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SECTION 1

# PHYSICAL AND CHEMICAL PROPERTIES 

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1.1 MOLAR GAS CONSTANT ..... 1.2
1.2 ESTIMATION OF CRITICAL TEMPERATURE FROM EMPIRICAL CORRELATION ..... 1.2
1.3 CRITICAL PROPERTIES FROMGROUP-CONTRIBUTION METHOD1.3
1.4 REDLICH-KWONG EQUATION OF STATE 1.5
1.5 P-V-T PROPERTIES OF A GAS MIXTURE 1.8
1.6 DENSITY OF A GAS MIXTURE ..... 1.12
1.7 ESTIMATION OF LIQUIDDENSITY 1.14
1.8 ESTIMATION OF IDEAL-GAS HEAT CAPACITY 1.15
1.9 HEAT CAPACITY OF REAL GASES ..... 1.20
1.10 LIQUID HEAT CAPACITY- GENERALIZED CORRELATION 1.22
1.11 ENTHALPY DIFFERENCE FOR IDEALGAS 1.24
1.12 ESTIMATION OF HEAT OFVAPORIZATION 1.24
1.13 PREDICTION OF VAPORPRESSURE 1.27
1.14 ENTHALPY ESTIMATION-GENERALIZED METHOD 1.29
1.15 ENTROPY INVOLVING A PHASECHANGE 1.31
1.16 ABSOLUTE ENTROPY FROM HEATCAPACITIES 1.33
1.17 EXPANSION UNDER ISENTROPIC
CONDITIONS ..... 1.36
1.18 CALCULATION OF FUGACITIES ..... 1.38
1.19 ACTIVITY COEFFICIENTS FROM THE SCATCHARD-HILDEBRAND EQUATION ..... 1.40
1.20 ACTIVITY-COEFFICIENT-CORRELATION

EQUATIONS AND LIQUID-LIQUID EQUILIBRIUM DATA 1.44
1.21 ACTIVITY-COEFFICIENT-CORRELATION EQUATIONS AND VAPOR-LIQUID EQUILIBRIUM DATA 1.46
1.22 CONVERGENCE-PRESSURE VAPOR-LIQUID EQUILIBRIUM K VALUES 1.49
1.23 HEAT OF FORMATION FROM ELEMENTS 1.64
1.24 STANDARD HEAT OF REACTION, STANDARD FREE-ENERGY CHANGE, AND EQUILIBRIUM CONSTANT 1.67
1.25 STANDARD HEAT OF REACTION FROM HEAT OF FORMATION-AQUEOUS SOLUTIONS 1.68
1.26 STANDARD HEAT OF REACTION FROM HEAT OF COMBUSTION 1.68
1.27 STANDARD HEAT OF FORMATION FROM HEAT OF COMBUSTION 1.70
1.28 HEAT OF ABSORPTION FROM SOLUBILITY DATA 1.71
1.29 ESTIMATION OF LIQUID VISCOSITY AT HIGH TEMPERATURES 1.73
1.30 VISCOSITY OF NONPOLAR AND POLAR GASES AT HIGH PRESSURE 1.73
1.31 THERMAL CONDUCTIVITY OF GASES 1.75
1.32 THERMAL CONDUCTIVITY OF LIQUIDS 1.76
1.33 DIFFUSION COEFFICIENTS FOR BINARY GAS SYSTEMS AT LOW PRESSURES 1.77
1.34 ESTIMATION OF SURFACE TENSION OF A PURE LIQUID 1.78
REFERENCES 1.79

### 1.1 MOLAR GAS CONSTANT

Calculate the molar gas constant $R$ in the following units:
a. $(\mathrm{atm})\left(\mathrm{cm}^{3}\right) /(\mathrm{g} \cdot \mathrm{mol})(\mathrm{K})$
b. $(\mathrm{psia})\left(\mathrm{ft}^{3}\right) /(\mathrm{lb} \cdot \mathrm{mol})\left({ }^{\circ} \mathrm{R}\right)$
c. $(\mathrm{atm})\left(\mathrm{ft}^{3}\right) /(\mathrm{lb} \cdot \mathrm{mol})(\mathrm{K})$
d. $\mathrm{kWh} /(\mathrm{lb} \cdot \mathrm{mol})\left({ }^{\circ} \mathrm{R}\right)$
e. $\mathrm{hp} \cdot \mathrm{h} /(\mathrm{lb} \cdot \mathrm{mol})\left({ }^{\circ} \mathrm{R}\right)$
f. $(\mathrm{kPa})\left(\mathrm{m}^{3}\right) /(\mathrm{kg} \cdot \mathrm{mol})(\mathrm{K})$
g. $\mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})(\mathrm{K})$

## Calculation Procedure

1. Assume a basis. Assume gas is at standard conditions, that is, $1 \mathrm{~g} \cdot \mathrm{~mol}$ gas at $1 \mathrm{~atm}(101.3 \mathrm{kPa})$ pressure and $0^{\circ} \mathrm{C}\left(273 \mathrm{~K}\right.$, or $\left.492^{\circ} \mathrm{R}\right)$, occupying a volume of 22.4 L .
2. Compute the gas constant. Apply suitable conversion factors and obtain the gas constant in various units. Use $P V=R T$; that is, $R=P V / T$. Thus,
a. $R=(1 \mathrm{~atm})[22.4 \mathrm{~L} /(\mathrm{g} \cdot \mathrm{mol})]\left(1000 \mathrm{~cm}^{3} / \mathrm{L}\right) / 273 \mathrm{~K}=82.05(\mathrm{~atm})\left(\mathrm{cm}^{3}\right) /(\mathrm{g} \cdot \mathrm{mol})(\mathrm{K})$
b. $R=(14.7 \mathrm{psia})\left[359 \mathrm{ft}^{3} /(\mathrm{lb} \cdot \mathrm{mol})\right] / 492^{\circ} \mathrm{R}=10.73(\mathrm{psia})\left(\mathrm{ft}^{3}\right) /(\mathrm{lb} \cdot \mathrm{mol})\left({ }^{\circ} \mathrm{R}\right)$
c. $R=(1 \mathrm{~atm})\left[359 \mathrm{ft}^{3} /(\mathrm{lb} \cdot \mathrm{mol})\right] / 273 \mathrm{~K}=1.315(\mathrm{~atm})\left(\mathrm{ft}^{3}\right) /(\mathrm{lb} \cdot \mathrm{mol})(\mathrm{K})$
d. $R=\left[10.73(\mathrm{psia})\left(\mathrm{ft}^{3}\right) /(\mathrm{lb} \cdot \mathrm{mol})\left({ }^{\circ} \mathrm{R}\right)\right]\left(144 \mathrm{in}^{2} / \mathrm{ft}^{2}\right)\left[3.77 \times 10^{-7} \mathrm{kWh} /(\mathrm{ft} \cdot \mathrm{lbf})\right]=5.83 \times 10^{-4} \mathrm{kWh} /$ $(\mathrm{lb} \cdot \mathrm{mol})\left({ }^{\circ} \mathrm{R}\right)$
e. $R=\left[5.83 \times 10^{-4} \mathrm{kWh} /(\mathrm{lb} \cdot \mathrm{mol})\left({ }^{\circ} \mathrm{R}\right)\right](1 / 0.746 \mathrm{hp} \cdot \mathrm{h} / \mathrm{kWh})=7.82 \times 10^{-4} \mathrm{hp} \cdot \mathrm{h} /(\mathrm{lb} \cdot \mathrm{mol})\left({ }^{\circ} \mathrm{R}\right)$
f. $R=(101.325 \mathrm{kPa} / \mathrm{atm})[22.4 \mathrm{~L} /(\mathrm{g} \cdot \mathrm{mol})][1000 \mathrm{~g} \cdot \mathrm{~mol} /(\mathrm{kg} \cdot \mathrm{mol})] /(273 \mathrm{~K})\left(1000 \mathrm{~L} / \mathrm{m}^{3}\right)=$ $8.31(\mathrm{kPa})\left(\mathrm{m}^{3}\right) /(\mathrm{kg} \cdot \mathrm{mol})(\mathrm{K})$
g. $R=\left[7.82 \times 10^{-4} \mathrm{hp} \cdot \mathrm{h} /(\mathrm{lb} \cdot \mathrm{mol})\left({ }^{\circ} \mathrm{R}\right)\right]\left[6.4162 \times 10^{5} \mathrm{cal} /(\mathrm{hp} \cdot \mathrm{h})\right][1 / 453.6 \mathrm{lb} \cdot \mathrm{mol} /(\mathrm{g} \cdot \mathrm{mol})]$ $\left(1.8^{\circ} \mathrm{R} / \mathrm{K}\right)=1.99 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})(\mathrm{K})$

## ESTIMATION OF CRITICAL TEMPERATURE EMPIRICAL CORRELATION

Predict the critical temperature of (a) n-eicosane, (b) 1-butene, and (c) benzene using the empirical correlation of Nokay. The Nokay relation is

$$
\log T_{c}=A+B \log S G+C \log T_{b}
$$

where $T_{c}$ is critical temperature in kelvins, $T_{b}$ is normal boiling point in kelvins, and $S G$ is specific gravity of liquid hydrocarbons at $60^{\circ} \mathrm{F}$ relative to water at the same temperature. As for $A, B$, and $C$, they are correlation constants given in Table 1.1.

TABLE 1.1 Correlation Constants for Nokay's Equation

| Family of compounds | $A$ | $B$ | $C$ |
| :--- | :---: | ---: | ---: |
| Alkanes (paraffins) | 1.359397 | 0.436843 | 0.562244 |
| Cycloalkanes (naphthenes) | 0.658122 | -0.071646 | 0.811961 |
| Alkenes (olefins) | 1.095340 | 0.277495 | 0.655628 |
| Alkynes (acetylenes) | 0.746733 | 0.303809 | 0.799872 |
| Alkadienes (diolefins) | 0.147578 | -0.396178 | 0.994809 |
| Aromatics | 1.057019 | 0.227320 | 0.669286 |

## Calculation Procedure

1. Obtain normal boiling point and specific gravity. Obtain $T_{b}$ and $S G$ for these three compounds from, for instance, Reid, Prausnitz, and Sherwood [1]. These are (a) for $n$-eicosane $\left(\mathrm{C}_{20} \mathrm{H}_{42}\right)$, $T_{b}=617 \mathrm{~K}$ and $S G=0.775$; (b) for 1-butene $\left(\mathrm{C}_{4} \mathrm{H}_{8}\right), T_{b}=266.9 \mathrm{~K}$ and $S G=0.595$; and (c) for benzene $\left(\mathrm{C}_{6} \mathrm{H}_{6}\right), T_{b}=353.3 \mathrm{~K}$ and $S G=0.885$.
2. Compute critical temperature using appropriate constants from Table 1.1. Thus (a) for $n$-eicosane:

$$
\log T_{c}=1.359397+0.436843 \log 0.775+0.562244 \log 617=2.87986
$$

so $T_{c}=758.3 \mathrm{~K}\left(905^{\circ} \mathrm{F}\right)$. (b) For 1-butene:

$$
\log T_{c}=1.095340+0.277495 \log 0.595+0.655628 \log 266.9=2.62355
$$

so $T_{c}=420.3 \mathrm{~K}\left(297^{\circ} \mathrm{F}\right)$. (c) For benzene:
$\log T_{c}=1.057019+0.22732 \log 0.885+0.669286 \log 353.3=2.75039$
so $T_{c}=562.8 \mathrm{~K}\left(553^{\circ} \mathrm{F}\right)$

Related Calculations. This procedure may be used to estimate the critical temperature of hydrocarbons containing a single family of compounds, as shown in Table 1.1. Tests of the equation on paraffins in the range $\mathrm{C}_{1}-\mathrm{C}_{20}$ and various other hydrocarbon families in the range $\mathrm{C}_{3}-\mathrm{C}_{14}$ have shown average and maximum deviations of about 6.5 and $35^{\circ} \mathrm{F}$ ( 3.6 and 19 K ), respectively.

### 1.3 CRITICAL PROPERTIES FROM GROUP-CONTRIBUTION METHOD

Estimate the critical properties of $p$-xylene and $n$-methyl-2-pyrrolidone using Lydersen's method of group contributions.

## Calculation Procedure

1. Obtain molecular structure, normal boiling point $T_{b}$, and molecular weight $M W$. From handbooks, for $p$-xylene $\left(\mathrm{C}_{8} \mathrm{H}_{10}\right), \mathrm{MW}=106.16, T_{b}=412.3 \mathrm{~K}$, and the structure is


For $n$-methyl-2-pyrrolidone $\left(\mathrm{C}_{5} \mathrm{H}_{9} \mathrm{NO}\right), \mathrm{MW}=99.1, T_{b}=475.0 \mathrm{~K}$, and the structure is

2. Sum up structural contributions of the individual property increments from Table 1.2, pp. 1.6 and 1.7. The calculations can be set out in the following arrays, in which $N$ stands for the number of groups. For $p$-xylene:

| Group type | $N$ | $\Delta T$ | $\Delta P$ | $\Delta V$ | $(N)(\Delta T)$ | $(N)(\Delta P)$ | $(N)(\Delta V)$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $-\mathrm{CH}_{3}$ (nonring) | 2 | 0.020 | 0.227 | 55 | 0.04 | 0.454 | 110 |
| $-\stackrel{1}{\mathrm{C}}=(\text { ring })$ | 2 | 0.011 | 0.154 | 36 | 0.022 | 0.308 | 72 |
|  | 4 | 0.011 | 0.154 | 37 | 0.044 | 0.616 | 148 |
| Total |  |  |  |  | 0.106 | 1.378 | 330 |

For $n$-methyl-2-pyrrolidone:

| Group type | $N$ | $\Delta T$ | $\Delta P$ | $\Delta V$ | $(N)(\Delta T)$ | $(N)(\Delta P)$ | $(N)(\Delta V)$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :---: |
| $-\mathrm{CH}_{3}$ (nonring) | 1 | 0.020 | 0.227 | 55 | 0.020 | 0.227 | 55 |
| $-\mathrm{CH}_{2}$ - (ring) | 3 | 0.013 | 0.184 | 44.5 | 0.039 | 0.552 | 133.5 |
| $\mathrm{C}=\mathrm{O}$ (ring) | 1 | 0.033 | 0.2 | 50 | 0.033 | 0.20 | 50 |
| $-\mathrm{N}-$ (ring) | 1 | 0.007 | 0.13 | 32 | $\underline{0.007}$ | $\frac{0.13}{32}$ |  |
| Total |  |  |  |  | 0.099 | 1.109 | $\underline{270.5}$ |

3. Compute the critical properties. The formulas are

$$
\begin{aligned}
T_{c} & =T_{b}\left\{\left[(0.567)+\Sigma(N)(\Delta T)-[\Sigma(N)(\Delta T)]^{2}\right\}^{-1}\right. \\
P_{c} & =\operatorname{MW}[0.34+(N)(\Delta P)]^{-2} \\
V_{c} & =[40+(N)(\Delta V)] \\
Z_{c} & =P_{c} V_{c} / R T_{c}
\end{aligned}
$$

where $T_{c}, P_{c}, V_{c}$, and $Z_{c}$ are critical temperature, critical pressure, critical volume, and critical compressibility factor, respectively. Thus, for $p$-xylene,

$$
\begin{aligned}
T_{c} & =412.3\left[0.567+0.106-(0.106)^{2}\right]^{-1} \\
& =623.0 \mathrm{~K}\left(661.8^{\circ} \mathrm{F}\right)(\text { literature value is } 616.2 \mathrm{~K}) \\
P_{c} & \left.=106.16(0.34+1.378)^{-2}=35.97 \mathrm{~atm}(3644 \mathrm{kPa}) \text { (literature value is } 34.7 \mathrm{~atm}\right) \\
V_{c} & =40+330 \\
& =370 \mathrm{~cm}^{3} /(\mathrm{g} \cdot \mathrm{~mol})\left[5.93 \mathrm{ft}^{3} /(\mathrm{lb} \cdot \mathrm{~mol})\right]\left[\text { literature value }=379 \mathrm{~cm}^{3} /(\mathrm{g} \cdot \mathrm{~mol})\right]
\end{aligned}
$$

And since $R=82.06\left(\mathrm{~cm}^{3}\right)(\mathrm{atm}) /(\mathrm{g} \cdot \mathrm{mol})(\mathrm{K})$,

$$
Z_{c}=(35.97)(370) /(82.06)(623)=0.26
$$

For $n$-methyl-2-pyrrolidone,

$$
\begin{aligned}
& T_{c}=475\left[0.567+0.099-(0.099)^{2}\right]^{-1}=723.9 \mathrm{~K}\left(843^{\circ} \mathrm{F}\right) \\
& P_{c}=99.1(0.34+1.109)^{-2}=47.2 \operatorname{atm}(4780 \mathrm{kPa}) \\
& V_{c}=40+270.5=310.5 \mathrm{~cm}^{3} /(\mathrm{g} \cdot \mathrm{~mol})\left[4.98 \mathrm{ft}^{3} /(\mathrm{lb} \cdot \mathrm{~mol})\right] \\
& Z_{c}=(47.2)(310.5) /(82.06)(723.9)=0.247
\end{aligned}
$$

Related Calculations. Extensive comparisons between experimental critical properties and those estimated by several other methods have shown that the Lydersen group-contribution method is the most accurate. This method is relatively easy to use for both hydrocarbons and organic compounds in general, provided that the structure is known. Unlike Nokay's correlation (see Example 1.2), it can be readily applied to hydrocarbons containing characteristics of more than a single family, such as an aromatic with olefinic side chains. A drawback of the Lydersen method, however, is that it cannot distinguish between isomers of similar structure, such as 2,3-dimethylpentane and 2,4-dimethylpentane.

Based on tests with paraffins in the $\mathrm{C}_{1}-\mathrm{C}_{20}$ range and other hydrocarbons in the $\mathrm{C}_{3}-\mathrm{C}_{14}$ range, the average deviation from experimental data for critical pressure is $18 \mathrm{lb} / \mathrm{in}^{2}(124 \mathrm{kPa})$, and the maximum error is around $70 \mathrm{lb} / \mathrm{in}^{2}(483 \mathrm{kPa})$. In general, the accuracy of the correlation is lower for unsaturated compounds than for saturated ones. As for critical temperature, the typical error is less than 2 percent; it can range up to 5 percent for nonpolar materials of relatively high molecular weight (e.g., 7100). Accuracy of the method when used with multifunctional polar groups is uncertain.

### 1.4 REDLICH-KWONG EQUATION OF STATE

Estimate the molar volume of isopropyl alcohol vapor at $10 \mathrm{~atm}(1013 \mathrm{kPa})$ and $473 \mathrm{~K}\left(392^{\circ} \mathrm{F}\right)$ using the Redlich-Kwong equation of state. For isopropyl alcohol, use 508.2 K as the critical temperature $T_{c}$ and 50 atm as the critical pressure $P_{c}$. The Redlich-Kwong equation is

$$
P=R T /(V-b)-a / T^{0.5} V(V-b)
$$

where $P$ is pressure, $T$ is absolute temperature, $V$ is molar volume, $R$ is the gas constant, and $a$ and $b$ are equation-of-state constants given by

$$
a=0.4278 R^{2} T_{c}^{2.5} / P_{c} \quad \text { and } \quad b=0.0867 R T_{c} / P_{c}
$$

TABLE 1.2 Critical-Property Increments—Lydersen's Structural Contributions

| Symbols | $\Delta T$ | $\Delta P$ | $\Delta V$ |
| :---: | :---: | :---: | :---: |
| Nonring increments |  |  |  |
| $-\mathrm{CH}_{3}$ | 0.020 | 0.227 | 55 |
| $-\stackrel{\mathrm{C}}{\mathrm{C}} \mathrm{H}_{2}$ | 0.020 | 0.227 | 55 |
|  | 0.012 | 0.210 | 51 |
| $-\stackrel{i}{\mathrm{C}}-$ | 0.00 | 0.210 | 41 |
| $=\stackrel{\mathrm{C}}{\mathrm{C}} \mathrm{H}_{2}$ | 0.018 | 0.198 | 45 |
| $=\stackrel{1}{\mathrm{C}} \mathrm{H}$ | 0.018 | 0.198 | 45 |
| $=\stackrel{1}{\mathrm{C}}-$ | 0.0 | 0.198 | 36 |
| $=\mathrm{C}=$ | 0.0 | 0.198 | 36 |
| $\equiv \mathrm{CH}$ | 0.005 | 0.153 | (36) |
| $\equiv \mathrm{C}$ - | 0.005 | 0.153 | (36) |
| Ring increments |  |  |  |
| $-\mathrm{CH}_{2}-$ | 0.013 | 0.184 | 44.5 |
| $-\stackrel{1}{\mathrm{C}} \mathrm{H}$ | 0.012 | 0.192 | 46 |
|  | (-0.007) | (0.154) | (31) |
| I | (-0.007) | (0.154) |  |
| $=\stackrel{1}{\mathrm{C}} \mathrm{H}$ | 0.011 | 0.154 | 37 |
| $=\stackrel{\mathrm{l}}{\mathrm{C}}-$ | 0.011 | 0.154 | 36 |
| $=\mathrm{C}=$ | 0.011 | 0.154 | 36 |
| Halogen increments |  |  |  |
| -F | 0.018 | 0.221 | 18 |
| $-\mathrm{Cl}$ | 0.017 | 0.320 | 49 |
| $-\mathrm{Br}$ | 0.010 | (0.50) | (70) |
| -I | 0.012 | (0.83) | (95) |
| Oxygen increments |  |  |  |
| - OH (alcohols) | 0.082 | 0.06 | (18) |
| - OH (phenols) | 0.031 | (-0.02) | (3) |
| - $\mathrm{O}-$ (nonring) | 0.021 | 0.16 | 20 |
| - O - (ring) | (0.014) | (0.12) | (8) |
| $-\mathrm{C}=\mathrm{O} \text { (nonring) }$ | 0.040 | 0.29 | 60 |
| $-\stackrel{\mathrm{C}}{\mathrm{C}}=\mathrm{O} \text { (ring) }$ | (0.033) | (0.2) | (50) |
| $\mathrm{HC}=\mathrm{O}$ (aldehyde) | 0.048 | 0.33 | 73 |
| -COOH (acid) | 0.085 | (0.4) | 80 |
| - COO - (ester) | 0.047 | 0.47 | 80 |
| $=\mathrm{O}$ (except for combinations above) | (0.02) | (0.12) | (11) |

TABLE 1.2 Critical-Property Increments—Lydersen's Structural Contributions (Continued)

| Symbols | $\Delta T$ | $\Delta P$ | $\Delta V$ |
| :---: | :---: | :---: | :---: |
| Nitrogen increments |  |  |  |
| $-\mathrm{NH}_{2}$ | 0.031 | 0.095 | 28 |
| $-\mathrm{NH} \text { (nonring) }$ | 0.031 | 0.135 | (37) |
| $-\stackrel{1}{\mathrm{~N}} \mathrm{H} \text { (ring) }$ | (0.024) | (0.09) | (27) |
| $-\stackrel{1}{N}-\text { (nonring) }$ | 0.014 | 0.17 | (42) |
| $-{ }_{-}^{\prime} \mathrm{N}-$ (ring) | (0.007) | (0.13) | (32) |
| $-\mathrm{CN}$ | (0.060) | (0.36) | (80) |
| $-\mathrm{NO}_{2}$ | (0.055) | (0.42) | (78) |
| Sulfur increments |  |  |  |
| -SH | 0.015 | 0.27 | 55 |
| -S- (nonring) | 0.015 | 0.27 | 55 |
| -S- (ring) | (0.008) | (0.24) | (45) |
| $=\mathrm{S}$ | (0.003) | (0.24) | (47) |

Miscellaneous


Note: There are no increments for hydrogen. All bonds shown as free are connected with atoms other than hydrogen. Values in parentheses are based on too few experimental data to be reliable.

Source: A. L. Lydersen, U. of Wisconsin Eng. Exp. Station, 1955.
when the critical temperature is in kelvins, the critical pressure is in atmospheres, and $R$ is taken as $82.05(\mathrm{~atm})\left(\mathrm{cm}^{3}\right) /(\mathrm{g} \cdot \mathrm{mol})(\mathrm{K})$.

In an alternate form, the Redlich-Kwong equation is written as

$$
Z=1 /(1-h)-(A / B)[h /(1+h)]
$$

where $h=b / V=B P / Z, B=b / R T, A / B=a / b R T^{1.5}$, and $Z$, the compressibility factor, is equal to $P V / R T$.

## Calculation Procedure

1. Calculate the compressibility factor $Z$. Since the equation is not explicit in $Z$, solve for it by an iterative procedure. For Trial 1, assume that $Z=0.9$; therefore,

$$
h=0.0867\left(P / P_{c}\right) / Z\left(T / T_{c}\right)=\frac{0.087(10 / 50)}{(0.9)(473 / 508.2)}=0.0208
$$

Substituting for the generalized expression for $A / B$ in the Redlich-Kwong equation,

$$
\begin{aligned}
Z & =\frac{1}{1-h}-\left[\frac{\left(0.4278 R^{2} T_{c}^{2.5} / P_{c}\right)}{\left(0.0867 R T_{c} / P_{c}\right)\left(R T^{1.5}\right)}\right]\left(\frac{h}{1+h}\right) \\
& =\frac{1}{1-h}-(4.9343)\left(T_{c} / T\right)^{1.5}\left(\frac{h}{1+h}\right) \\
& =\frac{1}{1-0.0208}-\left[(4.9343)\left(\frac{508.2}{473}\right)^{1.5}\right]\left[\frac{0.0208}{1+0.0208}\right] \\
& =0.910
\end{aligned}
$$

For Trial 2, then, assume that $Z=0.91$; therefore,

$$
h=\frac{0.0867(10 / 50)}{0.91(473 / 508.2)}=0.0205
$$

and

$$
Z=\frac{1}{1-0.0205}-(4.9343)(508.2 / 473)^{1.5} \frac{0.0205}{1+0.0205}=0.911
$$

which is close enough.
2. Calculate molar volume. By the definition of $Z$,

$$
\begin{aligned}
V & =Z R T / P \\
& =(0.911)(82.05)(473) /(10) \\
& =3535.6 \mathrm{~cm}^{3} /(\mathrm{g} \cdot \mathrm{~mol})\left[3.536 \mathrm{~m}^{3} /(\mathrm{kg} \cdot \mathrm{~mol}) \text { or } 56.7 \mathrm{ft}^{3} /(\mathrm{lb} \cdot \mathrm{~mol})\right]
\end{aligned}
$$

Related Calculations. This two-constant equation of Redlich-Kwong is extensively used for engineering calculations and enjoys wide popularity. Many modifications of the Redlich-Kwong equations of state, such as those by Wilson, Barnes-King, Soave, and Peng-Robinson, have been made and are discussed in Reid et al. [1]. The constants for the equation of state may be obtained by leastsquares fit of the equation to experimental $P-V-T$ data. However, such data are often not available. When this is the case, estimate the constants on the basis of the critical properties, as shown in the example.

### 1.5 P-V-T PROPERTIES OF A GAS MIXTURE

A gaseous mixture at $25^{\circ} \mathrm{C}(298 \mathrm{~K})$ and $120 \mathrm{~atm}(12,162 \mathrm{kPa})$ contains $3 \%$ helium, $40 \%$ argon, and $57 \%$ ethylene on a mole basis. Compute the volume of the mixture per mole using the following: (a) ideal-gas law, (b) compressibility factor based on pseudoreduced conditions (Kay's method),
(c) mean compressibility factor and Dalton's law, (d) van der Waal's equation and Dalton's law, and
(e) van der Waal's equation based on averaged constants.

## Calculation Procedure

1. Solve the ideal-gas law for volume. By definition, $V=R T / P$, where $V$ is volume per mole, $T$ is absolute temperature, $R$ is the gas constant, and $P$ is pressure. Then,

$$
V=\left[82.05\left(\mathrm{~cm}^{3}\right)(\mathrm{atm}) /(\mathrm{g} \cdot \mathrm{~mol})(\mathrm{K})\right] 298 \mathrm{~K} / 120 \mathrm{~atm}=203.8 \mathrm{~cm}^{3} /(\mathrm{g} \cdot \mathrm{~mol})
$$

2. Calculate the volume using Kay's method. In this method, $V$ is found from the equation $V=Z R T / P$, where $Z$, the compressibility factor, is calculated on the basis of pseudocritical constants that are computed as mole-fraction-weighted averages of the critical constants of the pure compounds. Thus, $T_{c}^{\prime}=\Sigma Y_{i} T_{c, i}$ and similarly for $P_{c}^{\prime}$ and $Z_{c}^{\prime}$, where the subscript $c$ denotes critical, the prime denotes pseudo, the subscript $i$ pertains to the $i$ th component, and $Y$ is mole fraction. Purecomponent critical properties can be obtained from handbooks. The calculations can then be set out as a matrix:

| Component, $i$ | $Y_{i}$ | $T_{c, i}(\mathrm{~K})$ | $Y_{i} T_{c, i}(\mathrm{~K})$ | $P_{c, i}(\mathrm{~atm})$ | $Y_{i} P_{c, i}(\mathrm{~atm})$ | $Z_{c, i}$ | $Y_{i} Z_{c, i}$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| He | 0.03 | 5.2 | 0.16 | 2.24 | 0.07 | 0.301 | 0.009 |
| A | 0.40 | 150.7 | 60.28 | 48.00 | 19.20 | 0.291 | 0.116 |
| $\mathrm{C}_{2} \mathrm{H}_{4}$ | $\underline{0.57}$ | 283.0 | $\underline{161.31}$ | 50.50 | $\underline{28.79}$ | 0.276 | $\underline{0.157}$ |
| $\Sigma=$ | 1.00 |  | 221.75 |  | 48.06 |  | 0.282 |

Then the reduced temperature $T_{r}=T / T_{c}^{\prime}=298 / 221.75=1.34$, and the reduced pressure $P_{r}=$ $P / P_{c}^{\prime}=120 / 48.06=2.50$. Now $Z_{c}^{\prime}=0.282$. Refer to the generalized compressibility plots in Figs. 1.2 and 1.3 , which pertain respectively to $Z_{c}^{\prime}$ values of 0.27 and 0.29 . Figure 1.2 gives a $Z$ of 0.71 , and Fig. 1.3 gives a $Z$ of 0.69 . By linear interpolation, then, $Z$ for the present case is 0.70 . Therefore, the mixture volume is given by

$$
V=Z R T / P=(0.70)(82.05)(298) / 120=138.8 \mathrm{~cm}^{3} /(\mathrm{g} \cdot \mathrm{~mol})
$$

3. Calculate the volume using the mean compressibility factor and Dalton's law. Dalton's law states that the total pressure exerted by a gaseous mixture is equal to the sum of the partial pressures. In using this method, assume that the partial pressure of a component of a mixture is equal to the product of its mole fraction and the total pressure. Thus the method consists of calculating the partial pressure for each component, calculating the reduced pressure and reduced temperature, finding the corresponding compressibility factor for each component (from a conventional compressibility-factor chart in a handbook), and then taking the mole-fraction-weighted average of those compressibility factors and using that average value to find $V$. The calculations can be set out in matrix form, employing the critical properties from the matrix in step 2:

|  |  | Partial <br> pressure | Reduced <br> pressure <br> $\left(p_{i}=P Y_{i}\right)$ | Reduced <br> $\left(p_{i} / P_{c, i}\right)$ | (emperature <br> $\left(T / T_{c, i}\right)$ | Compressibility <br> factor $\left(Z_{i}\right)$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| Component $(i)$ | $Y_{i}$ | $Z_{i} Y_{i}$ |  |  |  |  |
| Helium | 0.03 | 3.6 | 1.61 | 57.3 | 1.000 | 0.030 |
| Argon | 0.40 | 48.0 | 1.00 | 1.98 | 0.998 | 0.399 |
| Ethylene | $\underline{0.57}$ | $\underline{68.4}$ | 1.35 | 1.05 | 0.368 | $\underline{0.210}$ |
| Total | 1.00 | 120.0 |  |  |  | 0.639 |



FIGURE 1.1 Generalized compressibility factor; $Z_{c}=0.27$; low-pressure range. (Lydersen et al., University of Wisconsin Engineering Experiment Station, 1955.)

Therefore

$$
V=Z R T / P=(0.639)(82.05)(298) / 120=130.2 \mathrm{~cm}^{3} /(\mathrm{g} \cdot \mathrm{~mol})
$$

4. Calculate the volume using van der Waal's equation and Dalton's law. Van der Waal's equation is

$$
P=R T /(V-b)-a / V^{2}
$$

where $a$ and $b$ are van der Waal constants, available from handbooks, that pertain to a given substance. The values for helium, argon, and ethylene are as follows (for calculations with pressure in atmospheres, volume in cubic centimeters, and quantity in gram-moles):

|  | van der Waal constant |  |
| :--- | :---: | :---: |
| Component | $a$ | $b$ |
| Helium | $0.0341 \times 10^{6}$ | 23.7 |
| Argon | $1.350 \times 10^{6}$ | 32.3 |
| Ethylene | $4.480 \times 10^{6}$ | 57.2 |

For a mixture obeying Dalton's law, the equation can be rewritten as

$$
P=R T\left[\frac{Y_{\mathrm{He}}}{\left(V-Y_{\mathrm{He}} b_{\mathrm{He}}\right)}+\frac{Y_{\mathrm{A}}}{\left(V-Y_{\mathrm{A}} b_{\mathrm{A}}\right)}+\frac{Y_{\mathrm{Eth}}}{\left(V-Y_{\mathrm{Eth}} b_{\mathrm{Eth}}\right)}\right]-\left(\frac{1}{V^{2}}\right)\left(Y_{\mathrm{He}}^{2} a_{\mathrm{He}}+Y_{\mathrm{A}}^{2} a_{\mathrm{A}}+Y_{\mathrm{Eth}}^{2} a_{\mathrm{Eth}}\right)
$$

Upon substitution,

$$
\begin{aligned}
120= & (82.05)(298)\left[\frac{0.03}{V-(0.03)(23.7)}+\frac{0.40}{V-(0.4)(32.3)}+\frac{0.57}{V-(0.57)(57.2)}\right] \\
& -\frac{1}{V^{2}}\left[(0.0341)\left(10^{6}\right)\left(0.03^{2}\right)+(1.35)\left(10^{6}\right)\left(0.4^{2}\right)+(4.48)\left(10^{6}\right)\left(0.57^{2}\right)\right]
\end{aligned}
$$

Solving for volume by trial and error,

$$
V=150.9 \mathrm{~cm}^{3} /(\mathrm{g} \cdot \mathrm{~mol})\left[2.42 \mathrm{ft}^{3} /(\mathrm{lb} \cdot \mathrm{~mol})\right]
$$

5. Calculate the volume using van der Waal's equation with averaged constants. In this method it is convenient to rearrange the van der Waal equation into the form

$$
V^{3}-\left(b_{\text {avg }}+R T / P\right) V^{2}+a_{\text {avg }} V / P-a_{\text {avg }} b_{\text {avg }} / P=0
$$

For $a_{\text {avg }}$, take the expression $\left[\Sigma Y_{i}\left(a_{i}\right)^{0.5}\right]^{2}$; for $b_{\text {avg }}$, use the straightforward mole-fraction-weighted linear average $\Sigma Y_{i} b_{i}$. Thus, taking the values of $a_{i}$ and $b_{i}$ from the martix in step 4,

$$
\begin{aligned}
a_{\text {avg }} & =\left[(0.03)\left(0.0341 \times 10^{6}\right)^{0.5}+(0.40)\left(1.350 \times 10^{6}\right)^{0.5}+(0.57)\left(4.48 \times 10^{6}\right)^{0.5}\right]^{2} \\
& =2.81 \times 10^{6} \\
b_{\text {avg }} & =(0.03)(23.7)+(0.4)(32.3)+(0.57)(57.2) \\
& =46.23
\end{aligned}
$$

Upon substitution,

$$
V^{3}-[46.23+(82.05)(298) / 120] V^{2}+\left(2.81 \times 10^{6}\right) V / 120-\left(2.81 \times 10^{6}\right)(46.23) / 120=0
$$

Trial-and-error solution gives

$$
V=137 \mathrm{~cm}^{3} /(\mathrm{g} \cdot \mathrm{~mol})\left[2.20 \mathrm{ft}^{3} /(\mathrm{lb} \cdot \mathrm{~mol})\right]
$$

Related Calculations. This illustration outlines various simple techniques for estimating $P-V-T$ properties of gaseous mixtures. Obtain the compressibility factor from the generalized correspondingstate correlation, as shown in step 2.

The ideal-gas law is a simplistic model that is applicable to simple molecules at low pressure and high temperature. As for Kay's method, which in general is superior to the others, it is basically suitable for nonpolar/nonpolar mixtures and some polar/polar mixtures, but not for nonpolar/polar ones. Its average error ranges from about 1 percent at low pressures to 5 percent at high pressures and to as much as 10 percent when near the critical pressure.


FIGURE 1.2 Generalized compressibility factor; $Z_{c}=0.27$; high-pressure range. (Lydersen et al., University of Wisconsin Engineering Experiment Station, 1955.)

For a quick estimate one may compute the pseudocritical parameters for the mixture using Kay's mole-fraction-averaging mixing rule and obtain the compressibility factor from the generalized corresponding-state correlation as shown in step 2.

### 1.6 DENSITY OF A GAS MIXTURE

Calculate the density of a natural gas mixture containing $32.1 \%$ methane, $41.2 \%$ ethane, $17.5 \%$ propane, and $9.2 \%$ nitrogen (mole basis) at $500 \mathrm{psig}(3,550 \mathrm{kPa})$ and $250^{\circ} \mathrm{F}(394 \mathrm{~K})$.


FIGURE 1.3 Generalized compressibility factor; $Z_{c}=0.29$. (Lydersen et al., University of Wisconsin Engineering Experiment Station, 1955.)

## Calculation Procedure

1. Obtain the compressibility factor for the mixture. Employ Kay's method, as described in step 2 of Example 1.5. Thus $Z$ is found to be 0.933 .
2. Calculate the mole-fraction-weighted average molecular weight for the mixture. The molecular weights of methane, ethane, propane, and nitrogen are 16, 30, 44, and 28, respectively. Therefore, average molecular weight $M^{\prime}=(0.321)(16)+(0.412)(30)+(0.175)(44)+(0.092)(28)=27.8$ $\mathrm{lb} / \mathrm{mol}$.
3. Compute the density of the mixture. Use the formula

$$
\rho=M^{\prime} P / Z R T
$$

where $\rho$ is density, $P$ is pressure, $R$ is the gas constant, and $T$ is absolute temperature. Thus,

$$
\begin{aligned}
\rho & =(27.8)(500+14.7) /(0.933)(10.73)(250+460) \\
& =2.013 \mathrm{lb} / \mathrm{ft}^{3}\left(32.2 \mathrm{~kg} / \mathrm{m}^{3}\right)
\end{aligned}
$$

Related Calculations. Use of the corresponding-states three-parameter graphic correlation developed by Lydersen, Greenkorn, and Hougen (Figs. 1.1, 1.2, and 1.3) gives fairly good results for predicting the gas-phase density of nonpolar pure components and their mixtures. Errors are within 4 to 5 percent. Consequently, this generalized correlation can be used to perform related calculations, except in the regions near the critical point. For improved accuracy in estimating $P-V-T$ properties of pure components and their mixtures, use the Soave-modified Redlich-Kwong equation or the LeeKesler form of the Bendict-Webb-Rubin (B-W-R) generalized equation. For hydrocarbons, either of the two are accurate to within 2 to 3 percent, except near the critical point; for nonhydrocarbons, the Lee-Kesler modification of the B-W-R equation is recommended, the error probably being within a few percent except for polar molecules near the critical point. However, these equations are fairly complex and therefore not suitable for hand calculation. For a general discussion of various corresponding-state and analytical equations of state, see Reid et al. [1].

### 1.7 ESTIMATION OF LIQUID DENSITY

Estimate the density of saturated liquid ammonia at $37^{\circ} \mathrm{C}\left(310 \mathrm{~K}\right.$, or $\left.99^{\circ} \mathrm{F}\right)$ using (a) the Gunn-Yamada generalized correlation, and (b) the Rackett equation. The Gunn-Yamada correlation [16] is

$$
V / V_{\mathrm{Sc}}=V_{r}^{(0)}(1-\omega \Gamma)
$$

where $V$ is the liquid molar specific volume in cubic centimeters per gram-mole; $\omega$ is the acentric factor; $\Gamma$ is as defined below; $V_{\mathrm{Sc}}$ is a scaling parameter equal to $\left(R T_{c} / P_{c}\right)(0.2920-0.0967 \omega)$, where $R$ is the gas constant, $P$ is pressure, and the subscript $c$ denotes a critical property; and $V_{r}^{(0)}$ is a function whose value depends on the reduced temperature $T / T_{c}$ :

$$
\begin{aligned}
V_{r}^{(0)}= & 0.33593-0.33953\left(T / T_{c}\right)+1.51941\left(T / T_{c}\right)^{2}-2.02512\left(T / T_{c}\right)^{3} \\
& +1.11422\left(T / T_{c}\right)^{4} \quad \text { for } 0.2 \leq T / T_{c} \leq 0.8
\end{aligned}
$$

or

$$
\begin{aligned}
V_{r}^{(0)}= & 1.0+1.3\left(1-T / T_{c}\right)^{0.5} \log \left(1-T / T_{c}\right)-0.50879\left(1-T / T_{c}\right) \\
& -0.91534\left(1-T_{r}\right)^{2} \quad \text { for } 0.8 \leq T / T_{c} \leq 1.0
\end{aligned}
$$

and

$$
\Gamma=0.29607-0.09045\left(T / T_{c}\right)-0.04842\left(T / T_{c}\right)^{2} \quad \text { for } 0.2 \leq T / T_{c} \leq 1.0
$$

The Rackett equation [17] is

$$
V_{\text {sat liq }}=V_{c} Z_{c}^{\left(1-T / T_{c}\right)^{0.2857}}
$$

where $V_{\text {sat liq }}$ is the molar specific volume for saturated liquid, $V_{c}$ is the critical molar volume, and $Z_{c}$ is the critical compressibility factor. Use these values for ammonia: $T_{c}=405.6 \mathrm{~K}, P_{c}=111.3 \mathrm{~atm}$, $Z_{c}=0.242, V_{c}=72.5 \mathrm{~cm}^{3} /(\mathrm{g} \cdot \mathrm{mol})$, and $\omega=0.250$.

## Calculation Procedure

## 1. Compute saturated-liquid density using the Gunn-Yamada equation

$$
\begin{aligned}
V_{\mathrm{Sc}} & =(82.05)(405.6)[0.2920-(0.0967)(0.250)] / 111.3 \\
& =80.08 \mathrm{~cm}^{3} /(\mathrm{g} \cdot \mathrm{~mol})
\end{aligned}
$$

and the reduced temperature is given by

$$
\begin{aligned}
T / T_{c} & =(37+273) / 405.6 \\
& =0.764
\end{aligned}
$$

Therefore,

$$
\begin{aligned}
V_{r}^{(0)} & =0.33593-(0.33953)(0.764)+(1.51941)(0.764)^{2}-(2.02512)(0.764)^{3}+(1.11422)(0.764)^{4} \\
& =0.4399 \\
\Gamma & =0.29607-0.09045(0.764)-0.04842(0.764)^{2}=0.1987
\end{aligned}
$$

and the saturated liquid volume is given by

$$
\begin{aligned}
V & =(0.4399)(80.08)[1-(0.250)(0.1987)] \\
& =33.48 \mathrm{~cm}^{3} /(\mathrm{g} \cdot \mathrm{~mol})
\end{aligned}
$$

Finally, letting $M$ equal the molecular weight, the density of liquid ammonia is found to be

$$
\rho=M / V=17 / 33.48=0.508 \mathrm{~g} / \mathrm{cm}^{3}\left(31.69 \mathrm{lb} / \mathrm{ft}^{3}\right)
$$

(The experimental value is $0.5834 \mathrm{~g} / \mathrm{cm}^{3}$, so the error is 12.9 percent.)

## 2. Compute saturated-liquid density using the Rackett equation

$$
V_{\mathrm{sat}}=(72.5)(0.242)^{(1-0.764)^{0.2857}}=28.34 \mathrm{~cm}^{3} /(\mathrm{g} \cdot \mathrm{~mol})
$$

So

$$
\rho=17 / 28.34=0.5999 \mathrm{~g} / \mathrm{cm}^{3}\left(37.45 \mathrm{lb} / \mathrm{ft}^{3}\right) \quad(\text { error }=2.8 \text { percent })
$$

Related Calculations. Both the Gunn-Yamada and Rackett equations are limited to saturated liquids. At or below a $T_{r}$ of 0.99 , the Gunn-Yamada equation appears to be quite accurate for nonpolar as well as slightly polar compounds. With either equation, the errors for nonpolar compounds are generally within 1 percent. The correlation of Yen and Woods [18] is more general, being applicable to compressed as well as saturated liquids.

### 1.8 ESTIMATION OF IDEAL-GAS HEAT CAPACITY

Estimate the ideal-gas heat capacity $C_{p}^{\circ}$ of 2-methyl-1,3-butadiene and $n$-methyl-2-pyrrolidone at $527^{\circ} \mathrm{C}$ ( 800 K , or $980^{\circ} \mathrm{F}$ ) using the group-contribution method of Rihani and Doraiswamy. The Rihani-Doraiswamy method is based on the equation

$$
C_{p}^{\circ}=\sum_{i} N_{i} a_{i}+\sum_{i} N_{i} b_{i} T+\sum_{i} N_{i} c_{i} T^{2}+\sum_{i} N_{i} d_{i} T^{3}
$$

where $N_{i}$ is the number of groups of type $i, T$ is the temperature in kelvins, and $a_{i}, b_{i}, c_{i}$, and $d_{i}$ are the additive group parameters given in Table 1.3.

TABLE 1.3 Group Contributions to Ideal-Gas Heat Capacity

| Symbol | Coefficients |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  | $a$ | $b \times 10^{2}$ | $c \times 10^{4}$ | $d \times 10^{6}$ |
| Aliphatic hydrocarbon groups |  |  |  |  |
| $-\mathrm{CH}_{3}$ | 0.6087 | 2.1433 | $-0.0852$ | 0.01135 |
| $-\stackrel{\stackrel{1}{\mathrm{C}} \mathrm{H}_{2}}{ }$ | 0.3945 | 2.1363 | -0.1197 | 0.002596 |
| $=\mathrm{CH}_{2}$ | 0.5266 | 1.8357 | -0.0954 | 0.001950 |
|  | -3.5232 | 3.4158 | -0.2816 | 0.008015 |
|  | -5.8307 | 4.4541 | -0.4208 | 0.012630 |
|  | 0.2773 | 3.4580 | -0.1918 | 0.004130 |
|  | -0.4173 | 3.8857 | -0.2783 | 0.007364 |
|  | -3.1210 | 3.8060 | -0.2359 | 0.005504 |
|  | 0.9377 | 2.9904 | -0.1749 | 0.003918 |
|  | -1.4714 | 3.3842 | -0.2371 | 0.006063 |
|  | 0.4736 | 3.5183 | $-0.3150$ | 0.009205 |
| $\mathrm{H}^{\prime}$ |  |  |  |  |
| $\mathrm{C}=\mathrm{C}=\mathrm{CH}_{2}$ | 2.2400 | 4.2896 | -0.2566 | 0.005908 |
|  | 2.6308 | 4.1658 | -0.2845 | 0.007277 |
|  | -3.1249 | 6.6843 | -0.5766 | 0.017430 |
| $\equiv \mathrm{CH}$ | 2.8443 | 1.0172 | -0.0690 | 0.001866 |
| $-\mathrm{C} \equiv$ | -4.2315 | 7.8689 | -0.2973 | 0.00993 |

TABLE 1.3 Group Contributions to Ideal-Gas Heat Capacity (Continued)

| Symbol | Coefficients |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  | $a$ | $b \times 10^{2}$ | $c \times 10^{4}$ | $d \times 10^{6}$ |
| Aromatic hydrocarbon groups |  |  |  |  |
| $\mathrm{HC}^{*}$ | -1.4572 | 1.9147 | -0.1233 | 0.002985 |
| $-\mathrm{C}^{\star}$ | -1.3883 | 1.5159 | -0.1069 | 0.002659 |
| $\leftrightarrow \mathrm{C}^{\prime \prime}$ | 0.1219 | 1.2170 | -0.0855 | 0.002122 |
| Oxygen-containing groups |  |  |  |  |
| -OH | 6.5128 | $-0.1347$ | 0.0414 | $-0.001623$ |
| -O- | 2.8461 | -0.0100 | 0.0454 | -0.002728 |
| $\begin{gathered} \mathrm{H} \\ \stackrel{1}{\mathrm{C}}=\mathrm{O} \end{gathered}$ | 3.5184 | 0.9437 | 0.0614 | -0.006978 |
| $\mathrm{C}=\mathrm{O}$ | 1.0016 | 2.0763 | -0.1636 | 0.004494 |
|  | 1.4055 | 3.4632 | -0.2557 | 0.006886 |
|  | 2.7350 | 1.0751 | 0.0667 | -0.009230 |
| $0^{+}$ | -3.7344 | 1.3727 | -0.1265 | 0.003789 |
| Nitrogen-containing groups |  |  |  |  |
| - $\mathrm{C} \equiv \mathrm{N}$ | 4.5104 | 0.5461 | 0.0269 | $-0.003790$ |
| $-\mathrm{N} \equiv \mathrm{C}$ | 5.0860 | 0.3492 | 0.0259 | -0.002436 |
| $-\mathrm{NH}_{2}$ | 4.1783 | 0.7378 | 0.0679 | -0.007310 |
| NH | -1.2530 | 2.1932 | -0.1604 | 0.004237 |
| $\mathrm{N}-$ | -3.4677 | 2.9433 | $-0.2673$ | 0.007828 |
| $\mathrm{N}_{\Delta}^{*}$ | 2.4458 | 0.3436 | 0.0171 | -0.002719 |
| $-\mathrm{NO}_{2}$ | 1.0898 | 2.6401 | -0.1871 | 0.004750 |

TABLE 1.3 Group Contributions to Ideal-Gas Heat Capacity (Continued)

| Symbol | Coefficients |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  | $a$ | $b \times 10^{2}$ | $c \times 10^{4}$ | $d \times 10^{6}$ |
| Sulfur-containing groups |  |  |  |  |
| -SH | 2.5597 | 1.3347 | -0.1189 | 0.003820 |
| -S- | 4.2256 | 0.1127 | -0.0026 | -0.000072 |
| 2 |  |  |  |  |
| S | 4.0824 | -0.0301 | 0.0731 | -0.006081 |
| 5 |  |  |  |  |
| $-\mathrm{SO}_{3} \mathrm{H}$ | 6.9218 | 2.4735 | 0.1776 | -0.022445 |
| Halogen-containing groups |  |  |  |  |
| -F | 1.4382 | 0.3452 | -0.0106 | -0.000034 |
| $-\mathrm{Cl}$ | 3.0660 | 0.2122 | -0.0128 | 0.000276 |
| $-\mathrm{Br}$ | 2.7605 | 0.4731 | -0.0455 | 0.001420 |
| -I | 3.2651 | 0.4901 | -0.0539 | 0.001782 |
| Contributions due to ring formation (for cyclics only) |  |  |  |  |
| Three-membered ring | -3.5320 | -0.0300 | 0.0747 | -0.005514 |
| Four-membered ring | -8.6550 | 1.0780 | 0.0425 | -0.000250 |
| Five-membered ring: |  |  |  |  |
| c-Pentane | -12.2850 | 1.8609 | -0.1037 | 0.002145 |
| c-Pentene | -6.8813 | 0.7818 | -0.0345 | 0.000591 |
| Six-membered ring: |  |  |  |  |
| c-Hexane | -13.3923 | 2.1392 | -0.0429 | -0.001865 |
| c-Hexene | -8.0238 | 2.2239 | -0.1915 | 0.005473 |

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## Calculation Procedure

1. Obtain the molecular structure from a handbook, and list the number and type of groups. For 2-methyl-1,3-butadiene, the structure is

and the groups are


For $n$-methyl-2-pyrrolidone, the structure is

and the groups are

and a 5-membered (pentene) ring.
2. Sum up the group contributions for each compound. Obtain the values of $a, b, c$, and $d$ from Table 1.3, and set out the calculations in a martix:

|  | $N$ | $a$ | $b \times 10^{2}$ | $c \times 10^{4}$ | $d \times 10^{6}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 2-Methyl-1,3-butadiene: |  |  |  |  |  |
| $-\mathrm{CH}_{3}$ | 1 | 0.6087 | 2.1433 | $-0.0852$ | 0.01135 |
| $\backslash$ |  |  |  |  |  |
| $\mathrm{HC}=\mathrm{CH}_{2}$ | 1 | 0.2773 | 3.4580 | -0.1918 | 0.004130 |
| $\backslash$ |  |  |  |  |  |
| $\mathrm{C}=\mathrm{CH}_{2}$ | 1 | -0.4173 | 3.8857 | -0.2783 | 0.007364 |
| / |  |  |  |  |  |
| $\sum^{(N)}$ (group parameter) |  | 0.4687 | 9.4870 | $-0.5553$ | 0.02284 |
| $n$-Methyl-2-pyrrolidone: |  |  |  |  |  |
| 5-membered (pentene) ring | 1 | -6.8813 | 0.7818 | $-0.0345$ | 0.000591 |
| $-\mathrm{CH}_{3}$ | 1 | 0.6087 | 2.1433 | $-0.0852$ | 0.01135 |
| $-\stackrel{\stackrel{1}{\mathrm{C}} \mathrm{H}_{2}}{ }$ | 3 | 0.3945 | 2.1363 | -0.1197 | 0.002596 |
| 1 |  |  |  |  |  |
| $-\mathrm{C}=\mathrm{O}$ | 1 | 1.0016 | 2.0763 | $-0.1636$ | 0.004494 |
| 1 |  |  |  |  |  |
| N- | 1 | -3.4677 | 2.9433 | -0.2673 | 0.007828 |
| 1 |  |  |  |  |  |
| $\sum^{(N)}$ (group parameter) |  | -7.5552 | 14.3536 | -0.9097 | 0.026859 |

3. Compute the ideal-gas heat capacity for each compound. Refer to the equation in the statement of the problem. Now, $T=527+273=800 \mathrm{~K}$. Then, for 2-methyl-1,3-butadiene,

$$
\begin{aligned}
C_{p}^{\circ} & =0.4687+\left(9.4870 \times 10^{-2}\right)(800)+\left(-0.5553 \times 10^{-4}\right)(800)^{2}+\left(0.02284 \times 10^{-6}\right)(800)^{3} \\
& =52.52 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{~mol})(\mathrm{K})\left[52.52 \mathrm{Btu} /(\mathrm{lb} \cdot \mathrm{~mol})\left({ }^{\circ} \mathrm{F}\right)\right]
\end{aligned}
$$

And for n-methyl-2-pyrrolidone,

$$
\begin{aligned}
C_{p}^{\circ} & =-7.5552+\left(14.3536 \times 10^{-2}\right)(800)+\left(-0.9097 \times 10^{-4}\right)(800)^{2}+\left(0.02686 \times 10^{-6}\right)(800)^{3} \\
& =62.81 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{~mol})(\mathrm{K})\left[62.81 \mathrm{Btu} /(\mathrm{lb} \cdot \mathrm{~mol})\left({ }^{\circ} \mathrm{F}\right)\right]
\end{aligned}
$$

Related Calculations. The Rihani-Doraiswamy method is applicable to a large variety of compounds, including heterocyclics; however, it is not applicable to acetylenics. It predicts to within 2 to 3 percent accuracy. Accuracy levels are somewhat less when predicting at temperatures below about $300 \mathrm{~K}\left(80^{\circ} \mathrm{F}\right)$. Good accuracy is obtainable using the methods of Benson [25] and of Thinh [26].


FIGURE 1.4 Isothermal pressure correction to the molar heat capacity of gases. (Perry and Chilton-Chemical Engineers' Handbook, McGraw-Hill, 1973.)

### 1.9 HEAT CAPACITY OF REAL GASES

Calculate the heat capacity $C_{p}$ of ethane vapor at $400 \mathrm{~K}\left(260^{\circ} \mathrm{F}\right)$ and $50 \mathrm{~atm}(5065 \mathrm{kPa})$. Also estimate the heat-capacity ratio $C_{p} / C_{v}$ at these conditions. The ideal-gas heat capacity for ethane is given by

$$
C_{p}^{\circ}=2.247+\left(38.201 \times 10^{-3}\right) T-\left(11.049 \times 10^{-6}\right) T^{2}
$$

where $C_{p}^{\circ}$ is in $\mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})(\mathrm{K})$, and $T$ is in kelvins. For ethane, critical temperature $T_{c}=305.4 \mathrm{~K}$ and critical pressure $P_{c}=48.2 \mathrm{~atm}$.

## Calculation Procedure

1. Compute reduced temperature $\boldsymbol{T}_{r}$ and reduced pressure $\boldsymbol{P}_{r}$. Thus $T_{r}=T / T_{c}=400 /$ $305.4=1.310$, and $P_{r}=P / P_{c}=50 / 48.2=1.04$.
2. Obtain $\Delta C_{p}$ from Fig. 1.4. Thus $\Delta C_{p}=C_{p}-C_{p}^{\circ}=3 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})(\mathrm{K})$ at $T_{r}=1.31$ and $P_{r}=$ 1.04 .


FIGURE 1.5 Generalized heat-capacity differences, $C_{p}-C_{v}$. (Perry and Chilton-Chemical Engineers' Handbook, McGraw-Hill, 1973.)

## 3. Calculate ideal-gas heat capacity

$$
\begin{aligned}
C_{p}^{\circ} & =2.247+\left(38.201 \times 10^{-3}\right)(400)-\left(11.049 \times 10^{-6}\right)\left(400^{2}\right) \\
& =15.76 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{~mol})(\mathrm{K})
\end{aligned}
$$

## 4. Compute real-gas heat capacity

$$
C_{p}=\Delta C_{p}+C_{p}^{\circ}=3+15.76=18.76 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{~mol})(\mathrm{K})\left[18.76 \mathrm{Btu} /(\mathrm{lb} \cdot \mathrm{~mol})\left({ }^{\circ} \mathrm{F}\right)\right]
$$

5. Estimate heat-capacity ratio. From Fig. 1.5, $C_{p}-C_{v}=4$ at $T_{r}=1.31$ and $P_{r}=1.04$. So the real-gas heat-capacity ratio is

$$
\frac{C_{p}}{C_{v}}=\frac{C_{p}}{C_{p}-\left(C_{p}-C_{v}\right)}=\frac{18.76}{18.76-4}=1.27
$$

Note that the ideal-gas heat-capacity ratio is

$$
\frac{C_{p}^{\circ}}{C_{v}^{\circ}}=\frac{C_{p}^{\circ}}{\left(C_{p}^{\circ}-R\right)}=15.76 /(15.76-1.987)=1.144
$$

Related Calculations. This graphic correlation may be used to estimate the heat-capacity ratio of any nonpolar or slightly polar gas. The accuracy of the correlation is poor for highly polar gases and (as is true for correlations in general) near the critical region. For polar gases, the Lee-Kesler method [27] is suggested.

### 1.10 LIQUID HEAT CAPACITY—GENERALIZED CORRELATION

Estimate the saturated-liquid heat capacity of (a) n-octane and (b) ethyl mercaptan at $27^{\circ} \mathrm{C}\left(80.6^{\circ} \mathrm{F}\right)$ using the Yuan-Stiel corresponding-states correlation [19], given as

$$
C_{\sigma, L}-C_{p}^{\circ}=\left(\Delta C_{\sigma, L}\right)^{(0)}+\omega\left(\Delta C_{\sigma, L}\right)^{(1)}
$$

for nonpolar liquids, or

$$
\begin{aligned}
C_{\sigma, L}-C_{p}^{\circ}= & \left(\Delta C_{\sigma, L}\right)^{(0 p)}+\omega\left(\Delta C_{\sigma, L}\right)^{(1 p)}+X\left(\Delta C_{\sigma, L}\right)^{(2 p)}+X^{2}\left(\Delta C_{\sigma, L}\right)^{(3 p)} \\
& +\omega^{2}\left(\Delta C_{\sigma, L}\right)^{(4 p)}+X \omega\left(\Delta C_{\sigma, L}\right)^{(5 p)}
\end{aligned}
$$

for polar liquids, where $C_{\sigma, L}$ is saturated-liquid heat capacity and $C_{p}^{\circ}$ is ideal-gas heat capacity, both in calories per gram-mole kelvin; $\omega$ is the Pitzer acentric factor; the $\Delta C_{\sigma, L}$ terms are deviation functions for saturated-liquid heat capacity (given in Table 1.4); and $X$ is the Stiel polarity factor (from Table 1.5).

TABLE 1.4 Yuan and Stiel Deviation Functions for Saturated-Liquid Heat Capacity

| Reduced temperature | $\left(\Delta C_{\sigma}\right)^{(0)}$ | $\left(\Delta C_{\sigma}\right)^{(1)}$ | $\left(\Delta C_{\sigma}\right)^{(0 p)}$ | $\left(\Delta C_{\sigma}\right)^{(1 p)}$ | $\left(\Delta C_{\sigma}\right)^{(2 p)}$ | $\left(\Delta C_{\sigma}\right)^{(3 p)} \times 10^{-2}$ | $\left(\Delta C_{\sigma}\right)^{(4 p)}$ | $\left(\Delta C_{\sigma}\right)^{(5 p)}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 0.96 | 14.87 | 37.0 |  |  |  |  |  |  |
| 0.94 | 12.27 | 29.2 | 12.30 | 29.2 | -126 | * | * | * |
| 0.92 | 10.60 | 27.2 | 10.68 | 27.4 | -123 | * | * | * |
| 0.90 | 9.46 | 26.1 | 9.54 | 25.9 | -121 | * | * | * |
| 0.88 | 8.61 | 25.4 | 8.67 | 24.9 | -117.5 | * | * | * |
| 0.86 | 7.93 | 24.8 | 8.00 | 24.2 | -115 | * | * | * |
| 0.84 | 7.45 | 24.2 | 7.60 | 23.5 | -112.5 | * | * | * |
| 0.82 | 7.10 | 23.7 | 7.26 | 23.0 | -110 | * | * | * |
| 0.80 | 6.81 | 23.3 | 7.07 | 22.6 | -108 | * | * | * |
| 0.78 | 6.57 | 22.8 | 6.80 | 22.2 | -107 | * | * | * |
| 0.76 | 6.38 | 22.5 | 6.62 | 21.9 | -106 | * | * | * |
| 0.74 | 6.23 | 22.2 | 6.41 | 22.5 | -105 | -0.69 | -4.22 | -29.5 |
| 0.72 | 6.11 | 21.9 | 6.08 | 23.6 | -107 | 0.15 | -7.20 | -30.0 |
| 0.70 | 6.01 | 21.7 | 6.01 | 24.5 | -110 | 1.31 | -10.9 | -29.1 |
| 0.68 | 5.91 | 21.6 | 5.94 | 25.7 | -113 | 2.36 | -15.2 | -22.8 |
| 0.66 | 5.83 | 21.8 | 5.79 | 27.2 | -118 | 3.06 | -20.0 | -7.94 |
| 0.64 | 5.74 | 22.2 | 5.57 | 29.3 | -124 | 3.24 | -25.1 | 14.8 |
| 0.62 | 5.64 | 22.8 | 5.33 | 31.8 | -132 | 2.87 | -30.5 | 43.0 |
| 0.60 | 5.54 | 23.5 | 5.12 | 34.5 | -141 | 1.94 | -36.3 | 73.1 |
| 0.58 | 5.42 | 24.5 | 4.92 | 37.6 | -151 | 0.505 | -42.5 | 102 |
| 0.56 | 5.30 | 25.6 | 4.69 | 41.1 | -161 | -1.37 | -49.2 | 128 |
| 0.54 | 5.17 | 26.9 | 4.33 | 45.5 | -172 | -3.58 | -56.3 | 149 |
| 0.52 | 5.03 | 28.4 | 3.74 | 50.9 | -184 | -6.02 | -64.0 | 165 |
| 0.50 | 4.88 | 30.0 | 2.87 | 57.5 | -198 | -8.56 | -72.1 | 179 |
| 0.48 | 4.73 | 31.7 | 1.76 | 65.0 | -213 | -11.1 | -80.6 | 192 |
| 0.46 | 4.58 | 33.5 | 0.68 | 72.6 | -229 | -13.3 | -89.4 | 206 |
| 0.44 | 4.42 | 35.4 | 0.19 | 78.5 | -244 | -15.0 | -98.2 | 221 |
| 0.42 | 4.26 | 37.4 |  |  |  |  |  |  |
| 0.40 | 4.08 | 39.4 |  |  |  |  |  |  |

${ }^{*}$ Data not available for $\left(\Delta C_{\sigma}\right)^{(3 p)}$ to $\left(\Delta C_{\sigma}\right)^{(5 p)}$ above $T_{r}=0.74$; assume zero.
Source: R. C. Reid, J. M. Prausnitz, and T. K. Sherwood, Properties of Gases and Liquids, McGraw-Hill, New York, 1977.

TABLE 1.5 Stiel Polarity Factors of Some Polar Materials

| Material | Polarity factor | Material | Polarity factor |
| :--- | :---: | :--- | :---: |
| Methanol | 0.037 | Water | 0.023 |
| Ethanol | 0.0 | Hydrogen chloride | 0.008 |
| $n$-Propanol | -0.057 | Acetone | 0.013 |
| Isopropanol | -0.053 | Methyl fluoride | 0.012 |
| $n$-Butanol | -0.07 | Ethylene oxide | 0.012 |
| Dimethylether | 0.002 | Methyl acetate | 0.005 |
| Methyl chloride | 0.007 | Ethyl mercaptan | 0.004 |
| Ethyl chloride | 0.005 | Diethyl ether | -0.003 |
| Ammonia | 0.013 |  |  |

Source: R. C. Reid, J. M. Prausnitz, and T. K. Sherwood, Properties of Gases and Liquids, McGraw-Hill, New York, 1977.

For $n$-octane, $T_{c}=568.8 \mathrm{~K}, \omega=0.394, X=0$ (nonpolar liquid), and

$$
C_{p}^{\circ}=-1.456+\left(1.842 \times 10^{-1}\right) T-\left(1.002 \times 10^{-4}\right) T^{2}+\left(2.115 \times 10^{-8}\right) T^{3}
$$

where $T$ is in kelvins.
For ethyl mercaptan, $T_{c}=499 \mathrm{~K}, \omega=0.190$, and $X=0.004$ (slightly polar), and

$$
C_{p}^{\circ}=3.564+\left(5.615 \times 10^{-2}\right) T-\left(3.239 \times 10^{-5}\right) T^{2}+\left(7.552 \times 10^{-9}\right) T^{3}
$$

where $T$ is in kelvins.

## Calculation Procedure

1. Estimate the deviation functions. For $n$-octane, $T_{r}=(273+27) / 568.8=0.527$. From Table 1.4, using linear interpolation and the nonpolar terms,

$$
\left(\Delta C_{\sigma, L}\right)^{(0)}=5.08 \quad \text { and } \quad\left(\Delta C_{\sigma, L}\right)^{(1)}=27.9
$$

For ethyl mercaptan, $T_{r}=(273+27) / 499=0.60$. From Table 1.4 , for polar liquids,

$$
\begin{aligned}
& \left(\Delta C_{\sigma, L}\right)^{(0 p)}=5.12 \quad\left(\Delta C_{\sigma, L}\right)^{(1 p)}=34.5 \quad\left(\Delta C_{\sigma, L}\right)^{(2 p)}=-141 \\
& \left(\Delta C_{\sigma, L}\right)^{(3 p)}=0.0194 \quad\left(\Delta C_{\sigma, L}\right)^{(4 p)}=-36.3 \quad \text { and } \quad\left(\Delta C_{\sigma, L}\right)^{(5 p)}=73.1
\end{aligned}
$$

2. Compute ideal-gas heat capacity. For $n$-octane,

$$
\begin{aligned}
C_{p}^{\circ} & =-1.456+\left(1.842 \times 10^{-1}\right)(300)-\left(1.002 \times 10^{-4}\right)\left(300^{2}\right)+\left(2.115 \times 10^{-8}\right)\left(300^{3}\right) \\
& =45.36 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{~mol})(\mathrm{K})
\end{aligned}
$$

And for ethyl mercaptan,

$$
\begin{aligned}
C_{p}^{\circ} & =3.564+\left(5.615 \times 10^{-2}\right)(300)-\left(3.239 \times 10^{-5}\right)\left(300^{2}\right)+\left(7.552 \times 10^{-9}\right)\left(300^{3}\right) \\
& =17.7 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{~mol})(\mathrm{K})
\end{aligned}
$$

3. Compute saturated-liquid heat capacity. For $n$-octane,

$$
C_{\sigma, L}=5.08+(0.394)(27.9)+45.36=61.43 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{~mol})(\mathrm{K})
$$

The experimental value is $60 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})(\mathrm{K})$, so the error is 2.4 percent.
For ethyl mercaptan,

$$
\begin{aligned}
C_{\sigma, L}= & 5.12+(0.19)(34.5)+(0.004)(-141)+\left(0.004^{2}\right)(1.94)\left(10^{-2}\right) \\
& +\left(0.190^{2}\right)(-36.3)+(0.004)(0.19)(73.1)+17.7 \\
= & 27.6 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{~mol})(\mathrm{K})\left[27.6 \mathrm{Btu} /(\mathrm{lb} \cdot \mathrm{~mol})\left({ }^{\circ} \mathrm{F}\right)\right]
\end{aligned}
$$

The experimental value is $28.2 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})(\mathrm{K})$, so the error is 2.1 percent.

### 1.11 ENTHALPY DIFFERENCE FOR IDEAL GAS

Compute the ideal-gas enthalpy change for $p$-xylene between 289 and $811 \mathrm{~K}\left(61\right.$ and $1000^{\circ} \mathrm{F}$ ), assuming that the ideal-gas heat-capacity equation is (with $T$ in kelvins)

$$
C_{p}^{\circ}=-7.388+\left(14.9722 \times 10^{-2}\right) T-\left(0.8774 \times 10^{-4}\right) T^{2}+\left(0.019528 \times 10^{-6}\right) T^{3}
$$

## Calculation Procedure

1. Compute the ideal-gas enthalpy difference. The ideal-gas enthalpy difference $\left(H_{2}^{\circ}-H_{1}^{\circ}\right)$ is obtained by integrating the $C_{p}^{\circ}$ equation between two temperature intervals:

$$
\begin{aligned}
\left(H_{2}^{\circ}-H_{1}^{\circ}\right)= & \int_{T_{1}}^{T_{2}} C_{p}^{\circ} d t \\
= & \int_{T_{1}}^{T_{2}}\left[-7.388+(14.9772)\left(10^{-2}\right) T-(0.8774)\left(10^{-4}\right) T^{2}+(0.019528)\left(10^{-6}\right) T^{3}\right] d T \\
= & (-7.388)(811-289)+\left(14.9772 \times 10^{-2}\right)\left(811^{2}-289^{2}\right) / 2 \\
& -\left(0.8774 \times 10^{-4}\right)\left(811^{3}-289^{3}\right) / 3+\left(0.019528 \times 10^{-6}\right)\left(811^{4}-289^{4}\right) / 4 \\
= & 26,327 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{~mol})[47,400 \mathrm{Btu} /(\mathrm{lb} \cdot \mathrm{~mol})]
\end{aligned}
$$

The literature value is $26,284 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})$.

Related Calculations. Apply this procedure to compute enthalpy difference for any ideal gas. In absence of the ideal-gas heat-capacity equation, estimate $C_{p}^{\circ}$ using the Rihani-Doraiswamy groupcontribution method, Example 1.8.

### 1.12 ESTIMATION OF HEAT OF VAPORIZATION

Estimate the enthalpy of vaporization of acetone at the normal boiling point using the following relations, and compare your results with the experimental value of $7230 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})$.

1. Clapeyron equation and compressibility factor [20]:

$$
\Delta H_{v, b}=\left(R T_{c} \Delta Z_{v} T_{b, r} \ln P_{c}\right) /\left(1-T_{b, r}\right)
$$

TABLE 1.6 Values of $\Delta Z_{v}$ as a Function of Reduced Pressure

| $P_{r}$ | $Z_{v}-Z_{L}$ | $P_{r}$ | $Z_{v}-Z_{L}$ | $P_{r}$ | $Z_{v}-Z_{L}$ |
| :--- | :---: | :---: | :---: | :---: | :---: |
| 0 | 1.0 | 0.25 | 0.769 | 0.80 | 0.382 |
| 0.01 | 0.983 | 0.30 | 0.738 | 0.85 | 0.335 |
| 0.02 | 0.968 | 0.35 | 0.708 | 0.90 | 0.280 |
| 0.03 | 0.954 | 0.40 | 0.677 | 0.92 | 0.256 |
| 0.04 | 0.942 | 0.45 | 0.646 | 0.94 | 0.226 |
| 0.05 | 0.930 | 0.50 | 0.612 | 0.95 | 0.210 |
| 0.06 | 0.919 | 0.55 | 0.578 | 0.96 | 0.192 |
| 0.08 | 0.899 | 0.60 | 0.542 | 0.97 | 0.170 |
| 0.10 | 0.880 | 0.65 | 0.506 | 0.98 | 0.142 |
| 0.15 | 0.838 | 0.70 | 0.467 | 0.99 | 0.106 |
| 0.20 | 0.802 | 0.75 | 0.426 | 1.00 | 0.000 |

2. Chen method [21]:

$$
\Delta H_{v, b}=R T_{c} T_{b, r}\left(\frac{3.978 T_{b, r}-3.938+1.555 \ln P_{c}}{1.07-T_{b, r}}\right)
$$

3. Riedel method [22]:

$$
\Delta H_{v, b}=1.093 R T_{c}\left[T_{b, r} \frac{\left(\ln P_{c}-1\right)}{0.930-T_{b, r}}\right]
$$

4. Pitzer correlation:

$$
\Delta H_{v, b}=R T_{c}\left[7.08\left(1-T_{b, r}\right)^{0.354}+10.95 \omega\left(1-T_{b, r}\right)^{0.456}\right]
$$

where $\Delta H_{v, b}=$ enthalpy of vaporization at the normal boiling point in $\mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})$
$T_{c}=$ critical temperature in kelvins
$P_{c}=$ critical pressure in atmospheres
$\omega=$ Pitzer acentric factor
$R=$ gas constant $=1.987 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})(\mathrm{K})$
$T_{b, r}=T_{b} / T_{c}$, reduced temperature at the normal boiling point $T_{b}$
$\Delta Z_{v}=Z_{v}-Z_{L}$, the difference in the compressibility factor between the saturated vapor and saturated liquid at the normal boiling point, given in Table 1.6.

Also estimate the heat of vaporization of water at $300^{\circ} \mathrm{C}\left(572^{\circ} \mathrm{F}\right)$ by applying the Watson correlation:

$$
\frac{\Delta H_{2}}{\Delta H_{1}}=\left(\frac{1-T_{r, 2}}{1-T_{r, 1}}\right)^{0.38}
$$

where $\Delta H_{1}$ and $\Delta H_{2}$ are the heats of vaporization at reduced temperatures of $T_{r, 1}$ and $T_{r, 2}$, respectively.
Data for acetone are $T_{b}=329.7 \mathrm{~K}, T_{c}=508.7 \mathrm{~K}, P_{c}=46.6 \mathrm{~atm}$, and $\omega=0.309$. Data for water are $T_{b}=373 \mathrm{~K}, T_{c}=647.3 \mathrm{~K}$, and $\Delta H_{v, b}=9708.3 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})$.

## Calculation Procedure

1. Calculate reduced temperature $T_{b, r}$ and reduced pressure $P_{r}$ for the acetone at normal-boilingpoint conditions (1 atm) and obtain $\Delta Z_{v}$. Thus,

$$
T_{b, r}=\frac{329.7}{508.7}=0.648 \quad \text { and } \quad P_{r}=\frac{1}{46.6}=0.0215
$$

From Table 1.6, by extrapolation, $\Delta Z_{v}=0.966$.
2. Compute the heat of vaporization of acetone using the Clapeyron equation. From the preceding equation,

$$
\begin{aligned}
\Delta H_{v, b} & =(1.987)(508.7)(0.966)(0.648)(\ln 46.6) /(1-0.648) \\
& =6905 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{~mol})[12,430 \mathrm{Btu} /(\mathrm{lb} \cdot \mathrm{~mol})]
\end{aligned}
$$

Percent error is $100(7230-6905) / 7230$, or 4.5 percent.
3. Compute the heat of vaporization using the Chen method. Thus,

$$
\begin{aligned}
\Delta H_{v, b} & =(1.987)(508.7)(0.648)\left[\frac{(3.978)(0.648)-(3.938)+(1.555) \ln 46.6}{1.07-0.648}\right] \\
& =7160 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{~mol})[12,890 \mathrm{Btu} / \mathrm{lb} \cdot \mathrm{~mol})]
\end{aligned}
$$

Error is 1.0 percent.
4. Compute the heat of vaporization using the Riedel method. Thus,

$$
\begin{aligned}
\Delta H_{v, b} & =(1.093)(1.987)(508.7)\left\{0.648\left[\frac{\ln (46.6)-1}{0.930-0.648}\right]\right\} \\
& =7214 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{~mol})[12,985 \mathrm{Btu} /(\mathrm{lb} \cdot \mathrm{~mol})]
\end{aligned}
$$

Error is 0.2 percent.
5. Compute the heat of vaporization using the Pitzer correlation. Thus,

$$
\begin{aligned}
\Delta H_{v, b} & =(1.987)(508.7)\left[7.08(1-0.648)^{0.354}+(10.95)(0.309)(1-0.648)^{0.456}\right] \\
& =7069 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{~mol})[12,720 \mathrm{Btu} /(\mathrm{lb} \cdot \mathrm{~mol})]
\end{aligned}
$$

Error is 2.2 percent.
6. Compute the heat of vaporization of the water. Now, $T_{r, 1}=(100+273) / 647.3=0.576$ and $T_{r, 2}=(300+273) / 647.3=0.885$, where the subscript 1 refers to water at its normal boiling point and the subscript 2 refers to water at $300^{\circ} \mathrm{C}$. In addition, $\Delta H_{v, b}\left(=\Delta H_{1}\right)$ is given above as 9708.3 $\mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})$. Then, from the Watson correlation,

$$
\begin{aligned}
\Delta H_{v}\left(\text { at } 300^{\circ} \mathrm{C}\right) & =9708.3\left(\frac{1-0.885}{1-0.576}\right)^{0.38} \\
& =5913 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{~mol})[10,640 \mathrm{Btu} /(\mathrm{lb} \cdot \mathrm{~mol})]
\end{aligned}
$$

The value given in the steam tables is $5949 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})$, so the error is 0.6 percent.
Related Calculations. This illustration shows several techniques for estimating enthalpies of vaporization for pure liquids. The Clapeyron equation is inherently accurate, especially if $\Delta Z_{v}$ is obtained from reliable $P-V-T$ correlations. The other three techniques yield approximately the same error when averaged over many types of fluids and over large temperature ranges. They are quite satisfactory for engineering calculations. A comparison of calculated and experimental results for 89 compounds has shown average errors of 1.8 and 1.7 percent for the Riedel and Chen methods, respectively. For estimating $\Delta H_{v}$ at any other temperature from a single value at a given temperature, use the Watson correlation. Such a value is normally available at some reference temperature.

TABLE 1.7 Correlation Terms for the Lee-Kesler Vapor-Pressure Equation

| $T_{r}$ | $-\ln \left(P_{r}^{*}\right)^{(0)}$ | $-\ln \left(P_{r}^{*}\right)^{(1)}$ | $T_{r}$ | $-\ln \left(P_{r}^{*}\right)^{(0)}$ | $-\ln \left(P_{r}^{*}\right)^{(1)}$ |
| :--- | :---: | :---: | :---: | :---: | :---: |
| 1.00 | 0.000 | 0.000 | 0.60 | 3.568 | 3.992 |
| 0.98 | 0.118 | 0.098 | 0.58 | 3.876 | 4.440 |
| 0.96 | 0.238 | 0.198 | 0.56 | 4.207 | 4.937 |
| 0.94 | 0.362 | 0.303 | 0.54 | 4.564 | 5.487 |
| 0.92 | 0.489 | 0.412 | 0.52 | 4.951 | 6.098 |
| 0.90 | 0.621 | 0.528 | 0.50 | 5.370 | 6.778 |
| 0.88 | 0.757 | 0.650 | 0.48 | 5.826 | 7.537 |
| 0.86 | 0.899 | 0.781 | 0.46 | 6.324 | 8.386 |
| 0.84 | 1.046 | 0.922 | 0.44 | 6.869 | 9.338 |
| 0.82 | 1.200 | 1.073 | 0.42 | 7.470 | 10.410 |
| 0.80 | 1.362 | 1.237 | 0.40 | 8.133 | 11.621 |
| 0.78 | 1.531 | 1.415 | 0.38 | 8.869 | 12.995 |
| 0.76 | 1.708 | 1.608 | 0.36 | 9.691 | 14.560 |
| 0.74 | 1.896 | 1.819 | 0.34 | 10.613 | 16.354 |
| 0.72 | 2.093 | 2.050 | 0.32 | 11.656 | 18.421 |
| 0.70 | 2.303 | 2.303 | 0.30 | 12.843 | 20.820 |
| 0.68 | 2.525 | 2.579 |  |  |  |
| 0.66 | 2.761 | 2.883 |  |  |  |
| 0.64 | 3.012 | 3.218 |  |  |  |
| 0.62 | 3.280 | 3.586 |  |  |  |

Source: R. C. Reid, J. M. Prausnitz, and T. K. Sherwood, Properties of Gases and Liquids, McGraw-Hill, New York, 1977.

### 1.13 PREDICTION OF VAPOR PRESSURE

Estimate the vapor pressure of 1-butene at $100^{\circ} \mathrm{C}\left(212^{\circ} \mathrm{F}\right)$ using the vapor-pressure correlation of Lee and Kesler [23]. Also compute the vapor pressure of ethanol at $50^{\circ} \mathrm{C}\left(122^{\circ} \mathrm{F}\right)$ from the Thek-Stiel generalized correlation [24]. The Lee-Kesler equation is

$$
\left(\ln P_{r}^{*}\right)=\left(\ln P_{r}^{*}\right)^{(0)}+\omega\left(\ln P_{r}^{*}\right)^{(1)}
$$

at constant $T_{r}$, and the Thek-Stiel correlation for polar and hydrogen-bonded molecules is

$$
\begin{aligned}
\ln P_{r}^{*}= & \frac{\Delta H_{v b}}{R T_{c}\left(1-T_{b, r}\right)^{0.375}} \times\left(1.14893-0.11719 T_{r}-0.03174 T_{r}^{2}-\frac{1}{T_{r}}-0.375 \ln T_{r}\right) \\
& +\left[1.042 \alpha_{c}-\frac{0.46284 H_{v b}}{R T_{c}\left(1-T_{b, r}\right)^{0.375}}\right]\left[\frac{\left(T_{r}\right)^{A}-1}{A}+0.040\left(\frac{1}{T_{r}}-1\right)\right]
\end{aligned}
$$

where $P_{r}^{*}=P^{*} / P_{c}$, reduced vapor pressure, $P^{*}=$ vapor pressure at $T_{r}, P_{c}=$ critical pressure, $\omega=$ acentric factor, $T_{r}=T / T_{c}$, reduced temperature, $\left(\ln P_{r}^{*}\right)^{(0)}$ and $\left(\ln P_{r}^{*}\right)^{(1)}$ are correlation functions given in Table 1.7, $\Delta H_{v b}=$ heat of vaporization at normal boiling point $T_{b}, \alpha_{c}=$ a constant obtained from the Thek-Stiel equation from conditions $P^{*}=1$ atm at $T=T_{b}$,

$$
A=\left[5.2691+\frac{2.0753 \Delta H_{v b}}{R T_{c}\left(1-T_{b, r}\right)^{0.375}}-\frac{3.1738 T_{b, r} \ln P_{c}}{1-T_{b, r}}\right]
$$

and $T_{b, r}$ is the reduced normal boiling point.

## Calculation Procedure

1. Obtain critical properties and other necessary basic constants from Reid, Prausnitz, and Sherwood [1]. For 1-butene, $T_{c}=419.6 \mathrm{~K}, P_{c}=39.7 \mathrm{~atm}$, and $\omega=0.187$. For ethanol, $T_{b}=351.5 \mathrm{~K}$, $T_{c}=516.2 \mathrm{~K}, P_{c}=63 \mathrm{~atm}$, and $\Delta H_{v b}=9260 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})$.
2. Obtain correlation terms in the Lee-Kesler equation. From Table 1.7, interpolating linearily at $T_{r}=(273+100) / 419.6=0.889,\left(\ln P_{r}^{*}\right)^{(0)}=-0.698$ and $\left(\ln P_{r}^{*}\right)^{(1)}=-0.595$.
3. Compute the vapor pressure of 1-butene. Using the Lee-Kesler equation, $\left(\ln P_{r}^{*}\right)=-0.698+$ $(0.187)(-0.595)=-0.8093$, so

$$
P_{r}^{*}=0.4452 \quad \text { and } \quad P^{*}=(0.4452)(39.7)=17.67 \mathrm{~atm}(1790 \mathrm{kPa})
$$

The experimental value is 17.7 atm , so the error is only 0.2 percent.
4. Compute the constant $\boldsymbol{\alpha}_{\boldsymbol{c}}$ for ethanol. Now, when $T_{b, r}=351.5 / 516.2=0.681, P^{*}=1 \mathrm{~atm}$. So, in the Thek-Stiel equation, the $A$ term is

$$
5.2691+\left[\frac{(2.0753)(9260)}{(1.987)(516.2)(1-0.681)^{0.375}}-\frac{(3.1738)(0.681)(\ln 63)}{(1-0.681)}\right]=5.956
$$

at those conditions. Substituting into the full Thek-Stiel equation,

$$
\begin{aligned}
\ln \frac{1}{63}= & \frac{9260}{(1.987)(516.2)(1-0.681)^{0.375}} \\
& \times\left[1.14893-(0.11719)(0.681)-(0.03174)(0.681)^{2}-1 / 0.681-(0.375) \ln 0.681\right] \\
& +\left[1.042 \alpha_{c}-\frac{(0.46284)(9260)}{(1.987)(516.2)(1-0.681)^{0.375}}\right] \times\left[\frac{(0.681)^{5.956}-1}{5.956}+(0.040)(1 / 0.681-1)\right]
\end{aligned}
$$

Solving for $\alpha_{c}$, we find it to be 9.078 .
5. Compute the vapor pressure of ethanol. Now, $T_{r}=(273+50) / 516.2=0.626$. Substituting into the Thek-Stiel correlation,

$$
\begin{aligned}
\ln P_{r}^{*}= & \frac{9260}{(1.987)(516.2)(1-0.681)^{0.375}}\left[1.14893-0.11719(0.626)-0.03174(0.626)^{2}\right. \\
& \left.-\frac{1}{0.626}-0.375 \ln 0.626\right]+\left[1.042(9.078)-\frac{(0.46284)(9260)}{(1.987)(516.2)(1-0.681)^{0.375}}\right] \\
& \times\left[\frac{(0.626)^{5.956}-1}{5.956}+0.040\left(\frac{1}{0.626}-1\right)\right] \\
= & -5.37717
\end{aligned}
$$

Therefore, $P_{r}^{*}=0.00462$, so $P^{*}=(0.00462)(63)=0.2911 \mathrm{~atm}(29.5 \mathrm{kPa})$. The experimental value is 0.291 atm , so the error in this case is negligible.

Related Calculations. For nonpolar liquids, use the Lee-Kesler generalized correlation. For polar liquids and those having a tendency to form hydrogen bonds, the Lee-Kesler equation does not give satisfactory results. For predicting vapor pressure of those types of compounds, use the Thek-Stiel correlation. This method, however, requires heat of vaporization at the normal boiling point, besides critical constants. If heat of vaporization at the normal boiling point is not available, estimate using the

Pitzer correlation discussed in Example 1.12. If a heat-of-vaporization value at any other temperature is available, use the Watson correlation (Example 1.12) to obtain the value at the normal boiling point.

The Lee-Kesler and Thek-Stiel equations each can yield vapor pressures whose accuracy is within $\pm 1$ percent. The Antoine equations, based on a correlation with three constants, is less accurate; in some cases, the accuracy is within $\pm 4$ or 5 percent. For an example using the Antoine equation, see Example 3.1.

### 1.14 ENTHALPY ESTIMATION-GENERALIZED METHOD

Calculate (a) enthalpy $H_{V}$ of ethane vapor at $1000 \mathrm{psia}(6900 \mathrm{kPa})$ and $190^{\circ} \mathrm{F}(360 \mathrm{~K})$, (b) enthalpy $H_{L}$ of liquid ethane at $50^{\circ} \mathrm{F}(283 \mathrm{~K})$ and $450 \mathrm{psia}(3100 \mathrm{kPa})$. Use generalized enthalpy departure charts (Figs. 1.6 through 1.9) to estimate enthalpy values, and base the calculations relative to $\mathrm{H}=0$ for saturated liquid ethane at $-200^{\circ} \mathrm{F}$. The basic constants for ethane are molecular weight $\mathrm{MW}=$ 30.07, critical temperature $T_{c}=550^{\circ} \mathrm{R}$, critical pressure $P_{c}=709.8$ psia, and critical compressibility factor $Z_{c}=0.284$. Ideal-gas enthalpy $H^{\circ}$ (relative to saturated liquid ethane at $-200^{\circ} \mathrm{F}$ ) at $190^{\circ} \mathrm{F}=$ $383 \mathrm{Btu} / \mathrm{lb}$, and at $50^{\circ} \mathrm{F}=318 \mathrm{Btu} / \mathrm{lb}$.

## Calculation Procedure

## 1. Compute reduced temperature $T_{r}$ and reduced pressure $P_{r}$

a. For the vapor, $T_{r}=(190+459.7) / 550=1.18$, and $P_{r}=1000 / 709.8=1.41$.
b. For the liquid, $T_{r}=(50+459.7) / 550=0.927$, and $P_{r}=450 / 709.8=0.634$.

## 2. Obtain the enthalpy departure function

a. From Fig. 1.9, for $Z_{c}=0.29, T_{r}=1.18, P_{r}=1.41,\left(H^{\circ}-H\right) / T_{c}=2.73 \mathrm{Btu} /(\mathrm{lb} \cdot \mathrm{mol})\left({ }^{\circ} \mathrm{R}\right)$; and from Fig. 1.8, for $Z_{c}=0.27, T_{r}=1.18, P_{r}=1.41,\left(H^{\circ}-H\right) / T_{c}=2.80 \mathrm{Btu} /(\mathrm{lb} \cdot \mathrm{mol})\left({ }^{\circ} \mathrm{R}\right)$. Interpolating linearily for $Z_{c}=0.284,\left(H^{\circ}-H\right) / T_{c}=2.75$.
b. From Fig. 1.9, for $Z_{c}=0.29, P_{r}=0.634$, and $T_{r}=0.927$, in the liquid region, $\left(H^{\circ}-H\right) / T_{c}=$ $7.83 \mathrm{Btu} /(\mathrm{lb} \cdot \mathrm{mol})\left({ }^{\circ} \mathrm{R}\right)$; and from Fig. 1.8, for $Z_{c}=0.27, P_{r}=0.634$, and $T_{r}=0.927$, in the liquid region, $\left(H^{\circ}-H\right) / T_{c}=9.4 \mathrm{Btu} /(\mathrm{lb} \cdot \mathrm{mol})\left({ }^{\circ} \mathrm{R}\right)$. Interpolating for $Z_{c}=0.284,\left(H^{\circ}-H\right) / T_{c}=$ 8.3.

## 3. Compute enthalpy of vapor and liquid

a. Enthalpy of ethane vapor at $190^{\circ} \mathrm{F}$ and 1000 psia :

$$
\begin{aligned}
H_{v} & =H_{190^{\circ} \mathrm{F}}^{\circ}-\left(\frac{H^{\circ}-H}{T_{c}}\right)\left(\frac{T_{c}}{\mathrm{MW}}\right)=383-(2.75)(550) /(30.07) \\
& =332.7 \mathrm{Btu} / \mathrm{lb}(773,800 \mathrm{~J} / \mathrm{kg})
\end{aligned}
$$

b. Enthalpy of ethane liquid at $50^{\circ} \mathrm{F}$ and 450 psia :

$$
\begin{aligned}
H_{L} & =H_{50^{\circ} \mathrm{F}}^{\circ}-\left(\frac{H^{\circ}-H}{T_{c}}\right)\left(\frac{T_{c}}{\mathrm{MW}}\right)=318-(8.3)(550) /(30.07) \\
& =166 \mathrm{Btu} / \mathrm{lb}(386,100 \mathrm{~J} / \mathrm{kg})
\end{aligned}
$$



FIGURE 1.6 Enthalpy departure from ideal-gas state; $Z_{c}=0.23$. (Yen and Alexander-AICHE Journal 11:334, 1965.)

Related Calculations. This procedure may be used to estimate the enthalpy of any liquid or vapor for nonpolar or slightly polar compounds. Interpolation is required if $Z_{c}$ values lie between 0.23 , $0.25,0.27$, and 0.29 . However, extrapolation to $Z_{c}$ values less than 0.23 or higher than 0.29 should not be made, because serious errors may result. When estimating enthalpy departures for mixtures, estimate mixture pseudocritical properties by taking mole-fraction-weighted averages. Do not use this correlation for gases having a low critical temperature, such as hydrogen, helium, or neon.


FIGURE 1.7 Enthalpy departure from ideal-gas state; $Z_{c}=0.25$. (Yen and Alexander-AICHE Journal 11:334, 1965.)

### 1.15 ENTROPY INVOLVING A PHASE CHANGE

Calculate the molar entropies of fusion and vaporization for benzene. Having a molecular weight of 78.1 , benzene melts at $5.5^{\circ} \mathrm{C}$ with a heat of fusion of $2350 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})$. Its normal boiling point is $80.1^{\circ} \mathrm{C}$, and its heat of vaporization at that temperature is $94.1 \mathrm{cal} / \mathrm{g}$.

## Calculation Procedure

1. Calculate the entropy of fusion $\Delta S_{\text {fusion }}$. By definition, $\Delta S_{\text {fusion }}=\Delta H_{\text {fusion }} / T_{\text {fusion }}$, where the numerator is the heat of fusion and the denominator is the melting point in absolute temperature.


FIGURE 1.8 Enthalpy departure from ideal-gas state; $Z_{c}=0.27$. (Yen and Alexander-AICHE Journal 11:334, 1965.)

Thus

$$
\Delta S_{\text {fusion }}=\frac{2350}{(5.5+273)}=8.44 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{~mol})(\mathrm{K})\left[8.44 \mathrm{Btu} /(\mathrm{lb} \cdot \mathrm{~mol})\left({ }^{\circ} \mathrm{F}\right)\right]
$$

2. Calculate the entropy of vaporization $\boldsymbol{\Delta} \boldsymbol{S}_{\text {vap. }}$. By definition, $\Delta S_{\text {vap }}=\Delta H_{\text {vap }} / T_{\text {vap }}$, where the numerator is the heat of vaporization and the denominator is the absolute temperature at which the vaporization takes place. Since the heat of vaporization is given on a weight basis, it must be multiplied by the molecular weight to obtain the final result on a molar basis. Thus

$$
\Delta S_{\text {vap }}=\frac{(94.1)(78.1)}{(80.1+273)}=20.81 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{~mol})(\mathrm{K})\left[20.81 \mathrm{Btu} /(\mathrm{lb} \cdot \mathrm{~mol})\left({ }^{\circ} \mathrm{F}\right)\right]
$$

Related Calculations. This procedure can be used to obtain the entropy of phase change for any compound. If heat-of-vaporization data are not available, the molar entropy of vaporization for nonpolar liquids can be estimated via an empirical equation of Kistyakowsky:

$$
\Delta S_{\text {vap }}=8.75+4.571 \log T_{b}
$$

where $T_{b}$ is the normal boiling point in kelvins and the answer is in calories per gram-mole per kelvin. For benzene, the calculated value is 20.4 , which is in close agreement with the value found in step 2.

### 1.16 ABSOLUTE ENTROPY FROM HEAT CAPACITIES

Calculate the absolute entropy of liquid $n$-hexanol at $20^{\circ} \mathrm{C}\left(68^{\circ} \mathrm{F}\right)$ and $1 \mathrm{~atm}(101.3 \mathrm{kPa})$ from these heat-capacity data:

| Temperature, K | Phase | Heat capacity, <br> $\mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})(\mathrm{K})$ |
| :---: | :---: | :---: |
| 18.3 | Crystal | 1.695 |
| 27.1 | Crystal | 3.819 |
| 49.9 | Crystal | 8.670 |
| 76.5 | Crystal | 15.80 |
| 136.8 | Crystal | 24.71 |
| 180.9 | Crystal | 29.77 |
| 229.6 | Liquid | 46.75 |
| 260.7 | Liquid | 50.00 |
| 290.0 | Liquid | 55.56 |

The melting point of $n$-hexanol is $-47.2^{\circ} \mathrm{C}(225.8 \mathrm{~K})$, and its enthalpy of fusion is $3676 \mathrm{cal} /$ ( $\mathrm{g} \cdot \mathrm{mol}$ ). The heat capacity of crystalline $n$-hexanol $\left(C_{p}\right)_{\text {crystal }}$ at temperatures below 18.3 K may be estimated using the Debye-Einstein equation:

$$
\left(C_{p}\right)_{\text {crystal }}=a T^{3}
$$

where $a$ is an empirical constant and $T$ is the temperature in kelvins. The absolute entropy may be obtained from

$$
\begin{equation*}
S_{\mathrm{liq}, 20^{\circ} \mathrm{C}}^{\circ}=\int_{0}^{18.3}\left(C_{p} / T\right) d T+\int_{18.3}^{225.8}\left(C_{p} / T\right) d T+\Delta H_{\text {fusion }} / 225.8+\int_{225.8}^{(273+20)}\left(C_{p} / T\right) d T \tag{1.1}
\end{equation*}
$$

(A)
(B)
(C)
(D)
where $S_{\text {liq, } 20^{\circ} \mathrm{C}}^{\circ}=$ absolute entropy of liquid at $20^{\circ} \mathrm{C}(293 \mathrm{~K})$
$(\mathbf{A})=$ absolute entropy of crystalline $n$-hexanol at 18.3 K , from the Debye-Einstein equation
$(\mathbf{B})=$ entropy change between 18.3 K and fusion temperature, 225.8 K
$(\mathbf{C})=$ entropy change due to phase transformation (melting)
$(\mathbf{D})=$ entropy change of liquid $n$-hexanol from melting point to the desired temperature (293 K)

## Calculation Procedure

1. Estimate absolute entropy of crystalline n-hexanol. Since no experimental data are available below 18.3 K , estimate the entropy change below this temperature using the Debye-Einstein equation. Use the crystal entropy value of $1.695 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})\left({ }^{\circ} \mathrm{K}\right)$ at 18.3 K to evaluate the coefficient $a$. Hence $a=1.695 / 18.3^{3}=0.2766 \times 10^{-3}$. The " $\mathbf{A}$ " term in Eq. 1.1 therefore is

$$
\int_{0}^{18.3}\left[\left(0.2766 \times 10^{-3}\right) T^{3} / T\right] d T=\left(0.2766 \times 10^{-3}\right) 18.3^{3} / 3=0.565 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{~mol})(\mathrm{K})
$$

2. Compute entropy change between 18.3 K and fusion temperature. Plot the given experimental data on the crystal heat capacity versus temperature in kelvins and evaluate the integral (the "B" term


FIGURE 1.9 Enthalpy departure from ideal-gas state; $Z_{c}=0.29$. (Garcia-Rangel and Yen-Paper presented at 159th National Meeting of American Chemical Society, Houston, Tex., 1970.)
in Eq. 1.1) graphically. See Fig. 1.10. Thus,

$$
\int_{18.3}^{225.8}\left(C_{p} / T\right) d T=38.0 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{~mol})(\mathrm{K})
$$

3. Compute the entropy change due to phase transformation. In this case,

$$
\Delta H_{\text {fusion }} / 225.8=3676 / 225.8=16.28 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{~mol})(\mathrm{K})
$$

This is the "C" term in Eq. 1.1.


FIGURE 1.10 Calculation of absolute entropy from heat-capacity data (Example 1.16).
4. Compute the entropy change between 225.8 K and 293 K . Plot the given experimental data on the liquid heat capacity versus temperature in kelvins and evaluate the integral (the "D" term in Eq. 1.1) graphically. See Fig. 1.10. Thus,

$$
\int_{225.8}^{293}\left(C_{p} / T\right) d T=13.7 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{~mol})(\mathrm{K})
$$

5. Calculate the absolute entropy of liquid n-hexanol. The entropy value is obtained from the summation of the four terms; i.e., $S_{\text {liq }}^{\circ}, 20^{\circ} \mathrm{C}=0.565+38.0+16.28+13.7=68.5 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})(\mathrm{K})$ [68.5 Btu/(lb $\left.\cdot \mathrm{mol})\left({ }^{\circ} \mathrm{F}\right)\right]$.

Related Calculations. This general procedure may be used to calculate entropy values from heatcapacity data. However, in many situations involving practical computations, the entropy changes rather than absolute values are required. In such situations, the "A" term in Eq. 1.1 may not be needed. Entropy changes associated with phase changes, such as melting and vaporization, can be evaluated from the $\Delta H / T$ term (see Example 1.15).

### 1.17 EXPANSION UNDER ISENTROPIC CONDITIONS

Calculate the work of isentropic expansion when $1000 \mathrm{lb} \cdot \mathrm{mol} / \mathrm{h}$ of ethylene gas at 1500 psig $(10,450 \mathrm{kPa})$ and $104^{\circ} \mathrm{F}(313 \mathrm{~K})$ is expanded in a turbine to a discharge pressure of $150 \mathrm{psig}(1135 \mathrm{kPa})$. The ideal-gas heat capacity of ethylene is

$$
C_{p}^{\circ}=0.944+\left(3.735 \times 10^{-2}\right) T-\left(1.993 \times 10^{-5}\right) T^{2}
$$

where $C_{p}^{\circ}$ is in British thermal units per pound-mole per degree Rankine, and $T$ is temperature in degrees Rankine. Critical temperature $T_{c}$ is $282.4 \mathrm{~K}\left(508.3^{\circ} \mathrm{R}\right)$, critical pressure $P_{c}$ is 49.7 atm , and critical compressibility factor $Z_{c}$ is 0.276 .

## Calculation Procedure

1. Estimate degree of liquefaction, ifany. Since the expansion will result in cooling, the possibility of liquefaction must be considered. If it does occur, the final temperature will be the saturation temperature $T_{\text {sat }}$ corresponding to 150 psig . On the assumption that liquefaction has occurred from the expansion, the reduced saturation temperature $T_{r s}$ at the reduced pressure $P_{r}$ of $(150+14.7) /(49.7)(14.7)$, or 0.23 , is 0.81 from Fig. 1.1. Therefore, $T_{\text {sat }}=(0.81)(508.3)$ or $412^{\circ}$ R. Use the following equation to estimate the mole fraction of ethylene liquefied:

$$
\Delta S=0=\left(S_{1}^{\circ}-S_{1}\right)+\int_{T_{1}}^{T_{\text {sat }}}\left(C_{p}^{\circ} / T\right) d T-R \ln \left(P_{2} / P_{1}\right)-\left(S_{2}^{\circ}-S_{2}\right)_{S G}-x \Delta S_{\text {vap }}
$$

where $\left(S_{1}^{\circ}-S_{1}\right)$ and $\left(S_{2}^{\circ}-S_{2}\right)_{S G}$ are the entropy departure functions for gas at inlet conditions and saturation conditions, respectively; $\Delta S_{\text {vap }}$ is the entropy of vaporization at the saturation temperature; $x$ equals moles of ethylene liquefied per mole of ethylene entering the turbine; and $P_{1}$ and $P_{2}$ are the inlet and exhaust pressures. Obtain entropy departure functions from Fig. 1.11 at inlet and exhaust conditions. Thus, at inlet conditions, $T_{r 1}=(104+460) / 508.3=1.11$, and $P_{r 1}=(1500+14.7) /(14.7)(49.7)=2.07$, so $\left(S_{1}^{\circ}-S_{1}\right)=5.0 \mathrm{Btu} /(\mathrm{lb} \cdot \mathrm{mol})\left({ }^{\circ} \mathrm{R}\right)$. At outlet conditions, $T_{r 2}=0.81$, and $P_{r 2}=0.23$, so $\left(S_{2}^{\circ}-S_{2}\right)_{S G}=1.0 \mathrm{Btu} /(\mathrm{lb} \cdot \mathrm{mol})\left({ }^{\circ} \mathrm{R}\right)$ and $\left(S_{2}^{\circ}-S_{2}\right)_{S L}=13.7$ $\mathrm{Btu} /(\mathrm{lb} \cdot \mathrm{mol})\left({ }^{\circ} \mathrm{R}\right)$. The difference between these last two values is the entropy of vaporization at the saturation temperature $S_{\text {vap }}$.

Substituting in the entropy equation, $\Delta S=0=5.0+0.944 \ln (412 / 564)+\left(3.735 \times 10^{-2}\right)$ $(412-564)-(1 / 2)\left(1.993 \times 10^{-5}\right)\left(412^{2}-564^{2}\right)-1.987 \ln (164.7 / 1514.7)-1.0-x(13.7-1.0)$. Upon solving, $x=0.31$. Since the value of $x$ is between 0 and 1 , the assumption that liquefaction occurs is valid.
2. Compute the work of isentropic expansion. The work of isentropic expansion is obtained from enthalpy balance equation:

$$
\begin{aligned}
\text { Work } & =-\Delta H \\
& =-\left\{T_{c}\left[\left(H_{1}^{\circ}-H_{1}\right) / T_{c}\right]+\int_{T_{1}}^{T_{\text {sat }}} C_{p}^{\circ} d T-T_{c}\left[\left(H_{2}^{\circ}-H_{2}\right)_{S G} / T_{c}\right]-x \Delta H_{\text {vap }}\right\}
\end{aligned}
$$

where $\left(H_{1}^{\circ}-H_{1}\right) / T_{c}$ and $\left(H_{2}^{\circ}-H_{2}\right)_{S G} / T_{c}$ are enthalpy departure functions for gas at inlet conditions and saturation conditions, respectively; and $\Delta H_{\text {vap }}$ is enthalpy of vaporization at the saturation temperature $\left(=T \Delta S_{\text {vap }}\right)$.

The enthalpy departure functions, obtained as in Example 1.14, are

$$
\begin{aligned}
\left(H_{1}^{\circ}-H_{1}\right) / T_{c} & =6.1 \mathrm{Btu} /(\mathrm{lb} \cdot \mathrm{~mol})\left({ }^{\circ} \mathrm{R}\right) \\
\left(H_{2}^{\circ}-H_{2}\right)_{S G} / T_{c} & =0.9 \mathrm{Btu} /(\mathrm{lb} \cdot \mathrm{~mol})\left({ }^{\circ} \mathrm{R}\right)
\end{aligned}
$$



FIGURE 1.11 Entropy departure of gases and liquids; $Z_{c}=0.27$. (Hougen, Watson, Ragatz-Chemical Process Principles, Part II, Wiley, 1959.)

Substituting these in the enthalpy balance equation,

$$
\begin{aligned}
\text { Work }= & -\Delta H \\
= & -\left[(508.3)(6.1)+(412-564)(0.944)+(1 / 2)(3.735)\left(10^{-2}\right)\left(412^{2}-564^{2}\right)\right. \\
& \left.-(1 / 3)(1.993)\left(10^{-5}\right)\left(412^{3}-564^{3}\right)-(508.3)(0.9)-(0.31)(412)(13.7-1.0)\right] \\
= & 1165.4 \mathrm{Btu} /(\mathrm{lb} \cdot \mathrm{~mol})
\end{aligned}
$$

The power from the turbine equals $[1165.4 \mathrm{Btu} /(\mathrm{lb} \cdot \mathrm{mol})](1000 \mathrm{lb} \cdot \mathrm{mol} / \mathrm{h})(0.000393 \mathrm{hp} \cdot \mathrm{h} / \mathrm{Btu})=$ $458 \mathrm{hp}(342 \mathrm{~kW})$.

Related Calculations. When specific thermodynamic charts, namely, enthalpy-temperature, entropy-temperature, and enthalpy-entropy, are not available for a particular system, use the generalized enthalpy and entropy charts to perform expander-compressor calculations, as shown in this example.

### 1.18 CALCULATION OF FUGACITIES

Calculate fugacity of (a) methane gas at $50^{\circ} \mathrm{C}\left(122^{\circ} \mathrm{F}\right)$ and $60 \mathrm{~atm}(6080 \mathrm{kPa})$, (b) benzene vapor at $400^{\circ} \mathrm{C}\left(752^{\circ} \mathrm{F}\right)$ and $75 \mathrm{~atm}(7600 \mathrm{kPa})$, (c) liquid benzene at $428^{\circ} \mathrm{F}(493 \mathrm{~K})$ and $2000 \mathrm{psia}(13,800 \mathrm{kPa})$, and (d) each component in a mixture of $20 \%$ methane, $40 \%$ ethane, and $40 \%$ propane at $100^{\circ} \mathrm{F}(310 \mathrm{~K})$ and $300 \mathrm{psia}(2070 \mathrm{kPa})$ assuming ideal-mixture behavior. The experimental pressure-volume data for benzene vapor at $400^{\circ} \mathrm{C}\left(752^{\circ} \mathrm{F}\right)$ from very low pressures up to about 75 atm are represented by

$$
Z=\frac{P V}{R T}=1-0.0046 P
$$

where $Z$ is the compressibility factor and $P$ is the pressure in atmospheres.

## Calculation Procedure

1. Obtain the critical-property data. From any standard reference, the critical-property data are

| Compound | $T_{c}, \mathrm{~K}$ | $P_{c}$, atm | $P_{c}, \mathrm{kPa}$ | $Z_{c}$ |
| :--- | :---: | :---: | :---: | :---: |
| Benzene | 562.6 | 48.6 | 4924 | 0.274 |
| Methane | 190.7 | 45.8 | 4641 | 0.290 |
| Ethane | 305.4 | 48.2 | 4884 | 0.285 |
| Propane | 369.9 | 42.0 | 4256 | 0.277 |

2. Calculate the fugacity of the methane gas. Now, reduced temperature $T_{r}=T / T_{c}=(50+$ $273) / 190.7=1.69$, and reduced pressure $P_{r}=P / P_{c}=60 / 45.8=1.31$. From the generalized fugacity-coefficient chart (Fig. 1.12), the fugacity coefficient $f / P$ at the reduced parameters is 0.94 . (Ignore the fact that $Z_{c}$ differs slightly from the standard value of 0.27 ). Therefore, the fugacity $f=(0.94)(60)=56.4 \mathrm{~atm}(5713 \mathrm{kPa})$.


FIGURE 1.12 Fugacity coefficients of gases and liquids; $Z_{c}=0.27$. (Hougen, Watson, Ragatz-Chemical Process Principles, Part II, Wiley, 1959.)
3. Calculate the fugacity of the benzene vapor using the P-V-T relationship given in the statement of the problem. Start with the equation

$$
d \ln (f / P)_{T}=[(Z-1) d \ln P]_{T}
$$

Upon substituting the given $P-V-T$ relationship,

$$
d \ln (f / P)=(1-0.0046 P)(d \ln P)-d \ln P=-0.0046 P(d \ln P)
$$

Since $d P / P=d \ln P, d \ln (f / P)=-0.0046 d P$. Upon integration,

$$
\ln \left(f_{2} / P_{2}\right)-\ln \left(f_{1} / P_{1}\right)=-0.0046\left(P_{2}-P_{1}\right)
$$

From the definition of fugacity, $f / P$ approaches 1.0 as $P$ approaches 0 ; therefore, $\ln \left(f_{1} / P_{1}\right)$ approaches $\ln 1$ or 0 as $P_{1}$ approaches 0 . Hence $\ln \left(f_{2} / P_{2}\right)=-0.0046 P_{2}$, and $f_{2}=P_{2} \exp \left(-0.0046 P_{2}\right)$. So, when $P_{2}=75 \mathrm{~atm}$, fugacity $f=75 \exp [(-0.0046)(75)]=53.1 \mathrm{~atm}(5380 \mathrm{kPa})$.
4. Calculate the fugacity of the benzene vapor from the generalized correlation. Now $T_{r}=$ $(400+273) / 562.6=1.20$, and $P_{r}=75 / 48.6=1.54$. Ignoring the slight difference in $Z_{c}$ from Fig. 1.12, $f / P=0.78$. So fugacity $f=(0.78)(75)=58.5 \mathrm{~atm}(5926 \mathrm{kPa})$.
5. Calculate the fugacity of the liquid benzene from the generalized correlation. Now $T_{r}=$ $(428+460) /[(562.6)(1.8)]=0.88$, and $P_{r}=2000 /[(14.69)(48.6)]=2.80$. From Fig. $1.12, f / P=$ 0.2 . So fugacity $f=(0.2)(2000)=400 \mathrm{psia}(2760 \mathrm{kPa})$.
6. Calculate the fugacity of each component in the mixture. The calculations for this step can be set out as follows:

|  | Methane | Ethane | Propane |
| :--- | :---: | :---: | :---: |
| Mole fraction, $Y_{i}$ | 0.2 | 0.4 | 0.4 |
| Reduced temperature, $T_{r}=T / T_{c}$ | 1.63 | 1.02 | 0.84 |
| Reduced pressure, $P_{r}=P / P_{c}$ | 0.45 | 0.42 | 0.49 |
| Fugacity coefficient, $f_{i}^{\circ} / P$ (from Fig. 1.12) | 0.98 | 0.89 | 0.56 |
| Fugacity of pure component, |  |  |  |
| $\quad f_{i}^{\circ}=\left(f_{i}^{\circ} / P\right)(300)$, psia (kPa) | $294(2027)$ | $267(1841)$ | $168(1158)$ |
| Fugacity of component in the mixture, |  |  |  |
| $\quad f_{i}=Y_{i} f_{i}^{\circ}$, (ideal mixture), psia (kPa) | $58.8(405)$ | $106.8(736)$ | $67.2(463)$ |

Related Calculations. If experimental $P-V-T$ data are available, either as an analytical expression or as tabular values, the fugacity coefficient may be calculated by integrating the data (numerically or otherwise) as shown in step 3 above. However, if such data are not available, use the generalized fugacity coefficient chart to estimate fugacity values. Refer to Hougen, Watson, and Ragatz [4] for deviation-correction terms for values of $Z_{c}$ above and below the standard value of 0.27 .

The generalized-correlation method used in this example is fast and adequate for calculations requiring typical engineering accuracy. Fugacities can also be calculated by thermodynamically rigorous methods based on equations of state. Although these are cumbersome for hand calculation, they are commonly used for estimating vapor-phase nonidealities and making phase-equilibrium calculations. (Examples are given in Section 3, on phase equilibrium; in particular, see Examples 3.2 and 3.3.)

In the present example involving a mixture (part d), ideal behavior was assumed. For handling nonideal gaseous mixtures, volumetric data are required, preferably in the form of an equation of state at the temperature under consideration and as a function of composition and density, from zero density (lower integration limit) to the density of interest. These computations often require trial-and-error solutions and consequently are tedious for hand calculation.

TABLE 1.8 Vapor-Liquid Equilibrium Data for Benzene(1)/ $n$-Heptane(2) System at $80^{\circ} \mathrm{C}$

| Mole fraction of benzene <br> in liquid phase, $x_{1}$ | 0.000 | 0.0861 | 0.2004 | 0.3842 | 0.5824 | 0.7842 | 0.8972 | 1.000 |
| :--- | ---: | ---: | ---: | ---: | ---: | ---: | ---: | ---: |
| Mole fraction of benzene | 0.000 | 0.1729 | 0.3473 | 0.5464 | 0.7009 | 0.8384 | 0.9149 | 1.000 |
| $\quad$in vapor phase, $y_{1}$ |  |  |  |  |  |  |  |  |
| Total pressure, $P$ | 427.8 | 476.25 | 534.38 | 613.53 | 679.74 | 729.77 | 748.46 | 757.60 |
| $\quad$ mmHg: | 57.0 | 63.49 | 71.24 | 81.80 | 90.62 | 97.29 | 99.79 | 101.01 |
| $\mathrm{kPa}:$ |  |  |  |  |  |  |  |  |

### 1.19 ACTIVITY COEFFICIENTS FROM THE SCATCHARD-HILDEBRAND EQUATION

Experimental vapor-liquid-equilibrium data for benzene(1)/n-heptane(2) system at $80^{\circ} \mathrm{C}\left(176^{\circ} \mathrm{F}\right)$ are given in Table 1.8. Calculate the vapor compositions in equilibrium with the corresponding liquid compositions, using the Scatchard-Hildebrand regular-solution model for the liquid-phase activity coefficient, and compare the calculated results with the experimentally determined composition. Ignore the nonideality in the vapor phase. Also calculate the solubility parameters for benzene and $n$-heptane using heat-of-vaporization data.

The following data are available on the two components:

| Compound | Vapor pressure at $80^{\circ} \mathrm{C}$, mmHg | Normal boiling point, ${ }^{\circ} \mathrm{C}$ | Heat of vaporization at normal boiling point, $\mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})$ | Solubility parameter, $\left(\mathrm{cal} / \mathrm{cm}^{3}\right)^{1 / 2}$ | $\begin{gathered} \text { Liquid molar } \\ \text { volume at } 25^{\circ} \mathrm{C}, \\ {\left[\mathrm{~cm}^{3} /(\mathrm{g} \cdot \mathrm{~mol})\right]} \end{gathered}$ | Critical temperature $T_{c}, \mathrm{~K}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Benzene | 757.6 | 80.3 | 7352 | 9.16 | 89.4 | 562.1 |
| $n$-heptane | 427.8 | 98.6 | 7576 | 7.43 | 147.5 | 540.2 |

The Scatchard-Hildebrand regular-solution model expresses the liquid activity coefficients $\gamma_{i}$ in a binary mixture as

$$
\ln \gamma_{1}^{L}=\frac{V_{1}^{L} \phi_{2}^{2}}{R T}\left(\delta_{1}-\delta_{2}\right)^{2}
$$

and

$$
\ln \gamma_{2}^{L}=\frac{V_{2}^{L} \phi_{1}^{2}}{R T}\left(\delta_{1}-\delta_{2}\right)^{2}
$$

and the activity coefficient of liquid component $i$ in a multicomponent mixture as

$$
\ln \gamma_{i}^{L}=\frac{V_{i}^{L}}{R T}\left(\delta_{i}-\bar{\delta}\right)^{2}
$$

where $V_{i}^{L}=$ liquid molar volume of component $i$ at $25^{\circ} \mathrm{C}$
$R=$ gas constant
$T=$ system temperature
$\phi_{i}=$ molar volume fraction of component $i$ at $25^{\circ} \mathrm{C}=\left(x_{i} V_{i}^{L}\right) /\left(\Sigma x_{i} V_{i}^{L}\right)$
$\delta_{i}=$ solubility parameter of component $i$
$\bar{\delta}=$ a molar volume fraction average of $\delta_{i}=\Sigma \phi_{i} \delta_{i}$

The solubility parameter is defined as

$$
\delta_{i}=\left(\frac{\Delta H_{i}^{V}-298.15 R}{V_{i}^{L}}\right)^{1 / 2}
$$

where $\Delta H_{i}^{V}=$ heat of vaporization of component $i$ from saturated liquid to the ideal-gas state at $25^{\circ} \mathrm{C}, \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})$
$R=$ gas constant, $1.987 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})(\mathrm{K})$
$V_{i}^{L}=$ liquid molar volume of component $i$ at $25^{\circ} \mathrm{C}, \mathrm{cm}^{3} /(\mathrm{g} \cdot \mathrm{mol})$

## Calculation Procedure

1. Compute the liquid-phase activity coefficients. Using the given values of liquid molar volumes and solubility parameters, the activity coefficients are calculated for each of the eight liquid compositions in Table 1.8. For instance, when $x_{1}=0.0861$ and $x_{2}=1-x_{1}=0.914$, then $\phi_{1}=$ $(0.0861)(89.4) /[(0.0861)(89.4)+(0.914)(147.5)]=0.0540$ and $\phi_{2}=1-\phi_{1}=0.9460$. Therefore,

$$
\ln \gamma_{1}=\frac{(89.4)(0.9460)^{2}}{(1.987)(273+80)}(9.16-7.43)^{2}=0.341
$$

so $\gamma_{1}=1.407$, and

$$
\ln \gamma_{2}=\frac{(147.5)(0.054)^{2}}{(1.987)(273+80)}(9.16-7.43)^{2}=0.002
$$

so $\gamma_{2}=1.002$.
The activity coefficients for other liquid compositions are calculated in a similar fashion and are given in Table 1.9.
2. Compute the vapor-phase mole fractions. Assuming ideal vapor-phase behavior, $y_{1}=$ $x_{1} P_{1}^{\circ} \gamma_{1} / P$ and $y_{2}=x_{2} P_{2}^{\circ} \gamma_{2} / P=1-y_{1}$, where $P_{i}^{\circ}$ is the vapor pressure of component $i$. From Table 1.8, when $x_{1}=0.0861, P=476.25 \mathrm{mmHg}$. Therefore, the calculated vapor-phase mole fraction of benzene is $y_{1}=(0.0861)(757.6)(1.407) / 476.25=0.1927$. The mole fraction of $n$-heptane is ( $1-0.1927$ ) or 0.8073 . The vapor compositions in equilibrium with other liquid compositions are calculated in a similar fashion and are tabulated in Table 1.9. The last column in the table shows the deviation of the calculated composition from that determined experimentally.
3. Estimate heats of vaporization at $25^{\circ}$ C. Use the Watson equation:

$$
\Delta H_{\mathrm{vap}, 25^{\circ} \mathrm{C}}=\Delta H_{\mathrm{vap}, T N B P}\left[\frac{1-(273+25) / T_{c}}{1-T_{N B P} / T_{c}}\right]^{0.38}
$$

where $\Delta H_{\text {vap }}$ is heat of vaporization, and $T_{N B P}$ is normal boiling-point temperature.
Thus, for benzene,

$$
\Delta H_{\text {vap }, 25^{\circ} \mathrm{C}}=7353\left[\frac{1-298 / 562.1}{1-(273+80.3) / 562.1}\right]^{0.38}=8039 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{~mol})
$$

And for $n$-heptane,

$$
\Delta H_{\text {vap }, 25^{\circ} \mathrm{C}}=7576\left[\frac{1-298 / 540.2}{1-(273+98.6) / 540.2}\right]^{0.38}=8694 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{~mol})
$$

TABLE 1.9 Experimental and Calculated Vapor-Liquid Equilibrium Data for the Benzene(1) $/ n$-Heptane(2) System at $80^{\circ} \mathrm{C}$

|  |  |  |  |  | Percent deviation |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | $y_{1}^{\exp }$ | $\gamma_{1}$ | $\gamma_{2}$ | $y_{1}^{\text {calc }}$ | $\left(y_{1}^{\text {calc }}-y_{1}^{\exp }\right)(100) / y_{1}^{\exp }$ |
| 0.0000 | 0.0000 | 1.4644 | 1.0000 | 0.0000 | - |
| 0.0861 | 0.1729 | 1.4070 | 1.002 | 0.1927 | 11.5 |
| 0.2004 | 0.3473 | 1.3330 | 1.0110 | 0.3787 | 9.0 |
| 0.3842 | 0.5464 | 1.2224 | 1.0485 | 0.5799 | 6.1 |
| 0.5824 | 0.7009 | 1.1185 | 1.1412 | 0.7260 | 3.6 |
| 0.7842 | 0.8384 | 1.0379 | 1.3467 | 0.8450 | 0.8 |
| 0.8972 | 0.9194 | 1.0097 | 1.5607 | 0.9170 | -0.3 |
| 1.0000 | 1.0000 | 1.0000 | 1.8764 | 1.0000 | 0.00 |
|  |  |  |  |  | (Overall $=5.1 \%)$ |

Note: Superscript ${ }^{\text {exp }}$ means experimental; superscript ${ }^{\text {calc }}$ means calculated.
4. Compute the solubility parameters. By definition,

$$
\delta_{\text {benzene }}=\left[\frac{8039-(298.15)(1.987)}{89.4}\right]^{1 / 2}=9.13\left({\left.\mathrm{cal} / \mathrm{cm}^{3}\right)^{1 / 2}}^{1 / 2}\right.
$$

and

$$
\delta_{n \text {-heptane }}=\left[\frac{8694-(298.15)(1.987)}{147.5}\right]^{1 / 2}=7.41\left(\mathrm{cal} / \mathrm{cm}^{3}\right)^{1 / 2}
$$

These calculated values are reasonably close to the true values given in the statement of the problem.

Related Calculations. The regular-solution model of Scatchard and Hildebrand gives a fair representation of activity coefficients for many solutions containing nonpolar components. This procedure is suggested for estimating vapor-liquid equilibria if experimental data are not available. The solubility parameters and liquid molar volumes used as characteristic constants may be obtained from Table 1.10. For substances not listed there, the solubility parameters may be calculated from heat of vaporization and liquid molar volume data as shown in step 4.

For moderately nonideal liquid mixtures involving similar types of compounds, the method gives activity coefficients within $\pm 10$ percent. However, extension of the correlation to hydrogen-bonding compounds and highly nonideal mixtures can lead to larger errors.

When experimental equilibrium data on nonideal mixtures are not available, methods such as those based on Derr and Deal's analytical solution of groups (ASOG) [28] or the UNIFAC correlation (discussed in Example 3.4) may be used. Activity-coefficient estimation methods are also available in various thermodynamic-data packages, such as Chemshare. Further discussion may be found in Prausnitz [3] and in Reid, Prausnitz, and Sherwood [1].

The following two examples show how to use experimental equilibrium data to obtain the equation coefficients (as opposed to the activity coefficients themselves) for activity-coefficient correlation equations. Use of these correlations to calculate the activity coefficients and make phase-equilibrium calculations is discussed in Section 3.

TABLE 1.10 Selected Values of Solubility Parameters at $25^{\circ} \mathrm{C}$

| Formula | Substance | Liquid molar volume, $\mathrm{cm}^{3}$ | Molar heat of vaporization at $25^{\circ} \mathrm{C}$, kcal | Solubility parameter $\left(\mathrm{cal} / \mathrm{cm}^{3}\right)^{1 / 2}$ |
| :---: | :---: | :---: | :---: | :---: |
| Aliphatic hydrocarbons |  |  |  |  |
| $\mathrm{C}_{5} \mathrm{H}_{12}$ | $n$-Pentane | 116 | 6.40 | 7.1 |
|  | 2-Methyl butane (isopentane) | 117 | 6.03 | 6.8 |
|  | 2,2-Dimethyl propane (neopentane) | 122 | 5.35 | 6.2 |
| $\mathrm{C}_{6} \mathrm{H}_{14}$ | $n$-Hexane | 132 | 7.57 | 7.3 |
| $\mathrm{C}_{7} \mathrm{H}_{16}$ | $n$-Heptane | 148 | 8.75 | 7.4 |
| $\mathrm{C}_{8} \mathrm{H}_{18}$ | $n$-Octane | 164 | 9.92 | 7.5 |
|  | 2,2,4-Trimethylpentane <br> ("isooctane") | 166 | 8.40 | 6.9 |
| $\mathrm{C}_{16} \mathrm{H}_{34}$ | $n$-Hexadecane | 294 | 19.38 | 8.0 |
| $\mathrm{C}_{5} \mathrm{H}_{10}$ | Cyclopentane | 95 | 6.85 | 8.1 |
| $\mathrm{C}_{6} \mathrm{H}_{12}$ | Cyclohexane | 109 | 7.91 | 8.2 |
| $\mathrm{C}_{7} \mathrm{H}_{14}$ | Methylcyclohexane | 128 | 8.46 | 7.8 |
| $\mathrm{C}_{6} \mathrm{H}_{12}$ | 1-Hexene | 126 | 7.34 | 7.3 |
| $\mathrm{C}_{8} \mathrm{H}_{16}$ | 1-Octene | 158 | 9.70 | 7.6 |
| $\mathrm{C}_{6} \mathrm{H}_{10}$ | 1,5-Hexadiene | 118 | 7.6 | 7.7 |
| Aromatic hydrocarbons |  |  |  |  |
| $\mathrm{C}_{6} \mathrm{H}_{6}$ | Benzene | 89 | 8.10 | 9.2 |
| $\mathrm{C}_{7} \mathrm{H}_{8}$ | Toluene | 107 | 9.08 | 8.9 |
| $\mathrm{C}_{8} \mathrm{H}_{10}$ | Ethylbenzene | 123 | 10.10 | 8.8 |
|  | $o$-Xylene | 121 | 10.38 | 9.0 |
|  | $m$-Xylene | 123 | 10.20 | 8.8 |
|  | $p$-Xylene | 124 | 10.13 | 8.8 |
| $\mathrm{C}_{9} \mathrm{H}_{12}$ | $n$-Propyl benzene | 140 | 11.05 | 8.6 |
|  | Mesitylene | 140 | 11.35 | 8.8 |
| $\mathrm{C}_{8} \mathrm{H}_{8}$ | Styrene | 116 | 10.5 | 9.3 |
| $\mathrm{C}_{10} \mathrm{H}_{8}$ | Naphthalene | 123 |  | 9.9 |
| $\mathrm{C}_{14} \mathrm{H}_{10}$ | Anthracene | (150) |  | 9.9 |
| $\mathrm{C}_{14} \mathrm{H}_{10}$ | Phenanthrene | 158 |  | 9.8 |


| Fluorocarbons |  |  |  |  |
| :--- | :--- | :--- | :--- | :--- |
| $\mathrm{C}_{6} \mathrm{~F}_{14}$ | Perfluoro- $\boldsymbol{n}$-hexane | 205 | 7.75 | 5.9 |
| $\mathrm{C}_{7} \mathrm{~F}_{16}$ | Perfluoro- -heptane (pure) | 226 | 8.69 | 6.0 |
|  | Perfluoroheptane (mixture) |  |  | 5.85 |
| $\mathrm{C}_{6} \mathrm{~F}_{12}$ | Perfluorocyclohexane | 170 | 6.9 | 6.1 |
| $\mathrm{C}_{7} \mathrm{~F}_{14}$ | Perfluoro (methylcyclohexane) | 196 | 7.9 | 6.1 |


| Other fluorochemicals |  |  |  |  |
| :--- | :--- | :---: | :---: | ---: |
| $\left(\mathrm{C}_{4} \mathrm{~F}_{9}\right)_{3} \mathrm{~N}$ | Perfluoro tributylamine | 360 | 13.0 | 5.9 |
| $\mathrm{C}_{4} \mathrm{Cl}_{2} \mathrm{~F}_{6}$ | Dichlorohexafluorocyclobutane | 142 |  | 7.1 |
| $\mathrm{C}_{4} \mathrm{Cl}_{3} \mathrm{~F}_{7}$ | 2,2,3-Trichloroheptafluorobutane | 165 | 8.51 | 6.9 |
| $\mathrm{C}_{2} \mathrm{Cl}_{3} \mathrm{~F}_{3}$ | 1,1,2-Trichloro, 1,2,2-trifluoroethane | 120 | 6.57 | 7.1 |
| $\mathrm{C}_{7} \mathrm{~F}_{15} \mathrm{H}$ | Pentadecafluoroheptane | 215 | 9.01 | 6.3 |
| Other aliphatic halogen compounds |  |  |  |  |
| $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ | Methylene chloride | 64 | 6.84 | 9.8 |
| $\mathrm{CHCl}_{3}$ | Chloroform | 81 | 7.41 | 9.2 |
| $\mathrm{CCl}_{4}$ | Carbon tetrachloride | 97 | 7.83 | 8.6 |
| $\mathrm{CHBr}_{3}$ | Bromoform | 88 | 10.3 | 10.5 |

TABLE 1.10 Selected Values of Solubility Parameters at $25^{\circ} \mathrm{C}$ (Continued)

| Formula | Substance | Liquid molar volume, $\mathrm{cm}^{3}$ | Molar heat of vaporization at $25^{\circ} \mathrm{C}$, kcal | Solubility parameter $\left(\mathrm{cal} / \mathrm{cm}^{3}\right)^{1 / 2}$ |
| :---: | :---: | :---: | :---: | :---: |
| Other aliphatic halogen compounds |  |  |  |  |
| $\mathrm{CH}_{3} \mathrm{I}$ | Methyl iodide | 63 | 6.7 | 9.9 |
| $\mathrm{CH}_{2} \mathrm{I}_{2}$ | Methylene iodide | 81 |  | 11.8 |
| $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{Cl}$ | Ethyl chloride | 74 | 5.7 | 8.3 |
| $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{Br}$ | Ethyl bromide | 75 | 6.5 | 8.9 |
| $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{I}$ | Ethyl iodide | 81 | 7.7 | 9.4 |
| $\mathrm{C}_{2} \mathrm{H}_{4} \mathrm{Cl}_{2}$ | 1,2-Dichloroethane (ethylene chloride) | 79 | 8.3 | 9.9 |
| $\mathrm{C}_{2} \mathrm{H}_{4} \mathrm{Cl}_{2}$ | 1,1-Dichloroethane (ethylidene chloride) | 85 | 7.7 | 9.1 |
| $\mathrm{C}_{2} \mathrm{H}_{4} \mathrm{Br}_{2}$ | 1,2-Dibromoethane | 90 | 9.9 | 10.2 |
| $\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{Cl}_{3}$ | 1,1,1-Trichloroethane | 100 | 7.8 | 8.5 |

Source: J. Hildebrand, J. Prausnitz, and R. Scott, Regular and Related Solutions, (c) 1970 by Litton Educational Publishing Inc. Reprinted with permission of Van Nostrand Co.

### 1.20 ACTIVITY-COEFFICIENT-CORRELATION EQUATIONS AND LIQUID-LIQUID EQUILIBRIUM DATA

Calculate the coefficients of Van Laar equations and the three-suffix Redlich-Kister equations from experimental solubility data at $70^{\circ} \mathrm{C}\left(158^{\circ} \mathrm{F}\right.$, or 343 K$)$ for the water $(1) /$ trichloroethylene $(2)$ system. The Van Laar equations are

$$
\log \gamma_{1}=\frac{A_{1,2}}{\left(1+\frac{A_{1,2} X_{1}}{A_{2,1} X_{2}}\right)^{2}} \quad \log \gamma_{2}=\frac{A_{2,1}}{\left(1+\frac{A_{2,1} X_{2}}{A_{1,2} X_{1}}\right)^{2}}
$$

The Redlich-Kister equation is

$$
g^{E} / R T=X_{1} X_{2}\left[B_{1,2}+C_{1,2}\left(2 X_{1}-1\right)\right]
$$

From the relation $\ln \gamma_{i}=\left[\delta\left(g^{E} / R T\right) / \delta X_{i}\right]$

$$
\ln \gamma_{i}=X_{1} X_{2}\left[B_{1,2}+C_{1,2}\left(X_{1}-X_{2}\right)\right]+X_{2}\left[B_{1,2}\left(X_{2}-X_{1}\right)+C_{1,2}\left(6 X_{1} X_{2}-1\right)\right]
$$

In these equations, $\gamma_{1}$ and $\gamma_{2}$ are activity coefficients of components 1 and 2 , respectively, $X_{1}$ and $X_{2}$ are mole fractions of components 1 and 2, respectively, $A_{1,2}$ and $A_{2,1}$ are Van Laar coefficients, $B_{1,2}$ and $C_{1,2}$ are Redlich-Kister coefficients, $R$ is the gas constant, and $T$ is the absolute system temperature.

The solubility data at $70^{\circ} \mathrm{C}$ in terms of mole fraction are: mole fraction of water in water-rich phase $X_{1}^{W}=0.9998$; mole fraction of trichloroethylene in water-rich phase $X_{2}^{W}=0.0001848$; mole fraction of water in trichloroethylene-rich phase $X_{1}^{O}=0.007463$; and mole fraction of trichloroethylene in trichloroethylene-rich phase $X_{2}^{O}=0.9925$.

## Calculation Procedure

1. Estimate the Van Laar constants. In the water-rich phase,

$$
\begin{aligned}
& \log \gamma_{1}^{W}=\frac{A_{1,2}}{\left[1+\frac{\left(A_{1,2}\right)(0.9998)}{\left(A_{2,1}\right)(0.0001848)}\right]^{2}}=\frac{A_{1,2}}{\left[1+(5410.2)\left(A_{1,2}\right) / A_{2,1}\right]^{2}} \\
& \log \gamma_{2}^{W}=\frac{A_{2,1}}{\left[1+\frac{\left(A_{2,1}\right)(0.0001848)}{\left(A_{1,2}\right)(0.9998)}\right]^{2}}=\frac{A_{2,1}}{\left[1+(0.0001848)\left(A_{2,1}\right) / A_{1,2}\right]^{2}}
\end{aligned}
$$

In the trichloroethylene-rich phase,

$$
\begin{aligned}
& \log \gamma_{1}^{o}=\frac{A_{1,2}}{\left[1+\frac{\left(A_{1,2}\right)(0.007463)}{\left(A_{2,1}\right)(0.9925)}\right]^{2}}=\frac{A_{1,2}}{\left[1+(0.007520)\left(A_{1,2}\right) / A_{2,1}\right]^{2}} \\
& \log \gamma_{2}^{o}=\frac{A_{2,1}}{\left[1+\frac{\left(A_{2,1}\right)(0.9925)}{\left(A_{1,2}\right)(0.007463)}\right]^{2}}=\frac{A_{2,1}}{\left[1+(132.99)\left(A_{2,1}\right) / A_{1,2}\right]^{2}}
\end{aligned}
$$

Now, at liquid-liquid equilibria, the partial pressure of component $i$ is the same both in waterrich and organic-rich phases, and partial pressure $\bar{P}_{i}=P_{i}^{*} \gamma_{i} X_{i}$, where $P_{i}^{*}$ is the vapor pressure of component $i$. Hence $\gamma_{1}^{O} / \gamma_{1}^{W}=K_{1}=X_{1}^{W} / X_{1}^{O}=0.9998 / 0.007463=134$, and $\gamma_{2}^{O} / \gamma_{2}^{W}=K_{2}=$ $X_{2}^{W} / X_{2}^{O}=0.0001848 / 0.9925=0.0001862$.

From the Van Laar equation,

$$
\begin{aligned}
\log \gamma_{1}^{o}-\log \gamma_{1}^{W} & =\log K_{1} \\
& =\frac{A_{1,2}}{\left[1+(0.007520)\left(A_{1,2}\right) / A_{2,1}\right]^{2}}-\frac{A_{1,2}}{\left[1+(5410.2)\left(A_{1,2}\right) / A_{2,1}\right]^{2}}
\end{aligned}
$$

Substituting for $K_{1}$ and rearranging,

$$
\begin{equation*}
A_{1,2}^{2}+0.0246 A_{2,1}^{2}+132.9788 A_{1,2} A_{2,1}-62.5187 A_{1,2}^{2} A_{2,1}=0 \tag{1.2}
\end{equation*}
$$

Similarly,

$$
\begin{aligned}
\log \gamma_{2}^{O}-\log \gamma_{2}^{W} & =\log K_{2} \\
& =\frac{A_{2,1}}{\left[1+(132.99)\left(A_{2,1}\right) / A_{1,2}\right]^{2}}-\frac{A_{2,1}}{\left[1+(0.0001848)\left(A_{2,1}\right) / A_{1,2}\right]^{2}}
\end{aligned}
$$

Substituting for $K_{2}$ and rearranging,

$$
\begin{equation*}
A_{1,2}^{2}+0.02456 A_{2,1}^{2}+132.8999 A_{1,2} A_{2,1}+35.6549 A_{1,2} A_{2,1}^{2}=0 \tag{1.3}
\end{equation*}
$$

Solving Eqs. 1.2 and 1.3 simultaneously for the Van Laar constants, $A_{1,2}=2.116$ and $A_{2,1}=$ -3.710.

## 2. Estimate the Redlich-Kister coefficients

$$
\begin{align*}
\log \left(\gamma_{1}^{O} / \gamma_{1}^{W}\right) & =\log K_{1} \\
& =B_{1,2}\left(X_{2}^{2, O}-X_{2}^{2, W}\right)+C_{1,2}\left[\left(X_{2}^{2, O}\right)\left(4 X_{1}^{O}-1\right)-\left(X_{2}^{2, W}\right)\left(4 X_{1}^{W}-1\right)\right]  \tag{1.4}\\
\log \left(\gamma_{2}^{o} / \gamma_{2}^{W}\right) & =\log K_{2} \\
& =B_{1,2}\left(X_{1}^{2, O}-X_{1}^{2, W}\right)+C_{1,2}\left[\left(X_{1}^{2, O}\right)\left(1-4 X_{2}^{O}\right)-\left(X_{1}^{2, W}\right)\left(1-4 X_{2}^{W}\right)\right] \tag{1.5}
\end{align*}
$$

Substituting numerical values and simultaneously solving Eqs. 1.4 and 1.5 for the Redlich-Kister constants, $B_{1,2}=2.931$ and $C_{1,2}=0.799$.

Related Calculations. This illustration outlines the procedure for obtaining coefficients of a liquidphase activity-coefficient model from mutual solubility data of partially miscible systems. Use of such models to calculate activity coefficients and to make phase-equilibrium calculations is discussed in Section 3. This leads to estimates of phase compositions in liquid-liquid systems from limited experimental data. At ordinary temperature and pressure, it is simple to obtain experimentally the composition of two coexisting phases, and the technical literature is rich in experimental results for a large variety of binary and ternary systems near $25^{\circ} \mathrm{C}\left(77^{\circ} \mathrm{F}\right)$ and atmospheric pressure. Example 1.21 shows how to apply the same procedure with vapor-liquid equilibrium data.

### 1.21 ACTIVITY-COEFFICIENT-CORRELATION EQUATIONS AND VAPOR-LIQUID EQUILIBRIUM DATA

From the isothermal vapor-liquid equilibrium data for the ethanol(1)/toluene(2) system given in Table 1.11, calculate (a) vapor composition, assuming that the liquid phase and the vapor phase obey Raoult's and Dalton's laws, respectively, (b) the values of the infinite-dilution activity coefficients, $\gamma_{1}^{\infty}$ and $\gamma_{2}^{\infty}$, (c) Van Laar parameters using data at the azeotropic point as well as from the infinite-dilution activity coefficients, and (d) Wilson parameters using data at the azeotropic point as well as from the infinite-dilution activity coefficients.

TABLE 1.11 Vapor-Liquid Equilibria for Ethanol(1)/Toluene(2) System at $55^{\circ} \mathrm{C}$

| $P, \mathrm{mmHg}$ <br> (1) | $X_{1}^{\exp }$ <br> (2) | $\begin{gathered} Y_{1}^{\exp } \\ (3) \end{gathered}$ | $Y_{1} P$, mmHg <br> (4) | $Y_{2} P$, mmHg (5) | $Y_{1}$, ideal <br> (6) | $\ln \gamma_{1}^{\exp }$ <br> (7) | $\ln \gamma_{2}^{\exp }$ <br> (8) | $\begin{gathered} \left(\frac{G^{E}}{X_{1} X_{2} R T}\right)^{\exp } \\ \hline 9) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 114.7 | 0.0000 | 0.0000 | 0.0000 | 114.7 | 0.0000 | (2.441)* | 0.0000 | (2.441)* |
| 144.2 | 0.0120 | 0.2127 | 30.7 | 113.5 | 0.0233 | 2.213 | 0.002 | 2.407 |
| 194.6 | 0.0400 | 0.4280 | 83.3 | 111.3 | 0.0575 | 2.010 | 0.011 | 2.369 |
| 243.0 | 0.1000 | 0.5567 | 135.3 | 107.7 | 0.1151 | 1.577 | 0.043 | 2.182 |
| 294.5 | 0.4000 | 0.6699 | 197.3 | 97.2 | 0.3798 | 0.568 | 0.345 | 1.809 |
| 308.2 | 0.7490 | 0.7490 | 230.8 | 77.4 | 0.6795 | 0.097 | 0.988 | 1.706 |
| (Azeotrope) |  |  |  |  |  |  |  |  |
| 305.7 | 0.8400 | 0.7994 | 244.4 | 61.3 | 0.7683 | 0.040 | 1.206 | 1.686 |
| 295.2 | 0.9400 | 0.8976 | 265.0 | 30.2 | 0.8903 | 0.008 | 1.480 | 1.708 |
| 279.6 | 1.000 | 1.0000 | 279.6 | 0.0000 | 1.0000 | 0.000 | (1.711)* | (1.711)* |

[^0]For a binary system, the Van Laar equations are

$$
\log \gamma_{1}=\frac{A_{1,2}}{\left(1+\frac{A_{1,2} X_{1}}{A_{2,1} X_{2}}\right)^{2}} \quad \text { and } \quad \log \gamma_{2}=\frac{A_{2,1}}{\left(1+\frac{A_{2,1} X_{2}}{A_{1,2} X_{1}}\right)^{2}}
$$

or

$$
A_{1,2}=\log \gamma_{1}\left(1+\frac{X_{2} \log \gamma_{2}}{X_{1} \log \gamma_{1}}\right)^{2} \quad \text { and } \quad A_{2,1}=\log \gamma_{2}\left(1+\frac{X_{1} \log \gamma_{1}}{X_{2} \log \gamma_{2}}\right)^{2}
$$

The Wilson equations are

$$
\begin{aligned}
G^{E} / R T & =-X_{1} \ln \left(X_{1}+X_{2} G_{1,2}\right)-X_{2} \ln \left(X_{2}+X_{1} G_{1,2}\right) \\
\ln \gamma_{1} & =-\ln \left(X_{1}+X_{2} G_{1,2}\right)+X_{2}\left[\frac{G_{1,2}}{\left(X_{1}+X_{2} G_{1,2}\right)}-\frac{G_{2,1}}{\left(X_{2}+X_{1} G_{2,1}\right)}\right] \\
\ln \gamma_{2} & =-\ln \left(X_{2}+X_{1} G_{2,1}\right)-X_{1}\left[\frac{G_{1,2}}{\left(X_{1}+X_{2} G_{1,2}\right)}-\frac{G_{2,1}}{\left(X_{2}+X_{1} G_{2,1}\right)}\right] \\
G^{E} / X_{1} X_{2} R T & =\ln \gamma_{1} / X_{2}+\ln \gamma_{2} / X_{1}
\end{aligned}
$$

In these equations, $\gamma_{1}$ and $\gamma_{2}$ are activity coefficients of components 1 and 2 , respectively, $G^{E}$ is Gibbs molar excess free energy, $A_{1,2}$ and $A_{2,1}$ are Van Laar parameters, $G_{1,2}$ and $G_{2,1}$ are Wilson parameters, that is,

$$
G_{i, j}=\frac{V_{j}}{V_{i}} e^{-a_{i, j} / R T} \quad i \neq j
$$

$a_{i, j}$ are Wilson constants $\left(a_{i, j} \neq a_{j, i}\right.$ and $\left.G_{i, j} \neq G_{j, i}\right), X_{1}$ and $X_{2}$ are liquid-phase mole fractions of components 1 and 2, respectively, $Y_{1}$ and $Y_{2}$ are vapor-phase mole fractions of components 1 and 2, respectively, $R$ is the gas constant, and $T$ is the absolute system temperature.

## Calculation Procedure

1. Compute vapor compositions, ignoring liquid- and vapor-phase nonidealities. By Raoult's and Dalton's laws, $Y_{1}=X_{1} P_{1}^{O} / P, Y_{2}=X_{2} P_{2}^{O} / P$ or $Y_{2}=1-Y_{1}$, where $P^{O}$ is vapor pressure and $P$ is total system pressure. Now, $P_{1}^{O}=279.6 \mathrm{mmHg}$ (the value of pressure corresponding to $X_{1}=Y_{1}=1$ ), and $P_{2}^{O}=114.7 \mathrm{mmHg}$ (the value of pressure corresponding to $X_{2}=Y_{2}=1$ ).

The vapor compositions calculated using the preceding equations are shown in col. 6 of Table 1.11.
2. Compute logarithms of the activity coefficients from experimental $\boldsymbol{X}-\boldsymbol{Y}$ data. Assuming an ideal vapor phase, the activity coefficients are given as $\gamma_{1}=P Y_{1} / X_{1} P_{1}^{O}$ and $\gamma_{2}=P Y_{2} / X_{2} P_{2}^{O}$. The natural logarithms of the activity coefficients calculated using the preceding equations are shown in cols. 7 and 8 of Table 1.11.
3. Compute infinite-dilution activity coefficients. First, calculate $G^{E} / X_{1} X_{2} R T=\ln \gamma_{1} / X_{2}+$ $\ln \gamma_{2} / X_{1}$. The function $G^{E} / X_{1} X_{2} R T$ calculated using the preceding equation is tabulated in col. 9 of Table 1.11.

Next, obtain the infinite-dilution activity coefficients graphically by extrapolating $G^{E} / X_{1} X_{2} R T$ values to $X_{1}=0$ and $X_{2}=0$ (Fig. 1.13). Thus, $\ln \gamma_{1}^{\infty}=2.441$ and $\ln \gamma_{2}^{\infty}=1.711$, so $\gamma_{1}^{\infty}=11.48$ and $\gamma_{2}^{\infty}=5.53$.


FIGURE 1.13 Graphic solution for infinite-dilution activity coefficients (Example 1.21).
4. Calculate Van Laar parameters from azeotropic data. At the azeotropic point, $X_{1}=0.7490$, $X_{2}=1-X_{1}=0.251$, and $\ln \gamma_{1}=0.097$ and $\ln \gamma_{2}=0.988$ (see Table 1.11). Therefore,

$$
\begin{aligned}
A_{1,2} & =\frac{0.097}{2.303}\left[1+\frac{(0.251)(0.988)(2.303)}{(0.749)(0.097)(2.303)}\right]^{2} \\
& =0.820 \quad\left(\ln \gamma_{i}=2.303 \log \gamma_{i}\right)
\end{aligned}
$$

and

$$
\begin{aligned}
A_{2,1} & =\frac{0.988}{2.303}\left[1+\frac{(0.749)(0.097)(2.303)}{(0.251)(0.988)(2.303)}\right]^{2} \\
& =0.717
\end{aligned}
$$

5. Calculate Van Laar parameters from the infinite-dilution activity coefficients. By definition, $A_{1,2}=\log \gamma_{1}^{\infty}$ and $A_{2,1}=\log \gamma_{2}^{\infty}$. Therefore, $A_{1,2}=2.441 / 2.303=1.059$, and $A_{2,1}=$ $1.711 / 2.303=0.743$.
6. Calculate Wilson parameters from azeotropic data. From the azeotropic data,

$$
0.097=-\ln \left(0.749+0.251 G_{1,2}\right)+0.251\left[\frac{G_{1,2}}{\left(0.749+0.251 G_{1,2}\right)}-\frac{G_{2,1}}{\left(0.251+0.749 G_{2,1}\right)}\right]
$$

and

$$
0.988=-\ln \left(0.251+0.749 G_{2,1}\right)-0.749\left[\frac{G_{1,2}}{\left(0.749+0.251 G_{1,2}\right)}-\frac{G_{2,1}}{\left(0.251+0.749 G_{2,1}\right)}\right]
$$

Solving for $G_{1,2}$ and $G_{2,1}$ by trial and error gives $G_{1,2}=0.1260$ and $G_{2,1}=0.4429$.
7. Calculate Wilson parameters from the infinite-dilution activity coefficients. The equations are $\ln \gamma_{1}^{\infty}=2.441=-\ln G_{1,2}+1-G_{2,1}$, and $\ln \gamma_{2}^{\infty}=1.711=-\ln G_{2,1}+1-G_{1,2}$. Solving by trial and error, $G_{1,2}=0.1555$ and $G_{2,1}=0.4209$.

Related Calculations. These calculations show how to use vapor-liquid equilibrium data to obtain parameters for activity-coefficient correlations such as those of Van Laar and Wilson. (Use of liquidliquid equilibrium data for the same purpose is shown in Example 1.20.) If the system forms an azeotrope, the parameters can be obtained from a single measurement of the azeotropic pressure and the composition of the constant boiling mixture. If the activity coefficients at infinite dilution are available, the two parameters for the Van Laar equation are given directly, and the two in the case of the Wilson equation can be solved for as shown in the example.

In principle, the parameters can be evaluated from minimal experimental data. If vapor-liquid equilibrium data at a series of compositions are available, the parameters in a given excess-freeenergy model can be found by numerical regression techniques. The goodness of fit in each case depends on the suitability of the form of the equation. If a plot of $G^{E} / X_{1} X_{2} R T$ versus $X_{1}$ is nearly linear, use the Margules equation (see Section 3). If a plot of $X_{1} X_{2} R T / G^{E}$ is linear, then use the Van Laar equation. If neither plot approaches linearity, apply the Wilson equation or some other model with more than two parameters.

The use of activity-coefficient-correlation equations to calculate activity coefficients and make phase-equilibrium calculations is discussed in Section 3. For a detailed discussion, see Prausnitz [3].

### 1.22 CONVERGENCE-PRESSURE VAPOR-LIQUID EQUILIBRIUM K VALUES

In a natural-gas processing plant (Fig. 1.14), a $1000 \mathrm{lb} \cdot \mathrm{mol} / \mathrm{h}(453.6 \mathrm{~kg} \cdot \mathrm{~mol} / \mathrm{h})$ stream containing $5 \mathrm{~mol} \%$ nitrogen, $65 \%$ methane, and $30 \%$ ethane is compressed from $80 \mathrm{psia}\left(552 \mathrm{kPa}\right.$ ) at $70^{\circ} \mathrm{F}$ $(294 \mathrm{~K})$ to $310 \mathrm{psia}(2137 \mathrm{kPa})$ at $260^{\circ} \mathrm{F}(400 \mathrm{~K})$ and subsequently cooled in a heat-exchanger chilling train (a cooling-water heat exchanger and two refrigeration heat exchangers) to partially liquefy the feed stream. The liquid is disengaged from the vapor phase in a separating drum at 300 psia $(2070 \mathrm{kPa})$ and $-100^{\circ} \mathrm{F}(200 \mathrm{~K})$ and pumped to another part of the process. The vapor from the drum is directed to a 15 -tray absorption column.


FIGURE 1.14 Flow diagram for portion of natural-gas-processing plant (Example 1.22).

In the column, the vapor is countercurrently contacted with $250 \mathrm{~mol} / \mathrm{h}$ of liquid propane, which absorbs from the vapor feed 85 percent of its ethane content, 9 percent of its methane, and a negligible amount of nitrogen. The pressure of the bottom stream of liquid propane with its absorbed constituents is raised to $500 \mathrm{psia}(3450 \mathrm{kPa})$, and the stream is heated to $50^{\circ} \mathrm{F}(283 \mathrm{~K})$ in a heat exchanger before being directed to another section of the process. The vapor, leaving the overhead tower at $-60^{\circ} \mathrm{F}$ ( 222 K ), consists of unabsorbed constituents plus some vaporized propane from the liquid-propane absorbing medium.
a. In which heat exchanger of the chilling train does condensation start? Assume that the convergence pressure is $800 \mathrm{psia}(5520 \mathrm{kPa})$.
b. How much propane is in the vapor leaving the overhead of the column? Assume again that the convergence pressure is $800 \mathrm{psia}(5520 \mathrm{kPa})$.
c. Does any vaporization take place in the heat exchanger that heats the bottoms stream from the column?

Use convergence-pressure vapor-liquid equilibrium $K$-value charts (Figs. 1.15 through 1.26).

## Calculation Procedure

1. Calculate dew-point equilibrium for the feed. A vapor is at its dew-point temperature when the first drop of liquid forms upon cooling the vapor at constant pressure and the composition of the vapor remaining is the same as that of the initial vapor mixture. At dew-point conditions, $Y_{i}=N_{i}=K_{i} X_{i}$, or $X_{i}=N_{i} / K_{i}$, and $\Sigma N_{i} / K_{i}=1.0$, where $Y_{i}$ is the mole fraction of component $i$ in the vapor phase, $X_{i}$ is the mole fraction of component $i$ in the liquid phase, $N_{i}$ is the mole fraction of component $i$ in the original mixture, and $K_{i}$ is the vapor-liquid equilibrium $K$ value.

Calculate the dew-point temperature of the mixture at a pressure of 310 psia and an assumed convergence pressure of 800 psia . At various assumed temperatures and at a pressure of 310 psia , the $K$ values for methane, nitrogen, and ethane, as obtained from Figs. 1.15, 1.18, and 1.21, are listed in Table 1.12, as are the corresponding values of $N_{i} / K_{i}$. At the dew-point temperature, the latter will add up to 1.0. It can be seen from the table that the dew point lies between -60 and $-50^{\circ} \mathrm{F}(222$ and $227 \mathrm{~K})$. Therefore, the condensation will take place in the last heat exchanger in the train, because that one lowers the stream temperature from $-20^{\circ} \mathrm{F}(244 \mathrm{~K})$ to $-100^{\circ} \mathrm{F}(200 \mathrm{~K})$.
2. Estimate the compositions of the liquid and vapor phases leaving the separator. At the separator conditions, $-100^{\circ} \mathrm{F}$ and 310 psia , estimate the mole ratio of vapor to liquid $V / L$ from the relationship

$$
L_{i}=F_{i} /\left[1+(V / L) K_{i}\right]
$$

1.12 Calculation of Dew Point for Feed Gas in Example 1.22 (convergence pressure $=800 \mathrm{psia}$ )

| Component $i$ | Mole fraction $N_{i}$ | Assumed temperature |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | $0^{\circ} \mathrm{F}$ |  | $-50^{\circ} \mathrm{F}$ |  | $-100^{\circ} \mathrm{F}$ |  | $-60^{\circ} \mathrm{F}$ |  |
|  |  | $K_{i}$ | $N_{i} / K_{i}$ | $K_{i}$ | $N_{i} / K_{i}$ | $K_{i}$ | $N_{i} / K_{i}$ | $K_{i}$ | $N_{i} / K_{i}$ |
| Methane | 0.65 | 3.7 | 0.176 | 3.1 | 0.210 | 2.6 | 0.250 | 3.0 | 0.217 |
| Nitrogen | 0.05 | 18.0 | 0.003 | 16.0 | 0.003 | 12.0 | 0.004 | 15.0 | 0.003 |
| Ethane | 0.30 | 0.8 | 0.375 | 0.45 | 0.667 | 0.17 | 1.765 | 0.35 | 0.857 |
| Total | 1.00 |  | 0.554 |  | 0.880 |  | 2.019 |  | 1.077 |



FIGURE 1.15 $K$ values for nitrogen; convergence pressure $=800 \mathrm{psia}$. (Note: $1 \mathrm{psi}=6.895 \mathrm{kPa}$.) (Courtesy of NGPA.)


FIGURE 1.16 $K$ values for nitrogen; convergence pressure $=1000 \mathrm{psia}$. (Note: $1 \mathrm{psi}=6.895 \mathrm{kPa}$.) (Courtesy of NGPA.)


FIGURE 1.17 $K$ values for nitrogen; convergence pressure $=2000 \mathrm{psia}$. (Note: $1 \mathrm{psi}=6.895 \mathrm{kPa}$.) (Courtesy of NGPA.)


FIGURE $1.18 K$ values for methane; convergence pressure $=800 \mathrm{psia}$. (Note: $1 \mathrm{psi}=6.895 \mathrm{kPa}$.) (Courtesy of NGPA.)
where $L_{i}$ is moles of component $i$ in the liquid phase, $F_{i}$ is moles of component $i$ in the feed (given in the statement of the problem), and $K_{i}$ is the vapor-liquid equilibrium $K$ value for that component, obtainable from Figs. 1.15, 1.18, and 1.21. Use trial and error for finding $V / L$ : Using the known $F_{i}$ and $K_{i}$, assume a value of $V / L$ and calculate the corresponding $L_{i}$; add up these $L_{i}$ to obtain the total moles per hour of liquid, and subtract the total from $1000 \mathrm{~mol} / \mathrm{h}$ (given in the statement of the problem) to obtain the moles per hour of vapor; take the ratio of the two, and compare it with the assumed $V / L$ ratio. This trial-and-error procedure, leading to a $V / L$ of 2.2 , is summarized in Table 1.13. Thus the composition of the liquid phase leaving the separator (i.e., the $L_{i}$ corresponding


FIGURE $1.19 K$ values for methane; convergence pressure $=1000 \mathrm{psia}$. (Note: $1 \mathrm{psi}=6.985 \mathrm{kPa}$.) (Courtesy of NGPA.)
to a $V / L$ of 2.2 ) appears as the next-to-last column in that table. The vapor composition (expressed as moles per hour of each component), given in the last column, is found by subtracting the moles per hour in the liquid phase from the moles per hour of feed.
3. Estimate the amount of propane in the vapor leaving the column overhead. The vapor stream leaving the column overhead may be assumed to be at its dew point; in other words, the dew point of the overhead mixture is $-60^{\circ} \mathrm{F}$ and 295 psia . At the dew point, $\Sigma\left(Y_{i} / K_{i}\right)=1.0$. Designate $Y_{i}$,

TABLE 1.13 Equilibrium Flash Calculations for Example 1.22 (convergence pressure $=800 \mathrm{psia}$; feed rate $=1000 \mathrm{~mol} / \mathrm{h}$ )

| Component $i$ | $\begin{gathered} F_{i}, \\ \mathrm{lb} \cdot \mathrm{~mol} / \mathrm{h} \end{gathered}$ | $\begin{gathered} K_{i} \\ \text { at }-100^{\circ} \mathrm{F}, \\ 300 \mathrm{psia} \\ \hline \end{gathered}$ | $L_{i}, \mathrm{lb} \cdot \mathrm{mol} / \mathrm{h}$, at assumed $V / L$ ratio of |  |  |  |  | $V_{i}$, <br> $\mathrm{lb} \cdot \mathrm{mol} / \mathrm{h}$, at $V / L=2.2$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | 1 | 2 | 2.5 | 2.3 | 2.2 |  |
| Methane | 650 | 2.6 | 180.6 | 104.8 | 86.7 | 93.1 | 96.7 | 553.3 |
| Nitrogen | 50 | 12.0 | 3.8 | 2.0 | 1.6 | 1.7 | 1.8 | 48.2 |
| Ethane | 300 | 0.18 | 254.2 | 220.6 | 206.9 | 212.2 | 214.9 | 85.1 |
| Total | 1000 |  | 438.6 | 327.4 | 295.2 | 307 | 313.4 | 686.6 |
| $V=1000-L$ |  |  | 561.4 | 672.6 | 704.8 | 693 | 686.6 |  |
| Calculated $V / L$ |  |  | 1.280 | 2.054 | 2.388 | 2.257 | $\begin{aligned} & 2.191 \\ & \text { (close } \\ & \text { enough) } \end{aligned}$ |  |



FIGURE 1.20 $K$ values for methane; convergence pressure $=1500 \mathrm{psia}$. (Note: $1 \mathrm{psi}=6.895 \mathrm{kPa}).($ Courtesy of NGPA.)


FIGURE 1.21 $K$ values for ethane; convergence pressure $=800 \mathrm{psia}$. (Note: $1 \mathrm{psi}=6.895 \mathrm{kPa}$.) (Courtesy of NGPA.)


FIGURE 1.22 $K$ values for ethane; convergence pressure $=1000 \mathrm{psia} .($ Note: $1 \mathrm{psi}=6.895 \mathrm{kPa}).($ Courtesy of NGPA.)
the mole fraction of component $i$ in the column overhead, as $D_{i} / D$, where $D_{i}$ is the flow rate of component $i$ in the overhead stream and $D$ is the flow rate of the total overhead stream. Then the dewpoint equation can be rearranged into $\Sigma\left(D_{i} / K_{i}\right)=D$. Then the material balance and distribution of components in the vapor leaving the overhead can be summarized as in Table 1.14. (From a graph not shown, $K_{i}$ for propane at the dew point and 800 psia convergence pressure is 0.084 .) Since $\Sigma D_{i}=D$, the following equation can be written and solved for $D_{\mathrm{pr}}$, the flow rate of propane:

$$
206.6+11.9 D_{\mathrm{pr}}=564.5+D_{\mathrm{pr}}
$$



FIGURE 1.23 $K$ values for ethane; convergence pressure $=1500 \mathrm{psia}$. (Note: $1 \mathrm{psi}=6.895 \mathrm{kPa}$.) (Courtesy of NGPA.)

Thus $D_{\mathrm{pr}}$ is found to be $32.8 \mathrm{lb} \cdot \mathrm{mol} / \mathrm{h}(14.9 \mathrm{~kg} \cdot \mathrm{~mol} / \mathrm{h})$. (The amount of propane leaving the column bottom, needed for the next step in the calculation procedure, is $250-32.8$, or $217.2 \mathrm{lb} \cdot \mathrm{mol} / \mathrm{h}$.)
4. Compute the convergence pressure at the tower bottom. The convergence pressure is the pressure at which the vapor-liquid $K$ values of all components in the mixture converge to a value of $K=1.0$. The concept of convergence pressure is used empirically to account for the effect of composition. Convergence pressure can be determined by the critical locus of the system: For a binary mixture, the convergence pressure is the pressure corresponding to the system


FIGURE 1.24 $K$ values for propane; convergence pressure $=800 \mathrm{psia}$. $($ Note: $1 \mathrm{psi}=6.895 \mathrm{kPa}$. $)($ Courtesy of NGPA.)


FIGURE $1.25 K$ values for propane; convergence pressure $=1000 \mathrm{psia}$. (Note: $1 \mathrm{psi}=6.895 \mathrm{kPa}$.) (Courtesy of NGPA.)
temperature read from the binary critical locus. Critical loci of many hydrocarbon binaries are given in Fig. 1.27. This figure forms the basis for determining the convergence pressure for use with the $K$-value charts (Figs. 1.15 through 1.26).

Strictly speaking, the convergence pressure of a binary mixture equals the critical pressure of the mixture only if the system temperature coincides with the mixture critical temperature. For multicomponent mixtures, furthermore, the convergence pressure depends on both the temperature and the liquid composition of mixture. For convenience, a multicomponent mixture is treated as a pseudobinary mixture in this $K$-value approach. The pseudobinary mixture consists of a light component, which is the lightest component present in not less than 0.001 mol fraction in the liquid, and a pseudoheavy

TABLE 1.14 Overhead from Absorption Column in Example 1.22 (convergence pressure $=800 \mathrm{psia}$ )

|  | Amount in feed to <br> absorption column $F_{i}$, <br> $\mathrm{lb} \cdot \mathrm{mol} / \mathrm{h}$ | Fraction <br> absorbed | Quantity <br> absorbed $L_{i}$, <br> $\mathrm{lb} \cdot \mathrm{mol} / \mathrm{h}$ | Quantity in <br> overhead $D_{i}$, <br> $\mathrm{lb} \cdot \mathrm{mol} / \mathrm{h}$ | $K_{i}$ at <br> -60 F, <br> 295 psia | $D_{i} / K_{i}$ <br> Component $i$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| Nitrogen | 48.2 | 0 | 0 | 48.2 | 15 | 3.21 |
| Methane | 53.3 | 0.09 | 49.8 | 503.5 | 3 | 167.8 |
| Ethane | 85.1 | 0.85 | 72.3 | 12.8 | 0.36 | 35.6 |
| Propane | 0 | - | - | $D_{\mathrm{pr}}$ | 0.084 | $11.9 D_{\mathrm{pr}}$ <br> Total |



FIGURE 1.26 $K$ values for propane; convergence pressure $=1500 \mathrm{psia}$. (Note: $1 \mathrm{psi}=6.895 \mathrm{kPa}$.) (Courtesy of NGPA.)


FIGURE 1.27 Critical loci of binary mixtures. (Note: $1 \mathrm{psi}=6.895 \mathrm{kPa}$.) (Courtesy of NGPA.)
component that represents the remaining heavy components. The critical temperature and the critical pressure of the pseudoheavy component are defined as $T_{c, \text { heary }}=\Sigma W_{i} T_{c, i}$ and $P_{c, \text { heavy }}=\Sigma W_{i} P_{c, i}$, where $W_{i}$ is the weight fraction of component $i$ in the liquid phase on a lightest-component-free basis, and $T_{c, i}$ and $P_{c, i}$ are critical temperature and critical pressure of component $i$, respectively. The pseudocritical constants computed by following this procedure (outlined in Table 1.15) are $T_{c, \text { heary }}=186.7^{\circ} \mathrm{F}$ and $P_{c, \text { heary }}=633.1$ psia. Locate points $\left(T_{c, \text { light }}, P_{c, \text { light }}\right)$ and $\left(T_{c, \text { heary }}, P_{c, \text { heary }}\right)$ of the pseudobinary mixture on Fig. 1.27, and construct the critical locus by interpolating between the adjacent loci as shown by the dotted line. Read off convergence-pressure values corresponding to the system temperature from this critical locus. Thus, at 50 and $75^{\circ} \mathrm{F}$ ( 283 and 297 K ), the convergence pressures are about 1400 and 1300 psia ( 9653 and 8964 kPa ), respectively.

TABLE 1.15 Pseudocritical Constants for Tower Bottoms in Example 1.22

| Component | Flow rate $B_{i}, \mathrm{~mol} / \mathrm{h}$ | Molecular weight, lb/ (lb $\cdot \mathrm{mol}$ ) | Flow rate, lb/h | Critical temperature $T_{c, i},{ }^{\circ} \mathrm{F}$ | Critical pressure $P_{c, i}, \mathrm{psia}$ | Weight fraction $W_{i}$ | $W_{i} T_{c, i}$ | $W_{i} P_{c, i}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Methane | 49.8 | - | - | - | - | - | - | - |
| Ethane | 72.3 | 30.07 | 2174 | 90.3 | 709.8 | 0.169 | 15.3 | 120.0 |
| Propane | 217.2 | 49.09 | 10,662 | 206.3 | 617.4 | 0.831 | 171.4 | 513.1 |
| Total | 339.3 |  | 12,836 |  |  | 1.000 | 186.7 | 633.1 |

TABLE 1.16 Convergence-Pressure $K$ Values for Example 1.22

| Component | $K$ values |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $50^{\circ} \mathrm{F}, 500 \mathrm{psia}$ |  |  | $75^{\circ} \mathrm{F}, 500 \mathrm{psia}$ |  |  |
|  | $\begin{gathered} \text { Conv. press. } \\ =1000 \\ \text { psia } \end{gathered}$ | $\begin{gathered} \text { Conv. press. } \\ =1500 \\ \text { psia } \\ \hline \end{gathered}$ | $\begin{gathered} \text { Conv. press.* } \\ =1400 \\ \text { psia } \end{gathered}$ | $\begin{gathered} \text { Conv. press. } \\ =1000 \\ \text { psia } \end{gathered}$ | $\begin{gathered} \text { Conv. press. } \\ =1500 \\ \text { psia } \end{gathered}$ | $\begin{gathered} \text { Conv. press. }{ }^{*} \\ =1300 \\ \text { psia } \end{gathered}$ |
| $\mathrm{CH}_{4}$ | 2.9 | 4.1 | 3.86 | 3.05 | 4.4 | 3.86 |
| $\mathrm{C}_{2} \mathrm{H}_{6}$ | 0.95 | 0.93 | 0.93 | 1.18 | 1.2 | 1.19 |
| $\mathrm{C}_{3} \mathrm{H}_{8}$ | 0.36 | 0.32 | 0.33 | 0.46 | 0.38 | 0.41 |

*Values interpolated linearly.
5. Obtain convergence-pressure $\boldsymbol{K}$ values. Table 1.16 lists $K$ values of each component from the appropriate charts corresponding to given temperature and pressure at two convergence pressures, namely, 1000 and 1500 psia. Values are interpolated linearly for convergence pressures of 1400 psia (corresponding to $50^{\circ} \mathrm{F}$ ) and 1300 psia (corresponding to $75^{\circ} \mathrm{F}$ ).
6. Estimate bubble-point temperature of tower bottom stream after it leaves the pump and heat exchanger. At the bubble point, $\Sigma K_{i} X_{i}=1.0$, where $X_{i}$ is the mole fraction of component $i$ in the liquid mixture. Designate $X_{i}$ as $B_{i} / B$, where $B_{i}$ is the flow rate of component $i$ and $B$ is the flow rate of the total bottoms stream. Then the bubble-point equation can be rearranged into $\Sigma K_{i} B_{i}=B$. Using the $K_{i}$ values that correspond to temperatures of 50 and $75^{\circ} \mathrm{F}$ (from the previous step), we find $\Sigma K_{i} B_{i}$ at $50^{\circ} \mathrm{F}$ to be 331.1 and $\Sigma K_{i} B_{i}$ at $75^{\circ} \mathrm{F}$ to be 367.3 . However, at the bubble point, $\Sigma K_{i} B_{i}$ should be $339.3 \mathrm{~mol} / \mathrm{h}$, i.e., the amount of the total bottom stream. By linear interpolation, therefore, the bubble-point temperature is $56^{\circ} \mathrm{F}(286 \mathrm{~K})$. Since the temperature of the stream leaving the heat exchanger is $50^{\circ} \mathrm{F}(286 \mathrm{~K})$, no vaporization will take place in that exchanger.

Related Calculations. The convergence-pressure $K$-value charts provide a useful and rapid graphical approach for phase-equilibrium calculations. The Natural Gas Processors Suppliers Association has published a very extensive set of charts showing the vapor-liquid equilibrium $K$ values of each of the components methane to $n$-decane as functions of pressure, temperature, and convergence pressure. These charts are widely used in the petroleum industry. The procedure shown in this illustration can be used to perform similar calculations. See Examples 3.10 and 3.11 for straightforward calculation of dew points and bubble points, respectively.

## heat of formation from elements

Calculate the values of standard heat of formation $\Delta H_{f}^{\circ}$ and standard free energy of formation $\Delta G_{f}^{\circ}$ of 2-methyl propene (isobutene) from the elements at $400 \mathrm{~K}\left(260^{\circ} \mathrm{F}\right)$ :

$$
4 \mathrm{C}(s)+4 \mathrm{H}_{2}(g) \rightarrow \mathrm{C}_{4} \mathrm{H}_{8}(g)
$$

The standard heat of formation of a compound relative to its elements, all in their standard state of unit activities, is expressed as

$$
\Delta H_{f, T}^{\circ}=\left[\left(H_{T}^{\circ}-H_{0}^{\circ}\right)+\Delta H_{f, 0}^{\circ}\right]_{\text {compound }}-\left[\Sigma\left(H_{T}^{\circ}-H_{0}^{\circ}\right)\right]_{\text {elements }}
$$

where $\Delta H_{f, T}^{\circ}=$ standard heat of formation at temperature $T$
$H_{T}^{\circ}=$ enthalpy of compound or element at temperature $T$
$H_{0}^{\circ}=$ enthalpy of compound or element at 0 K
$\Delta H_{f, 0}^{\circ}=$ standard heat of formation at 0 K

The standard free energy of formation of a compound at a temperature $T$ from the elements at the same temperature is expressed as

$$
\left(\frac{\Delta G_{f}^{\circ}}{T}\right)_{T}=\left[\left(\frac{G_{T}^{\circ}-H_{0}^{\circ}}{T}\right)+\frac{\Delta H_{f, 0}^{\circ}}{T}\right]_{\text {compound }}-\left[\sum \frac{G_{T}^{\circ}-H_{0}^{\circ}}{T}\right]_{\text {elements }}
$$

where $\Delta G_{f}^{\circ}=$ standard free energy of formation at temperature $T$
$G_{T}^{\circ}=$ standard free energy of a compound or element at temperature $T$
Free-energy functions and enthalpy functions are given in Tables 1.17 and 1.18.

TABLE 1.17 Enthalpy above 0 K

|  | State | $\left(H_{T}^{\circ}-H_{0}^{\circ}\right), \mathrm{kg} \cdot \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})$ |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | 298.16 K | 400 K | 500 K | 600 K | 800 K | 1000 K | 1500 K |
| Methane | $g$ | 2.397 | 3.323 | 4.365 | 5.549 | 8.321 | 11.560 | 21.130 |
| Ethane | $g$ | 2.856 | 4.296 | 6.010 | 8.016 | 12.760 | 18.280 | 34.500 |
| Ethene (ethylene) | $g$ | 2.525 | 3.711 | 5.117 | 6.732 | 10.480 | 14.760 | 27.100 |
| Ethyne (acetylene) | $g$ | 2.3915 | 3.5412 | 4.7910 | 6.127 | 8.999 | 12.090 | 20.541 |
| Propane | $g$ | 3.512 | 5.556 | 8.040 | 10.930 | 17.760 | 25.670 | 48.650 |
| Propene (propylene) | $g$ | 3.237 | 4.990 | 7.076 | 9.492 | 15.150 | 21.690 | 40.570 |
| $n$-Butane | $g$ | 4.645 | 7.340 | 10.595 | 14.376 | 23.264 | 33.540 | 63.270 |
| 2-Methylpropane (isobutane) | $g$ | 4.276 | 6.964 | 10.250 | 14.070 | 23.010 | 33.310 | 63.050 |
| 1-Butene | $g$ | 4.112 | 6.484 | 9.350 | 12.650 | 20.370 | 29.250 | 54.840 |
| cis-2-Butene | $g$ | 3.981 | 6.144 | 8.839 | 12.010 | 19.510 | 28.230 | 53.620 |
| trans-2-Butene | $g$ | 4.190 | 6.582 | 9.422 | 12.690 | 20.350 | 29.190 | 54.710 |
| 2-Methylpropene (isobutene) | $g$ | 4.082 | 6.522 | 9.414 | 12.750 | 20.490 | 29.370 | 55.000 |
| $n$-Pentane | $g$ | 5.629 | 8.952 | 12.970 | 17.628 | 28.568 | 41.190 | 77.625 |
| 2-Methylbutane (isopentane) | $g$ | 5.295 | 8.596 | 12.620 | 17.300 | 28.300 | 41.010 | 77.740 |
| 2,2-Dimethylpropane (neopentane) | $g$ | 5.030 | 8.428 | 12.570 | 17.390 | 28.640 | 41.510 | 78.420 |
| $n$-Hexane | $g$ | 6.622 | 10.580 | 15.360 | 20.892 | 33.880 | 48.850 | 92.010 |
| 2-Methylpentane | $g$ | 6.097 | 10.080 | 14.950 | 20.520 | 33.600 | 48.700 |  |
| 3-Methylpentane | $g$ | 6.622 | 10.580 | 15.360 | 20.880 | 33.840 | 48.800 |  |
| 2,2-Dimethylbutane | $g$ | 5.912 | 9.880 | 14.750 | 20.340 | 33.520 | 48.600 |  |
| 2,3-Dimethylbutane | $g$ | 5.916 | 9.833 | 14.610 | 20.170 | 33.230 | 48.240 |  |
| Graphite | $s$ | 0.25156 | 0.5028 | 0.8210 | 1.1982 | 2.0816 | 3.0750 | 5.814 |
| Hydrogen, $\mathrm{H}_{2}$ | $g$ | 2.0238 | 2.7310 | 3.4295 | 4.1295 | 5.5374 | 6.9658 | 10.6942 |
| Water, $\mathrm{H}_{2} \mathrm{O}$ | $g$ | 2.3677 | 3.1940 | 4.0255 | 4.8822 | 6.6896 | 8.6080 | 13.848 |
| CO | $g$ | 2.0726 | 2.7836 | 3.4900 | 4.2096 | 5.7000 | 7.2570 | 11.3580 |
| $\mathrm{CO}_{2}$ | $g$ | 2.2381 | 3.1948 | 4.2230 | 5.3226 | 7.6896 | 10.2220 | 17.004 |
| $\mathrm{O}_{2}$ | 8 | 2.0698 | 2.7924 | 3.5240 | 4.2792 | 5.8560 | 7.4970 | 11.7765 |
| $\mathrm{N}_{2}$ | $g$ | 2.07227 | 2.7824 | 3.4850 | 4.1980 | 5.6686 | 7.2025 | 11.2536 |
| NO | $g$ | 2.1942 | 2.9208 | 3.6440 | 4.3812 | 5.9096 | 7.5060 | 11.6940 |

Note: $\quad H_{T}^{\circ}=$ molal enthalpy of the substance in its standard state, at temperature $T$. $H_{0}^{\circ}=$ molal enthalpy of the substance in its standard state, at 0 K .
Source: A. Hougen, K. M. Watson, and R. A. Ragatz, Chemical Process Principles, part III, Wiley, New York, 1959.

TABLE 1.18 Free-Energy Function and Standard Heat of Formation at 0 K

|  | State | $-\left(G_{T}^{\circ}-H_{0}^{\circ}\right) / T$ |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | 298.16 K | 400 K | 500 K | 600 K | 800 K | 1000 K | 1500 K | $\left(\Delta H_{f}^{\circ}\right)_{0}$ |
| Methane | $g$ | 36.46 | 38.86 | 40.75 | 42.39 | 45.21 | 47.65 | 52.84 | -15.987 |
| Ethane | $g$ | 45.27 | 48.24 | 50.77 | 53.08 | 57.29 | 61.11 | 69.46 | -16.517 |
| Ethene (ethylene) | $g$ | 43.98 | 46.61 | 48.74 | 50.70 | 54.19 | 57.29 | 63.94 | +14.522 |
| Ethyne (acetylene) | $g$ | 39.976 | 42.451 | 44.508 | 46.313 | 49.400 | 52.005 | 57.231 | +54.329 |
| Propane | $g$ | 52.73 | 56.48 | 59.81 | 62.93 | 68.74 | 74.10 | 85.86 | -19.482 |
| Propene (propylene) | $g$ | 52.95 | 56.39 | 59.32 | 62.05 | 67.04 | 71.57 | 81.43 | +8.468 |
| $n$-Butane | $g$ | 58.54 | 63.51 | 67.91 | 72.01 | 70.63 | 86.60 | 101.95 | -23.67 |
| 2-Methylpropane (isobutane) | $g$ | 56.08 | 60.72 | 64.95 | 68.95 | 76.45 | 83.38 | 98.64 | -25.30 |
| 1-Butene | $g$ | 59.25 | 63.64 | 67.52 | 71.14 | 77.82 | 83.93 | 97.27 | +4.96 |
| cis-2-Butene | $g$ | 58.67 | 62.89 | 66.51 | 69.94 | 76.30 | 82.17 | 95.12 | +3.48 |
| trans-2-Butene | $g$ | 56.80 | 61.31 | 65.19 | 68.84 | 75.53 | 81.62 | 94.91 | +2.24 |
| 2-Methylpropene (isobutene) | $g$ | 56.47 | 60.90 | 64.77 | 68.42 | 75.15 | 81.29 | 94.66 | +0.98 |
| $n$-Pentane | $g$ | 64.52 | 70.57 | 75.94 | 80.96 | 90.31 | 98.87 | 117.72 | -27.23 |
| 2-Methylbutane (isopentane) | $g$ | 64.36 | 70.67 | 75.28 | 80.21 | 89.44 | 97.96 | 116.78 | -28.81 |
| 2,2-Dimethylpropane (neopentane) | $g$ | 56.36 | 61.93 | 67.04 | 71.96 | 81.27 | 89.90 | 108.91 | -31.30 |
| $n$-Hexane | $g$ | 70.62 | 77.75 | 84.11 | 90.06 | 101.14 | 111.31 | 133.64 | -30.91 |
| 2-Methylpentane | $g$ | 70.50 | 77.2 | 83.3 | 89.1 | 100.1 | 110.3 | 132.5 | -32.08 |
| 3-Methylpentane | $g$ | 68.56 | 75.69 | 82.05 | 88.0 | 99.08 | 109.3 | 131.6 | -31.97 |
| 2,2-Dimethylbutane | $g$ | 65.79 | 72.3 | 78.3 | 84.1 | 95.0 | 105.1 | 127.4 | -34.65 |
| 2,3-Dimethylbutane | $g$ | 67.58 | 74.06 | 80.05 | 85.77 | 96.54 | 106.57 | 128.70 | -32.73 |
| Graphite | $s$ | 0.5172 | 0.824 | 1.146 | 1.477 | 2.138 | 2.771 | 4.181 | 0 |
| Hydrogen, $\mathrm{H}_{2}$ | $g$ | 24.423 | 26.422 | 27.950 | 29.203 | 31.186 | 32.738 | 35.590 | 0 |
| $\mathrm{H}_{2} \mathrm{O}$ | $g$ | 37.165 | 39.505 | 41.293 | 42.766 | 45.128 | 47.010 | 50.598 | -57.107 |
| CO | $g$ | 40.350 | 42.393 | 43.947 | 45.222 | 47.254 | 48.860 | 51.864 | -27.2019 |
| $\mathrm{CO}_{2}$ | $g$ | 43.555 | 45.828 | 47.667 | 49.238 | 51.895 | 54.109 | 58.481 | -93.9686 |
| $\mathrm{O}_{2}$ | $g$ | 42.061 | 44.112 | 45.675 | 46.968 | 49.044 | 50.697 | 53.808 | 0 |
| $\mathrm{N}_{2}$ | $g$ | 38.817 | 40.861 | 42.415 | 43.688 | 45.711 | 47.306 | 50.284 | 0 |
| NO | $g$ | 42.980 | 45.134 | 46.760 | 48.090 | 50.202 | 51.864 | 54.964 | +21.477 |

Note: $\quad G_{T}^{\circ}=$ molal free energy of the substance in its standard state, at temperature $T, \mathrm{~g} \cdot \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})$.
$H_{0}^{\circ}=$ molal enthalpy of the substance in its standard state, at $0 \mathrm{~K}, \mathrm{~g} \cdot \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})$.
$\left(\Delta H_{f}^{\circ}\right)_{0}=$ standard modal heat of formation at $0 \mathrm{~K}, \mathrm{~kg} \cdot \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})$.
Source: O. A. Hougen, K. M. Watson, and R. A. Ragatz, Chemical Process Principles, part III, Wiley, New York, 1959.

## Procedure

1. Tabulate free-energy and enthalpy functions. From Tables 1.17 and 1.18:

| Energy function | $\mathrm{C}_{4} \mathrm{H}_{8}(g)$ | $\mathrm{C}(s)$ | $\mathrm{H}_{2}(g)$ |
| :--- | :---: | :---: | :---: |
| $\left(G_{T}^{\circ}-H_{0}^{\circ}\right) / T, \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})(\mathrm{K})$ | -60.90 | -0.824 | -26.422 |
| $\Delta H_{f, 0}^{\circ}, \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})$ | 980 | 0 | 0 |
| $\left(H_{T}^{\circ}-H_{0}^{\circ}\right)_{400 \mathrm{~K}}, \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})$ | 6522 | 502.8 | 2731 |

2. Calculate standard heat of formation. Thus, $\Delta H_{f, 400 \mathrm{~K}}^{\circ}=(6522+980)-[(4)(502.8)+$ $(4)(2731)]=-5433.2 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})[-9779.8 \mathrm{Btu} /(\mathrm{lb} \cdot \mathrm{mol})]$.
3. Calculate standard free energy of formation. Thus, $\Delta G_{f}^{\circ} / T=(-60.90+980 / 400)-$ $[(4)(-0.824)+(4)(-26.422)]=50.534 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})(\mathrm{K})$. So, $\Delta G_{f}^{\circ}=(50.534)(400)=20,213.6 \mathrm{cal} /$ $(\mathrm{g} \cdot \mathrm{mol})[36,384 \mathrm{Btu} /(\mathrm{lb} \cdot \mathrm{mol})]$.

Related Calculations. Use this procedure to calculate standard heats and free energies of formation of any compound relative to its elements. The functions $\left(H_{T}^{\circ}-H_{0}^{\circ}\right),\left(G_{T}^{\circ}-H_{0}^{\circ}\right) / T$, and $\Delta H_{f, 0}^{\circ} / T$ not listed in Tables 1.17 and 1.18 may be found in other sources, such as Stull and Prophet [15].

### 1.24 STANDARD HEAT OF REACTION, STANDARD FREE-ENERGY CHANGE, AND EQUILIBRIUM CONSTANT

Calculate the standard heat of reaction $\Delta H_{T}^{\circ}$, the standard free-energy change $\Delta G_{T}^{\circ}$, and the reaction equilibrium constant $K_{T}$ for the water-gas shift reaction at $1000 \mathrm{~K}\left(1340^{\circ} \mathrm{F}\right)$ :

$$
\mathrm{CO}(g)+\mathrm{H}_{2} \mathrm{O}(g)=\mathrm{CO}_{2}(g)+\mathrm{H}_{2}(g)
$$

The standard heat of reaction is expressed as

$$
\Delta H_{T}^{\circ}=\Sigma\left[\left(H_{T}^{\circ}-H_{0}^{\circ}\right)+\Delta H_{f, 0}^{\circ}\right]_{\text {products }}-\Sigma\left[\left(H_{T}^{\circ}-H_{0}^{\circ}\right)+\Delta H_{f, 0}^{\circ}\right]_{\text {reactants }}
$$

The standard free-energy change is expressed as

$$
\Delta G^{\circ} / T=\Sigma\left[\left(G_{T}^{\circ}-H_{0}^{\circ}\right) / T+\Delta H_{f, 0}^{\circ} / T\right]_{\text {products }}-\Sigma\left[\left(G_{T}^{\circ}-H_{0}^{\circ}\right) / T+\Delta H_{f, 0}^{\circ} / T\right]_{\text {reactants }}
$$

The equilibrium constant is expressed as $K=e^{-\Delta G^{\circ} / R T}$, where the terms are as defined in Example 1.23.

## Calculation Procedure

1. Tabulate free-energy and enthalpy functions. From Tables 1.17 and 1.18:

| Energy function | $\mathrm{CO}_{2}(g)$ | $\mathrm{H}_{2}(g)$ | $\mathrm{CO}(g)$ | $\mathrm{H}_{2} \mathrm{O}(g)$ |
| :--- | :---: | :---: | :---: | :---: |
| $\left(G_{T}^{\circ}-H_{0}^{\circ}\right) / T$, | -54.109 | -32.738 | -48.860 | -47.010 |
| $\mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})(\mathrm{K})$ |  |  |  |  |
| $\Delta H_{f, 0}^{\circ}, \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})$ | $-93,968.6$ | 0 | $-27,201.9$ | $-57,107$ |
| $\left(H_{T}^{\circ}-H_{0}^{\circ}\right), \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})$ | 10,222 | 6965.8 | 7257 | 8608 |

2. Calculate standard heat of reaction. Thus, $\Delta H_{1000 \mathrm{~K}}^{\circ}=[(10,222.0)+(-93,968.6)+$ $(6,965.8)+(0)]-[(7,257.0)+(-27,201.9)+(8,608)+(-57,107)]=-8336.9 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})$ [ $-15,006.4 \mathrm{Btu} /(\mathrm{lb} \cdot \mathrm{mol})]$.
3. Calculate standard free-energy change. Thus, $\Delta G^{\circ} / 1000=[-54.109+(-93,968.6 /$ $1000)+(-32.738)+0 / 1000]-[-48.860+(-27201.9 / 1000+(-47.010)+(-57,107.0 /$ $1000)]=-0.638 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})(\mathrm{K})$. Therefore, $\Delta G_{1000 \mathrm{~K}}^{\circ}=-638.0 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})[-1148.4 \mathrm{Btu} /$ ( $\mathrm{lb} \cdot \mathrm{mol}$ )].
4. Calculate reaction equilibrium constant. Thus, $K_{1000 \mathrm{~K}}=e^{638 /(1.987)(1000)}=1.379$.

Related Calculations. Use this procedure to calculate heats of reaction and standard free-energy changes for reactions that involve components listed in Tables 1.17 and 1.18.

Heat of reaction, free-energy changes, and reaction equilibrium constants are discussed in more detail in Section 4 in the context of chemical-reaction equilibrium.

### 1.25 STANDARD HEAT OF REACTION FROM HEAT OF FORMATION-AQUEOUS SOLUTIONS

Calculate the standard heat of reaction $\Delta H^{\circ}$ for the following acid-base-neutralization reaction at standard conditions [ $\left.25^{\circ} \mathrm{C}, 1 \mathrm{~atm}(101.3 \mathrm{kPa})\right]$ :

$$
2 \mathrm{NaOH}(a q)+\mathrm{H}_{2} \mathrm{SO}_{4}(l)=\mathrm{Na}_{2} \mathrm{SO}_{4}(a q)+2 \mathrm{H}_{2} \mathrm{O}(l)
$$

## Calculation Procedure

1. Calculate the heat of reaction. The symbol $(a q)$ implies that the sodium hydroxide and sodium sulfate are in infinitely dilute solution. Therefore, the heat of solution must be included in the calculations. Data on both heat of formation and heat of solution at the standard conditions $\left(25^{\circ} \mathrm{C}\right.$ and 1 atm ) are available in Table 1.19. Since the answer sought is also to be at standard conditions, there is no need to adjust for differences in temperature (or pressure), and the equation to be used is simply

$$
\Delta H^{\circ}=\Sigma\left(\Delta H_{F}^{\circ}\right)_{\text {products }}+\Sigma\left(\Delta H_{s}^{\circ}\right)_{\text {dissolved products }}-\Sigma\left(\Delta H_{F}^{\circ}\right)_{\text {reactants }}-\Sigma\left(\Delta H_{s}^{\circ}\right)_{\text {dissolved reactants }}
$$

where $\Delta H_{F}^{\circ}$ is standard heat of formation, and $\Delta H_{s}^{\circ}$ is standard integral heat of solution at infinite dilution.

Thus, from Table 1.19 , and taking into account that there are 2 mol each of water and sodium hydroxide,

$$
\begin{aligned}
\Delta H^{\circ} & =[-330,900+2(-68,317)]+(-560)-[2(-101,990)+(-193,910)]-2(-10,246) \\
& =-49,712 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{~mol})[-89,482 \mathrm{Btu} /(\mathrm{lb} \cdot \mathrm{~mol})]
\end{aligned}
$$

The reaction is thus exothermic. To maintain the products at $25^{\circ} \mathrm{C}$, it will be necessary to remove 49,712 cal of heat per gram-mole of sodium sulfate produced.

Related Calculations. Use this general procedure to calculate heats of reaction for other aqueousphase reactions. Calculation of heat of reaction from standard heat of reaction is covered in Section 4 in the context of chemical-reaction equilibrium; see in particular Example 4.1.

## STANDARD HEAT OF REACTION FROM HEAT OF COMBUSTION

Calculate the standard heat of reaction $\Delta H^{\circ}$ of the following reaction using heat-of-combustion data:

$$
\underset{\text { (Methanol) }}{\mathrm{CH}_{3} \mathrm{OH}(l)}+\underset{\text { (Acetic acid) }}{\mathrm{CH}_{3} \mathrm{COOH}(l)}=\underset{\text { (Methyl acetate) }}{\mathrm{CH}_{3} \mathrm{OOCCH}_{3}(l)}+\underset{\text { (Water) }}{\mathrm{H}_{2} \mathrm{O}(l)}
$$

TABLE 1.19 Standard Heats of Formation and Standard Integral Heats of Solution at Infinite Dilution $\left(25^{\circ} \mathrm{C}, 1 \mathrm{~atm}\right)$

| Compound | Formula | State | $\begin{gathered} \Delta H_{f}^{\circ} \\ \mathrm{cal} /(\mathrm{g} \cdot \mathrm{~mol}) \end{gathered}$ | $\begin{gathered} \Delta H_{s}^{\circ}, \\ \mathrm{cal} /(\mathrm{g} \cdot \mathrm{~mol}) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: |
| Ammonia | $\mathrm{NH}_{3}$ | $g$ | -11,040 | -8,280 |
|  |  | $l$ | -16,060 | -3,260 |
| Ammonium nitrate | $\mathrm{NH}_{4} \mathrm{NO}_{3}$ | $s$ | -87,270 | 6,160 |
| Ammonium sulfate | $\left(\mathrm{NH}_{4}\right)_{2} \mathrm{SO}_{4}$ | $s$ | -281,860 | 1,480 |
| Calcium carbide | $\mathrm{CaC}_{2}$ | $s$ | -15,000 |  |
| Calcium carbonate | $\mathrm{CaCO}_{3}$ | $s$ | -288,450 |  |
| Calcium chloride | $\mathrm{CaCl}_{2}$ | $s$ | -190,000 | -19,820 |
| Calcium hydroxide | $\mathrm{Ca}(\mathrm{OH})_{2}$ | $s$ | -235,800 | -3,880 |
| Calcium oxide | CaO | $s$ | -151,900 | -19,400 |
| Carbon (graphite) | C | $s$ | 0 |  |
| Amorphous, in coke | C | $s$ | 2,600 |  |
| Carbon dioxide | $\mathrm{CO}_{2}$ | $g$ | -94,051.8 | -4,640 |
| Carbon disulfide | $\mathrm{CS}_{2}$ | $g$ | 27,550 |  |
|  |  | $l$ | 21,000 |  |
| Carbon monoxide | CO | $g$ | -26,416 |  |
| Carbon tetrachloride | $\mathrm{CCl}_{4}$ | $g$ | -25,500 |  |
|  |  | $l$ | -33,340 |  |
| Copper sulfate | $\mathrm{CuSO}_{4}$ | $s$ | -181,000 | -17,510 |
| Hydrochloric acid | HCl | $g$ | -22,063 | -17,960 |
| Hydrogen sulfide | $\mathrm{H}_{2} \mathrm{~S}$ | $g$ | -4,815 | -4,580 |
| Iron oxide | $\mathrm{Fe}_{3} \mathrm{O}_{4}$ | $s$ | -267,000 |  |
| Iron sulfate | $\mathrm{FeSO}_{4}$ | $s$ | -220,500 | -15,500 |
| Nitric acid | $\mathrm{HNO}_{3}$ | $l$ | -41,404 | -7,968 |
| Potassium chloride | KCl | $s$ | -104,175 | 4,115 |
| Potassium hydroxide | KOH | $s$ | -101,780 | -13,220 |
| Potassium nitrate | $\mathrm{KNO}_{3}$ | $s$ | -117,760 | 8,350 |
| Potassium sulfate | $\mathrm{K}_{2} \mathrm{SO}_{4}$ | $s$ | -342,660 | 5,680 |
| Sodium carbonate | $\mathrm{Na}_{2} \mathrm{CO}_{3}$ | $s$ | -270,300 | -5,600 |
|  | $\mathrm{Na}_{2} \mathrm{CO}_{3} \cdot 10 \mathrm{H}_{2} \mathrm{O}$ | $s$ | -975,600 | 16,500 |
| Sodium chloride | NaCl | $s$ | -98,232 | 930 |
| Sodium hydroxide | NaOH | $s$ | -101,990 | -10,246 |
| Sodium nitrate | $\mathrm{NaNO}_{3}$ | $s$ | -101,540 | -5,111 |
| Sodium sulfate | $\mathrm{Na}_{2} \mathrm{SO}_{4}$ | $s$ | -330,900 | -560 |
|  | $\mathrm{Na}_{2} \mathrm{SO}_{4} \cdot 10 \mathrm{H}_{2} \mathrm{O}$ | $s$ | -1,033,480 | 18,850 |
| Sulfur dioxide | $\mathrm{SO}_{2}$ | $g$ | -70,960 | 9,900 |
| Sulfur trioxide | $\mathrm{SO}_{3}$ | $g$ | -94,450 | -54,130 |
| Sulfuric acid | $\mathrm{H}_{2} \mathrm{SO}_{4}$ | $l$ | -193,910 | -22,990 |
| Water | $\mathrm{H}_{2} \mathrm{O}$ | $g$ | -57,798 |  |
|  |  | $l$ | -68,317 |  |
| Zinc sulfate | $\mathrm{ZnSO}_{4}$ | $s$ | -233,880 | -19,450 |

Source: F. D. Rossini et al., Selected Values of Chemical Thermodynamic Properties, National Bureau of Standards, Circular 500, 1952.

## Calculation Procedure

1. Obtain heats of combustion. Data on heats of combustion for both organic and inorganic compounds are given in numerous reference works. Thus:

| Compound | State | $\Delta H_{\text {combustion }}$, <br> $\mathrm{kcal} /(\mathrm{g} \cdot \mathrm{mol})$ |
| :--- | :---: | :---: |
| $\mathrm{CH}_{3} \mathrm{OH}$ | Liquid | -173.65 |
| $\mathrm{CH}_{3} \mathrm{COOH}$ | Liquid | -208.34 |
| $\mathrm{CH}_{3} \mathrm{OOCCH}$ |  | Liquid |

2. Calculate $\boldsymbol{\Delta} \boldsymbol{H}^{\circ}$. The heat of reaction is the difference between the heats of combustion of the reactants and of the products:

$$
\begin{gathered}
\Sigma \Delta H_{\text {combustion, reactants }}^{\circ}-\Sigma \Delta H_{\text {combustion, products }}^{\circ} \\
\text { So }, \Delta H^{\circ}=(-173.65)+(-208.34)-(-538.76)=156.77 \mathrm{kcal} /(\mathrm{g} \cdot \mathrm{~mol}) .
\end{gathered}
$$

Related Calculations. For a reaction between organic compounds, the basic thermochemical data are generally available in the form of standard heats of combustion. Use the preceding procedure for calculating the standard heats of reaction when organic compounds are involved, using the standard heats of combustion directly instead of standard heats of formation. Heat-of-formation data must be used when organic and inorganic compounds both appear in the reaction.

Calculation of heat of reaction from standard heat of reaction is covered in Section 4 in the context of chemical-reaction equilibrium; see in particular Example 4.1.

### 1.27 STANDARD HEAT OF FORMATION FROM HEAT OF COMBUSTION

Calculate the standard heats of formation of benzene $(l)$, methanol $(l)$, aniline $(l)$, methyl chloride $(g)$, and ethyl mercaptan $(l)$ using heat-of-combustion data, knowledge of the combustion products, and the equations in Table 1.20.

## Procedure

1. Obtain data on the heats of combustion, note the corresponding final combustion products, and select the appropriate equation in Table 1.20. From standard reference sources, the standard heats of combustion and the final products are as follows. The appropriate equation, A or B, is selected based on what the final combustion products are, i.e., where they are within col. 1 of Table 1.20.

| Compound (and number <br> of constituent atoms) | Combustion products | Heat of combustion, <br> $\mathrm{kcal} /(\mathrm{g} \cdot \mathrm{mol})$ | Equation to <br> be used |
| :--- | :--- | :---: | :---: |
| Benzene, $\mathrm{C}_{6} \mathrm{H}_{6}(l)$ | $\mathrm{CO}_{2}(g), \mathrm{H}_{2} \mathrm{O}(l)$ | 780.98 | A or B |
| Methanol, $\mathrm{CH}_{4} \mathrm{O}(l)$ | $\mathrm{CO}_{2}(g), \mathrm{H}_{2} \mathrm{O}(l)$ | 173.65 | A or B |
| Aniline, $\mathrm{C}_{6} \mathrm{H}_{7} \mathrm{~N}(l)$ | $\mathrm{CO}_{2}(g), \mathrm{H}_{2} \mathrm{O}(l), \mathrm{N}_{2}(g)$ | 812.0 | B |
| Methyl chloride, $\mathrm{CH}_{3} \mathrm{Cl}(g)$ | $\mathrm{CO}_{2}(g), \mathrm{H}_{2} \mathrm{O}(l), \mathrm{HCl}(a q)$ | 182.81 | A |
| Ethyl mercaptan, $\mathrm{C}_{2} \mathrm{H}_{6} \mathrm{~S}(l)$ | $\mathrm{CO}_{2}(g), \mathrm{H}_{2} \mathrm{O}(l), \mathrm{SO}_{2}(g)$ | 448.0 | B |

TABLE 1.20 Heat of Formation from Heat of Combustion

| Final products of the combustion |
| :---: | :---: |
| (1) | Equation for heat of formation $H_{f}^{\circ}, \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol}) ~(\mathbf{2})$.

Note: In the above equations, $\Delta H_{c}=$ heat of combustion corresponding to the final products in col. $1, a=$ atoms of carbon in the compound, $b=$ atoms of hydrogen, $c=$ atoms of bromine, $d=$ atoms of chlorine, $e=$ atoms of fluorine, $g=$ atoms of nitrogen, and $i=$ atoms of sulfur.
2. Calculate the heats of formation and compare with the literature values. This step can be set out in matrix form, as follows:

| Compound | Equation | Heat of formation, cal/(g $\cdot \mathrm{mol}$ ) |  |
| :---: | :---: | :---: | :---: |
|  |  | Calculated value | Literature value |
| Benzene ( $l$ ) | A | $\begin{aligned} = & -(-780.98)\left(10^{3}\right)-(94,051.8)(6) \\ & -(34,158.7)(6)=11,717 \end{aligned}$ | 11,630 |
| $\operatorname{Methanol}(l)$ | A | $\begin{aligned} = & -(-173.65)\left(10^{3}\right)-(94,051.8)(1) \\ & -(34,158.7)(4)=-57,036 \end{aligned}$ | -57,040 |
| Aniline( $l$ ) | B | $\begin{aligned} = & -(-812.0)\left(10^{3}\right)-(94,051.8)(6) \\ & -(34,158.7)(7)=8,578 \end{aligned}$ | 8,440 |
| Methyl chloride( $($ ) | A | $\begin{aligned} = & -(-182.81)\left(10^{3}\right)-(94,051.8)(1) \\ & -(34,158.7)(3)-(5,864.3)(1)=-19,582 \end{aligned}$ | -19,580 |
| Ethyl mercaptan(l) | B | $\begin{aligned} = & -(-448.0)\left(10^{3}\right)-(94,051.8)(2)- \\ & (34,158.7)(6)-(70,960)(1)=-16,015.8 \end{aligned}$ | -16,000 |

Related Calculations. This approach may be used to find the heat of formation of a compound all of whose constituent atoms are among the following: carbon, hydrogen, bromine, chlorine, fluorine, iodine, nitrogen, oxygen, and sulfur.

### 1.28 <br> HEAT OF ABSORPTION FROM SOLUBILITY DATA

Estimate the heat of absorption of carbon dioxide in water at $15^{\circ} \mathrm{C}\left(59^{\circ} \mathrm{F}\right.$, or 288 K$)$ from these solubility data:

| Temperature, ${ }^{\circ} \mathrm{C}$ | 0 | 5 | 10 | 15 | 20 |
| :--- | ---: | ---: | ---: | ---: | ---: |
| Henry constant, atm/mol-fraction | 728 | 876 | 1040 | 1220 | 1420 |

The formula is

$$
\Delta H_{\mathrm{abs}}=\left(\bar{h}_{i}-H_{i}\right)=R[d \ln H / d(1 / T)]
$$



FIGURE 1.28 Henry constant for carbon-dioxide/water system at $15^{\circ} \mathrm{C}$ (Example 1.28). Note: $1 \mathrm{~atm}=101.3 \mathrm{kPa}$.
where $\Delta H_{\text {abs }}$ is heat of absorption, $\bar{h}_{i}$ is partial molar enthalpy of component $i$ at infinite dilution in the liquid at a given temperature and pressure, $H_{i}$ is molar enthalpy of pure gas $i$ at the given temperature and pressure, $H$ is the Henry constant, the partial pressure of the gas divided by its solubility, $R$ is the gas constant, and $T$ is absolute temperature.

## Procedure

1. Determine $\boldsymbol{d} \ln \boldsymbol{H} / \boldsymbol{d}(\boldsymbol{I} / \boldsymbol{T})$. This is the slope of the plot of $\ln H$ against $1 / T$. A logarithmic plot based on the data given in the statement of the problem is shown in Fig. 1.28. The required slope is found to be $-2.672 \times 10^{3} \mathrm{~K}$.
2. Calculate the heat of absorption. Substitute directly into the formula. Thus,

$$
\begin{aligned}
\Delta H_{\mathrm{abs}} & =R[d \ln H / d(1 / T)]=1.987\left(-2.672 \times 10^{3}\right) \\
& =-5.31 \times 10^{3} \mathrm{cal} /(\mathrm{g} \cdot \mathrm{~mol})[9.56 \mathrm{Btu} /(\mathrm{lb} \cdot \mathrm{~mol})]
\end{aligned}
$$

Related Calculations. This procedure may be used for calculating the heats of solution from lowpressure solubility data where Henry's law in its simple form is obeyed.

### 1.29 ESTIMATION OF LIQUID VISCOSITY AT HIGH TEMPERATURES

Use the Letsou-Stiel high-temperature generalized correlation to estimate the viscosity of liquid benzene at $227^{\circ} \mathrm{C}\left(500 \mathrm{~K}, 440^{\circ} \mathrm{F}\right)$.

The correlation is expressed as

$$
\mu_{L} \psi=\left(\mu_{L} \psi\right)^{(0)}+\omega\left(\mu_{L} \psi\right)^{(1)}
$$

where $\left(\mu_{L} \psi\right)^{(0)}=0.015174-0.02135 T_{R}+0.0075 T_{R}^{2}$
$\left(\mu_{L} \psi\right)^{(1)}=0.042552-0.07674 T_{R}+0.0340 T_{R}^{2}$
$\mu_{L}=$ liquid viscosity at the reduced temperature, in centipoise (cP)
$\psi=\frac{T_{c}^{1 / 6}}{\left(M^{1 / 2} P_{c}^{2 / 3}\right)}$
$\omega=$ Pitzer accentric factor
$T_{c}=$ critical temperature, K
$P_{c}=$ critical pressure, atm
$M=$ molecular weight
Use these values for benzene: $T_{c}=562.6 \mathrm{~K}, P_{c}=48.6 \mathrm{~atm}, M=78.1$, and $\omega=0.212$.

## Calculation Procedure

1. Calculate the correlating parameters for the Letsou-Stiel method. By use of the equations outlined above,

$$
\begin{aligned}
\psi & =T_{c}^{1 / 6} /\left(M^{1 / 2} P_{c}^{2 / 3}\right)=(562.6)^{1 / 6} /(78.1)^{1 / 2}(48.6)^{2 / 3}=0.0244 \\
T_{R} & =T / T_{c}=(227+273) / 562.6=0.889 \\
\left(\mu_{L} \psi\right)^{(0)} & =0.015174-(0.02135)(0.889)+(0.0075)(0.889)^{2}=0.0021 \\
\left(\mu_{L} \psi\right)^{(1)} & =0.042552-(0.07674)(0.889)+(0.0340)(0.889)^{2}=0.0012
\end{aligned}
$$

2. Calculate the viscosity of liquid benzene. Thus, upon dividing through by $\psi$, we have the equation

$$
\begin{aligned}
\mu_{L} & =(1 / \psi)\left[\left(\mu_{L} \psi\right)^{(0)}+\omega\left(\mu_{L} \psi\right)^{(1)}\right] \\
& =(1 / 0.024)[(0.0021)+(0.212)(0.0012)]=0.0981 \mathrm{cP}
\end{aligned}
$$

Related Calculations. The Letsou-Stiel correlation is a fairly accurate method for estimating viscosities of liquids at relatively high temperatures, $T_{R}=0.75$ or higher. It has been tested on a large number of compounds and is reported to fit most materials up to a reduced temperature of about 0.9 , with an average error of $\pm 3$ percent.

### 1.30 VISCOSITY OF NONPOLAR AND POLAR GASES AT HIGH PRESSURE

Use the Jossi-Stiel-Thodos generalized correlation to estimate the vapor viscosity of (1) methane (a nonpolar gas) at 500 psig ( 35 atm abs ) and $250^{\circ} \mathrm{F}(394 \mathrm{~K})$, and (2) ammonia (a polar gas) at $340^{\circ} \mathrm{F}$ ( 444.4 K ) and 1980 psig ( 135.8 atm abs ). Experimentally determined viscosities for those two gases at low pressure and the same temperatures are $140 \mu \mathrm{P}$ for methane and $158 \mu \mathrm{P}$ for ammonia.

The Jossi-Stiel-Thodos correlation is summarized in these equations:
For nonpolar gases,

$$
\left[\left(\mu-\mu^{0}\right) \psi+1\right]^{0.25}=1.0230+0.2336 \rho_{R}+0.58533 \rho_{R}^{2}-0.040758 \rho_{R}^{3}+0.093324 \rho_{R}^{4}
$$

For polar gases,

$$
\begin{aligned}
& \left(\mu-\mu^{0}\right) \psi=1.656 \rho_{R}^{1.111} \quad \text { if } \rho_{R} \leq 0.1 \\
& \left(\mu-\mu^{0}\right) \psi=0.0607\left(9.045 \rho_{R}+0.63\right)^{1.739} \quad \text { if } 0.1 \leq \rho_{R} \leq 0.9 \\
& \log \left\{4-\log \left[\left(\mu-\mu^{0}\right) \psi\right]\right\}=0.6439-0.1005 \rho_{R}-D \quad \text { if } 0.9 \leq \rho_{R}<2.6
\end{aligned}
$$

where $D=0$ if $0.9 \leq \rho_{R} \leq 2.2$, or
$D=(0.000475)\left(\rho_{R}^{3}-10.65\right)^{2} \quad$ if $2.2<\rho_{R} \leq 2.6$
$\mu=$ viscosity of high-pressure (i.e., dense) gas, $\mu \mathrm{P}$
$\mu^{0}=$ viscosity of gas at low pressure, $\mu \mathrm{P}$
$\rho_{R}=$ reduced gas density, $\rho / \rho_{c}$ (which equals $V_{c} / V$ )
$\rho=$ density
$\rho_{c}=$ critical density
$V=$ specific volume
$V_{c}=$ critical specific volume
$\psi=T_{c}^{1 / 6} /\left(M^{1 / 2} P_{c}^{2 / 3}\right)$
$T_{c}=$ critical temperature, K
$P_{c}=$ critical pressure, atm
$M=$ molecular weight
Use these values for methane: $T_{c}=190.6 \mathrm{~K} ; P_{c}=45.4 \mathrm{~atm} ; V_{c}=99.0 \mathrm{~cm}^{3} /(\mathrm{g} \cdot \mathrm{mol}) ; Z_{c}=$ $0.288 ; M=16.04$. And use these values for ammonia: $T_{c}=405.6 \mathrm{~K} ; P_{c}=111.3 \mathrm{~atm} ; V_{c}=$ $72.5 \mathrm{~cm}^{3} /(\mathrm{g} \cdot \mathrm{mol}) ; Z_{c}=0.242 ; M=17.03$.

## Calculation Procedure

1. Calculate the nonideal compressibility factor for the methane and the ammonia. Use the generalized correlations shown in Figs. 1.1 through 1.3 in this chapter. For methane, $T_{R}=394 / 190.6=$ 2.07 , and $P_{R}=35 / 45.4=0.771$. From the statement of the problem, $Z_{c}=0.288$. Thus, by interpolation from Fig. 1.2 (for $Z_{c}=0.27$ ) and Fig. 1.3 (for $Z_{c}=0.29$ ), $Z$ is found to be 0.98 .

Similarly for ammonia, $T_{R}=444.4 / 405.6=1.10, P_{R}=135.8 / 111.3=1.22$, and $Z_{c}=0.242$. By extrapolation from Figs. 1.2 and $1.3, Z=0.65$.
2. Calculate the reduced density for the high-pressure gas. For methane, $\rho_{R}=\rho / \rho_{c}=\rho V_{c}=$ $P V_{c} / Z R T=(35)(99.0) /(0.98)(82.07)(394)=0.109$.

Similarly for ammonia, $\rho_{R}=P V_{c} / Z R T=(135.8)(72.5) /(0.65)(82.07)(444.4)=0.415$.
3. Calculate the parameter $\psi$. For methane, $\psi=T_{c}^{1 / 6} /\left(M^{1 / 2} P_{c}^{2 / 3}\right)=(190.6)^{1 / 6} /(16.04)^{1 / 2}$ $\times(45.4)^{2 / 3}=0.0471$.

And for ammonia, $\psi=(405.6)^{1 / 6} /(17.03)^{1 / 2}(111.3)^{2 / 3}=0.0285$.
4. Calculate the viscosity for the high-pressure methane, using the nonpolar equation. Thus, $\left[\left(\mu-\mu^{0}\right) \psi+1\right]^{0.25}=1.023+(0.2336)(0.109)+(0.58533)(0.109)^{2}-(0.040758)(0.109)^{3}+$ $(0.093324)(0.109)^{4}=1.0550$. And accordingly,

$$
\mu-\mu^{0}+\left[(1.0550)^{1 / 0.25}-1\right] / \psi=140+\left[(1.0550)^{1 / 0.25}-1\right] / 0.0471=145.07 \mu \mathrm{P}
$$

This correlation thus indicates that the pressure effect raises the viscosity of the methane by about 4 percent.
5. Calculate the viscosity for the high-pressure ammonia, using the appropriate polar equation. Because the reduced density $(0.415)$ lies between 0.1 and 0.9 , the appropriate equation is

$$
\left(\mu-\mu^{0}\right) \psi=0.0607\left(9.045 \rho_{R}+0.63\right)^{1.739}
$$

Thus, $\left.\left(\mu-\mu^{0}\right) \psi=0.0607(9.045)(0.415)+0.63\right]^{1.739}=0.7930$, so $\mu=\mu_{0}+0.7930 / \psi=158+$ $0.7930 / 0.0258=185.8 \mu \mathrm{P}$. This correlation thus predicts that the pressure effect raises the viscosity of the ammonia by about 18 percent.

### 1.31 THERMAL CONDUCTIVITY OF GASES

Use the modified Euken correlation to estimate the thermal conductivity of nitric oxide (NO) vapor at $300^{\circ} \mathrm{C}\left(573 \mathrm{~K}, 572^{\circ} \mathrm{F}\right)$ and $1 \mathrm{~atm}(101.3 \mathrm{kPa})$. At that temperature, the viscosity of nitric oxide is $32.7 \times 10^{-5} \mathrm{P}$.

The modified Euken correlation is

$$
\lambda M / \mu=3.52+1.32 C_{v}^{\circ}=3.52+1.32 C_{p}^{\circ} / \gamma
$$

where $M=$ molecular weight
$\mu=$ viscosity, P
$C_{p}^{\circ}, C_{v}^{\circ}=$ ideal-gas heat capacity at constant pressure and constant volume, respectively, $\mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol}) \mathrm{K}$
$\gamma=$ heat capacity ratio, equal to $C_{p}^{\circ} / C_{v}^{\circ}$
$\lambda=$ thermal conductivity, cal/(cm)(s)(K)

Use these values and relationships for nitric oxide: $M=30.01, C_{p}^{\circ}=6.461+2.358 \times 10^{-3} T$ (where $T$ is in kelvins), and $C_{v}^{\circ}=C_{p}^{\circ}-R=C_{p}^{\circ}-1.987$.

## Calculation Procedure

1. Calculate $C_{v}^{\circ}$. Thus, $C_{v}^{\circ}=C_{p}^{\circ}-R=6.461+\left(2.358 \times 10^{-3}\right)(300+273)-1.987=5.826$ $\mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})(\mathrm{K})$.
2. Calculate the thermal conductivity. Thus, upon rearranging the Eucken equation,

$$
\begin{aligned}
\lambda & =(\mu / M)\left(3.52+1.32 C_{v}^{\circ}\right) \\
& =\left[\left(32.7 \times 10^{-5}\right) / 30.01\right][3.52+(1.32)(5.826)] \\
& =1.22 \times 10^{-4} \mathrm{cal} /(\mathrm{cm})(\mathrm{s})(\mathrm{K})
\end{aligned}
$$

The experimentally determined value is reported as $1.07 \times 10^{-4} \mathrm{cal} /(\mathrm{cm})(\mathrm{s})(\mathrm{K})$. The error is thus 14 percent.

### 1.32 THERMAL CONDUCTIVITY OF LIQUIDS

Estimate the thermal conductivity of carbon tetrachloride at $10^{\circ} \mathrm{C}\left(283 \mathrm{~K}, 50^{\circ} \mathrm{F}\right)$ using the Robbins and Kingrea correlation:

$$
\lambda_{L}=[(88-4.94 \mathrm{H})(0.001) / \Delta S]\left[\left(0.55 / T_{R}\right)^{N}\right]\left[C_{p} \rho^{4 / 3}\right]
$$

where $\lambda_{L}=$ liquid thermal conductivity, $\mathrm{cal} /(\mathrm{cm})(\mathrm{s})(\mathrm{K})$
$T_{R}=$ reduced temperature, equal to $T / T_{c}$ where $T_{c}$ is critical temperature
$C_{p}=$ molal heat capacity of liquid, $\mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})(\mathrm{K})$
$\rho=$ molal liquid density, $(\mathrm{g} \cdot \mathrm{mol}) / \mathrm{cm}^{3}$
$\Delta S=\left(\Delta H_{v b} / T_{b}\right)+R \ln \left(273 / T_{b}\right), \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})(\mathrm{K})$
$\Delta H_{v b}=$ molal heat of vaporization at normal boiling point, $\mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})$
$T_{b}=$ normal boiling point, K
$H=$ empirical parameter whose value depends on molecular structure and is obtained from Table 1.21
$N=$ empirical parameter whose value depends on liquid density at $20^{\circ} \mathrm{C}$ (It equals 0 if the density is greater than $1.0 \mathrm{~g} / \mathrm{cm}^{3}$, and 1 otherwise.)

TABLE 1.21 $H$-factors for Robbins-Kingrea Correlation

| Functional group | Number of groups | H |
| :---: | :---: | :---: |
| Unbranched hydrocarbons: |  |  |
| Paraffins |  | 0 |
| Olefins |  | 0 |
| Rings |  | 0 |
| $\mathrm{CH}_{3}$ branches | 1 | 1 |
|  | 2 | 2 |
|  | 3 | 3 |
| $\mathrm{C}_{2} \mathrm{H}_{5}$ branches | 1 | 2 |
| $i-\mathrm{C}_{3} \mathrm{H}_{7}$ branches | 1 | 2 |
| $\mathrm{C}_{4} \mathrm{H}_{9}$ branches | 1 | 2 |
| F substitutions | 1 | 1 |
|  | 2 | 2 |
| Cl substitutions | 1 | 1 |
|  | 2 | 2 |
|  | 3 or 4 | 3 |
| Br substitutions | 1 | 4 |
|  | 2 | 6 |
| I substitutions | 1 | 5 |
| OH substitutions | 1 (iso) | 1 |
|  | 1 (normal) | -1 |
|  | 2 | 0 |
|  | 1 (tertiary) | 5 |
| Oxygen substitutions: |  |  |
| $-\mathrm{C}=\mathrm{O}$ (ketones, aldehydes) |  | 0 |
|  |  | 0 |
| -O- (ethers) |  | 2 |
| $\mathrm{NH}_{2}$ substitutions | 1 | 1 |

Source: Reprinted by permission from "Estimate Thermal Conductivity," Hydrocarbon Processing, May 1962, copyright 1962 by Gulf Publishing Co., all rights reserved.

Use these values for carbon tetrachloride: $T_{c}=556.4 \mathrm{~K}$, molecular weight $=153.8$, liquid density $=1.58 \mathrm{~g} / \mathrm{cm}^{3}$, molal heat capacity $=31.37 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})(\mathrm{K}), T_{b}=349.7 \mathrm{~K}, \Delta H_{v b}=7170$ $\mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})$

## Calculation Procedure

1. Obtain the structural constant H from Table 1.21. Since carbon tetrachloride is an unbranched hydrocarbon with three chlorine substitutions, $H$ has a value of 3 .
2. Calculate $\quad \Delta S$. Thus, $\Delta S=\left(\Delta H_{v b} / T_{b}\right)+R\left[\ln \left(273 / T_{b}\right)\right]=7170 / 349.7+1.987[\ln (273 /$ $349.7)]=20.0 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})(\mathrm{K})$.
3. Calculate the thermal conductivity. Thus,

$$
\begin{aligned}
\lambda_{L} & =[(88-4.94 H)(0.001) / \Delta S]\left[\left(0.55 / T_{R}\right)^{N}\right]\left[C_{p} \rho^{4 / 3}\right] \\
& =\{[88-(4.94)(3)][0.001] /[20.0]\}\left\{[0.55 /(283 / 556.4)]^{0}\right\}\left\{[31.37][1.58 / 153.8]^{4 / 3}\right\} \\
& =2.564 \times 10^{-6} \mathrm{cal} /(\mathrm{cm})(\mathrm{s})(\mathrm{K})
\end{aligned}
$$

The experimentally determined value is reported as $2.510 \times 10^{-6} \mathrm{cal} /(\mathrm{cm})(\mathrm{s})(\mathrm{K})$. The error is thus 2.2 percent.

### 1.33 DIFFUSION COEFFICIENTS FOR BINARY GAS SYSTEMS AT LOW PRESSURES

Estimate the diffusion coefficient of benzene vapor diffusing into air at $100^{\circ} \mathrm{F}$ and at atmospheric pressure using the following empirical correlation* for binary air-hydrocarbon systems at low pressures (less than 30 atm ):

$$
D_{A B}=\frac{0.0204 T^{1.75}\left(\frac{1}{M_{A}}+\frac{1}{M_{B}}\right)^{1 / 2}}{\left[\left(\Sigma_{A} V_{i}\right)^{1 / 3}+\left(\Sigma_{B} V_{i}\right)^{1 / 3}\right]^{2}}
$$

where $D_{A B}=$ diffusion component of component A (benzene) into component B (air), square feet per hour
$T=$ temperature, degrees Rankine
$M_{A}, M_{B}=$ molecular weights of components $A$ and $B$
$P=$ system pressure, pounds per square inch absolute
$\Sigma V_{i}=$ sum of atomic diffusion volumes shown in Table 1.22

## Calculation Procedure

1. Determine the diffusion volumes for benzene and air. Obtain the diffusion volumes for carbon, hydrogen, and an aromatic ring from Table 1.22. Weight the carbon and hydrogen in accordance with the number of atoms in the benzene molecule (six each), then add the diffusion increment for the aromatic ring (note that it is a negative number). The sum is the diffusion volume for benzene:
[^1]TABLE 1.22 Atomic Diffusion Volumes

| Molecule | Diffusion volume | Molecule | Diffusion volume |
| :---: | :---: | :---: | :---: |
| $\mathrm{H}_{2}$ | 7.07 | CO | 18.9 |
| He | 2.88 | $\mathrm{CO}_{2}$ | 26.9 |
| $\mathrm{~N}_{2}$ | 17.9 | $\mathrm{NH}_{3}$ | 14.9 |
| $\mathrm{O}_{2}$ | 16.6 | $\mathrm{Cl}_{2}$ | 37.7 |
| Air | 20.1 | $\mathrm{Br}_{2}$ | 67.2 |
| Ar | 16.1 | $\mathrm{SO}_{2}$ | 41.1 |
| $\mathrm{H}_{2} \mathrm{O}$ | 12.7 | $\mathrm{CCl}_{2} \mathrm{~F}_{2}$ | 114.8 |
| Atom | Volume increments, $V$ |  | Volume increment, $V$ |
| C | 16.5 | Cl | 19.5 |
| H | 1.98 | S | 17.0 |
| O | 5.48 | Aromatic ring | -20.2 |
| N | 5.69 | Heterocyclic ring | -20.2 |

$$
\begin{aligned}
\text { benzene } \Sigma V_{i}= & (6)(16.5) \\
& (\text { carbon })
\end{aligned} \underset{\text { (hydrogen) }}{(6)(1.98)}+\underset{\text { (aromatic ring) }}{(1)(-20.2)}=90.7
$$

As for air, its diffusion volume can be read directly from the table: 20.1.

## 2. Obtain the molecular weights

$\begin{array}{ll}\text { Component A (benzene): } & M_{A}=78.1 \\ \text { Component B (air): } & M_{B}=28.9\end{array}$
3. Calculate the diffusion coefficient. Substitute the values from steps 1 and 2 into the equation presented in the problem statement. Thus,

$$
\begin{aligned}
D_{A B} & =\frac{(0.0204)(100+459.7)^{1.75}(1 / 78.1+1 / 28.9)^{1 / 2}}{(14.69)\left[(90.7)^{1 / 3}+(20.1)^{1 / 3}\right]^{2}} \\
& =0.374 \mathrm{ft}^{2} / \mathrm{h}
\end{aligned}
$$

The experimentally determined value is reported as $0.372 \mathrm{ft}^{2} / \mathrm{h}$. The calculated value represents a deviation of 0.5 percent.

## ESTIMATION OF SURFACE TENSION OF A PURE LIQUID

Estimate the surface tension, $\sigma$, of $n$-butane at $20^{\circ} \mathrm{C}$ using the generalized corresponding state correlation of Brock and Bird [32] and the Miller relationship [33]. The correlation and the relationship are as follows:

$$
\sigma=\left[\left(P_{c}^{2 / 3}\right)\right]\left[T_{c}^{1 / 3}\right]\left[\left(1-T / T_{c}\right)^{11 / 9}\right][K]
$$

where $K$ is defined as follows:

$$
K=0.1196\left\{1+\left[\left(T_{b} / T_{c}\right) \ln \left(P_{c} / 1.01325\right)\right] /\left[1-T_{b} / T_{c}\right]\right\}-0.279
$$

where $\sigma=$ surface tension in dynes $/ \mathrm{cm}$
$P_{c}=$ critical pressure, bar
$T_{c}=$ critical temperature, K
$T_{b}=$ normal boiling point, K
Use the following physical data: $T_{c}=425.5 \mathrm{~K}, P_{c}=37.5$ bar, and $T_{b}=272.7 \mathrm{~K}$.

## Calculation Procedure

## 1. Calculate $K$

$$
\begin{aligned}
K & =0.1196\left[1+\frac{(272.7 / 425.7) \ln (37.5 / 1.01325)}{(1-272.7 / 425.2)}\right]-0.279 \\
& =0.612
\end{aligned}
$$

## 2. Calculate the surface tension

$$
\begin{aligned}
\sigma & =(37.5)^{2 / 3} \times(425.2)^{1 / 3}(1-293 / 425.2)^{11 / 9} \times 0.612 \\
& =12.36 \text { dyne } / \mathrm{cm}
\end{aligned}
$$

The experimentally determined value is reported as 12.46 . The calculated value represents an error of $+0.9 \%$.

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## SECTION 2

## STOICHIOMETRY*

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| 2.1 | MATERIAL BALANCE-NO CHEMICAL |
| :--- | :--- |
|  | REACTIONS INVOLVED 2.2 |
| 2.2 | MATERIAL BALANCE-CHEMICAL |
|  | REACTIONS INVOLVED 2.3 |
| 2.3 | MATERIAL BALANCE-INCOMPLETE |
|  | DATA ON COMPOSITION OR FLOW |
|  | RATE 2.4 |
| 2.4 | USE OF A TIE ELEMENT IN |
|  | MATERIAL-BALANCE |
|  | CALCULATIONS 2.5 |
| 2.5 | MATERIAL BALANCE-CHEMICAL |
|  | REACTION AND A RECYCLE STREAM |
|  | INVOLVED 2.6 |
| 2.6 MATERIAL BALANCE-CHEMICAL |  |

REACTION, RECYCLE STREAM, AND PURGE STREAM INVOLVED 2.7

### 2.7 USE OF ENERGY BALANCE WITH

 MATERIAL BALANCE 2.92.8 MATERIAL BALANCE-LINKING RECYCLE AND PURGE WITH REACTION SELECTIVITY AND CONVERSION 2.10
2.9 COMBUSTION OF COAL FUEL IN A FURNACE 2.14
2.10 COMBUSTION OF FUEL OIL IN A FURNACE 2.17
2.11 COMBUSTION OF NATURAL GAS IN A FURNACE 2.18

The first law of thermodynamics is the basis for material- or energy-balance calculations. Usually there is no significant transformation of mass to energy, and for a material balance, the first law can be reduced to the form

$$
\text { Mass in }=\text { mass out }+ \text { accumulation }
$$

A similar equation can be used to express the energy balance

$$
\text { Energy in (above datum) }+ \text { energy generated }=\text { energy out (above datum) }
$$

Energy balances differ from mass balances in that the total mass is known but the total energy of a component is difficult to express. Consequently, the heat energy of a material is usually expressed relative to its standard state at a given temperature. For example, the heat content, or enthalpy, of steam is expressed relative to liquid water at $273 \mathrm{~K}\left(32^{\circ} \mathrm{F}\right)$ at a pressure equal to its own vapor pressure.

Regardless of how complicated a material-balance system may appear, the use of a systematic approach can resolve it into a number of independent equations equal to the number of unknowns. One suitable stepwise approach is (1) state the problem, (2) list available data, (3) draw a sketch of the system, (4) define the system boundaries, (5) establish the bases for the system parameters,

[^2](6) write component material balances, (7) write an overall material balance, (8) solve the equations, and (9) make another mass balance as a check.

### 2.1 MATERIAL BALANCE-NO CHEMICAL REACTIONS INVOLVED

A slurry containing 25 percent by weight of solids is fed into a filter. The filter cake contains 90 percent solids and the filtrate contains 1 percent solids. Make a material balance around the filter for a slurry feed rate of $2000 \mathrm{~kg} / \mathrm{h}(4400 \mathrm{lb} / \mathrm{h})$. For that feed rate, what are the corresponding flow rates for the cake and the filtrate?

## Calculation Procedure

1. Sketch the system, showing the available data, indicating the unknowns, defining the system boundary, and establishing the basis for the calculations. When no chemical reactions are involved, the balances are based on the masses of individual chemical compounds appearing in more than one incoming or outgoing stream. Components appearing in only one incoming and one outgoing stream can be lumped together as though they are one component to simplify calculations and increase precision. A convenient unit of mass is selected, usually the kilogram or pound, and all components are expressed in that unit.

As the basis for a continuous process, always choose a unit of time or a consistent set of flow rates per unit of time. For batch processes, the appropriate basis is 1 batch. In the present (continuous) process, let the basis be 1 h . Let $C$ be the mass flow rate of filter cake and $F$ the mass flow rate of filtrate, in kilograms per hour. Figure 2.1 is a sketch of the system.
2. Set up and solve the material-balance equations. This is a steady-state operation, so accumulation equals zero and the amount of mass in equals the amount of mass out (per unit of time). Since there are two unknowns, $C$ and $F$, two independent equations must be written. One will be an overall balance; the other can be either a liquid balance (the option chosen in this example) or a solids balance.

Overall balance: $\quad$ Filtrate out + cake out $=$ slurry in, or $F+C=2000 \mathrm{~kg} / \mathrm{h}(4400 \mathrm{lb} / \mathrm{h})$.
Liquid balance: Liquid in filtrate + liquid in cake $=$ liquid in slurry, or (wt fraction liquid in filtrate) (mass of filtrate) $+(\mathrm{wt}$ fraction liquid in cake)(mass of cake) $=(\mathrm{wt}$ fraction liquid in slurry)(mass of slurry), or $(1.0-0.01) F+(1.0-0.90) C=(1.0-0.25)(2000)$.

Simultaneous solving of the two equations, $F+C=2000$ and $0.99 F+0.1 C=1500$, gives $F$ to be $1460.7 \mathrm{~kg} / \mathrm{h}(3214 \mathrm{lb} / \mathrm{h})$ of filtrate and $C$ to be $539.3 \mathrm{~kg} / \mathrm{h}(1186 \mathrm{lb} / \mathrm{h})$ of cake.
3. Check the results. It is convenient to check the answers by substituting them into the equation not used above, namely, the solids balance. Thus, solid in filtrate + solid in cake $=$ solid in slurry, or $0.01(1460.7)+0.9(539.3)=0.25(2000)$. The answers, therefore, are correct.


FIGURE 2.1 Material balance for filter (Example 2.1).

### 2.2 MATERIAL BALANCE-CHEMICAL REACTIONS INVOLVED

Natural gas consisting of $95 \%$ methane and $5 \%$ nitrogen by volume is burned in a furnace with $15 \%$ excess air. How much air at $289 \mathrm{~K}\left(61^{\circ} \mathrm{F}\right)$ and $101.3 \mathrm{kPa}(14.7 \mathrm{psia})$ is required if the fuel consumption is $10 \mathrm{~m}^{3} / \mathrm{s}\left(353 \mathrm{ft}^{3} / \mathrm{s}\right)$ measured at 289 K and 101.3 kPa ? Make an overall material balance and calculate the quantity and composition of the flue gas.

## Calculation Procedure

1. Sketch the system, setting out the available data, indicating the unknowns, defining the system boundary, and establishing the basis for the calculations. For a process involving chemical reactions, the usual procedure is to express the compositions of the streams entering and leaving the process in molar concentrations. The balances are made in terms of the largest components remaining unchanged in the reactions. These can be expressed as atoms $(\mathrm{S})$, ions $\left(\mathrm{SO}_{4}^{2-}\right)$, molecules $\left(\mathrm{O}_{2}\right)$, or other suitable units.

Whenever the reactants involved are not present in the proper stoichiometric ratios, the limiting reactant should be determined and the excess quantities of the other reactants calculated. Unconsumed reactants and inert materials exit with the products in their original form.

By convention, the amount of excess reactant in a reaction is always defined on the basis of the reaction going to 100 percent completion for the limiting reactant. The degree of completion is not a factor in determining or specifying the excess of reactants. For example, if methane is burned with 10 percent excess air, the volume of air needed to burn the methane is calculated as though there is total combustion of methane to carbon dioxide and water.

In the present problem, let the basis be 1 s . Let $A$ and $F$ be the volumetric flow rates for air and flue gas, in cubic meters per second. Figure 2.2 is a sketch of the system. The data are as follows:

Natural gas at 289 K and $101.3 \mathrm{kPa}=10 \mathrm{~m}^{3} / \mathrm{s}$
$95 \% \mathrm{CH}_{4} \quad \mathrm{MW}=16$
$5 \% \mathrm{~N}_{2} \quad \mathrm{MW}=28$
Air at 289 K and $101.3 \mathrm{kPa}=A \mathrm{~m}^{3} / \mathrm{s}$
$21 \% \mathrm{O}_{2} \quad \mathrm{MW}=32$
$79 \% \mathrm{~N}_{2} \quad \mathrm{MW}=28$
$\mathrm{R}=8.314 \mathrm{~kJ} /(\mathrm{kg} \cdot \mathrm{mol})(\mathrm{K}) \quad$ (ideal-gas constant)
2. Convert the natural gas flow rate to kilogram-moles per second. At the conditions of this problem, the ideal-gas law can be used. Thus, $n=P V / R T$, where $n$ is number of moles, $P$ is pressure, $V$ is volume, $R$ is the gas constant, and $T$ is absolute temperature.

For $\mathrm{CH}_{4}, n=(101.3 \mathrm{kPa})\left[\left(10 \mathrm{~m}^{3} / \mathrm{s}\right)(0.95)\right] /[8.314 \mathrm{~kJ} /(\mathrm{kg} \cdot \mathrm{mol})(\mathrm{K})](289 \mathrm{~K})=0.40 \mathrm{~kg} \cdot \mathrm{~mol} / \mathrm{s}$. For $\mathrm{N}_{2}$, since the volumetric composition is $95 \% \mathrm{CH}_{4}$ and $5 \% \mathrm{~N}_{2}, n=(0.05 / 0.95)(0.40)=$ $0.02 \mathrm{~kg} \cdot \mathrm{~mol} / \mathrm{s}$.


FIGURE 2.2 Material balance for furnace (Example 2.2).
3. Determine the amount of oxygen required and the airflow rate. The combustion reaction for $\mathrm{CH}_{4}$ is $\mathrm{CH}_{4}+2 \mathrm{O}_{2} \rightarrow \mathrm{CO}_{2}+2 \mathrm{H}_{2} \mathrm{O}$. Thus $0.40 \mathrm{~mol} / \mathrm{s}$ of $\mathrm{CH}_{4}$ requires $2(0.40)$, or $0.80, \mathrm{~mol} / \mathrm{s}$ of $\mathrm{O}_{2}$ for stoichiometric combustion. Since 15 percent excess air is specified, the number of moles of oxygen in the air is $(1.15)(0.80)$, or $0.92, \mathrm{~kg} \cdot \mathrm{~mol} / \mathrm{s}$. The amount of nitrogen in with the air is $[(0.79 \mathrm{~mol} \mathrm{~N} / 2 \mathrm{~mol}$ air $) /(0.21 \mathrm{~mol} \mathrm{O} 2 / \mathrm{mol}$ air $)]\left(0.92 \mathrm{~kg} \cdot \mathrm{~mol} / \mathrm{s}_{2}\right)=3.46 \mathrm{~kg} \cdot \mathrm{~mol} / \mathrm{s}$. Total moles in the incoming air are $0.92+3.46=4.38 \mathrm{~kg} \cdot \mathrm{~mol} / \mathrm{s}$. Finally, using the ideal-gas law to convert to volumetric flow rate, $V=n R T / P=(4.38)(8.314)(289) / 101.3=103.9 \mathrm{~m}^{3} / \mathrm{s}\left(3671 \mathrm{ft}^{3} / \mathrm{s}\right)$ of air.
4. Set up the material balance and calculate the composition and quantity of the flue gas. Convert to a mass basis because it is always true (unless there is a conversion between mass and energy) that from a mass standpoint the input equals the output plus the accumulation. In the present problem, there is no accumulation. The output (the flue gas) includes nitrogen from the air and from the natural gas, plus the 15 percent excess oxygen, plus the reaction products, namely, $0.40 \mathrm{~mol} / \mathrm{SO}_{2}$ and $2(0.40)=$ $0.80 \mathrm{~mol} / \mathrm{s}$ water.

Select 1 s as the basis. Then the inputs and outputs are as follows:

| Component | Kilogram-moles | $\times$ | Kilograms per mole $=$ Kilograms |
| :--- | :---: | :---: | :---: |
|  |  | Inputs |  |
| Natural gas: | 0.40 |  |  |
| $\mathrm{CH}_{4}$ | 0.02 | 28 | 6.40 |
| $\mathrm{~N}_{2}$ |  |  | 0.56 |
| Air: | 3.46 | 28 | 96.88 |
| $\mathrm{~N}_{2}$ | 0.92 | 32 | 29.44 |
| $\mathrm{O}_{2}$ |  |  | 133.28 |
| Total |  |  |  |
|  |  |  |  |
|  |  |  |  |
| Flue gas: | $(3.46+0.02)$ | 28 | 97.44 |
| $\mathrm{~N}_{2}$ | $0.92-0.80)$ | 32 | 3.84 |
| $\mathrm{O}_{2}$ | 0.40 | 44 | 17.60 |
| $\mathrm{CO}_{2}$ | 0.80 | 18 | 14.40 |
| $\mathrm{H}_{2} \mathrm{O}$ |  |  | 133.28 |
| Total |  |  |  |

The accumulation is zero. The overall material balance is $133.28=133.28+0$. The total quantity of flue gas, therefore, is $133.28 \mathrm{~kg} / \mathrm{s}(293 \mathrm{lb} / \mathrm{s})$.

Related Calculations. The composition of the flue gas as given above is by weight. If desired, the composition by volume (which, indeed, is the more usual basis for expressing gas composition) can readily be obtained by calculating the moles per second of nitrogen (molar and volumetric compositions are equal to each other).

For more complex chemical reactions, it may be necessary to make mass balances for each molecular or atomic species rather than for the compounds.

### 2.3 MATERIAL BALANCE-INCOMPLETE DATA ON COMPOSITION OR FLOW RATE

Vinegar with a strength of $4.63 \%$ (by weight) acetic acid is pumped into a vat to which 1000 kg ( 2200 lb ) of $36.0 \%$ acetic acid is added. The resulting mixture contains $8.50 \%$ acid. How much of this $8.50 \%$ acid solution is in the vat?

## Calculation Procedure

1. List the available data, establish a basis for the calculations, and assign letters for the unknown quantities. In many situations, such as in this example, some streams entering or leaving a process may have incomplete data to express their compositions or flow rates. The usual procedure is to write material balances as in the preceding examples but to assign letters to represent the unknown quantities. There must be one independent material balance written for each unknown in order to have a unique solution.

The present problem is a batch situation, so let the basis be 1 batch. There are two inputs: an unknown quantity of vinegar having a known composition ( $4.63 \%$ acetic acid) and a known amount of added acetic acid [1000 $\mathrm{kg}(2200 \mathrm{lb})]$ of known composition ( $36.0 \%$ acid). There is one output: a final batch of unknown quantity but known composition ( $8.50 \%$ acid). Let $T$ represent the kilograms of input vinegar and $V$ the size of the final batch in kilograms.
2. Set up and solve the material-balance equations. Two independent material balances can be set up, one for acetic acid or for water and the other for the overall system.

Acetic acid: $\quad$ Input $=$ output, or $0.0463 T+0.360(1000 \mathrm{~kg})=0.0850 \mathrm{~V}$
Water: Input $=$ output, or $(1-0.0463) T+(1-0.360)(1000 \mathrm{~kg})=(1-0.0850) \mathrm{V}$
Overall: $\quad$ Input $=$ output, or $T+1000=V$
Use the overall balance and one of the others, say, the one for acetic acid. By substitution, then, $0.0463 T+0.360(1000)=0.0850(T+1000)$; so $T$ is found to be 7106 kg vinegar, and $V=T+$ $1000=8106 \mathrm{~kg}(17,833 \mathrm{lb})$ solution in the vat.
3. Check the results. It is convenient to make the check by substituting into the equation not used above, namely, the water balance:

$$
(1-0.0463)(7106)+(1-0.360)(1000)=(1-0.0850)(8106)
$$

Thus, the results check.

### 2.4 USE OF A TIE ELEMENT IN MATERIAL-BALANCE CALCULATIONS

The spent catalyst from a catalytic-cracking reactor is taken to the regenerator for reactivation. Coke deposited on the catalyst in the reactor is removed by burning with air, and the flue gas is vented. The coke is a mixture of carbon and high-molecular-weight tars considered to be hydrocarbons. For the following conditions, calculate the weight percent of hydrogen in the coke. Assume that the coke on the regenerated catalyst has the same composition as the coke on the spent catalyst:

| Carbon on spent catalyst | $1.50 \mathrm{wt} \%$ |
| :--- | :---: |
| Carbon on regenerated catalyst | $0.80 \mathrm{wt} \%$ |
| Air from blower | $150,000 \mathrm{~kg} / \mathrm{h}(330,000 \mathrm{lb} / \mathrm{h})$ |
| Hydrocarbon feed to reactor | $300,000 \mathrm{~kg} / \mathrm{h}(660,000 \mathrm{lb} / \mathrm{h})$ |
| Flue gas analysis (dry basis): |  |
| $\mathrm{CO}_{2}$ | $12.0 \mathrm{vol} \%$ |
| CO | $6.0 \mathrm{vol} \%$ |
| $\mathrm{O}_{2}$ | $0.7 \mathrm{vol} \%$ |
| $\mathrm{~N}_{2}$ | $\frac{81.3}{} \quad$ |
|  |  |
|  |  |
|  |  |

Assume that all oxygen not reported in flue gas analysis reacted with hydrogen in the coke to form water. All oxygen is reported as $\mathrm{O}_{2}$ equivalent. Assume that air is $79.02 \%$ nitrogen and $20.98 \%$ oxygen.

## Calculation Procedure

1. Select a basis and a tie component, and write out the relevant equations involved. Select $100 \mathrm{~kg} \cdot \mathrm{~mol}$ dry flue gas as the basis. Since nitrogen passes through the system unreacted, select it as the tie component. That is, the other components of the system can be referred to nitrogen as a basis, thus simplifying the calculations.

Since dry flue gas is the basis, containing $\mathrm{CO}_{2}$ and CO , the relevant reactions and the quantities per 100 mol flue gas are

$$
\begin{aligned}
& \underset{12 \mathrm{~kg} \cdot \mathrm{~mol}}{\mathrm{C}}+\underset{12 \mathrm{~kg} \cdot \mathrm{~mol}}{\mathrm{O}_{2}} \rightarrow \underset{12 \mathrm{~kg} \cdot \mathrm{~mol}}{\mathrm{C}_{2}} \\
& \underset{6 \mathrm{~kg} \cdot \mathrm{~mol}}{\mathrm{C}}+\underset{\underset{3 \mathrm{~kg} \cdot \mathrm{~mol}}{1 / 2 \mathrm{O}_{2}}}{ } \rightarrow \underset{ }{6 \mathrm{~kg} \cdot \mathrm{~mol}}
\end{aligned}
$$

2. Calculate the amount of oxygen in the entering air. The total moles of nitrogen in the entering air must equal the total moles in the flue gas, namely, $81.3 \mathrm{~kg} \cdot \mathrm{~mol}$. Since air is $79.02 \%$ nitrogen and $20.98 \%$ oxygen, the oxygen amounts to $(20.98 / 79.02)(81.3)$, or $21.59 \mathrm{~kg} \cdot \mathrm{~mol}$.
3. Calculate the amount of oxygen that leaves the system as water. The number of kilogrammoles of oxygen in the regenerator exit gases should be the same as the number in the entering air, that is, 21.59. Therefore, the oxygen not accounted for in the dry analysis of the flue gas is the oxygen converted to water. The dry analysis accounts for 12 mol oxygen as $\mathrm{CO}_{2}, 3 \mathrm{~mol}$ as CO , and 0.7 mol as unreacted oxygen. Thus the water leaving the system in the (wet) flue gas accounts for $(21.59-12-3-0.7)=5.89 \mathrm{~mol}$ oxygen.
4. Calculate the weight percent of hydrogen in the coke. Since 2 mol water is produced per mole of oxygen reacted, the amount of water in the wet flue gas is $2(5.89)=11.78 \mathrm{~mol}$. This amount of water contains 11.78 mol hydrogen or $(11.78)[2.016 \mathrm{~kg} /(\mathrm{kg} \cdot \mathrm{mol})]=23.75 \mathrm{~kg}$ hydrogen.

Now, the amount of carbon associated with this is the 12 mol that reacted to form $\mathrm{CO}_{2}$ plus the 6 mol that reacted to form CO or $(12+6)[12.011 \mathrm{~kg} /(\mathrm{kg} \cdot \mathrm{mol})]=216.20 \mathrm{~kg}$ carbon. Therefore, the weight percent of hydrogen in the coke is $(100)(23.75) /(23.75+216.0)=9.91$ percent.

## MATERIAL BALANCE-CHEMICAL REACTION a RECYCLE STREAM INVOLVED

In the feed-preparation section of an ammonia plant, hydrogen is produced from methane by a combination steam-reforming/partial-oxidation process. Enough air is used in partial oxidation to give a $3: 1$ hydrogen-nitrogen molar ratio in the feed to the ammonia unit. The hydrogen-nitrogen mixture is heated to reaction temperature and fed into a fixed-bed reactor where 20 percent conversion of reactants to ammonia is obtained per pass. After leaving the reactor, the mixture is cooled and the ammonia removed by condensation. The unreacted hydrogen-nitrogen mixture is recycled and mixed with fresh feed. On the basis of $100 \mathrm{~kg} \cdot \mathrm{~mol} / \mathrm{h}(220 \mathrm{lb} \cdot \mathrm{mol} / \mathrm{h})$ of fresh feed, make a material balance and determine the ammonia-production and recycle rates.


FIGURE 2.3 Material balance for ammonia plant with no purge stream (Example 2.5).

## Calculation Procedure

1. Sketch the system, showing the available data, indicating the unknowns, and establishing the system boundary. Since one of the answers sought is the recycle rate, the system boundary must be selected in such a way as to be crossed by the recycle stream.

Since the feed is a $3: 1$ ratio, the $100 \mathrm{~mol} / \mathrm{h}$ will consist of $25 \mathrm{~mol} / \mathrm{h}$ of nitrogen and $75 \mathrm{~mol} / \mathrm{h}$ of hydrogen. Let $x$ equal the moles per hour of ammonia produced and $y$ the moles per hour of recycle. The sketch and the system boundary are shown in Fig. 2.3.
2. Determine the amount of ammonia produced. Set out the ammonia-production reaction, namely, $\mathrm{N}_{2}+3 \mathrm{H}_{2} \rightarrow 2 \mathrm{NH}_{3}$. Thus 4 mol hydrogen-nitrogen mixture in a $3: 1$ ratio (as is the case for the feed in this example) will yield 2 mol ammonia. Since the system boundary is drawn in such a way that the exiting and reentering recycle streams offset each other algebraically, the net output from the system, consisting of liquid ammonia, must equal the net input, consisting of fresh feed. The amount $x$ of ammonia produced per hour thus can be determined by straightforward stoichiometry: $x=$ $\left[100 \mathrm{~kg} \cdot \mathrm{~mol} / \mathrm{h}\left(\mathrm{H}_{2}+\mathrm{N}_{2}\right)\right]\left[(2 \mathrm{~mol} \mathrm{NH} 3) / 4 \mathrm{~mol}\left(\mathrm{H}_{2}+\mathrm{N}_{2}\right)\right]$, or $x=50 \mathrm{~kg} \cdot \mathrm{~mol} / \mathrm{h}(110 \mathrm{lb} \cdot \mathrm{mol} / \mathrm{h}) \mathrm{NH}_{3}$.
3. Determine the recycle rate. The total feed to the heater and reactor consists of $(100+y)$ $\mathrm{kg} \cdot \mathrm{mol} / \mathrm{h}$. Twenty percent of this feed is converted to ammonia, and during that conversion, 2 mol ammonia is produced per 4 mol feed (inasmuch as it consists of 3:1 hydrogen-nitrogen mixture). Therefore, the amount of ammonia produced equals $[0.20(100+y)]\left[\left(2 \mathrm{~mol} \mathrm{NH}_{3}\right) / 4 \mathrm{~mol}\left(\mathrm{H}_{2}+\mathrm{N}_{2}\right)\right]$. Ammonia production is $50 \mathrm{~kg} \cdot \mathrm{~mol} / \mathrm{h}$, so solving this equation for $y$ gives a recycle rate of $400 \mathrm{~kg} \cdot \mathrm{~mol} / \mathrm{h}(880 \mathrm{lb} \cdot \mathrm{mol} / \mathrm{h})$.
4. Check the results. A convenient way to check is to set up an overall mass balance. Since there is no accumulation, the input must equal the output. Input $=\left(25 \mathrm{~kg} \cdot \mathrm{~mol} / \mathrm{h} \mathrm{N}_{2}\right)(28 \mathrm{~kg} / \mathrm{mol})+$ $\left(75 \mathrm{~kg} \cdot \mathrm{~mol} / \mathrm{h} \mathrm{H}_{2}\right)(2 \mathrm{~kg} / \mathrm{mol})=850 \mathrm{~kg} / \mathrm{h}$, and output $=(50 \mathrm{~kg} \cdot \mathrm{~mol} / \mathrm{h} \mathrm{NH} 33)(17 \mathrm{~kg} / \mathrm{mol})=850 \mathrm{~kg} / \mathrm{h}$. The results thus check.

Related Calculations. It is also possible to calculate the recycle rate in the preceding example by making a material balance around the reactor-condenser system.

The ratio of the quantity of material recycled to the quantity of fresh feed is called the "recycle ratio." In the preceding problem, the recycle ratio is $400 / 100$, or 4.

### 2.6 MATERIAL BALANCE-CHEMICAL REACTION, RECYCLE STREAM, AND PURGE STREAM INVOLVED

In the Example 2.5 for producing ammonia, the amount of air fed is set by the stoichiometric ratio of hydrogen to nitrogen for the ammonia feed stream. In addition to nitrogen and oxygen, the air

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FIGURE 2.4 Material balance for ammonia plant with purge stream (Example 2.6).
contains inert gases, principally argon, that gradually build up in the recycle stream until the process is affected adversely. It has been determined that the concentration of argon in the reactor must be no greater than 4 mol argon per 100 mol hydrogen-nitrogen mixture. Using the capacities given in the preceding example, calculate the amount of the recycle stream that must be vented to meet the concentration requirement. The fresh feed contains 0.31 mol argon per 100 mol hydrogen-nitrogen mixture. Also calculate the amount of ammonia produced.

## Calculation Procedure

1. Select the basis for calculation and sketch the system, showing the available data and indicating the unknowns. For ease of comparison with the preceding example, let the basis be $100.31 \mathrm{~kg} \cdot \mathrm{~mol} / \mathrm{h}$ total fresh feed, consisting of $100 \mathrm{~mol}\left(\mathrm{H}_{2}+\mathrm{N}_{2}\right)$ and 0.31 mol argon (A). Let $x$ equal the moles of $\mathrm{NH}_{3}$ produced per hour, $y$ the moles of $\mathrm{H}_{2}+\mathrm{N}_{2}$ recycled per hour, $w$ the moles of A recycled per hour, and $z$ the moles of $\mathrm{H}_{2}+\mathrm{N}_{2}$ purged per hour. The sketch is Fig. 2.4.
2. Calculate the amount of recycle stream that must be vented. As noted in the preceding example, the conversion per pass through the reactor is 20 percent. Therefore, for every 100 mol $\left(\mathrm{H}_{2}+\mathrm{N}_{2}\right)$ entering the heater-reactor-condenser train, 20 mol will react to form ammonia and 80 mol will leave the condenser to be recycled or purged. All the argon will leave with this recycle-and-purge stream. Since the maximum allowable argon level in the reactor input is 4 mol argon per 100 mol $\left(\mathrm{H}_{2}+\mathrm{N}_{2}\right)$, there will be 4 mol argon per $80 \mathrm{~mol}\left(\mathrm{H}_{2}+\mathrm{N}_{2}\right)$ in the recycle-and-purge stream.

Under steady-state operating conditions, the argon purged must equal the argon entering in the fresh feed. The moles of argon in the purge equals $(4 / 80) z=0.05 z$. Therefore, $0.05 z=0.31$, so $z=6.2 \mathrm{~mol} / \mathrm{h}\left(\mathrm{H}_{2}+\mathrm{N}_{2}\right)$ purged. The total purge stream consists of $6.2 \mathrm{~mol} / \mathrm{h}\left(\mathrm{H}_{2}+\mathrm{N}_{2}\right)$ plus $0.31 \mathrm{~mol} / \mathrm{h}$ argon.
3. Calculate the amount of $\boldsymbol{H}_{2}+N_{2}$ recycled. The moles of $\mathrm{H}_{2}+\mathrm{N}_{2}$ in the feed to the reactor is 100 mol fresh feed plus $y \mathrm{~mol}$ recycle. Of this, 80 percent is to be either purged or recycled; that is, $0.80(100+y)=y+z=y+6.2$. Therefore $y=369 \mathrm{~mol} / \mathrm{h}\left(\mathrm{H}_{2}+\mathrm{N}_{2}\right)$ recycled.

Although not needed for the solution of this problem, the amount of argon in the recycle can be calculated as a matter of interest. Total argon entering the reactor is $0.31+w \mathrm{~mol}$; then, according to the argon limitation stipulated, $0.31+w=0.04(100+369)$, so $w=18.45 \mathrm{~mol} / \mathrm{h}$.
4. Calculate the amount of ammonia produced. Of the $100+y \mathrm{~mol}\left(\mathrm{H}_{2}+\mathrm{N}_{2}\right)$ (in the stoichiometric $3: 1$ ratio) entering the reactor, 20 percent is converted to ammonia. The reaction is
$\mathrm{N}_{2}+3 \mathrm{H}_{2} \rightarrow 2 \mathrm{NH}_{3}$, so 4 mol reactants yields 2 mol ammonia. Therefore, total ammonia production is $0.20(100+y)(2 / 4)=0.20(100+369)(2 / 4)=46.9 \mathrm{~mol} / \mathrm{h}$.
5. Check the results. It is convenient to check by making an overall mass balance. The input per hour consists of $100 \mathrm{~mol}\left(\mathrm{H}_{2}+\mathrm{N}_{2}\right)$ in a 3:1 ratio plus 0.31 mol A; that is, $\left(75 \mathrm{~mol}_{2}\right)(2 \mathrm{~kg} / \mathrm{mol})+$ $\left(25 \mathrm{~mol} \mathrm{~N} \mathrm{~N}_{2}\right)(28 \mathrm{~kg} / \mathrm{mol})+(0.31 \mathrm{~mol} \mathrm{~A})(40 \mathrm{~kg} / \mathrm{mol})=862.4 \mathrm{~kg}$. The output per hour consists of 46.9 mol ammonia plus a vent-stream mixture of $6.2 \mathrm{~mol}\left(\mathrm{H}_{2}+\mathrm{N}_{2}\right)$ (in a 3:1 ratio) and 0.31 mol A; that is, $\left(46.9 \mathrm{~mol} \mathrm{NH}_{3}\right)(17 \mathrm{~kg} / \mathrm{mol})+(3 / 4)\left[6.2 \mathrm{~mol}\left(\mathrm{H}_{2}+\mathrm{N}_{2}\right)\right]\left(2 \mathrm{~kg} \mathrm{H}_{2} / \mathrm{mol}\right)+(1 / 4)(6.2)\left(28 \mathrm{~kg} \mathrm{~N}_{2} / \mathrm{mol}\right)+$ $(0.31 \mathrm{~mol} \mathrm{~A})(40 \mathrm{~kg} / \mathrm{mol})=862.4 \mathrm{~kg}$.

There is no accumulation in the system, so input should equal output. Since $862.4 \mathrm{~kg}=862.4 \mathrm{~kg}$, the results thus check.

### 2.7 USE OF ENERGY BALANCE WITH MATERIAL BALANCE

A particular crude oil is heated to $510 \mathrm{~K}\left(458^{\circ} \mathrm{F}\right)$ and charged at $10 \mathrm{~L} / \mathrm{h}\left(0.01 \mathrm{~m}^{3} / \mathrm{h}\right.$, or $\left.2.6 \mathrm{gal} / \mathrm{h}\right)$ to the flash zone of a laboratory distillation tower. The flash zone is at an absolute pressure of 110 kPa ( 16 psi ). Determine the percent vaporized and the amounts of the overhead and bottoms streams. Assume that the vapor and liquid are in equilibrium.

## Calculation Procedure

1. Select the approach to be employed. In this problem there is not enough information available to employ a purely material-balance approach. Instead, use an energy balance as well. Such an approach is especially appropriate in cases such as this one in which some of the components undergo a phase change.

From the American Petroleum Institute's (API) Technical Data Book-Petroleum Refining, specific heats, specific gravities, latent heats of vaporization, and percent vaporization can be obtained, for a given oil, as a function of flash-zone temperature (percent vaporization and flash-zone temperature are functionally related because the flash vaporization takes place adiabatically). This suggests a trial-and-error procedure: Assume a flash-zone temperature and the associated percent vaporization; then make an energy balance to check the assumptions. Finally, complete the material balance.
2. Assume a flash-zone temperature and percent vaporization, and obtain the data for the system at those conditions. Assume, for a first guess, that 30 percent (by volume) of the feed is vaporized. The API Data Book indicates that for this oil, the corresponding flash-zone temperature is $483 \mathrm{~K}\left(410^{\circ} \mathrm{F}\right)$; the fraction vaporized has a latent heat of vaporization of $291 \mathrm{~kJ} / \mathrm{kg}$ ( $125 \mathrm{Btu} /$ lb ) and a density of $0.750 \mathrm{~kg} / \mathrm{L}\left(750 \mathrm{~kg} / \mathrm{m}^{3}\right.$, or $\left.47.0 \mathrm{lb} / \mathrm{ft}^{3}\right)$ and a specific heat of $2.89 \mathrm{~kJ} /$ $(\mathrm{kg})(\mathrm{K})\left[0.69 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)\right]$. The unvaporized portion has a density of $0.892 \mathrm{~kg} / \mathrm{L}\left(892 \mathrm{~kg} / \mathrm{m}^{3}\right.$, or $\left.55.8 \mathrm{lb} / \mathrm{ft}^{3}\right)$ and a specific heat of $2.68 \mathrm{~kJ} /(\mathrm{kg})(\mathrm{K})$ [ $\left.0.64 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)\right]$. In addition, the feed has a density of $0.850 \mathrm{~kg} / \mathrm{L}\left(850 \mathrm{~kg} / \mathrm{m}^{3}\right.$, or $\left.53.1 \mathrm{lb} / \mathrm{ft}^{3}\right)$ and a specific heat of $2.85 \mathrm{~kJ} /(\mathrm{kg})(\mathrm{K})[0.68 \mathrm{Btu} /$ (lb) $\left.\left({ }^{\circ} \mathrm{F}\right)\right]$.
3. Make an energy balance. For convenience, use the flash temperature, 483 K , as the datum temperature. The energy brought into the system by the feed, consisting of sensible-heat energy with reference to the datum temperature, must equal the energy in the vapor stream (its latent heat plus its sensible heat) plus the energy in the bottoms stream (its sensible heat). However, since the flash temperature is the datum, and since both the vapor and the bottoms streams are at the datum temperature, neither of those product streams has a sensible-heat term associated with it. Thus the
energy balance on the basis of $1 \mathrm{~h}(10 \mathrm{~L})$ is as follows:

$$
\begin{aligned}
& (10 \mathrm{~L})(0.850 \mathrm{~kg} / \mathrm{L})[2.85 \mathrm{~kJ} /(\mathrm{kg})(\mathrm{K})](510 \mathrm{~K}-483 \mathrm{~K})=(3 \mathrm{~L})(0.750 \mathrm{~kg} / \mathrm{L})\{(291 \mathrm{~kJ} / \mathrm{kg}) \\
& \quad+[2.89 \mathrm{~kJ} /(\mathrm{kg})(\mathrm{K})](483 \mathrm{~K}-483 \mathrm{~K})\}+(7 \mathrm{~L})(0.892 \mathrm{~kg} / \mathrm{L})[2.68 \mathrm{~kJ} /(\mathrm{kg})(\mathrm{K})](483 \mathrm{~K}-483 \mathrm{~K})
\end{aligned}
$$

Or, $654=655+0$. Since this is within the limits of accuracy, the assumption of 30 percent vaporized is correct.
4. Make the material balance to determine the amount in the overhead and bottoms streams. On the basis of 1 h , the mass in is $(10 \mathrm{~L})(0.850 \mathrm{~kg} / \mathrm{L})=8.5 \mathrm{~kg}$. The mass out consists of the mass that becomes vaporized (the overhead) plus the mass that remains unvaporized (the bottoms). The overhead is $(3 \mathrm{~L})(0.750 \mathrm{~kg} / \mathrm{L})=2.25 \mathrm{~kg}(4.96 \mathrm{lb})$. The bottoms stream is $(7 \mathrm{~L})(0.892 \mathrm{~kg} / \mathrm{L})=$ $6.24 \mathrm{~kg}(13.76 \mathrm{lb})$. Thus, $8.5 \mathrm{~kg}=(2.25+6.24) \mathrm{kg}$. The material balance is consistent, within the limits of accuracy.

Related Calculations. The problem can be worked in similar fashion using values from enthalpy tables. In this case, the datum temperature is below the flash-zone temperature; therefore, sensible heat in the two exiting streams must be taken into account.

### 2.8 MATERIAL BALANCE-LINKING RECYCLE AND PURGE WITH REACTION SELECTIVITY AND CONVERSION

Benzene is to be produced from toluene according to the reaction


The reaction is carried out in the gas phase and normally operates at around $700^{\circ} \mathrm{C}$ and 40 bar. Some of the benzene formed undergoes a secondary reversible reaction to an unwanted byproduct, diphenyl, according to the reaction

$$
\underset{\text { benzene }}{2 \mathrm{C}_{6} \mathrm{H}_{6}} \rightleftarrows \underset{\text { diphenyl }}{\mathrm{C}_{12} \mathrm{H}_{10}}+\underset{\text { hydrogen }}{\mathrm{H}_{2}}
$$

Laboratory studies indicate that a hydrogen-toluene ratio of 5 at the reactor inlet is required to prevent excessive coke formation in the reactor. Even with a large excess of hydrogen, the toluene cannot be forced to complete conversion. The laboratory studies indicate that the selectivity (i.e., fraction of toluene reacted that is converted to benzene) is related to the conversion (i.e., fraction of toluene fed that is reacted) according to

$$
S=1-\frac{0.0036}{(1-X)^{1.544}}
$$

where $S=$ selectivity
$X=$ conversion
The reactor effluent is thus likely to contain hydrogen, methane, benzene, toluene, and diphenyl. Because of the large differences in volatility of these components, it seems likely that partial condensation will allow the effluent to be split into a vapor stream containing predominantly hydrogen and methane and a liquid stream containing predominantly benzene, toluene, and diphenyl.

The hydrogen in the vapor stream is a reactant and hence should be recycled to the reactor inlet (see flow diagram). The methane enters the process as a feed impurity and is also a byproduct from
the primary reaction and must be removed from the process. The hydrogen-methane separation is likely to be expensive, but the methane can be removed from the process by means of a purge (see flow diagram).


The liquid stream can be separated readily into pure components by distillation, with the benzene taken off as product, the diphenyl as an unwanted byproduct, and the toluene recycled. It is possible to recycle the diphenyl to improve selectivity, but we will assume that is not done here.

The hydrogen feed contains methane as an impurity at a mole fraction of 0.05 . The production rate of benzene required is $265 \mathrm{kmol} \mathrm{h}^{-1}$.

Assume initially that a phase split can separate the reactor effluent into a vapor stream containing only hydrogen and methane and a liquid stream containing only benzene, toluene, and diphenyl and that the liquid separation system can produce essentially pure products.

For a conversion in the reactor of 0.75 :

1. Determine the relation between the fraction of vapor from the phase split sent to purge $(\alpha)$ and the fraction of methane in the recycle and purge ( $y$ ).
2. Given the assumptions, estimate the composition of the reactor effluent for fraction of methane in the recycle and purge of 0.4.

## Calculation Procedure

1. Calculate the benzene selectivity from toluene. Let $P_{\mathrm{B}}$ be the production rate of benzene. Then,

$$
\begin{array}{lrcc}
\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CH}_{3}+\mathrm{H}_{2} & \longrightarrow \mathrm{C}_{6} \mathrm{H}_{6}+\mathrm{C}_{6} \mathrm{H}_{6} & +\mathrm{CH}_{4} \\
\quad \frac{P_{\mathrm{B}}}{S} & \frac{P_{\mathrm{B}}}{S} & P_{\mathrm{B}} & P_{\mathrm{B}}\left(\frac{1}{S}-1\right) \\
2 \mathrm{C}_{6} \mathrm{H}_{6} & \rightleftarrows & P_{\mathrm{B}} \\
P_{\mathrm{B}}\left(\frac{1}{S}-1\right) & & \frac{\mathrm{C}_{12} \mathrm{H}_{10}}{2}\left(\frac{1}{S}-1\right) & +\frac{\mathrm{H}_{2}}{2}\left(\frac{1}{S}-1\right)
\end{array}
$$

For $X=0.75$,

$$
\begin{aligned}
S & =1-\frac{0.0036}{(1-0.75)^{1.544}} \\
& =0.9694
\end{aligned}
$$

For more on calculation of selectivities, see Section 4 in this book.

## 2. Calculate the amount of toluene to be fed to the reactor

$$
\text { fresh toluene feed }=\frac{P_{\mathrm{B}}}{S}
$$

and

$$
\text { toluene recycle }=R_{\mathrm{T}}
$$

Then

$$
\text { toluene entering the reactor }=\frac{P_{\mathrm{B}}}{S}+R_{\mathrm{T}}
$$

and

$$
\text { toluene in reactor effluent }=\left(\frac{P_{\mathrm{B}}}{S}+R_{\mathrm{T}}\right)(1-X)=R_{\mathrm{T}}
$$

For $P_{\mathrm{B}}=265 \mathrm{kmol} \mathrm{h}^{-1}, X=0.75$, and $S=0.9694$,

$$
R_{\mathrm{T}}=91.12 \mathrm{kmol} \mathrm{~h}^{-1}
$$

Therefore,

$$
\begin{aligned}
\text { toluene entering the reactor } & =\frac{265}{0.9694}+91.12 \\
& =364.5 \mathrm{kmol} \mathrm{~h}^{-1}
\end{aligned}
$$

3. Find the amount of hydrogen to be fed, as a function of the phase split that is sent to purge, $\alpha$

$$
\begin{aligned}
\text { hydrogen entering the reactor } & =5 \times 364.5 \\
& =1823 \mathrm{kmol} \mathrm{~h}^{-1} \\
\text { net hydrogen consumed in reaction } & =\frac{P_{\mathrm{B}}}{S}-\frac{P_{\mathrm{B}}}{2}\left(\frac{1}{S}-1\right) \\
& =\frac{P_{\mathrm{B}}}{S}\left(1-\frac{1-S}{2}\right) \\
& =269.2 \mathrm{kmol} \mathrm{~h}^{-1}
\end{aligned}
$$

Therefore,

$$
\begin{aligned}
\text { hydrogen in reactor effluent } & =1823-269.2 \\
& =1554 \mathrm{kmol} \mathrm{~h}^{-1} \\
\text { hydrogen lost in purge } & =1554 \alpha
\end{aligned}
$$

Thus,

$$
\text { hydrogen feed to the process }=1554 \alpha+269.2
$$

## 4. Find the fraction $y$ of methane in the purge and recycle, as a function of $\alpha$

$$
\text { methane feed to process as an impurity }=(1554 \alpha+269.2) \frac{0.05}{0.95}
$$

and

$$
\text { methane produced by reactor }=\frac{P_{\mathrm{B}}}{S}
$$

So,

$$
\begin{aligned}
\text { methane in purge } & =\frac{P_{\mathrm{B}}}{S}+(1554 \alpha+269.2) \frac{0.05}{0.95} \\
& =81.79 \alpha+287.5 \\
\text { total flow rate of purge } & =1554 \alpha+81.79 \alpha+287.5 \\
& =1636 \alpha+287.5
\end{aligned}
$$

The fraction of methane in the purge (and recycle) as a function of $\alpha$ is thus

$$
y=\frac{81.79 \alpha+287.5}{1636 \alpha+287.5}
$$

The graph shows a plot of this equation. As the purge fraction $\alpha$ is increased, the flow rate of purge increases, but the concentration of methane in the purge and recycle decreases. This variation (along with reactor conversion) is an important degree of freedom in the optimization of reaction and separation systems.


## 5. For an $\alpha$ of 0.4, find the amount of methane in the reactor effluent

mole fraction of methane in vapor from phase separator $=0.4$
Therefore,

$$
\begin{aligned}
\text { methane in reactor effluent } & =\frac{0.4}{0.6} \times 1554 \\
& =1036 \mathrm{kmol} \mathrm{~h}^{-1}
\end{aligned}
$$

## 6. Find the amount of diphenyl in the reactor effluent

$$
\begin{aligned}
\text { diphenyl in reactor effluent } & =\frac{P_{\mathrm{B}}}{2}\left(\frac{1}{S}-1\right) \\
& =4 \mathrm{kmol} \mathrm{~h}^{-1}
\end{aligned}
$$

7. Summarize the composition of the reactor effluent. The estimated composition of the reactor effluent is given in the table. These results assume that all separations in the phase split are sharp.

| Component | Flow rate $\left(\mathrm{kmol} \mathrm{h}^{-1}\right)$ |
| :--- | :---: |
| Hydrogen | 1554 |
| Methane | 1036 |
| Benzene | 265 |
| Toluene | 91 |
| Diphenyl | 4 |

Source: Adapted from Smith, Chemical Process Design, McGraw-Hill.

## COMBUSTION OF COAL FUEL IN A FURNACE

A coal has the following ultimate analysis: $\mathrm{C}=0.8339, \mathrm{H}_{2}=0.0456, \mathrm{O}_{2}=0.0505, \mathrm{~N}_{2}=0.0103$, $\mathrm{S}=0.0064$, ash $=0.0533$, total $=1.000$. This coal is burned in a steam-boiler furnace. Determine the weight of air required for theoretically perfect combustion, the weight of gas formed per pound of coal burned, and the volume of flue gas at the boiler exit temperature of $600^{\circ} \mathrm{F}$ ( 589 K ) per pound of coal burned; the air required with 20 percent excess air and the volume of gas formed with this excess; and the $\mathrm{CO}_{2}$ percentage in the flue gas on a dry and wet basis.

## Calculation Procedure

1. Compute the weight of oxygen required per pound of coal. To find the weight of oxygen required for theoretically perfect combustion of coal, set up the following tabulation, based on the ultimate analysis of the coal:

| Element | $\times$ | Molecular-weight <br> ratio | $=$ | Pounds $\mathrm{O}_{2}$ <br> required |
| :--- | ---: | ---: | ---: | ---: |
| $\mathrm{C} ; 0.8339$ | $\times$ | $32 / 12$ | $=$ | 2.2237 |
| $\mathrm{H}_{2} ; 0.0456$ | $\times$ | $16 / 2$ | $=$ | 0.3648 |
| $\mathrm{O}_{2} ; 0.0505 ;$ decreases external $\mathrm{O}_{2}$ required |  |  | $=$ | -0.0505 |
| $\mathrm{~N}_{2} ; 0.0103 ;$ is inert in combustion and is ignored |  |  |  |  |
| $\mathrm{S} ; 0.0064$ | $\times$ | $32 / 32$ | $=$ | 0.0064 |
| Ash; $0.0533 ;$ is inert in combustion and is ignored |  |  |  |  |
| Total 1.0000 |  |  |  |  |
| Pounds external $\mathrm{O}_{2}$ per lb fuel |  |  | 2.5444 |  |

Note that of the total oxygen needed for combustion, 0.0505 lb is furnished by the fuel itself and is assumed to reduce the total external oxygen required by the amount of oxygen present in the fuel. The molecular-weight ratio is obtained from the equation for the chemical reaction of the element with oxygen in combustion. Thus, for carbon, $\mathrm{C}+\mathrm{O}_{2} \rightarrow \mathrm{CO}_{2}$, or $12+32=44$, where 12 and 32 are the molecular weights of C and $\mathrm{O}_{2}$, respectively.
2. Compute the weight of air required for perfect combustion. Air at sea level is a mechanical mixture of various gases, principally $23.2 \%$ oxygen and $76.8 \%$ nitrogen by weight. The nitrogen associated with the 2.5444 lb of oxygen required per pound of coal burned in this furnace is the product of the ratio of the nitrogen and oxygen weights in the air and 2.5444, or (2.5444) $(0.768 / 0.232)=8.4219 \mathrm{lb}$. Then the weight of air required for perfect combustion of $1 \mathrm{lb} \mathrm{coal}=$ sum of nitrogen and oxygen required $=8.4219+2.5444=10.9663 \mathrm{lb}$ of air per pound of coal burned.
3. Compute the weight of the products of combustion. Find the products of combustion by addition:

| Fuel constituents | + | Oxygen | $\rightarrow$ | Products of combustion |
| :--- | :---: | :---: | :---: | :---: |
| $\mathrm{C} ; 0.8339$ | + | 2.2237 | $\rightarrow$ | $\mathrm{CO}_{2}=3.0576 \mathrm{lb}$ |
| $\mathrm{H} ; 0.0456$ | + | 0.3648 | $\rightarrow$ | $\mathrm{H}_{2} \mathrm{O}=0.4104$ |
| $\mathrm{O}_{2} ; 0.0505 ;$ this is not a product of combustion |  |  |  |  |
| $\mathrm{N}_{2} ; 0.0103 ;$ inert but passes through furnace |  | 0.0064 | $\rightarrow$ | $\mathrm{SO}_{2}=0.0103$ |
| $\mathrm{~S} ; 0.0064$ | + |  | $=\mathrm{N}_{2}=8.4219$ |  |
| Outside nitrogen from step 2 |  |  | $=11.9130$ |  |
| Pounds of flue gas per pound of coal burned |  |  |  |  |

4. Convert the flue-gas weight to volume. Use Avogadro's law, which states that under the same conditions of pressure and temperature, 1 mol (the molecular weight of a gas expressed in pounds) of any gas will occupy the same volume.

At 14.7 psia and $32^{\circ} \mathrm{F}, 1 \mathrm{~mol}$ of any gas occupies $359 \mathrm{ft}^{3}$. The volume per pound of any gas at these conditions can be found by dividing 359 by the molecular weight of the gas and correcting for the gas temperature by multiplying the volume by the ratio of the absolute flue-gas temperature and the atmospheric temperature. To change the weight analysis (step 3) of the products of combustion to volumetric analysis, set up the calculation thus:

| Products | Weight, <br> lb | Molecular <br> weight | Temperature correction | Volume at <br> $600^{\circ} \mathrm{F}, \mathrm{ft}^{3}$ |
| :--- | :---: | :---: | :---: | :---: |
| $\mathrm{CO}_{2}$ | 3.0576 | 44 | $(359 / 44)(3.0576)(2.15)$ | $=53.8$ |
| $\mathrm{H}_{2} \mathrm{O}$ | 0.4104 | 18 | $(359 / 18)(0.4104)(2.15)$ | $=17.6$ |
| $\mathrm{Total}^{2}$ | 8.4322 | 28 | $(359 / 28)(8.4322)(2.15)$ | $=233.0$ |
| $\mathrm{SO}_{2}$ | 0.0128 | 64 | $(359 / 64)(0.0128)(2.15)$ | $=\underline{0.17}$ |
| Cubic feet of flue gas per pound of coal burned |  | $=304.57$ |  |  |

In this calculation, the temperature correction factor $2.15=($ absolute flue-gas temperature $) /($ absolute atmospheric temperature $), \mathrm{R}=(600+460) /(32+460)$. The total weight of $\mathrm{N}_{2}$ in the flue gas is the sum of the $\mathrm{N}_{2}$ in the combustion air and the fuel, or $8.4219+0.0103=8.4322 \mathrm{lb}$. This value is used in computing the flue-gas volume.
5. Compute the $\boldsymbol{C O}_{\mathbf{2}}$ content of the flue gas. The volume of $\mathrm{CO}_{2}$ in the products of combustion at $600^{\circ} \mathrm{F}$ is $53.8 \mathrm{ft}^{3}$ as computed in step 4 , and the total volume of the combustion products is $304.57 \mathrm{ft}^{3}$. Therefore, the percent $\mathrm{CO}_{2}$ on a wet basis (i.e., including the moisture in the combustion products) $=$ $\mathrm{ft}^{3} \mathrm{CO}_{2} /$ total $\mathrm{ft}^{3}=53.8 / 304.57=0.1765$, or 17.65 percent.

The percent $\mathrm{CO}_{2}$ on a dry, or Orsat, basis is found in the same manner except that the weight of $\mathrm{H}_{2} \mathrm{O}$ in the products of combustion, 17.6 lb from step 4, is subtracted from the total gas weight. Or, percent $\mathrm{CO}_{2}$, dry, or Orsat, basis $=(53.8) /(304.57-17.6)=0.1875$, or 18.75 percent.
6. Compute the air required with the stated excess flow. With 20 percent excess air, the airflow required $=(0.20+1.00)($ airflow with no excess $)=1.20(10.9663)=13.1596 \mathrm{lb}$ of air per pound of coal burned. The airflow with no excess is obtained from step 2.
7. Compute the weight of the products of combustion. The excess air passes through the furnace without taking part in the combustion and increases the weight of the products of combustion per pound of coal burned. Therefore, the weight of the products of combustion is the sum of the weight of the combustion products without the excess air and the product of (percent excess air)(air for perfect combustion, lb ); or using the weights from steps 3 and 2 , respectively,$=11.9130+(0.20)(10.9663)=$ 14.1063 lb of gas per pound of coal burned with 20 percent excess air.
8. Compute the volume of the combustion products and the percent $\mathrm{CO}_{2}$. The volume of the excess air in the products of combustion is obtained by converting from the weight analysis to the volumetric analysis and correcting for temperature as in step 4, using the air weight from step 2 for perfect combustion and the excess-air percentage, or $(10.9663)(0.20)(359 / 28.95)(2.15)=58.5 \mathrm{ft}^{3}$ $\left(1.66 \mathrm{~m}^{3}\right)$. In this calculation, the value 28.95 is the molecular weight of air. The total volume of the products of combustion is the sum of the column for perfect combustion, step 4 , and the excess-air volume, above, or $304.57+58.5=363.07 \mathrm{ft}^{3}\left(10.27 \mathrm{~m}^{3}\right)$.

Using the procedure in step 5 , the percent $\mathrm{CO}_{2}$, wet basis, $=53.8 / 363.07=14.8$ percent. The percent $\mathrm{CO}_{2}$, dry basis, $=53.8 /(363.07-17.6)=15.6$ percent.

Related Calculations. Use the method given here when making combustion calculations for any type of coal-bituminous, semibituminous, lignite, anthracite, cannel, or coking-from any coal field in the world used in any type of furnace-boiler, heater, process, or waste-heat. When the air used for combustion contains moisture, as is usually true, this moisture is added to the combustionformed moisture appearing in the products of combustion. Thus, for $80^{\circ} \mathrm{F}(300 \mathrm{~K})$ air of 60 percent relative humidity, the moisture content is 0.013 lb per pound of dry air. This amount appears in the products of combustion for each pound of air used and is a commonly assumed standard in combustion calculations.

A fuel oil has the following ultimate analysis: $\mathrm{C}=0.8543, \mathrm{H}_{2}=0.1131, \mathrm{O}_{2}=0.0270, \mathrm{~N}_{2}=0.0022$, $\mathrm{S}=0.0034$, total $=1.0000$. This fuel oil is burned in a steam-boiler furnace. Determine the weight of air required for theoretically perfect combustion, the weight of gas formed per pound of oil burned, and the volume of flue gas at the boiler exit temperature of $600^{\circ} \mathrm{F}(589 \mathrm{~K})$ per pound of oil burned; the air required with 20 percent excess air and the volume of gas formed with this excess; and the $\mathrm{CO}_{2}$ percentage in the flue gas on a dry and wet basis.

## Calculation Procedure

1. Compute the weight of oxygen required per pound of oil. The same general steps as given in the previous Calculation Procedure will be followed. Consult that procedure for a complete explanation of each step. Using the molecular weight of each element, the following table can be set up:

2. Compute the weight of air required for perfect combustion. The weight of nitrogen associated with the required oxygen $=(3.1593)(0.768 / 0.232)=10.4583 \mathrm{lb}$. The weight of air required $=$ $10.4583+3.1593=13.6176 \mathrm{lb}$ per pound of oil burned.
3. Compute the weight of the products of combustion. As before:

| Fuel constituents + oxygen $=$ |  |  | Products of combustion |
| :--- | :---: | :---: | :---: |
| $\mathrm{C} ; 0.8543+2.2781$ | $=$ | 3.1324 | $\mathrm{CO}_{2}$ |
| $\mathrm{H}_{2} ; 0.1131+0.9148$ | $=$ | 1.0179 | $\mathrm{H}_{2} \mathrm{O}$ |
| $\mathrm{O}_{2} ; 0.270 ;$ not a product of combustion |  |  |  |
| $\mathrm{N}_{2} ; 0.0022 ;$ inert but passes through furnace | $=$ | 0.0022 | $\mathrm{~N}_{2}$ |
| $\mathrm{~S} ; 0.0034+0.0034$ | $=$ | 0.0068 | $\mathrm{SO}_{2}$ |
| Outside $\mathrm{N}_{2}$ from step 2 | $=$ | 10.458 | $\mathrm{~N}_{2}$ |
| Pounds of flue gas per pound of oil burned | $=$ | 14.6173 |  |

4. Convert the flue-gas weight to volume. As before:

| Products | Weight, <br> lb | Molecular <br> weight | Temperature correction |  | Volume at <br> $600^{\circ} \mathrm{F}, \mathrm{ft}^{3}$ |
| :--- | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{CO}_{2}$ | 3.1324 | 44 | $(359 / 44)(3.1324)(2.15)$ | $=$ | 55.0 |
| $\mathrm{H}_{2} \mathrm{O}$ | 1.0179 | 18 | $(359 / 18)(1.0179)(2.15)$ | $=$ | 43.5 |
| $\mathrm{~N}_{2}$ (total) | 10.460 | 28 | $(359 / 28)(10.460)(2.15)$ | $=$ | 288.5 |
| $\mathrm{SO}_{2}$ | 0.0068 | 64 | $(359 / 64)(0.0068)(2.15)$ | $=$ | $\underline{0.82}$ |
| Cubic feet of flue gas per pound of oil burned | $=$ | 387.82 |  |  |  |

In this calculation, the temperature correction factor $2.15=$ (absolute flue-gas temperature)/ (absolute atmospheric temperature) $=(600+460) /(32+460)$. The total weight of $\mathrm{N}_{2}$ in the flue gas is the sum of the $\mathrm{N}_{2}$ in the combustion air and the fuel, or $10.4583+0.0022=10.4605 \mathrm{lb}$.
5. Compute the $\boldsymbol{C O}_{2}$ content of the flue gas. The $\mathrm{CO}_{2}$, wet basis, $=55.0 / 387.82=0.142$, or 14.2 percent. The $\mathrm{CO}_{2}$, dry basis, $=55.0 /(387.2-43.5)=0.160$, or 16.0 percent.
6. Compute the air required with stated excess flow. The pounds of air per pound of oil with 20 percent excess air $=(1.20)(13.6176)=16.3411 \mathrm{lb}$ air per pound of oil burned.
7. Compute the weight of the products of combustion. The weight of the products of combustion $=$ product weight for perfect combustion, $\mathrm{lb}+$ (percent excess air)(air for perfect combustion, lb ) $=$ $14.6173+(0.20)(13.6176)=17.3408 \mathrm{lb}$ flue gas per pound of oil burned with 20 percent excess air.
8. Compute the volume of the combustion products and the percent $\mathrm{CO}_{2}$. The volume of excess air in the products of combustion is found by converting from the weight to the volumetric analysis and correcting for temperature as in step 4 , using the air weight from step 2 for perfect combustion and the excess-air percentage, or $(13.6176)(0.20)(359 / 28.95)(2.15)=72.7 \mathrm{ft}^{3}\left(2.06 \mathrm{~m}^{3}\right)$. Add this to the volume of the products of combustion found in step 4 , or $387.82+72.70=460.52 \mathrm{ft}^{3}\left(13.03 \mathrm{~m}^{3}\right)$.

Using the procedure in step 5 , the percent $\mathrm{CO}_{2}$, wet basis, $=55.0 / 460.52=0.1192,11.92$ percent. The percent $\mathrm{CO}_{2}$, dry basis, $=55.0 /(460.52-43.5)=0.1318$, or 13.18 percent.

Related Calculations. Use the method given here when making combustion calculations for any type of fuel oil-paraffin-base, asphalt-base, Bunker C, No. 2, 3, 4, or 5-from any source, domestic or foreign, in any type of furnace-boiler, heater, process, or waste-heat. When the air used for combustion contains moisture, as is usually true, this moisture is added to the combustion-formed moisture appearing in the products of combustion. Thus, for $80^{\circ} \mathrm{F}$ air of 60 percent relative humidity, the moisture content is 0.013 lb per pound of dry air. This amount appears in the products of combustion for each pound of air used and is a commonly assumed standard in combustion calculations.

### 2.11 COMBUSTION OF NATURAL GAS IN A FURNACE

A natural gas has the following volumetric analysis at $60^{\circ} \mathrm{F}: \mathrm{CO}_{2}=0.004, \mathrm{CH}_{4}=0.921, \mathrm{C}_{2} \mathrm{H}_{6}=$ $0.041, \mathrm{~N}_{2}=0.034$, total $=1.000$. This natural gas is burned in a steam-boiler furnace. Determine the weight of air required for theoretically perfect combustion, the weight of gas formed per pound of natural gas burned, and the volume of the flue gas at the boiler exit temperature of $650^{\circ} \mathrm{F}$ per pound of natural gas burned; the air required with 20 percent excess air and the volume of gas formed with this excess; and the $\mathrm{CO}_{2}$ percentage in the flue gas on a dry and wet basis.

## Procedure

1. Compute the weight of oxygen required per pound of gas. The same general steps as given in the previous Calculation Procedures will be followed, except that they will be altered to make allowances for the differences between natural gas and coal.

The composition of the gas is given on a volumetric basis, which is the usual way of expressing a fuel-gas analysis. To use the volumetric-analysis data in combustion calculations, they must be converted to a weight basis. This is done by dividing the weight of each component by the total weight of the gas. A volume of $1 \mathrm{ft}^{3}$ of the gas is used for this computation. Find the weight of each

TABLE 2.1 Properties of Combustion Elements

| Element or compound | Formula | Molecular weight | At $14.7 \mathrm{psia}, 60^{\circ} \mathrm{F}$ |  | Nature |  | Heat value, Btu |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | Weight, $\mathrm{lb} / \mathrm{ft}^{3}$ | $\begin{aligned} & \text { Volume, } \\ & \mathrm{ft}^{3} / \mathrm{lb} \end{aligned}$ | Gas or solid | Combustible | $\begin{gathered} \text { Per } \\ \text { pound } \end{gathered}$ | $\begin{aligned} & \text { Per } \mathrm{ft}^{3} \mathrm{at} \\ & 14.7 \mathrm{psia}^{2} \\ & 60^{\circ} \mathrm{F} \end{aligned}$ | Per <br> mole |
| Carbon | C | 12 | - | - | S | Yes | 14,540 | - | 174,500 |
| Hydrogen | $\mathrm{H}_{2}$ | 2.02* | 0.0053 | 188 | G | Yes | 61,000 | 325 | 123,100 |
| Sulfur | S | 32 | - | - | S | Yes | 4,050 | - | 129,600 |
| Carbon monoxide | CO | 28 | 0.0739 | 13.54 | G | Yes | 4,380 | 323 | 122,400 |
| Methane | $\mathrm{CH}_{4}$ | 16 | 0.0423 | 23.69 | G | Yes | 24,000 | 1,012 | 384,000 |
| Acetylene | $\mathrm{C}_{2} \mathrm{H}_{2}$ | 26 | 0.0686 | 14.58 | G | Yes | 21,500 | 1,483 | 562,000 |
| Ethylene | $\mathrm{C}_{2} \mathrm{H}_{4}$ | 28 | 0.0739 | 13.54 | G | Yes | 22,200 | 1,641 | 622,400 |
| Ethane | $\mathrm{C}_{2} \mathrm{H}_{6}$ | 30 | 0.0792 | 12.63 | G | Yes | 22,300 | 1,762 | 668,300 |
| Oxygen | $\mathrm{O}_{2}$ | 32 | 0.0844 | 11.84 | G |  |  |  |  |
| Nitrogen | $\mathrm{N}_{2}$ | 28 | 0.0739 | 13.52 | G |  |  |  |  |
| $\mathrm{Air}^{\dagger}$ | - | 29 | 0.0765 | 13.07 | G |  |  |  |  |
| Carbon dioxide | $\mathrm{CO}_{2}$ | 44 | 0.1161 | 8.61 | G |  |  |  |  |
| Water | $\mathrm{H}_{2} \mathrm{O}$ | 18 | 0.0475 | 21.06 | G |  |  |  |  |

*For most practical purposes, the value of 2 is sufficient.
${ }^{\dagger}$ The molecular weight of 29 is merely the weighted average of the molecular weight of the constituents.
Source: P. W. Swain and L. N. Rowley, "Library of Practical Power Engineering" (collection of articles published in Power).
component and the total weight of $1 \mathrm{ft}^{3}$ as follows, using the properties of the combustion elements and compounds given in Table 2.1:

| Component | Percent by <br> volume | Density, <br> $\mathrm{lb} / \mathrm{ft}^{3}$ | Component weight, lb <br> $=$ col. $2 \times$ col. 3 |
| :--- | :---: | :---: | :--- |
| $\mathrm{CO}_{2}$ | 0.004 | 0.1161 | 0.0004644 |
| $\mathrm{CH}_{4}$ | 0.921 | 0.0423 | 0.0389583 |
| $\mathrm{C}_{2} \mathrm{H}_{6}$ | 0.041 | 0.0792 | 0.0032472 |
| $\mathrm{~N}_{2}$ | $\underline{0.034}$ | 0.0739 | $\underline{0.0025026}$ |
| Total | 1.000 |  | $0.0451725 \mathrm{lb} / \mathrm{ft}^{3}$ |

$$
\begin{aligned}
\text { Percent } \mathrm{CO}_{2} & =0.0004644 / 0.0451725=0.01026, \quad \text { or } 1.03 \text { percent } \\
\text { Percent } \mathrm{CH}_{4} \text { by weight } & =0.0389583 / 0.0451725=0.8625, \quad \text { or } 86.25 \text { percent } \\
\text { Percent } \mathrm{C}_{2} \mathrm{H}_{6} \text { by weight } & =0.0032472 / 0.0451725=0.0718, \quad \text { or } 7.18 \text { percent } \\
\text { Percent } \mathrm{N}_{2} \text { by weight } & =0.0025026 / 0.0451725
\end{aligned}
$$

The sum of the weight percentages $=1.03+86.25+7.18+5.54=100.00$. This sum checks the accuracy of the weight calculation, because the sum of the weights of the component parts should equal 100 percent.

Next, find the oxygen required for combustion. Since both the $\mathrm{CO}_{2}$ and $\mathrm{N}_{2}$ are inert, they do not take part in the combustion; they pass through the furnace unchanged. Using the molecular weights of the remaining compounds in the gas and the weight percentages, we have:

## STOICHIOMETRY*

| Compound | $\times$ | Molecular-weight <br> ratio | $=$ | Pounds $\mathrm{O}_{2}$ <br> required |
| :--- | :---: | :---: | :---: | :---: |
| $\mathrm{CH}_{4} ; 0.8625$ | $\times$ | $64 / 16$ | $=$ | 3.4500 |
| $\mathrm{C}_{2} \mathrm{H}_{6} ; 0.0718$ | $\times$ | $112 / 30$ | $=$ | $\underline{0.2920}$ |
| Pounds of external $\mathrm{O}_{2}$ required per pound fuel |  |  | $=$ | 3.7420 |

In this calculation, the molecular-weight ratio is obtained from the equation for the combustion chemical reaction, or $\mathrm{CH}_{4}+2 \mathrm{O}_{2}=\mathrm{CO}_{2}+2 \mathrm{H}_{2} \mathrm{O}$, that is, $16+64=44+36$, and $\mathrm{C}_{2} \mathrm{H}_{6}+{ }^{7} / 2 \mathrm{O}_{2}=$ $2 \mathrm{CO}_{2}+3 \mathrm{H}_{2} \mathrm{O}$, that is, $30+112=88+54$.
2. Compute the weight of air required for perfect combustion. The weight of nitrogen associated with the required oxygen $=(3.742)(0.768 / 0.232)=12.39 \mathrm{lb}$. The weight of air required $=12.39+$ $3.742=16.132 \mathrm{lb}$ per pound of gas burned.
3. Compute the weight of the products of combustion. Use the following relation:

| Fuel constituents |  |  |  | Products of <br> combustion |
| :--- | :--- | :--- | ---: | ---: |
| $\mathrm{CO}_{2} ; 0.0103 ;$ inert but passes through the furnace |  |  | Oxygen | $=$ |
| $\mathrm{CH}_{4} ; 0.8625$ | + | 3.45 | $=$ | 0.010300 |
| $\mathrm{C}_{2} \mathrm{H}_{6} ; 0.003247$ | + | 0.2920 | $=$ | 4.312500 |
| $\mathrm{~N}_{2} ; 0.0554 ;$ inert but passes through the furnace |  |  | $=$ | 0.032447 |
| Outside $\mathrm{N}_{2}$ from step 2 |  | $=$ | $\underline{12.390000}$ |  |
| Pounds of flue gas per pound of natural gas burned |  |  |  |  |

4. Convert the flue-gas weight to volume. The products of complete combustion of any fuel that does not contain sulfur are $\mathrm{CO}_{2}, \mathrm{H}_{2} \mathrm{O}$, and $\mathrm{N}_{2}$. Using the combustion equation in step 1, compute the products of combustion thus: $\mathrm{CH}_{4}+2 \mathrm{O}_{2}=\mathrm{CO}_{2}+\mathrm{H}_{2} \mathrm{O} ; 16+64=44+36$; or the $\mathrm{CH}_{4}$ burns to $\mathrm{CO}_{2}$ in the ratio of 1 part $\mathrm{CH}_{4}$ to $44 / 16$ parts $\mathrm{CO}_{2}$. Since, from step 1, there is $0.03896 \mathrm{lb} \mathrm{CH}_{4} \mathrm{perft}^{3}$ natural gas, this forms $(0.03896)(44 / 16)=0.1069 \mathrm{lb} \mathrm{CO}_{2}$. Likewise, for $\mathrm{C}_{2} \mathrm{H}_{6},(0.003247)(88 / 30)=0.00952 \mathrm{lb}$. The total $\mathrm{CO}_{2}$ in the combustion products $=0.00464+0.1069+0.00952=0.11688 \mathrm{lb}$, where the first quantity is the $\mathrm{CO}_{2}$ in the fuel.

Using a similar procedure for the $\mathrm{H}_{2} \mathrm{O}$ formed in the products of combustion by $\mathrm{CH}_{4}$, $(0.03896)(36 / 16)=0.0875 \mathrm{lb}$. For $\mathrm{C}_{2} \mathrm{H}_{6},(0.003247)(54 / 30)=0.005816 \mathrm{lb}$. The total $\mathrm{H}_{2} \mathrm{O}$ in the combustion products $=0.0875+0.005816=0.093316 \mathrm{lb}$.

Step 2 shows that $12.39 \mathrm{lbN}_{2}$ is required per pound of fuel. Since $1 \mathrm{ft}^{3}$ of the fuel weighs 0.04517 lb , the volume of gas that weighs 1 lb is $1 / 0.04517=22.1 \mathrm{ft}^{3}$. Therefore, the weight of $\mathrm{N}_{2}$ per cubic foot of fuel burned $=12.39 / 22.1=0.560 \mathrm{lb}$. This, plus the weight of $\mathrm{N}_{2}$ in the fuel, step 1 , is $0.560+0.0025=0.5625 \mathrm{lb} \mathrm{N}_{2}$ in the products of combustion.

Next, find the total weight of the products of combustion by taking the sum of the $\mathrm{CO}_{2}, \mathrm{H}_{2} \mathrm{O}$, and $\mathrm{N}_{2}$ weights, or $0.11688+0.09332+0.5625=0.7727 \mathrm{lb}$. Now convert each weight to cubic feet at $650^{\circ} \mathrm{F}$, the temperature of the combustion products, or:

| Products | Weight, <br> lb | Molecular <br> weight | Temperature correction | Volume at <br> $650^{\circ} \mathrm{F}, \mathrm{ft}^{3}$ |
| :--- | :---: | :---: | :---: | ---: |
| $\mathrm{CO}_{2}$ | 0.11688 | 44 | $(379 / 44)(0.11688)(2.255)$ | $=2.265$ |
| $\mathrm{H}_{2} \mathrm{O}$ | 0.09332 | 18 | $(379 / 18)(0.09332)(2.255)$ | $=4.425$ |
| $\mathrm{~N}_{2}$ (total) | 0.5625 | 28 | $(379 / 28)(0.5625)(2.255)$ | $=17.190$ |
| Cubic feet of flue gas per cubic foot of natural-gas fuel | $=23.880$ |  |  |  |

In this calculation, the value of 379 is used in the molecular-weight ratio because at $60^{\circ} \mathrm{F}$ and 14.7 psia the volume of 1 lb of any gas $=379 /$ gas molecular weight. The fuel gas used is initially at $60^{\circ} \mathrm{F}$ and 14.7 psia . The ratio $2.255=(650+460) /(32+460)$.
5. Compute the $\boldsymbol{C O}_{2}$ content of the flue gas. The $\mathrm{CO}_{2}$, wet basis, $=2.265 / 23.88=0.0947$, or 9.47 percent. The $\mathrm{CO}_{2}$, dry basis, $=2.265 /(23.88-4.425)=0.1164$, or 11.64 percent.
6. Compute the air required with the stated excess flow. The pounds of air per pound of natural gas with 20 percent excess air $=(1.20)(16.132)=19.3584 \mathrm{lb}$ air per pound of natural gas, or $19.3584 / 22.1=0.875 \mathrm{lb}$ of air per cubic foot of natural gas $\left(14.02 \mathrm{~kg} / \mathrm{m}^{3}\right)$. See step 4 for an explanation of the value 22.1 .
7. Compute the weight of the products of combustion. Weight of the products of combustion $=$ product weight for perfect combustion, $\mathrm{lb}+$ (percent excess air)(air for perfect combustion, lb$)=$ $16.80+(0.20)(16.132)=20.03 \mathrm{lb}$.
8. Compute the volume of the combustion products and the percent $\mathrm{CO}_{2}$. The volume of excess air in the products of combustion is found by converting from the weight to the volumetric analysis and correcting for temperature as in step 4 , using the air weight from step 2 for perfect combustion and the excess-air percentage, or $(16.132 / 22.1)(0.20)(379 / 28.95)(2.255)=4.31 \mathrm{ft}^{3}$. Add this to the volume of the products of combustion found in step 4 , or $23.88+4.31=28.19 \mathrm{ft}^{3}\left(0.80 \mathrm{~m}^{3}\right)$.

Using the procedure in step 5 , the percent $\mathrm{CO}_{2}$, wet basis, $=2.265 / 28.19=0.0804$, or 8.04 percent. The percent $\mathrm{CO}_{2}$, dry basis, $=2.265 /(28.19-4.425)=0.0953$, or 9.53 percent.

Related Calculations. Use the method given here when making combustion calculations for any type of gas used as a fuel-natural gas, blast-furnace gas, coke-oven gas, producer gas, water gas, sewer gas-from any source, domestic or foreign, in any type of furnace-boiler, heater, process, or waste-heat. When the air used for combustion contains moisture, as is usually true, this moisture is added to the combustion-formed moisture appearing in the products of combustion. Thus, for $80^{\circ} \mathrm{F}$ $(300 \mathrm{~K})$ air of 60 percent relative humidity, the moisture content is 0.013 lb per pound of dry air. This amount appears in the products of combustion for each pound of air used and is a commonly assumed standard in combustion calculations.

## STOICHIOMETRY*

# PHASE EOUILIBRIUM 

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### 3.1 VAPOR-LIQUID EQUILIBRIUM RATIOS FOR IDEAL-SOLUTION BEHAVIOR 3.1

3.2 FUGACITY OF PURE LIQUID 3.3
3.3 NONIDEAL GAS-PHASE MIXTURES 3.4
3.4 NONIDEAL LIQUID MIXTURES 3.5
3.5 K VALUE FOR IDEAL LIQUID PHASE, NONIDEAL VAPOR PHASE 3.7
3.6 K VALUE FOR IDEAL VAPOR PHASE, NONIDEAL LIQUID PHASE 3.8
3.7 THERMODYNAMIC CONSISTENCY OF EXPERIMENTAL VAPOR-LIQUID EQUILIBRIUM DATA 3.8
3.8 ESTIMATING INFINITE-DILUTION ACTIVITY COEFFICIENTS 3.10
3.9 ESTIMATING THE PARAMETERS FOR THE WILSON-EQUATION MODEL FOR ACTIVITY COEFFICIENTS 3.11
3.10 CALCULATING DEW POINT WHEN LIQUID PHASE IS IDEAL 3.12
3.11 CALCULATING BUBBLE POINT WHEN VAPOR PHASE IS IDEAL 3.14
3.12 BINARY PHASE DIAGRAMS FOR VAPOR-LIQUID EQUILIBRIUM 3.15
3.13 MULTICOMPONENT LIQUID-LIQUID EQUILIBRIUM 3.18
3.14 CALCULATIONS FOR ISOTHERMAL FLASHING 3.19
REFERENCES 3.20

### 3.1 VAPOR-LIQUID EQUILIBRIUM RATIOS FOR IDEAL-SOLUTION BEHAVIOR

Assuming ideal-system behavior, calculate the $K$ values and relative volatility for the benzene-toluene system at $373 \mathrm{~K}\left(212^{\circ} \mathrm{F}\right)$ and $101.3 \mathrm{kPa}(1 \mathrm{~atm})$.

## Calculation Procedure

1. Determine the relevant vapor-pressure data. Design calculations involving vapor-liquid equilibrium (VLE), such as distillation, absorption, or stripping, are usually based on vapor-liquid equilibrium ratios, or $K$ values. For the $i$ th species, $K_{i}$ is defined as $K_{i}=y_{i} / x_{i}$, where $y_{i}$ is the mole fraction of that species in the vapor phase and $x_{i}$ is its mole fraction in the liquid phase. Sometimes the design calculations are based on relative volatility $\alpha_{i, j}$, which equals $K_{i} / K_{j}$, the subscripts $i$ and $j$ referring to two different species. In general, $K$ values depend on temperature and pressure and the compositions of both phases.

When a system obeys Raoult's law and Dalton's law, it is known as an "ideal system" (see Related Calculations for guidelines). Then $K_{i}=P_{i}^{\circ} / P$, and $\alpha_{i, j}=P_{i}^{\circ} / P_{j}^{\circ}$, where $P_{i}^{\circ}$ is the vapor pressure of the (pure) $i$ th component at the system temperature and $P$ is the total pressure.

One way to obtain the necessary vapor-pressure data for benzene and toluene is to employ the Antoine equation:

$$
\log _{10} P^{\circ}=A-B /(t+C)
$$

(See also Section 1.) When $P^{\circ}$ is in millimeters of mercury and $t$ is temperature in degrees Celsius, the following are the values for the constants $A, B$, and $C$ :

|  | $A$ | $B$ | $C$ |
| :--- | :---: | :---: | :---: |
| Benzene | 6.90565 | 1211.033 | 220.790 |
| Toluene | 6.95464 | 1424.255 | 219.482 |

Then, at 373 K (i.e., $100^{\circ} \mathrm{C}$ ),

$$
\log _{10} P_{\text {benzzene }}^{\circ}=6.90565-1211.033 /(100+220.790)=3.1305
$$

and $P_{\text {benzene }}^{\circ}$ therefore equals $1350.5 \mathrm{mmHg}(180.05 \mathrm{kPa})$. Similarly,

$$
\log _{10} P_{\text {toluene }}^{\circ}=6.95464-1424.255 /(100+219.482)=2.4966
$$

so $P_{\text {toluene }}^{\circ}$ equals $313.8 \mathrm{mmHg}(41.84 \mathrm{kPa})$.
2. Divide vapor pressures by total pressure to obtain $\boldsymbol{K}$ values. Total pressure $P$ is 1 atm , or 760 mmHg . Therefore, $K_{\text {benzene }}=1350.5 / 760=1.777$, and $K_{\text {toluene }}=313.8 / 760=0.413$.
3. Calculate relative volatility of benzene with respect to toluene. Divide the vapor pressure of benzene by that of toluene. Thus, $\alpha_{\text {benzene-toluene }}=1350.5 / 313.8=4.304$.

Related Calculations. Many systems deviate from the ideal solution behavior in either or both phases, so the $K$ values given by $K_{i}=P_{i}^{\circ} / P$ are not adequate. The rigorous thermodynamic definition of $K$ is

$$
K_{i}=\gamma_{i} f_{i}^{\circ} / \phi_{i} P
$$

where $\gamma_{i}$ is the activity coefficient of the $i$ th component in the liquid phase, $f_{i}^{\circ}$ is the fugacity of pure liquid $i$ at system temperature $T$ and pressure $P$, and $\phi_{i}$ is the fugacity coefficient of the $i$ th species in the vapor phase.

In this definition, the activity coefficient takes account of nonideal liquid-phase behavior; for an ideal liquid solution, the coefficient for each species equals 1 . Similarly, the fugacity coefficient represents deviation of the vapor phase from ideal gas behavior and is equal to 1 for each species when the gas obeys the ideal gas law. Finally, the fugacity takes the place of vapor pressure when the pure vapor fails to show ideal gas behavior, either because of high pressure or as a result of vapor-phase association or dissociation. Methods for calculating all three of these follow.

The vapor-phase fugacity coefficient can be neglected when the system pressure is low [e.g., less than $100 \mathrm{psi}(689.5 \mathrm{kPa})$, generally] and the system temperature is not below a reduced temperature of 0.8 . The pure-liquid fugacity is essentially equal to the vapor pressure at system temperatures up to a reduced temperature of 0.7 . Unfortunately, however, many molecules (among them hydrogen fluoride and some organic acids) associate in the vapor phase and behave nonideally even under the preceding conditions. There is no widely recognized listing of all such compounds. As for nonideality in the liquid phase, perhaps the most important cause of it is hydrogen bonding. For general rules of thumb for predicting hydrogen bonding, see R. H. Ewell, J. M. Harrison, and L. Berg, Ind. Eng. Chem. 36(10):871, 1944.

### 3.2 FUGACITY OF PURE LIQUID

Calculate the fugacity of liquid hydrogen chloride at $40^{\circ} \mathrm{F}(277.4 \mathrm{~K})$ and $200 \mathrm{psia}(1379 \mathrm{kPa})$. (The role of fugacity in phase equilibrium is discussed under Related Calculations in Example 3.1).

## Calculations Procedure

1. Calculate the compressibility factor. For components whose critical temperature is greater than the system temperature,

$$
f^{\circ}=v P^{\circ} \exp \left[V\left(P-P^{\circ}\right) / R T\right]
$$

where $f^{\circ}$ is the pure-liquid fugacity, $v$ is the fugacity coefficient for pure vapor at the system temperature, $P^{\circ}$ is the vapor pressure at that temperature, $V$ is the liquid molar volume, $P$ is the system pressure, and $T$ is the absolute temperature.

Thermodynamically, the fugacity coefficient is given by

$$
\ln v=\int_{0}^{P^{\circ}} \frac{Z-1}{P} d P
$$

where $Z$ is the compressibility factor. This integral has been evaluated for several equations of state. For instance, for the Redlich-Kwong equation, which is very popular in engineering design and is employed here, the relationship is

$$
\ln v=(Z-1)-\ln \left(Z-B P^{\circ}\right)-\frac{A^{2}}{B} \ln \left(1+\frac{B P^{\circ}}{Z}\right)
$$

where $A^{2}=0.4278 / T_{r}^{2.5} P_{c}$
$B=0.0867 / T_{r} P_{c}$
$T_{r}=$ reduced temperature $\left(T / T_{c}\right)$
$T_{c}=$ critical temperature
$P_{c}=$ critical pressure
The compressibility factor $Z$ is calculated by solving the following cubic equation (whose symbols are as defined above):

$$
Z^{3}-Z^{2}+\left[A^{2} P^{\circ}-B P^{\circ}\left(1+B P^{\circ}\right)\right] Z+\left(A^{2} P^{\circ}\right)\left(B P^{\circ}\right)=0
$$

The critical temperature of HCl is $584^{\circ} \mathrm{R}$, so the reduced temperature at $40^{\circ} \mathrm{F}$ is $(460+40) / 584$ or 0.85616 . The critical pressure of HCl is 1206.9 psia . Then, $A^{2}=0.4278 /\left[0.85616^{2.5}(1206.9)\right]=$ $5.226 \times 10^{-4}$, and $B=0.0867 /(0.85616 \times 1206.9)=8.391 \times 10^{-5}$. The vapor pressure $P^{\circ}$ of HCl at $40^{\circ} \mathrm{F}$, is 423.3 psia, so $A^{2} P^{\circ}=0.2212, B P^{\circ}=0.03552, A^{2} P^{\circ}-B P^{\circ}\left(1+B P^{\circ}\right)=0.1844$, and $\left(A^{2} P\right)\left(B P^{\circ}\right)=7.857 \times 10^{-3}$. The cubic equation thus becomes $Z^{3}-Z^{2}+0.1844 Z+7.856 \times$ $10^{-3}=0$.

This equation can be solved straightforwardly or by trial and error. The largest real root is the compressibility factor for the vapor; in this case, $Z=0.73431$.
2. Calculate the fugacity coefficient. Using the preceding relationship based on the RedlichKwong equation,

$$
\begin{aligned}
\ln v & =(0.73431-1)-\ln (0.73431-0.03552)-\frac{5.226 \times 10^{-4}}{8.391 \times 10^{-5}} \ln \left(1+\frac{0.03552}{0.73431}\right) \\
& =-0.2657+0.3584-0.2942=-0.2015
\end{aligned}
$$

Therefore, $v=0.8175$.
3. Calculate the fugacity. The density of saturated vapor at $40^{\circ} \mathrm{F}$ is $55 \mathrm{lb} / \mathrm{ft}^{3}$, and the molecular weight of HCl is 36.46 . Therefore, the liquid molar volume $V$ is $36.46 / 55=0.663 \mathrm{ft}^{3} /(\mathrm{lb} \cdot \mathrm{mol})$. The gas constant $R$ is $10.73(\mathrm{psia})\left(\mathrm{ft}^{3}\right) /(\mathrm{lb} \cdot \mathrm{mol})\left({ }^{\circ} \mathrm{R}\right)$. Therefore,

$$
\exp \left[V\left(P-P^{\circ}\right) / R T\right]=\exp \left[\frac{0.663(200-423.3)}{10.73(460+40)}\right]=0.9728
$$

Finally, using the equation for fugacity at the beginning of this problem, $f^{\circ}=0.8175 \times 423.3 \times$ $0.9728=336.6 \mathrm{psi}(2321 \mathrm{kPa})$.

The exponential term, 0.9728 in this equation, is known as the "Poynting correction." It is greater than unity if system pressure is greater than the vapor pressure. The fugacity coefficient $v$ is always less than unity. Depending on the magnitudes of $v$ and the Poynting correction, fugacity of pure liquid $f^{\circ}$ can thus be greater or less than the vapor pressure.

Related Calculations. This procedure is valid only for those components whose critical temperature is above the system temperature. When the system temperature is instead above the critical temperature, generalized fugacity-coefficient graphs can be used. However, such an approach introduces the concept of hypothetical liquids. When accurate results are needed, experimental measurements should be made. The Henry constant, which can be experimentally determined, is simply $\gamma^{\infty} f^{\circ}$, where $\gamma^{\infty}$ is the activity coefficient at infinite dilution (see Example 3.8).

Use of generalized fugacity coefficients (e.g., see Example 1.18) eliminates some computational steps. However, the equation-of-state method used here is easier to program on a programmable calculator or computer. It is completely analytical, and use of an equation of state permits the computation of all the thermodynamic properties in a consistent manner.

### 3.3 NONIDEAL GAS-PHASE MIXTURES

Calculate the fugacity coefficients of the components in a gas mixture containing $80 \% \mathrm{HCl}$ and $20 \%$ dichloromethane (DCM) at $40^{\circ} \mathrm{F}(277.4 \mathrm{~K})$ and $200 \mathrm{psia}(1379 \mathrm{kPa})$.

## Calculation Procedure

1. Calculate the compressibility factor for the mixture. In a manner similar to that used in the previous problem, an expression for the fugacity coefficient in vapor mixtures can be derived from any equation of state applicable to such mixtures. If the Redlich-Kwong equation of state is used, the expression is

$$
\ln \phi_{i}=(Z-1) \frac{B_{i}}{B}-\ln (Z-B P)-\frac{A^{2}}{B}\left(\frac{2 A_{i}}{A}-\frac{B_{i}}{B}\right) \ln \left(1+\frac{B P}{Z}\right)
$$

where $\phi_{i}=$ the fugacity coefficient of the $i$ th component in the vapor

$$
\begin{aligned}
A_{i}^{2} & =0.4278 / T_{r, i}^{2.5} P_{c, i} \\
B_{i} & =0.0867 / T_{r, i} P_{c, i} \\
A & =\Sigma y_{i} A_{i} \\
B & =\Sigma y_{i} B_{i}
\end{aligned}
$$

$T_{r, i}=$ the reduced temperature of component $i\left(T / T_{c, i}\right)$
$T_{c, i}=$ the critical temperature of component $i$
$P_{c, i}=$ the critical pressure of component $i$
$y_{i}=$ the mole fraction of component $i$ in the vapor mixture.
The compressibility factor $Z$ is calculated by solving the cubic equation:

$$
Z^{3}-Z^{2}+\left[A^{2} P-B P(1+B P)\right] Z+\left(A^{2} P\right)(B P)=0
$$

The relevant numerical inputs are:

|  | HCl | DCM |
| :--- | :--- | :--- |
| Critical temperature $T_{c, i},{ }^{\circ} \mathrm{R}$ | 584 | 933 |
| Critical pressure $P_{c, i}, \mathrm{psia}$ | 1206.9 | 893 |
| Reduced temperature $T_{r, i}$ at $40^{\circ} \mathrm{F}$ | 0.8562 | 0.5359 |
| $A_{i}$, equal to $\left(0.4278 / T_{r, i}^{2.5} P_{c, i}\right)^{1 / 2}$ | 0.02286 | 0.04774 |
| $B_{i}$, equal to $0.0867 / T_{r, i} P_{c, i}$ | $8.390 \times 10^{-5}$ | $1.812 \times 10^{-4}$ |
| Mole fraction $y_{i}$ | 0.8 | 0.2 |

Then, $A=y_{1} A_{1}+y_{2} A_{2}=0.0278, B=y_{1} B_{1}+y_{2} B_{2}=1.0336 \times 10^{-4}, A^{2} P=(0.0278)^{2}(200)$ $=0.1546, B P=\left(1.0336 \times 10^{-4}\right)(200)=0.02067, A^{2} P-B P(1+B P)=0.1335$, and $\quad\left(A^{2} P\right)$ $\times(B P)=0.003195$. The cubic equation becomes $Z^{3}-Z^{2}+0.1335 Z+0.003195=0$.

This equation can be solved straightforwardly or by trial and error. The largest real root is the compressibility factor; in this case, $Z=0.8357$.
2. Calculate the fugacity coefficients. Substituting into the preceding relationship based on the Redlich-Kwong equation,

$$
\begin{aligned}
\ln \phi_{i}= & (0.8357-1) B_{i} / 1.0336 \times 10^{-4}-\ln (0.8357-0.02067) \\
& -\left(0.0278^{2} / 1.0336 \times 10^{-4}\right)\left[\left(2 A_{i} / 0.0278\right)\right. \\
& \left.-\left(B_{i} / 1.0336 \times 10^{-4}\right)\right][\ln (1+0.02067 / 0.8357)] \\
= & -1589.6 B_{i}+0.2045-0.1827\left(71.94 A_{i}-9674.9 B_{i}\right)
\end{aligned}
$$

Letting subscript 1 correspond to HCl and subscript 2 to DCM , the equation yields $\ln \phi_{1}=$ -0.08095 and $\ln \phi_{2}=-0.3905$. Therefore, $\phi_{1}=0.9222$ and $\phi_{2}=0.6767$.

Related Calculations. Certain compounds, such as acetic acid and hydrogen fluoride, are known to form dimers, trimers, or other oligomers by association in the vapor phase. Simple equations of state are not adequate for representing the nonideality in systems containing such compounds. Unfortunately, there is no widely recognized listing of all such compounds.

### 3.4 NONIDEAL LIQUID MIXTURES

Calculate the activity coefficients of chloroform and acetone at $0^{\circ} \mathrm{C}$ in a solution containing $50 \mathrm{~mol} \%$ of each component, using the Wilson-equation model. The Wilson constants for the system (with subscript 1 pertaining to chloroform and subscript 2 to acetone) are

$$
\begin{aligned}
& \lambda_{1,2}-\lambda_{1,1}=-332.23 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{~mol})[-1390 \mathrm{~kJ} /(\mathrm{kg} \cdot \mathrm{~mol})] \\
& \lambda_{1,2}-\lambda_{2,2}=-72.20 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{~mol})[-302.1 \mathrm{~kJ} /(\mathrm{kg} \cdot \mathrm{~mol})]
\end{aligned}
$$

## Calculation Procedure

1. Compute the $\boldsymbol{G}_{i, j}$ parameters for the Wilson equation. General engineering practice is to establish liquid-phase nonideality through experimental measurement of vapor-liquid equilibrium. Models with adjustable parameters exist for adequately representing most nonideal-solution behavior. Because of these models, the amount of experimental information needed is not excessive (see Example 3.9, which shows procedures for calculating such parameters from experimental data).

One such model is the Wilson-equation model, which is applicable to multicomponent systems while having the attraction of entailing only parameters that can be calculated from binary data alone. Another attraction is that the Wilson constants are approximately independent of temperature. This model is

$$
\ln \gamma_{i}=1-\ln \sum_{j=1}^{N} x_{j} G_{j, i}-\sum_{j=1}^{N}\left(x_{j} G_{i, j} / \sum_{k} x_{k} G_{k, j}\right)
$$

where $\gamma_{i}$ is the activity coefficient of the $i$ th component, $x_{i}$ is the mole fraction of that component, and $G_{i, j}=V_{i} / V_{j} \exp \left[-\left(\lambda_{i, j}-\lambda_{j, j}\right) / R T\right]$, with $V_{i}$ being the liquid molar volume of the $i$ th component and $\left(\lambda_{i, j}-\lambda_{j, j}\right)$ being the Wilson constants. Note that $\lambda_{i, j}=\lambda_{j, i}$, but that $G_{i, j}$ is not equal to $G_{j, i}$.

For a binary system, $N=2$ and $\left(x_{i}+x_{j}\right)=1.0$, and the model becomes

$$
\ln \gamma_{1}=-\ln \left(x_{1}+x_{2} G_{2,1}\right)+x_{2}\left[\frac{G_{2,1}}{x_{1}+x_{2} G_{2,1}}-\frac{G_{1,2}}{x_{2}+x_{1} G_{1,2}}\right]
$$

and

$$
\ln \gamma_{2}=-\ln \left(x_{2}+x_{1} G_{1,2}\right)+x_{1}\left[\frac{G_{1,2}}{x_{2}+x_{1} G_{1,2}}-\frac{G_{2,1}}{x_{1}+x_{2} G_{2,1}}\right]
$$

where

$$
G_{1,2}=\frac{V_{1}}{V_{2}} \exp \left(-\frac{\lambda_{1,2}-\lambda_{2,2}}{R T}\right) \quad \text { and } \quad G_{2,1}=\frac{V_{2}}{V_{1}} \exp \left(-\frac{\lambda_{1,2}-\lambda_{1,1}}{R T}\right)
$$

At $0^{\circ} \mathrm{C}, V_{1}=71.48 \mathrm{cc} /(\mathrm{g} \cdot \mathrm{mol})$ and $V_{2}=78.22 \mathrm{cc} /(\mathrm{g} \cdot \mathrm{mol})$. Therefore, for the chloroform/ acetone system,

$$
G_{1,2}=\frac{71.48}{78.22} \exp \left(-\frac{(-72.20)}{(1.9872)(273.15)}\right)=1.0438
$$

and

$$
G_{2,1}=\frac{78.22}{71.48} \exp \left(-\frac{(-332.23)}{(1.9872)(273.15)}\right)=2.0181
$$

2. Calculate the activity coefficients. The mole fractions $x_{1}$ and $x_{2}$ each equal 0.5 . Therefore, $x_{1}+x_{2} G_{2,1}=1.509$, and $x_{2}+x_{1} G_{1,2}=1.022$. Substituting into the Wilson model,

$$
\ln \gamma_{1}=-\ln 1.509+0.5\left(\frac{2.0181}{1.509}-\frac{1.0438}{1.022}\right)=-0.2534
$$

Therefore, $\gamma_{1}=0.7761$. And,

$$
\ln \gamma_{2}=-\ln 1.022+0.5\left(\frac{1.0438}{1.022}-\frac{2.0181}{1.509}\right)=-0.1798
$$

Therefore, $\gamma_{2}=0.8355$.
This system, where the activity coefficients are less than unity, is an example of negative deviation from ideal behavior.

Related Calculations. When the Wilson model is used for systems with more than two components, it is important to remember that the $G_{i, j}$ summations must be made over every possible pair of components (also, remember that $G_{i, j} \neq G_{j, i}$ ).

A limitation on the Wilson equation is that it is not applicable to systems having more than one liquid phase. The NRTL model, which is similar to the Wilson equation, may be used for systems forming two liquid phases.

An older model for predicting liquid-phase activity coefficients is that of Van Laar, in which (for two components) $\ln \gamma_{1}=A_{1,2} /\left(1+A_{1,2} x_{1} / A_{2,1} x_{2}\right)^{2}$, with the $A$ 's being constants to be determined from experimental data. This model can handle systems having more than one liquid phase. Another older model is that of Margules, available in "two-suffix" and "three-suffix" versions. These are (for two components), respectively, $\ln \gamma_{1}=A x_{2}^{2}$ and $\ln \gamma_{1}=x_{2}^{2}\left[A_{1,2}+2\left(A_{2,1}-A_{1,2}\right) x_{1}\right]$. Ternary versions of these older models are available, but extending the Van Laar and Margules correlations to multicomponent systems is in general rather awkward.

Fredenslund and coworkers have developed the UNIFAC correlation, which is satisfactory for those systems covered by the extensive amount of experimental data in their work. For details, see A. Fredenslund, J. Gmehling, and P. Rasumssen, Vapor-Liquid Equilibria Using UNIFAC, Elsevier Scientific Publishing Co., Amsterdam, 1977.

### 3.5 K VALUE FOR IDEAL LIQUID PHASE, NONIDEAL VAPOR PHASE

Assuming the liquid phase but not the vapor phase to be ideal, calculate the $K$ values for HCl and dichloromethane (DCM) in a system at $200 \mathrm{psia}(1,379 \mathrm{kPa})$ and $40^{\circ} \mathrm{F}(277.4 \mathrm{~K})$ and whose vapor composition is $80 \mathrm{~mol} \% \mathrm{HCl}$. Also calculate the relative volatility. Compare the calculated values with those which would exist if the system showed ideal behavior.

## Calculation Procedure

1. Set out the relevant form of the thermodynamic definition of $\boldsymbol{K}$ value. Refer to the rigorous definition of $K$ value given under Related Calculations in Example 3.1. When the liquid phase is ideal, then $\gamma_{i}=1$. Thus the relevant form is

$$
K_{i}=f_{i}^{\circ} / \phi_{i} P
$$

where $f_{i}^{\circ}$ is the fugacity of pure liquid $i$ at system temperature and pressure, $\phi_{i}$ is the fugacity coefficient of the $i$ th species in the vapor phase, and $P$ is the system pressure. Let subscript 1 pertain to HCl and subscript 2 pertain to DCM.
2. Determine the pure-liquid fugacities and the vapor-phase fugacity coefficients. The fugacity of HCl at 200 psia and $40^{\circ} \mathrm{F}$ was calculated in Example 3.2 to be 336.6 psi . The same procedure can be employed to find $f_{2}^{\circ}$, the pure-liquid fugacity of DCM. With reference to that example, $A^{2}=0.04774$ and $B_{2}=1.812 \times 10^{-4}$; the vapor pressure of $D C M$ at $40^{\circ} \mathrm{F}$ is 3.28 psi . The resulting cubic equation for compressibility factor yields a $Z$ of 0.993 ; the Redlich-Kwong relationship yields a $v_{2}$ of 0.993 . The liquid molar volume of DCM at $40^{\circ} \mathrm{F}$ is $1.05 \mathrm{ft}^{3} /(\mathrm{lb} \cdot \mathrm{mol})$, so the Poynting correction is calculated to be 1.039 , and the resulting value for $f_{2}^{\circ}$ emerges as $3.38 \mathrm{psi}(23.3 \mathrm{kPa})$. As for the fugacity coefficients, they were calculated in Example 3.3 to be $\phi_{1}=0.9222$ and $\phi_{2}=0.6767$.
3. Calculate the $K$ values and relative volatility. Using the equation in step $1, K_{1}=336.6 /$ $(0.9222)(200)=1.82$, and $K_{2}=3.38 /(0.6767)(200)=0.025$. From the definition in Example 3.1, relative volatility $\alpha_{1,2}=K_{1} / K_{2}=1.82 / 0.025=72.8$.
4. Compare these results with those which would prevail if the system were ideal. As indicated in Example 3.1, the $K$ value based on ideal behavior is simply the vapor pressure of the component divided by the system pressure. Vapor pressures of HCl and DCM at $40^{\circ} \mathrm{F}$ are, respectively, 423.3 and 3.28 psia. Thus $K_{1}^{\text {ideal }}=423.3 / 200=2.12, K_{2}^{\text {ideal }}=3.28 / 200=0.016$, and $\alpha_{1,2}^{\text {ideal }}=2.12 / 0.016=$ 133.

It may be seen that under the system conditions that prevail in this case, the actual relative volatility is considerably lower than it would be if the system were ideal.

### 3.6 K VALUE FOR IDEAL VAPOR PHASE, NONIDEAL LIQUID PHASE

Assuming the vapor phase but not the liquid phase to be ideal, calculate the $K$ values for ethanol and water in an $80 \%$ ethanol solution at $500 \mathrm{mmHg}(66.7 \mathrm{kPa})$ and $70^{\circ} \mathrm{C}\left(158^{\circ} \mathrm{F}, 343 \mathrm{~K}\right)$. Also calculate the relative volatility, and compare the calculated values with those which would exist if the system showed ideal behavior.

## Calculation Procedure

1. Set out the relevant form of the thermodynamic definition of $\boldsymbol{K}$ value. At this low system pressure, the vapor-phase nonideality is negligible. Since neither component has a very high vapor pressure at the system temperature, and since the differences between the vapor pressures and the system pressure are relatively small, the pure-liquid fugacities can be taken to be essentially the same as the vapor pressures.

Refer to the rigorous definition of $K$ value given under Related Calculations in Example 3.1. Taking into account the assumptions in the preceding paragraph, this definition simplifies into $K_{i}=\gamma_{i} P_{i} / P$, where $\gamma_{i}$ is the activity coefficient of the $i$ th component in the liquid phase, $P_{i}$ is the vapor pressure of that component, and $P$ is the system pressure.
2. Determine the activity coefficients and the vapor pressures. The activity coefficients can be calculated from the Wilson-equation model, as discussed in Example 3.4, or by one of the other methods discussed in the same example under Related Calculations. For instance, the experimentally determined Van Laar constants for the ethanol/water system are $A_{1,2}=1.75$ and $A_{2,1}=0.91$, where subscripts 1 and 2 refer to ethanol and water, respectively. So the Van Laar model discussed there becomes $\ln \gamma_{1}=1.75 /[1+(1.75)(0.08) /(0.91)(0.2)]^{2}$, and (by interchanging subscripts) $\ln \gamma_{2}=0.91 /[1+(0.91)(0.2) /(1.75)(0.8)]^{2}$. Accordingly, $\gamma_{1}=1.02$, and $\gamma_{2}=2.04$.

From tables, the vapor pressures of ethanol and water at $70^{\circ} \mathrm{C}$ are 542 and 233 mmHg , respectively.
3. Calculate the $\boldsymbol{K}$ values and relative volatility. Using the equation in step $1, K_{1}=$ $(1.02)(542) / 500=1.11$, and $K_{2}=(2.04)(233) / 500=0.95$.

From the definition in Example 3.1, relative volatility $\alpha_{1,2}=K_{1} / K_{2}=1.11 / 0.95=1.17$.
4. Compare these results with those which would prevail if the system were ideal. As indicated in that example, the $K$ value based on ideal behavior is simply the vapor pressure of the component divided by the system pressure. Thus $K_{1}^{\text {ideal }}=542 / 500=1.084, K_{2}^{\text {ideal }}=233 / 500=0.466$, and $\alpha_{1,2}^{\text {ideal }}=1.084 / 0.466=2.326$. Under the system conditions that prevail in this case, actual relative volatility is considerably lower than the ideal-system value.

Related Calculations. As computer-based computation has become routine, a growing trend in the determination of $K$ values has been the use of of cubic equations of state, such as the Peng-Robinson, for calculating the fugacities of the components in each phase. Such calculations are mathematically complex and involve iteration.

### 3.7 THERMODYNAMIC CONSISTENCY OF EXPERIMENTAL VAPOR-LIQUID EQUILIBRIUM DATA

Vapor-liquid equilibrium data for the ethanol/water system (subscripts 1 and 2 , respectively) at $70^{\circ} \mathrm{C}$ $\left(158^{\circ} \mathrm{F}, 343 \mathrm{~K}\right)$ are given in the three left columns of Table 3.1. Check to see if the data are thermodynamically consistent.

TABLE 3.1 Ethanol/Water System at $70^{\circ} \mathrm{C}$ (Examples 3.7 and 3.8)

| Experimental data |  |  | Calculated results |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Mole fraction <br> ethanol in <br> Pressure $P$, <br> mmHg | Mole fraction <br> ethanol in <br> vapor $y_{1}$ | $\gamma_{1}$, <br> $P y_{1} / P_{1}^{\circ} x_{1}$ | $\gamma_{2}$, <br> $P y_{2} / P_{2}^{\circ} x_{2}$ | $\ln \left(\gamma_{1} / \gamma_{2}\right)$ | $\ln \gamma_{1} / x_{2}^{2}$ | $-\ln \gamma_{2} / x_{1}^{2}$ |
| 362.5 | 0.062 | 0.374 | 4.034 | 1.038 | 1.357 | 1.585 | - |
| 399.0 | 0.095 | 0.439 | 3.402 | 1.062 | 1.165 | 1.495 | - |
| 424.0 | 0.131 | 0.482 | 2.878 | 1.085 | 0.976 | 1.400 | - |
| 450.9 | 0.194 | 0.524 | 2.247 | 1.143 | 0.676 | 1.246 | - |
| 468.0 | 0.252 | 0.552 | 1.891 | 1.203 | 0.452 | 1.139 | - |
| 485.5 | 0.334 | 0.583 | 1.564 | 1.305 | 0.181 | 1.008 | - |
| 497.6 | 0.401 | 0.611 | 1.399 | 1.387 | 0.009 | 0.936 | - |
| 525.9 | 0.593 | 0.691 | 1.131 | 1.714 | -0.416 | - | -1.532 |
| 534.3 | 0.680 | 0.739 | 1.071 | 1.870 | -0.557 | - | -1.354 |
| 542.7 | 0.793 | 0.816 | 1.030 | 2.070 | -0.698 | - | -1.157 |
| 543.1 | 0.810 | 0.826 | 1.022 | 2.135 | -0.737 | - | -1.156 |
| 544.5 | 0.943 | 0.941 | 1.002 | 2.419 | -0.881 | - | -0.993 |
| 544.5 | 0.947 | 0.945 | 1.002 | 2.425 | -0.883 | - | -0.988 |

## Calculation Procedure

1. Select the criterion to be used for thermodynamic consistency. Deviations from thermodynamic consistency arise as a result of experimental errors. Impurities in the samples used for vaporliquid equilibrium measurements are often the source of error. A complete set of vapor-liquid equilibrium data includes temperature $T$, pressure $P$, liquid composition $x_{i}$, and vapor composition $y_{i}$. Usual practice is to convert these data into activity coefficients by the following equation, which is a rearranged form of the equation that rigorously defines $K$ values (i.e., defines the ratio $y_{i} / x_{i}$ under Related Calculations in Example 3.1):

$$
\gamma_{i}=\phi_{i} P y_{i} / f_{i}^{\circ} x_{i}
$$

The fugacity coefficients $\phi_{i}$ are estimated using procedures described in Example 3.3. Fugacity $f_{i}^{\circ}$ of pure liquid is calculated using procedures described in Example 3.2. Assuming that $\phi_{i}$ and $f_{i}^{\circ}$ are correctly calculated, the $\gamma_{i}$ obtained using the preceding equation must obey the GibbsDuhem equation. The term "thermodynamically consistent data" is used to refer to data that obey that equation.

At constant temperature, the Gibbs-Duhem equation can be rearranged to give the approximate equality

$$
\int_{0}^{1} \ln \frac{\gamma_{1}}{\gamma_{2}} d x_{1}=0
$$

(This would be an exact equality if both temperature and pressure were constant, but that would be inconsistent with the concept of vapor-liquid equilibrium.) In other words, the net area under the curve $\ln \left(\gamma_{1} / \gamma_{2}\right)$ versus $x_{1}$ should be zero. This means that the area above and below the $x$ axis must be equal. Since real data entail changes in system pressure and are subject to experimental errors and errors in estimating $f_{i}^{\circ}$ and $\phi_{i}$, the preceding requirement cannot be expected to be exactly satisfied. However, the deviation should not be more than a few percent of the total absolute area.
2. Determine the system activity coefficients, and plot the natural logarithm of their ratio against liquid-phase ethanol content. As in the previous example, and for the reasons discussed there, the
system pressures and vapor pressures in the present example are such that the vapor pressure may be used for $f^{\circ}$ and $\phi_{i}=1$. Activity coefficients calculated from the experimental data, as well as $\ln \left(\gamma_{1} / \gamma_{2}\right)$ values, are also given in Table 3.1. A plot of $\ln \left(\gamma_{1} / \gamma_{2}\right)$ versus $x_{1}$ is shown in Fig. 3.1.


FIGURE 3.1 Area test for thermodynamic consistency of data on ethanol(1)/water(2) system (Example 3.7).

## 3. Determine and evaluate the net area under

the plot. By measurement, the area above the $x$ axis is 0.295 , and the area below it is 0.325 . Net area is $0.295-0.325=0.03$. The total absolute area is $0.295+0.325=0.62$. Net area as a percent of total area is thus 5 percent. This figure is small enough that the data can be assumed to be thermodynamically consistent.

Related Calculations. When vapor-liquid equilibrium data are taken under isobaric rather than isothermal conditions, as is often the case, the right-hand side of the preceding Gibbs-Duhem equation cannot as readily be taken to approximate zero. Instead, the equation should be taken as

$$
\int_{0}^{1} \ln \left(\frac{\gamma_{1}}{\gamma_{2}}\right) d x=\int_{x=0}^{x=1}\left(\frac{\Delta H}{R T^{2}}\right) d T
$$

where $\Delta H$ is the heat of mixing.
For some systems, the integral on the right-hand side may indeed be neglected, i.e., set equal to zero. These include systems consisting of chemically similar components with low values for the heat of mixing and ones in which the boiling points of pure components are close together. In general, however, this will not be the case.

Since the enthalpy of mixing necessary for the evaluation of the integral is often not available, the integral can instead be estimated as $1.5\left(\Delta T_{\max }\right) / T_{\min }$. Here, $T_{\min }$ is the lowest-boiling temperature in the isobaric system. Usually, this will be the boiling temperature of the lower-boiling component. In cases of low-boiling azeotropes, it is the boiling temperature of the azeotrope. Moreover, $\Delta T_{\max }$ is the maximum difference of boiling points in the total composition range of the isobaric system. Usually, this will be the boiling-point difference of the pure components. For azeotropic systems, $\Delta T_{\max }$ is the difference between the boiling temperature of the azeotrope and the component boiling most distant from it.

The preceding test for thermodynamic data treats the data set as a whole. It does not determine whether individual data points are consistent. A point-consistency test has been proposed, but it is too cumbersome for manual calculations.

## ESTIMATING INFINITE-DILUTION ACTIVITY COEFFICIENTS

Estimate the infinite-dilution activity coefficients of ethanol and water at $70^{\circ} \mathrm{C}\left(158^{\circ} \mathrm{F}, 343 \mathrm{~K}\right)$ using the data given in the left three columns of Table 3.1.

## Calculation Procedure

1. Determine the system activity coefficients, calculate the ratios $\ln \gamma_{1} / x_{2}^{2},-\ln \gamma_{2} / x_{1}^{2}$, and $\boldsymbol{\operatorname { l n }}\left(\gamma_{1} / \gamma_{2}\right)$, and plot them against $\boldsymbol{x}_{\boldsymbol{1}}$. In a binary system, the infinite-dilution activity


FIGURE 3.2 Determining infinite-dilution activity coefficients by extrapolation (Example 3.8).
coefficients are defined as

$$
\gamma_{1}^{\infty}=\lim _{x_{1} \rightarrow 0} \gamma_{1} \quad \text { and } \quad \gamma_{2}^{\infty}=\lim _{x_{1} \rightarrow 1} \gamma_{2}
$$

They are generally calculated for two reasons: First, activity coefficients in the very dilute range are experimentally difficult to measure but are commonly needed when designing separation systems, and estimation of infinite-dilution activity coefficients is needed for meaningful extrapolation of whatever experimental data are available. Second, these coefficients are useful when estimating the parameters that are required in several mathematical models used for determining activity coefficients.

One way to estimate infinite-dilution activity coefficients is related to the preceding example on thermodynamic consistency; in addition, it takes advantage of the fact that the plot of $\ln \gamma_{1} / x_{2}^{2}$ versus $x_{1}$ is considerably more linear than is $\ln \gamma_{1}$ versus $x_{1}$.

The first step is to calculate $\ln \gamma_{1} / x_{2}^{2}$, $-\ln \gamma_{2} / x_{1}^{2}$, and $\ln \left(\gamma_{1} / \gamma_{2}\right)$. The results are shown in Table 3.1 and plotted as a function of $x_{1}$ in Fig. 3.2.
2. Extrapolate the two curves relating to $\gamma_{1}$ so that they converge on a common point at $x_{1}=0$ and the two curves relating to $\gamma_{2}$ so that they converge at $x_{1}=1$. Determine these two points of convergence and find their antilogarithms. The extrapolations are carried out in Fig. 3.2. The point of convergence along $x_{1}=0$ that corresponds to $\ln \gamma_{1}^{\infty}$ is 1.75 , so $\gamma_{1}^{\infty}$ is 5.75. The point of convergence along $x_{1}=1$ that corresponds to $-\ln \gamma_{2}^{\infty}$ is -0.91 , so $\gamma_{2}^{\infty}$ is 2.48 .

### 3.9 ESTIMATING THE PARAMETERS FOR THE WILSON-EQUATION MODEL FOR ACTIVITY COEFFICIENTS

Calculate the Wilson constants for the ethanol/water system using the infinite-dilution activity coefficients calculated in the preceding example: $\gamma_{1}^{\infty}=5.75$ and $\gamma_{2}^{\infty}=2.48$, with subscript 1 pertaining to ethanol.

## Calculation Procedure

1. Rearrange the Wilson-equation model so that its constants can readily be calculated from infinite-dilution activity coefficients. In Example 3.4, given Wilson constants were employed in the Wilson-equation model to calculate the activity coefficients for the two components of a binary nonideal liquid mixture. The present example, in essence, reverses the procedure; it employs known activity coefficients (at infinite dilution) in order to calculate Wilson constants, so that these can be employed to determine activity coefficients in other situations concerning the same two components.

As shown in the Example 3.4, $G_{1,2}=\left(V_{1} / V_{2}\right) \exp \left[-\left(\lambda_{1,2}-\lambda_{2,2}\right) R T\right]$. This can be rearranged into $\lambda_{1,2}-\lambda_{2,2}=-R T \ln \left(G_{1,2} V_{2} / V_{1}\right)$. Similarly, $\lambda_{1,2}-\lambda_{1,1}=-R T \ln \left(G_{2,1} V_{1} / V_{2}\right)$. Moreover, at infinite dilution, when $x_{1}$ and $x_{2}$, respectively, equal zero, the Wilson-equation model becomes $G_{1,2}+$ $\ln G_{2,1}=1-\ln \gamma_{1}^{\infty}$, and $G_{2,1}+\ln G_{1,2}=1-\ln \gamma_{2}^{\infty}$.

Thus the problem consists of first calculating $G_{1,2}$ and $G_{2,1}$ from the known values of $\gamma_{1}^{\infty}$ and $\gamma_{2}^{\infty}$ and then employing the calculated $G$ values to determine the Wilson constants, $\lambda_{1,2}-\lambda_{1,1}$ and $\lambda_{1,2}-\lambda_{2,2}$.
2. Calculate the $\boldsymbol{G}$ values. This calculation, involving a transcendental function, must be made by trial and error. Since $\ln \gamma_{1}^{\infty}=\ln 5.75=1.75$ and $\ln \gamma_{2}^{\infty}=\ln 2.48=0.91$, the preceding $G$ equations become $G_{1,2}+\ln G_{2,1}=1-1.75=-0.75$, and $G_{2,1}+\ln G_{1,2}=1-0.91=0.09$. The procedure consists of guessing a value for $G_{1,2}$, then using this value in the first equation to calculate a $G_{2,1}$, then using this $G_{2,1}$ in the second equation to calculate a $G_{1,2}$ (designated $G_{1,2}^{*}$ ), and repeating these steps until the difference between (guessed) $G_{1,2}$ and (calculated) $G_{1,2}^{*}$ becomes sufficiently small.

Start with $G_{1,2}$ guessed to be 1.0. Then $G_{2,1}=\exp (-0.75-1)=0.1738, G_{1,2}^{*}=\exp (0.09-$ $0.1738)=0.9196$, and $G_{1,2}^{*}-G_{1,2}=0.9196-1=-0.0804$. Next, guess $G_{1,2}$ to be 0.9 . Then $G_{2,1}=0.192, G_{1,2}^{*}=0.903$, and $G_{1,2}^{*}-G_{1,2}=0.003$. Next, guess $G_{1,2}$ to be 0.9036 (by linear interpolation). Then $G_{2,1}=0.1914, G_{1,2}^{*}=0.9036$, and $G_{1,2}^{*}-G_{1,2}=0$. Hence the solution is $G_{1,2}=0.9036$ and $G_{2,1}=0.1914$.
3. Calculate the Wilson constants. At $70^{\circ} \mathrm{C}(343 \mathrm{~K})$, the temperature at which the activity coefficients were determined, $V_{1}=62.3 \mathrm{cc} /(\mathrm{g} \cdot \mathrm{mol})$, and $V_{2}=18.5 \mathrm{cc} /(\mathrm{g} \cdot \mathrm{mol})$. Then $\lambda_{1,2}-$ $\lambda_{2,2}=-R T \ln \left(G_{1,2} V_{1} / V_{2}\right)=-(1.987) 343 \ln [0.9036(18.5) / 62.3]=897 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})[3724 \mathrm{~kJ} /$ $(\mathrm{kg} \cdot \mathrm{mol})]$, and $\lambda_{1,2}-\lambda_{1,1}=-(1.987) 343 \ln [0.1914(62.3) / 18.5]=299 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})[1251 \mathrm{~kJ} /$ $(\mathrm{kg} \cdot \mathrm{mol})]$.

Related Calculations. The constants for the binary Margules and Van Laar models for predicting activity coefficients (see Related Calculations under Example 3.4) are simply the natural logarithms of the infinite-dilution activity coefficients: $A_{1,2}=\ln \gamma_{1}^{\infty}$ and $A_{2,1}=\ln \gamma_{2}^{\infty}$.

The Wilson, Margules, and Van Laar procedures described in this example are suitable for manual calculation. However, to take full advantage of all the information available from whatever vaporliquid equilibrium data are at hand, statistical procedures for estimating the parameters should instead be employed, with the aid of digital computers. These procedures fall within the domain of nonlinear regression analysis.

In such an analysis, one selects a suitable objective function and then varies the parameters so as to maximize or minimize the function. Theoretically, the objective function should be derived using the statistical principles of maximum-likelihood estimation. In practice, however, it is satisfactory to use a weighted-least-squares analysis, as follows:

Usually, the liquid composition and the temperature are assumed to be error-free independent variables. Experimental values of vapor composition and total pressure are employed to calculate vapor-phase fugacity coefficients and pure-liquid fugacities. Then one uses trial and error in guessing parameters in the activity-coefficient model to be determined so as to arrive at parameter values that minimize the weighted sums of the squared differences between (1) experimental values of total pressure and of vapor mole fractions and (2) the values of pressure and mole fraction that are calculated on the basis of the model-generated activity coefficients. For several algorithms for minimizing the sum of squares, see D. M. Himmelblau, Applied Nonlinear Programming, McGraw-Hill, New York, 1972.

## CALCULATING DEW POINT WHEN LIQUID PHASE IS IDEAL

Calculate the dew point of a vapor system containing $80 \mathrm{~mol} \%$ benzene and $20 \mathrm{~mol} \%$ toluene at $1000 \mathrm{mmHg}(133.3 \mathrm{kPa})$.

## Calculation Procedure

1. Select a temperature, and test its suitability by trial and error. The dew point of a system at pressure $P$ whose vapor composition is given by mole fractions $y_{i}$ is that temperature at which there
is onset of condensation. Mathematically, it is that temperature at which

$$
\sum_{i=1}^{N} \frac{y_{i}}{K_{i}}=1
$$

where the $K_{i}$ are vapor-liquid equilibrium ratios as defined in Example 3.1.
When the liquid phase is ideal, $K_{i}$ depends only on the temperature, the pressure, and the vapor composition. The procedure for determining the dew point in such a case is to (1) guess a temperature; (2) calculate the $K_{i}$, which equal $f_{i}^{\circ} / \phi_{i} P$, where $f_{i}^{\circ}$ is the fugacity of pure liquid $i$ at the system temperature and pressure, $\phi_{i}$ is the fugacity coefficient of the $i$ th species in the vapor phase, and $P$ is the system pressure; and (3) check if the preceding dew-point equation is satisfied. If it is not, repeat the procedure with a different guess.

For this system, $f_{i}^{\circ}$ may be assumed to be the same as the vapor pressure. The vapor phase can be assumed to be ideal, that is, $\phi_{i}=1$. (For a discussion of the grounds for these assumptions, see Example 3.6).

The boiling points of benzene and toluene at 1000 mmHg are first calculated (for instance, by using the Antoine equation, as discussed in Example 3.1). They are $89^{\circ} \mathrm{C}$ and $141^{\circ} \mathrm{C}$, respectively. As a first guess at the dew-point temperature, try a linear interpolation of these boiling points: $T=(0.8)(89)+$ $(0.2)(141)$, which approximately equals 100 . Let subscript 1 refer to benzene; subscript 2 to toluene.

At $100^{\circ} \mathrm{C}, P_{1}^{\circ}=1350 \mathrm{mmHg}$ and $P_{2}^{\circ}=314 \mathrm{mmHg}$ (see Example 3.1). Therefore, $K_{1}=$ $1350 / 1000=1.35$ and $K_{2}=314 / 1000=0.314$. Moreover, the dew-point equation becomes $\left(y_{1} / K_{1}\right)$ $+\left(y_{2} / K_{2}\right)=(0.8) /(1.35)+(0.2) /(0.314)=1.230$.

Since this sum is greater than 1 , the $K$ values are too low. So the vapor pressures and, accordingly, the assumed temperature are too low.
2. Repeat the trial-and-error procedure with the aid of graphic interpolation until the dew-point temperature is found. As the next estimate of the dew point, try $110^{\circ} \mathrm{C}$. At this temperature, $K_{1}=$ 1.756 and $K_{2}=0.428$, as found via the procedure outlined in the previous step. Then $\left(y_{1} / K_{1}\right)+$ $\left(y_{2} / K_{2}\right)=0.923$. Since the sum is less than 1 , the assumed temperature is too high.

Next plot $\left(y_{1} / K_{1}\right)+\left(y_{2} / K_{2}\right)$ against temperature, as shown in Fig. 3.3. Linear interpolation of


FIGURE 3.3 Trial-and-error solution for dew point (Example 3.10). the first two trial values suggests $107.5^{\circ} \mathrm{C}$ as the next guess. At this temperature, $K_{1}=1.647$ and $K_{2}=0.397$, and $\left(y_{1} / K_{1}\right)+\left(y_{2} / K_{2}\right)=0.989$.

The second and third guess points on Fig. 3.3 suggest that the next guess be $107.1^{\circ} \mathrm{C}$. At this temperature, $K_{1}=1.630$ and $K_{2}=0.392$, and $\left(y_{1} / K_{1}\right)+\left(y_{2} / K_{2}\right)=1.001$. Thus, the dew point can be taken as $107.1^{\circ} \mathrm{C}\left(380.3 \mathrm{~K}\right.$ or $\left.224.8^{\circ} \mathrm{F}\right)$.

As a matter of interest, the liquid that condenses at the dew point has the composition $x_{i}=$ $y_{i} / K_{i}$, where the $x_{i}$ are the liquid-phase mole fractions. In this case, $x_{1}=0.8 / 1.630=0.49$ and $x_{2}=0.2 / 0.392=0.51(=1-0.49)$.

Related Calculations. When the liquid phase is nonideal, the $K$ values depend on the liquid composition, in this case the dew composition, which is not known. The procedure then is to guess both the liquid composition and the temperature and to check not only whether the dew-point equation is satisfied, but also whether the values of $x_{i}$ calculated by the equations $x_{i}=y_{i} / K_{i}$ are the


FIGURE 3.4 Logic diagram for determining dew point (Example 3.10).
same as the guessed values. (When there is no other basis for the initial guess of the dew composition, an estimate of it may be obtained by dew-point calculations presuming an ideal liquid phase, as outlined above.) Such nonideal liquid-phase dew-point calculations are usually carried out using a digital computer. A logic diagram for dew-point determination is shown in Fig. 3.4.

## CALCULATING BUBBLE POINT WHEN VAPOR PHASE IS IDEAL

Calculate the bubble point of a liquid system containing $80 \mathrm{~mol} \%$ ethanol and $20 \mathrm{~mol} \%$ water at $500 \mathrm{mmHg}(66.7 \mathrm{kPa})$.

## Procedure

1. Select a temperature, and test its suitability by trial and error. The bubble point of a system at pressure $P$ and whose liquid composition is given by mole fractions $x_{i}$ is that temperature at which there is onset of vaporization. Mathematically, it is the temperature such that

$$
\sum_{i=1}^{N} K_{i} x_{i}=1
$$

where the $K_{i}$ are vapor-liquid equilibrium ratios.

When the vapor phase is ideal, the $K_{i}$ are independent of the vapor composition. In such a case, the procedure for bubble-point determination is to (1) guess a temperature; (2) calculate the $K_{i}$, which equal $\gamma_{i} f_{i}^{\circ} / P$, where $\gamma_{i}$ is the activity coefficient of the $i$ th component in the liquid phase, $f_{i}^{\circ}$ is the fugacity of pure liquid $i$ at system temperature and pressure, and $P$ is the system pressure; and (3) check if the preceding bubble-point equation is satisfied. If it is not, repeat the procedure with a different guess.

For this system, $f_{i}^{\circ}$ may be assumed to be the same as the vapor pressure (for a discussion of the grounds for this assumption, see Example 3.6). Activity coefficients can be calculated using the Wilson, Margules, or Van Laar equations (see Example 3.4).

From vapor-pressure calculations, the boiling points of ethanol and water at 500 mmHg are $68^{\circ} \mathrm{C}$ and $89^{\circ} \mathrm{C}$, respectively. As a first guess at the bubble-point temperature, try a linear interpolation of the boiling points: $T=(0.8)(68)+(0.2)(89)$, which is approximately equal to 72 . Let subscript 1 refer to ethanol and subscript 2 to water. At $72^{\circ} \mathrm{C}$, activity coefficients calculated via the Van Laar equation are 1.02 for ethanol and 2.04 for water. From tables or calculation, the vapor pressures are 589 and 254 mmHg . Then $K_{1}=(1.02)(589) / 500=1.202$ and $K_{2}=(2.04)(254) / 500=1.036$, and the bubble-point equation becomes $K_{1} x_{1}+K_{2} x_{2}=(1.202)(0.8)+(1.036)(0.2)=1.169$.

Since this is greater than 1, the $K$ values are too high. This means that the vapor pressures and, accordingly, the assumed temperature are too high.
2. Repeat the trial-and-error procedure until the bubble-point temperature is found. As a second guess, try $67^{\circ} \mathrm{C}$. Assume that because the temperature difference is small, the activity coefficients remain the same as in step 1. At $67^{\circ} \mathrm{C}$, the vapor pressures are 478 and 205 mmHg . Then, $K_{1}=0.9746$ and $K_{2}=0.8344$, as found by the procedure outlined in the previous step. Then $K_{1} x_{1}+K_{2} x_{2}=$ 0.9466 . Since this sum is less than 1 , the assumed temperature is too low.

As a next estimate, try $68^{\circ} \mathrm{C}$. At this temperature, $K_{1}=1.039$ and $K_{2}=0.891$, and $K_{1} x_{1}+K_{2} x_{2}=$ 1.009.

Finally, at $68.3^{\circ} \mathrm{C}, K_{1}=1.030$ and $K_{2}=0.883$, and $K_{1} x_{1}+K_{2} x_{2}=1.0006$. This is very close to 1.0 , so $68.3^{\circ} \mathrm{C}\left(341.5 \mathrm{~K}\right.$ or $\left.154.9^{\circ} \mathrm{F}\right)$ can be taken as the bubble point.

As a matter of interest, the vapor that is generated at the bubble point has the composition $y_{i}=$ $K_{i} x_{i}$, where the $y_{i}$ are the vapor-phase mole fractions. In this case, $y_{1}=(1.030)(0.8)=0.82$ and $y_{2}=(0.883)(0.2)=0.18(=1.0-0.82)$.

Related Calculations. When the vapor phase is nonideal, the $K$ values depend on the vapor composition, in this case the bubble composition, which is unknown. The procedure then is to guess both the vapor composition and the temperature and to check not only whether the bubble-point equation is satisfied, but also whether the values of $y_{i}$ given by the equations $y_{i}=K_{i} x_{i}$ are the same as the guess values. (When there is no other basis for guessing the bubble composition, an estimate based on calculations that presume an ideal vapor phase may be used, as outlined above.) As in the case of nonideal dew points, nonideal bubble points are calculated using a digital computer. Figure 3.5 shows a logic diagram for computing bubble points.

### 3.12 BINARY PHASE DIAGRAMS FOR VAPOR-LIQUID EQUILIBRIUM

A two-phase binary mixture at $100^{\circ} \mathrm{C}\left(212^{\circ} \mathrm{F}\right.$ or 373 K$)$ and $133.3 \mathrm{kPa}(1.32 \mathrm{~atm}$ or 1000 mmHg$)$ has an overall composition of $68 \mathrm{~mol} \%$ benzene and $32 \mathrm{~mol} \%$ toluene. Determine the mole fraction benzene in the liquid phase and in the vapor phase.

## Calculation Procedure

1. Obtain (or plot from data) a phase diagram for the benzene/toluene system. Vapor-liquid equilibrium behavior of binary systems can be represented by a temperature-composition diagram at


FIGURE 3.5 Logic diagram for determining bubble point (Example 3.11).
a given constant pressure (such as Fig. 3.6) or by a pressure-composition diagram at a given constant temperature (such as Fig. 3.7).

Curve $A B C$ in each figure represents the states of saturated-liquid mixtures; it is called the "bubble-point curve" because it is the locus of bubble points in the temperature-composition diagram. Curve $A D C$ represents the states of saturated vapor; it is called the "dewpoint curve" because it is the locus of the dew points. The bubble- and dew-point curves converge at the two ends, which represent the saturation points of the two pure components. Thus in Fig. 3.6, point $A$ corresponds to the boiling point of toluene at 133.3 kPa , and point $C$ corresponds to the boiling point of benzene. Similarly, in Fig. 3.7, point $A$ corresponds to the vapor pressure of toluene at $100^{\circ} \mathrm{C}$, and point $C$ corresponds to the vapor pressure of benzene.

The regions below $A B C$ in Fig. 3.6 and above $A B C$ in Fig. 3.7 represent subcooled liquid; no vapor is present. The regions above $A D C$ in Fig. 3.6 and below $A D C$ in Fig. 3.7 represent superheated vapor; no liquid is present. The area between the curves is the region where both liquid and vapor phases coexist.


FIGURE 3.6 The benzene-toluene system at 1000 mmHg (133 kPa) (Example 3.12).


FIGURE 3.7 The benzene-toluene system at $100^{\circ} \mathrm{C}$ (Example 3.12).
2. Determine vapor and liquid compositions directly from the diagram. If a system has an overall composition and temperature or pressure such that it is in the two-phase region, such as the conditions at point $E$ in either diagram, it will split into a vapor phase whose composition is given by point $D$ and a liquid phase whose composition is given by point $B$, where line $B D$ is the horizontal (constant-temperature or constant-pressure) line passing through $E$.

Related Calculations. The relative amounts of vapor and liquid present at equilibrium are given by $($ moles of liquid $) /($ moles of vapor $)=($ length of line $E D) /($ length of line $B E)$.

Figures 3.6 and 3.7 have shapes that are characteristic for ideal systems. Certain nonideal systems deviate so much from these as to form maxima or minima at an intermediate composition rather than at one end or the other of the diagram. Thus the dew-point and bubble-point curves meet at this intermediate composition as well as at the ends. Such a composition is called an "azeotropic composition."

The example discussed here pertains to binary systems. By contrast, multicomponent vapor-liquid equilibrium behavior cannot easily be represented on diagrams and instead is usually calculated at a given state by using the procedures described in the preceding two examples.

Phase equilibrium is important in design of distillation columns. Such design is commonly based on use of an $x y$ diagram, a plot of equilibrium vapor composition $y$ versus liquid composition $x$ for a given binary system at a given pressure. An $x y$ diagram can be prepared from a temperature-composition or a pressurecomposition diagram, such as Figs. 3.6 and 3.7. Select a value of $x$; find the bubble-point condition (temperature on Fig. 3.6, for instance) for that value on curve $A B C$; then move horizontally to curve $A D C$ in order to find the equilibrium value of $y$; and then plot that $y$ as ordinate versus that $x$ as abscissa. Figure 3.8 shows the $x y$ diagram for the benzene/toluene system.


FIGURE 3.8 $x y$ diagram for benzene-toluene system at 1 atm (Example 3.12).

### 3.13 MULTICOMPONENT LIQUID-LIQUID EQUILIBRIUM

Develop a design method for calculating multicomponent liquid-liquid equilibrium.

## Calculation Procedure

1. Establish what equations must be satisfied. Ideal solutions or solutions exhibiting negative deviation from ideal behavior cannot form two liquid phases. Instead, strong positive deviation is necessary for two or more liquid phases to exist together.

Calculations of multicomponent liquid-liquid equilibrium are needed in the design of liquid (solvent) extraction systems. Since these operations take place considerably below the bubble point, it is not necessary to consider the equilibrium-vapor phase. The equations to be solved are: Material balances:

$$
\phi x_{i}^{(1)}+(1-\phi) x_{i}^{(2)}=Z_{i}
$$

Equilibrium relationships:

$$
\gamma_{i}^{(1)} x_{i}^{(1)}=\gamma_{i}^{(2)} x_{i}^{(2)}
$$

Constraints:

$$
\sum_{i=1}^{N} x_{i}^{(1)}=\sum_{i=1}^{N} x_{i}^{(2)}=1
$$

In these equations, $\phi$ is the mole fraction of phase 1 (i.e., the moles of phase 1 per total moles), $Z_{i}$ is the mole fraction of the $i$ th species in the total system, $x_{i}^{(1)}$ is the mole fraction of the $i$ th species in phase $1, x_{i}^{(2)}$ is the mole fraction of the $i$ th species in phase $2, \gamma_{i}^{(1)}$ is the activity coefficient of the $i$ th species in phase 1 , and $\gamma_{i}^{(2)}$ is its activity coefficient in phase 2.
2. Set out the calculation procedure. The preceding equations are rearranged to facilitate the solution according to the following procedure: (1) guess the liquid compositions of both phases, (2) calculate the activity coefficients in both phases at the solution temperature, (3) solve the following nonlinear equation for $\phi$ :

$$
\begin{aligned}
F(\phi) & =\sum_{i=1}^{N}\left[x_{i}^{(1)}-x_{i}^{(2)}\right] \\
& =\sum_{i=1}^{N} \frac{z_{i}\left[1-\gamma_{i}^{(1)} / \gamma_{i}^{(2)}\right]}{\phi+(1-\phi) \gamma_{i}^{(1)} / \gamma_{i}^{(2)}} \\
& =0
\end{aligned}
$$

(4) calculate the liquid compositions from

$$
x_{i}^{(1)}=\frac{Z_{i}}{\phi+(1-\phi) \gamma_{i}^{(1)} / \gamma_{i}^{(2)}}
$$

and

$$
x_{i}^{(2)}=x_{i}^{(1)} \gamma_{i}^{(1)} / \gamma_{i}^{(2)}
$$

and (5) if the calculated values in step 4 are not the same as the guessed values from step 1, repeat the procedure with different guesses.

Any nonlinear equation-solving techniques can be used in the preceding procedure, which is usually carried out with a digital computer.

Related Calculations. Graphic representation of liquid-liquid equilibrium is convenient only for binary systems and isothermal ternary systems. Detailed discussion of such diagrams appears in A. W. Francis, Liquid-Liquid Equilibrium, Interscience, New York, 1963. Thermodynamic correlations of liquid-liquid systems using available models for liquid-phase nonideality are not always satisfactory, especially when one is trying to extrapolate outside the range of the data.

Of interest in crystallization calculations is solid-liquid equilibrium. When the solid phase is a pure component, the following thermodynamic relationship holds:

$$
\ln \frac{1}{\gamma_{i} x_{i}}=\frac{\Delta H_{i}}{R T}\left(1-\frac{T}{T_{i}^{*}}\right)-\frac{\Delta C_{i}}{R}\left[\left(\frac{T_{i}^{*}}{T}-1\right)-\ln \left(\frac{T_{i}^{*}}{T}\right)\right]
$$

where $x_{i}$ is the saturation mole fraction of the $i$ th component in equilibrium with pure solid, $\gamma_{i}$ is the activity coefficient of the $i$ th species with reference to pure solid at absolute temperature $T, R$ is the universal gas constant, $T_{i}^{*}$ is the triple-point temperature of the component, $\Delta H_{i}$ is its heat of fusion at $T_{i}^{*}$, and $\Delta C_{i}$ is the difference between the specific heats of pure liquid and solid. For many substances, the second term on the right-hand side of the equation is negligible and can be omitted. With such a simplification, the equation can be rewritten as

$$
x_{i}=\frac{\exp \left[\frac{\Delta H_{i}}{R T_{i}^{*}}\left(1-\frac{T_{i}^{*}}{T}\right)\right]}{\gamma_{i}}
$$

Often the melting point and the heat of fusion at the melting point are used as estimates of $T_{i}^{*}$ and $\Delta H_{i}$. It should be noted that the latter equation is nonlinear, since $\gamma_{i}$ on the right-hand side is a function of $x_{i}$. Hence the determination of $x_{i}$ calls for an iterative numerical procedure, such as the Newton-Raphson or the secant methods.

### 3.14 CALCULATIONS FOR ISOTHERMAL FLASHING

A mixture containing $50 \mathrm{~mol} \%$ benzene and $50 \mathrm{~mol} \%$ toluene exists at $1 \mathrm{~atm}(101.3 \mathrm{kPa})$ and $100^{\circ} \mathrm{C}$ $\left(212^{\circ} \mathrm{F}\right.$ or 373 K$)$. Calculate the compositions and relative amounts of the vapor and liquid phases.

## Calculation Procedure

1. Calculate the mole fraction in the vapor phase. When the components of the system are soluble in each other in the liquid state (as is the case for benzene and toluene), so that there is only one liquid phase, then the moles of vapor $V$ per total moles can be calculated from the equation

$$
\sum_{i=1}^{N}\left[Z_{i}\left(1-K_{i}\right) /\left(1-V+V K_{i}\right)\right]=0
$$

where $Z_{i}$ is the mole fraction of the $i$ th component in the total system and $K_{i}$ is the $K$ value of the $i$ th component, as discussed in the first example in this section.

Since the pressure is not high, ideal-system $K$ values can be used, and these are independent of composition. From the above-mentioned example, $K_{1}=1.777$ and $K_{2}=0.413$, where the subscript 1 refers to benzene and subscript 2 to toluene.

For a binary system, as in this case, the preceding summation equation becomes $Z_{1}\left(1-K_{1}\right) /$ $\left(1-V+V K_{1}\right)+Z_{2}\left(1-K_{2}\right) /\left(1-V+V K_{2}\right)=0, \quad$ or $\quad 0.5(1-1.777) /(1-V+1.777 V)+$ $0.5(1-0.413) /(1-V+0.413 V)=0$. By algebra, $V=0.208$, so 20.8 percent of the system will be in the vapor phase.
2. Calculate the liquid composition. The liquid composition can be calculated from the equation $x_{i}=Z_{i} /\left(1-V+V K_{i}\right)$. For benzene, $x_{1}=0.5 /[1-0.208+(0.208)(1.777)]=0.430$, and for toluene, $x_{2}=0.5 /[1-0.208+(0.208)(0.413)]=0.570$ (or, of course, for a binary mixture, $\left.x_{2}=1-x_{1}=0.570\right)$.
3. Calculate the vapor composition. The vapor composition can be calculated directly from the defining equation for $K$ values in rearranged form: $y_{i}=K_{i} x_{i}$. For benzene, $y_{1}=K_{1} x_{1}=$ $1.777(0.430)=0.764$, and for toluene, $y_{2}=K_{2} x_{2}=0.413(0.570)=0.236$ (or, of course, for a binary mixture, $\left.y_{2}=1-y_{1}=0.236\right)$.

Related Calculations. If the system is such that two liquid phases form, then the defining equation for $V$ above must be replaced by a pair of equations in which the unknowns are $V$ and $\phi$, the latter being the moles of liquid phase 1 per total liquid moles:

$$
\sum_{i=1}^{N} Z_{i}\left[1-K_{i}^{(1)}\right] /\left[\phi(1-V)+(1-\phi)(1-V) K_{i}^{(1)} / K_{i}^{(2)}+V K_{i}^{(1)}\right]=0
$$

and

$$
\sum_{i=1}^{N} Z_{i}\left[1-K_{i}^{(1)} / K_{i}^{(2)}\right] /\left[\phi(1-V)+(1-\phi)(1-V) K_{i}^{(1)} / K_{i}^{(2)}+V K_{i}^{(1)}\right]=0
$$

In addition, the equation for liquid composition becomes $x_{i}^{(1)}=Z_{i} /[\phi(1-V)+(1-\phi)$ $\left.(1-V) K_{i}^{(1)} / K_{i}^{(2)}+V K_{i}^{(1)}\right]$. In these three equations, the superscripts 1 and 2 refer to the two liquid phases.

In systems where more than one liquid phase exists, the $K$ values are not independent of composition. In such a case, it is necessary to use a trial-and-error procedure, guessing the composition of all the phases, calculating a $K$ value for the equilibrium of each liquid phase with the vapor phase, solving the equations for $V$ and $\phi$, and then calculating the compositions of the phases by the equations for the $x_{i}$ and $y_{i}$ and seeing if these calculations agree with the guesses. This procedure should be carried out using a computer.

In the case of adiabatic rather than isothermal flashing, when the total enthalpy of the system rather than its temperature is specified, the equations associated with isothermal flash are solved jointly with an enthalpy-balance equation, treating the temperature as another variable. The general enthalpy balance is

$$
\begin{aligned}
& H_{F}=V H_{V}[1-V]\left[\phi H_{L}^{(1)}+(1-\phi) H_{L}^{(2)}\right], \text { where } \\
& \qquad H_{V}=\sum_{i=1}^{N} h_{v, i} y_{i}+\Delta h_{d} \text { and } H_{L}^{(k)}=\sum_{i=1}^{N} h_{L, i} x_{i}^{(k)}+\Delta h_{m}^{(k)}
\end{aligned}
$$

where $h_{v, i}$ is ideal-gas enthalpy per mole of pure $i$ th component, $h_{L, i}$ is the enthalpy per mole of pure liquid of $i$ th component, $\Delta h_{d}$ is enthalpy departure from ideal-gas state per mole of vapor of composition given by the $y_{i}$, and $\Delta h_{m}^{(k)}$ is the heat of mixing per mole of liquid phase having the composition given by the $x_{i}^{(k)}, k$ taking the values 1 and 2 if there are two liquid phases or the value 1 if there is only one liquid phase. Very often the heat of mixing is negligible. A convenient procedure for adiabatic flash is to perform isothermal flashes at a series of temperatures to find the temperature at which the enthalpy balance is satisfied.

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## SECTION 4

# CHEMICAL-REACTION EQUILIBRIUM* 

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4.1 HEAT OF REACTION 4.2
4.2 HEAT OF FORMATION FOR UNCOMMON COMPOUNDS 4.4

### 4.3 STANDARD GIBBS FREE-ENERGY

 CHANGE OF REACTION 4.54.4 ESTIMATION OF EQUILIBRIUM COMPOSITIONS 4.6
4.5 ACTIVITIES BASED ON MIXED STANDARD STATES 4.7
4.6 EFFECTS OF TEMPERATURE AND
PRESSURE ON EQUILIBRIUM
COMPOSITION 4.9

Chemical engineers make reaction-equilibria calculations to find the potential yield of a given reaction, as a function of temperature, pressure, and initial composition. In addition, the heat of reaction is often obtained as an integral part of the calculations. Because the calculations are made from thermodynamic properties that are accessible for most common compounds, the feasibility of a large number of reactions can be determined without laboratory study. Normally, thermodynamic feasibility should be determined before obtaining kinetic data in the laboratory, and if a given set of reaction conditions does not yield a favorable final mixture of products and reactants, the reaction-equilibria principles indicate in what direction one or more of the conditions should be changed.

The basic sequence of equilibria calculations consists of (1) determining the standard-state Gibbs free-energy change $\Delta G^{\circ}$ for the reaction under study at the temperature of interest (since this step commonly includes calculation of the standard enthalpy change of reaction $\Delta H^{\circ}$, an example of that calculation is included below), (2) determining the equilibrium constant $K$ from $\Delta G^{\circ}$, (3) relating the equilibria compositions to $K$, and (4) evaluating how this equilibrium composition changes as a function of temperature and pressure. A frequent complication is the need to deal with simultaneous or heterogeneous reactions or both.

[^3]
### 4.1 HEAT OF REACTION

Evaluate the heat of reaction of $\mathrm{CO}(\mathrm{g})+2 \mathrm{H}_{2}(\mathrm{~g}) \rightarrow \mathrm{CH}_{3} \mathrm{OH}(\mathrm{g})$ at $600 \mathrm{~K}\left(620^{\circ} \mathrm{F}\right)$ and 10.13 MPa (100 atm).

## Calculation Procedure

1. Calculate the heat of reaction at $298 \mathrm{~K}, \Delta \mathrm{H}_{298}^{\circ}$. Calculating heat of reaction is a multistep process. One starts with standard heats of formation at 298 K , calculates the standard heat of reaction, and then adjusts for actual system temperature and pressure.

The heat of reaction at 298 K is commonly referred to as the "standard heat of reaction." It can be calculated readily from the standard heats of formation ( $\Delta H_{f 298}^{\circ}$ ) of the reaction components; these standard heats of formation are widely tabulated. Thus, Perry and Chilton [7] show $\Delta H_{f 298}^{\circ}$ for $\mathrm{CH}_{3} \mathrm{OH}$ and CO to be -48.08 and $-26.416 \mathrm{kcal} /(\mathrm{g} \cdot \mathrm{mol})$, respectively (the heat of formation of hydrogen is zero, as is the case for all other elements). The standard heat of reaction is the sum of the heats of formation of the reaction products minus the heats of formation of the reactants. In this case,

$$
\begin{aligned}
\Delta H_{298}^{\circ} & =-48.08-[-26.416+2(0)] \\
& =-21.664 \mathrm{kcal} /(\mathrm{g} \cdot \mathrm{~mol})
\end{aligned}
$$

2. Calculate the heat-capacity constants. The heat capacity per mole of a given substance $C_{p}$ can be expressed as a function of absolute temperature $T$ by equations of the form $C_{p}=a+b T+c T^{2}+$ $d T^{3}$. Values of the constants are tabulated in the literature. Thus Sandler [10] shows the following values for the substances in this example:

|  | $\mathrm{CH}_{3} \mathrm{OH}$ | CO | $\mathrm{H}_{2}$ |
| :--- | :---: | :---: | :---: |
| $a$ | 4.55 | 6.726 | 6.952 |
| $b\left(\times 10^{2}\right)$ | 2.186 | 0.04001 | -0.04576 |
| $c\left(\times 10^{5}\right)$ | -0.291 | 0.1283 | 0.09563 |
| $d\left(\times 10^{9}\right)$ | -1.92 | -0.5307 | -0.2079 |

In this step, we are determining the constants for the equation $\Delta C_{p}=\Delta a+\Delta b T+\Delta c T^{2}+$ $\Delta d T^{3}$, where $\Delta a$ (for instance) equals $\sum a_{\text {products }}-\sum a_{\text {reactants }}$. Thus, for the reaction in this example, $\Delta a=4.55-6.726-2(6.952)=-16.08 ; \Delta b=[2.186-0.04001+2(0.04576)] \times$ $10^{-2}=2.2375 \times 10^{-2} ; \Delta c=[-0.291-0.1283-2(0.09563)] \times 10^{-5}=-0.61056 \times 10^{-5} ; \quad$ and $\Delta d=[-1.92+0.5307+2(0.2079)] \times 10^{-9}=-0.9735 \times 10^{-9}$. The resulting $\Delta C_{p}$ is in cal/ $(\mathrm{g} \cdot \mathrm{mol})(\mathrm{K})$ (rather than in kcal).
3. Calculate the standard heat of reaction at $600 \mathrm{~K}, \Delta \boldsymbol{H}_{600}^{\circ}$. This step combines the results of the previous two, via the equation

$$
\Delta H_{T}^{\circ}=\Delta H_{298}^{\circ}+\int_{298}^{T}\left[\Delta a+\Delta b T+\Delta c T^{2}+\Delta d T^{3}\right] d T
$$

Integration gives the equation

$$
\begin{aligned}
\Delta H_{T}= & \Delta H_{298}^{\circ}+\Delta a(T-298)+\frac{\Delta b}{2}\left(T^{2}-298^{2}\right) \\
& +\frac{\Delta c}{3}\left(T^{3}-298^{3}\right)+\frac{\Delta d}{4}\left(T^{4}-298^{4}\right)
\end{aligned}
$$

Therefore,

$$
\begin{aligned}
\Delta H_{600}^{\circ}= & -21,664-16.08(600-298)+\left(\frac{2.2375 \times 10^{-2}}{2}\right)\left(600^{2}-298^{2}\right) \\
& -\left(\frac{0.61056 \times 10^{-5}}{3}\right)\left(600^{3}-298^{3}\right)-\left(\frac{0.9735 \times 10^{-9}}{4}\right)\left(600^{4}-298^{4}\right) \\
= & -2.39 \times 10^{4} \mathrm{cal} /(\mathrm{g} \cdot \mathrm{~mol})\left[-1.00 \times 10^{8} \mathrm{~J} /(\mathrm{kg} \cdot \mathrm{~mol})\right. \\
& \left.\quad \text { or }-4.30 \times 10^{4} \mathrm{Btu} /(\mathrm{lb} \cdot \mathrm{~mol})\right]
\end{aligned}
$$

4. Calculate the true heat of reaction by correcting $\Delta H_{600}^{\circ}$ for the effect of pressure. The standard heats of formation, from which $\Delta H_{600}^{\circ}$ was calculated, are based on a pressure of 1 atm . The actual pressure in this case is 100 atm . The correction equation is $\Delta H_{600,100 \mathrm{~atm}}=\Delta H_{600}^{\circ}-\Delta H^{1}$, where the correction factor $\Delta H^{1}$ is in turn defined as follows: $\Delta H^{1}=\Delta H^{\circ}+\omega \Delta H^{\prime}$. In the latter equation, $\Delta H^{\circ}$ and $\Delta H^{\prime}$ are parameters whose values depend on the reduced temperature and reduced pressure, while $\omega$ is the acentric factor. Generalized correlations that enable the calculation of $\Delta H^{\circ}$ and $\Delta H^{\prime}$ can be found, for instance, in Smith and Van Ness [11], and $\omega$ is tabulated in the literature. Analogously to the approach in step 2 , the calculation is based on the sum of the values for the reaction products minus the sum of the values for the reactants.

For the present example, the values are as follows:

| Component | $\omega$ | $\Delta H^{\circ}$ | $\Delta H^{\prime}$ | $\Delta H^{1}, \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})$ |
| :---: | :--- | :---: | :---: | :---: |
| $\mathrm{CH}_{3} \mathrm{OH}$ | 0.556 | 1222 | 305.5 | 1392 |
| CO | 0.041 | 0 | 0 | 0 |
| $\mathrm{H}_{2}$ | 0 | 0 | 0 | 0 |

Therefore, $\Delta H^{1}$ for this example is 1392 . In turn,

$$
\begin{aligned}
\Delta H_{600,100 \mathrm{~atm}}= & -2.39 \times 10^{4}-1392 \\
= & -2.529 \times 10^{4} \mathrm{cal} /(\mathrm{g} \cdot \mathrm{~mol})\left[-1.058 \times 10^{8} \mathrm{~J} /(\mathrm{kg} \cdot \mathrm{~mol})\right. \\
& \quad \text { or }-4.55 \mathrm{Btu} /(\mathrm{lb} \cdot \mathrm{~mol})]
\end{aligned}
$$

Related Calculations. When reactants enter at a temperature different from that of the exiting products, the enthalpy changes that are due to this temperature difference should be computed independently and added to $\Delta H_{298 \mathrm{~K}}^{\circ}$, along with the pressure deviations of enthalpy.

When heat capacities of enthalpies of formation are not tabulated, a group-contribution method such as that in the following example may be used.

### 4.2 HEAT OF FORMATION FOR UNCOMMON COMPOUNDS

Assuming that tabulated heat-of-formation data are not available for ethanol, n-propanol, and $n$-butanol, use the group-contribution approach of Benson to estimate these data at 298 K .

## Calculation Procedure

1. Draw structural formulas for the chemical compounds. Take the formulas from a chemical dictionary, chemistry textbook, or similar source. For this example, they are



2. Identify all groups in each formula. A group is defined here as a polyvalent atom (ligancy $\geq 2$ ) in a molecule together with all of its ligands. Thus the ethanol molecule has one each of three kinds of groups: (1) a carbon atom linked to one other carbon atom and to three hydrogen atoms, the notation for this group being $\mathrm{C}-(\mathrm{C})(\mathrm{H})_{3} ;(2)$ a carbon atom linked to one other carbon atom and to an oxygen atom and to two hydrogen atoms, which can be expressed as $\mathrm{C}-(\mathrm{C})(\mathrm{O})(\mathrm{H})_{2}$; and (3) an oxygen atom linked to a carbon atom and to a hydrogen atom, which can be expressed as $\mathrm{O}-(\mathrm{C})(\mathrm{H})$.

The $n$-propanol molecule has one each of four kinds of groups: $\mathrm{C}-(\mathrm{C})(\mathrm{H})_{3}, \mathrm{C}-(\mathrm{C})_{2}(\mathrm{H})_{2}$, $\mathrm{C}-(\mathrm{C})(\mathrm{O})(\mathrm{H})_{2}$, and $\mathrm{O}-(\mathrm{C})(\mathrm{H})$. And the $n$-butanol molecule differs from the $n$-propanol molecule only in that it has two (rather than one) of the $\mathrm{C}-(\mathrm{C})_{2}(\mathrm{H})_{2}$ groups.
3. For each molecule, add up the partial heats offormation for its constituent groups. The partial heats of formation can be found in Benson [2]. Adding these up for a given molecule gives an estimate of the heat of formation for that molecule.

For ethanol, the result is as follows:

| $\mathrm{C}-(\mathrm{C})(\mathrm{H})_{3}$ | $-10.20 \mathrm{kcal} /(\mathrm{g} \cdot \mathrm{mol})$ |
| :--- | :--- |
| $\mathrm{C}-(\mathrm{C})(\mathrm{O})(\mathrm{H})_{2}$ | -8.1 |
| $\mathrm{O}-(\mathrm{C})(\mathrm{H})$ | -37.9 |
| $\Delta H_{f 298}^{\circ}=$ | $-56.2 \mathrm{kcal} /(\mathrm{g} \cdot \mathrm{mol})\left[-2.35 \times 10^{8} \mathrm{~J} / \mathrm{kg} \cdot \mathrm{mol}\right)$ <br>  |

For $n$-propanol:

| $\mathrm{C}-(\mathrm{C})(\mathrm{H})_{3}$ | -10.20 |
| :--- | :--- |
| $\mathrm{C}-(\mathrm{C})_{2}(\mathrm{H})_{2}$ | -4.93 |
| $\mathrm{C}-(\mathrm{C})(\mathrm{O})(\mathrm{H})_{2}$ | -8.1 |
| $\mathrm{O}-(\mathrm{C})(\mathrm{H})$ | $\underline{-37.9}$ |
| $\Delta H_{f 298}^{\circ}=$ | $-61.13 \mathrm{kcal} /(\mathrm{g} \cdot \mathrm{mol})\left[-2.556 \times 10^{8} \mathrm{~J} /(\mathrm{kg} \cdot \mathrm{mol})\right.$ <br>  |

And for $n$-butanol:

| $\mathrm{C}-(\mathrm{C})(\mathrm{H})_{3}$ | -10.20 |
| :--- | :--- |
| $2\left[\mathrm{C}-(\mathrm{C})_{2}(\mathrm{H})_{2}\right]=2(-4.93)=$ | -9.86 |
| $\mathrm{C}-(\mathrm{C})(\mathrm{O})(\mathrm{H})_{2}$ | -8.1 |
| $\mathrm{O}-(\mathrm{C})(\mathrm{H})$ | -37.9 |
| $\Delta H_{f 298}^{\circ}=$ | $-66.06 \mathrm{kcal} /(\mathrm{g} \cdot \mathrm{mol})\left[-2.762 \times 10^{8} \mathrm{~J} /(\mathrm{kg} \cdot \mathrm{mol})\right.$ <br>  |

Related Calculations. As an indicator of the degree of accuracy of this method, the observed values for ethanol, $n$-propanol, and $n$-butanol are $-2.35 \times 10^{8},-2.559 \times 10^{8}$, and $-2.83 \times 10^{8} \mathrm{~J} /(\mathrm{kg} \cdot \mathrm{mol})$, respectively. Deviations may be as high as $\pm 1.25 \times 10^{7} \mathrm{~J} /(\mathrm{kg} \cdot \mathrm{mol})$. Benson's method may also be used to estimate ideal-gas heat capacities.

### 4.3 STANDARD GIBBS FREE-ENERGY CHANGE OF REACTION

Calculate the standard Gibbs free-energy change $\Delta G^{\circ}$ for the reaction $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OH} \rightarrow \mathrm{CH}_{2}=\mathrm{CH}_{2}+$ $\mathrm{H}_{2} \mathrm{O}$ at $443 \mathrm{~K}\left(338^{\circ} \mathrm{F}\right)$.

## Calculation Procedure

1. Calculate $\Delta H_{298}^{\circ}$ for the reaction, and set out an equation for $\Delta H_{T}^{\circ}$ as a function of temperature T. This step directly employs the procedures developed in the preceding examples. Thus $\Delta H_{298}^{\circ}$ is found to be $1.0728 \times 10^{4} \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})$, and the required equation is

$$
\begin{aligned}
\Delta H_{T}^{\circ}= & \Delta H_{298}^{\circ}+\Delta a(T-298)+(\Delta b / 2)\left(T^{2}-298^{2}\right) \\
& +(\Delta c / 3)\left(T^{3}-298^{3}\right)+(\Delta d / 4)\left(T^{4}-298^{4}\right)
\end{aligned}
$$

The calculated numerical values of the heat-capacity constants are $\Delta a=3.894, \Delta b=-0.01225$, $\Delta c=0.7381 \times 10^{-5}$, and $\Delta d=-1.4287 \times 10^{-9}$. Therefore, after arithmetic partial simplification, the equation becomes (with the answer emerging in calories per gram-mole)

$$
\Delta H_{T}^{\circ}=1.0049 \times 10^{4}+\Delta a T+(\Delta b / 2) T^{2}+(\Delta c / 3) T^{3}+(\Delta d / 4) T^{4}
$$

2. Calculate $\Delta G_{298}^{\circ}$ for the reaction. This can be determined in a straightforward manner from tabulated data on standard Gibbs free energies of formation at $298 \mathrm{~K}, \Delta G_{f 298}^{\circ}$. The answer is the sum of the values for the reaction products minus the sum of the values for the reactants. Thus Perry and Chilton [7] show $\Delta G_{f 298}^{\circ}$ for ethanol, ethylene, and water to be, respectively, $-40.23,16.282$, and $-54.635 \mathrm{kcal} /(\mathrm{g} \cdot \mathrm{mol})$. Accordingly, $\Delta G_{298}^{\circ}=(16.282-54.635)-(-40.23)=1.877 \mathrm{kcal} /$ $(\mathrm{g} \cdot \mathrm{mol})\left[7.854 \times 10^{6} \mathrm{~J} /(\mathrm{kg} \cdot \mathrm{mol})\right.$ or $\left.3.3786 \times 10^{3} \mathrm{Btu} /(\mathrm{lb} \cdot \mathrm{mol})\right]$.
3. Calculate $\Delta G^{\circ}$ at the reaction temperature, $443 K$. The equation used is

$$
\Delta G^{\circ}=\Delta H_{0}-\Delta a T \ln T-(\Delta b / 2) T^{2}-(\Delta c / 6) T^{3}-(\Delta d / 12) T^{4}-I R T
$$

where $\Delta H_{0}$ is the integration constant that is determined for the $\Delta H_{T}^{\circ}$ equation in step 1 (that is, 1.0049 $\times 10^{4}$ ), R is the universal gas constant, the heat-capacity constants ( $\Delta a$, etc.) are as determined in step 1 , and $I$ is a constant yet to be determined.

To determine $I$, substitute into the equation the (known) values pertaining to $\Delta G^{\circ}$ at 298 K . Thus $1.877 \times 10^{3} \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})=1.0049 \times 10^{4}-(3.894)(298) \ln 298-1 / 2(-0.01225)(298)^{2}-$ $(1 / 6)\left(0.7381 \times 10^{-5}\right)(298)^{3}-(1 / 12)\left(-1.4287 \times 10^{-9}\right)(298)^{4}-(1.987)(298)(I)$. Solving for $I$, it is found to be 3.503 .

Finally, insert this value into the equation and solve for $\Delta G^{\circ}$ at 443 K . Thus $\Delta G^{\circ}=1.0049 \times$ $10^{4}-(3.894)(443) \ln 443-1 / 2(-0.01225)(443)^{2}-(1 / 6)\left(0.7381 \times 10^{-5}\right)(443)^{3}-(1 / 12)(-1.4287 \times$ $\left.10^{-9}\right)(443)^{4}-(1.987)(443)(3.503)=-2.446 \times 10^{3} \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol}) \quad\left[\right.$ or $-1.0237 \times 10^{7} \mathrm{~J} /(\mathrm{kg} \cdot \mathrm{mol})$ or $-4.4019 \mathrm{Btu} /(\mathrm{lb} \cdot \mathrm{mol})$ ].

Related Calculations. $\Delta G_{298}^{\circ}$ may also be calculated via the relationship $\Delta G_{298}^{\circ}=\Delta H_{298}^{\circ}-$ $T \Delta S_{298}^{\circ}$, where $S$ is entropy. Values for $S$ can be found in the literature, or $\Delta S_{298}^{\circ}$ can be estimated by Benson's group-contribution method (see example for estimating $\Delta H_{f 298}^{\circ}$ by that method above). However, the deviations for entropy values calculated by Benson's method are high compared with those for $\Delta H_{f 298}^{\circ}$, so when such group methods are used in the course of calculating $\Delta G_{298}^{\circ}$, only qualitative feasibility studies are possible, based on these rules-of-thumb: (1) if $\Delta G_{T}^{\circ}$ is less than zero, the reaction is clearly feasible; (2) if the value is less than $4.184 \times 10^{7} \mathrm{~J} /(\mathrm{kg} \cdot \mathrm{mol}$ ) [or $1.8 \times$ $\left.10^{4} \mathrm{Btu} /(\mathrm{lb} \cdot \mathrm{mol})\right]$, the reaction should be studied further; and (3) if the value is greater than $4.184 \times$ $10^{7} \mathrm{~J} /(\mathrm{kg} \cdot \mathrm{mol})$, the reaction is feasible only under exceptional circumstances. (Thus, in the present example, the reaction appears unfavorable at 298 K , but much more promising at 443 K .)

The Gibbs free-energy change of reaction may be related to the heat of reaction by $d\left(\Delta G^{\circ} / R T\right) / d T=-\Delta H^{\circ} / R T^{2}$. And if $\Delta H^{\circ}$ is constant, or if changes in $\Delta G^{\circ}$ are needed over a small temperature range, then a given $\Delta G^{\circ}$ value at a known temperature $T_{1}$ may be used to obtain $\Delta G^{\circ}$ at a different temperature $T_{v}$ via the relationship, $\Delta G_{v} / R T_{v}=\Delta G^{\circ} / R T_{1}-\left(\Delta H^{\circ} / R\right)\left[\left(1 / T_{v}\right)-\right.$ $\left.\left(1 / T_{1}\right)\right]$.

### 4.4 ESTIMATION OF EQUILIBRIUM COMPOSITIONS

Estimate the equilibrium composition of the reaction $n$-pentane $\rightarrow$ neopentane, at $500 \mathrm{~K}\left(440^{\circ} \mathrm{F}\right)$ and 10.13 $\mathrm{MPa}(100 \mathrm{~atm})$, if the system initially contains $1 \mathrm{~g} \cdot \mathrm{~mol} n$-pentane. Ignore other isomerization reactions.

## Calculation Procedure

1. Calculate $\boldsymbol{\Delta} \boldsymbol{G}^{\circ}$ at 500 K . This step is carried out as outlined in the previous example. Accordingly, $\Delta G_{500}^{\circ}$ is found to be $330.54 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})$ [or $13.83 \times 10^{6} \mathrm{~J} /(\mathrm{kg} \cdot \mathrm{mol})$ or 594.97 Btu/ ( $\mathrm{lb} \cdot \mathrm{mol}$ )].
2. Determine the equilibrium constant $K$. This step consists of solving the equation $K=\exp$ $\left(-\Delta G^{\circ} / R T\right)$. Thus $K=\exp [-330.54 /(1.987)(500)]=0.717$.
3. Express mole fractions in terms of the reaction-progress variable $\boldsymbol{x}$. The reaction-progress variable $x$ is a measure of the extent to which a reaction has taken place. In the present example, $x$ would be 0 if the "equilibrium" mixture consisted solely of $n$-pentane; it would be 1 if the mixture consisted solely of neopentane (i.e., if all the $n$-pentane had reacted). It is defined as $\int_{n_{o, i}}^{n f, i} d n / v_{i}$, where $n$ is number of moles of component $i$, subscripts $o$ and $f$ refer to initial and final states, respectively, and $v_{i}$ is the stoichiometric number for component $i$, which is equal to its stoichiometric coefficient in that reaction but with the convention that reactants are given a minus sign. In the present example, $v_{n \text {-pentane }}=-1$ and $v_{\text {neopentane }}=1$, and $n_{o, n \text {-pentane }}=1$ and $n_{o, \text { neopentane }}=0$. Since a given system (such as the system in this example) is characterized by a particular value of the reaction-progress variable,
the integrals described above (an integral can be written for each component) must equal each other for that system.

In the present case,

$$
\int_{1}^{n f, n \text {-pentane }} d n_{n-\text {-pentane }} /-1=\int_{0}^{n f, \text { neopentane }} d n_{\text {neopentane }} / 1=x
$$

Carrying out the two integrations and solving for the two $n_{f}$ values in terms of $x$, we find $n_{f, n \text {-pentane }}=$ $(1-x)$, and $n_{f, \text { neopentane }}=x$. Total moles at equilibrium equals $(1-x)+x=1$. Thus the mole fractions $y_{i}$ at equilibrium are $(1-x) / 1=(1-x)$ for $n$-pentane and $x / 1=x$ for neopentane. [This procedure is valid for any system, however complicated. In the present simple example, it is intuitively clear that at equilibrium, the two $n_{f}$ values must be $(1-x)$ and $x$.]
4. Estimate the final composition by using the Lewis-Randall rule. By definition, $K=\Pi \hat{a}_{i}^{v i}$, where the $\hat{a}_{i}$ are the activities of the components within the mixture, and the $\nu_{i}$ are the stoichiometric numbers as defined above. Then, using $101.3 \mathrm{kPa}(1 \mathrm{~atm})$ as the standard-state fugacity, $K=\left(\hat{f} / f^{\circ}\right)_{\text {neopentane }} /\left(\hat{f} / f^{\circ}\right)_{n \text {-pentane }}=(y \hat{\phi} P)_{\text {neopentane }} /(y \hat{\phi} P)_{n \text {-pentane }}$, where $f$ is fugacity, $y$ is mole fraction, $\phi$ is fugacity coefficient, $P$ is system pressure, the caret symbol ${ }^{\wedge}$ denotes the value of $f$ or $\phi$ in solution, and the superscript ${ }^{\circ}$ denotes standard state, normally taken 1 atm .

The Lewis-Randall rule assumes that the fugacity of a component in solution is directly proportional to its mole fraction. Under this assumption, $\hat{\phi}_{i}=\phi_{i}$. Therefore (and noting that $P$ cancels in numerator and denominator), $K=(y \phi)_{\text {neopentane }} /(y \phi)_{n \text {-pentane }}$. The $\phi$ can be calculated by methods outlined in Section 3 (or by use of Pitzer correlations); they are found to be 0.505 for neopentane and 0.378 for $n$-pentane. Therefore, substituting into the equation for $K, 0.717=0.505 y_{\text {neopentane }} / 0.378 y_{n \text {-pentane }}=$ $0.505 x / 0.378(1-x)$. Solving for $x$, it is found to be 0.349 . Therefore, the equilibrium composition consists of 0.349 mole fraction neopentane and $(1-0.349)=0.651$ mole fraction $n$-pentane.

Related Calculations. If the standard heat of reaction $\Delta H^{\circ}$ is known at a given $T$ and $K$ is known at that temperature, a reasonable estimate for $K$ (designated $K_{1}$ ) at a not-too-distant temperature $T_{1}$ can be obtained via the equation $\ln \left(K / K_{1}\right)=\left(-\Delta H^{\circ} / R\right)\left[(1 / T)-\left(1 / T_{1}\right)\right]$, where the heat of reaction is assumed to be constant over the temperature range of interest.

Occasionally, laboratory-measured values of $K$ are available. These can be used to determine either or both constants of integration ( $\Delta H_{0}$ and $I$ ) in the calculations for $\Delta G$.

As for the calculation of equilibrium composition, the Lewis-Randall-rule assumption in step 4 is a simplification. The rigorous calculation instead requires use of $\hat{\phi}$, the values of fugacity coefficient as they actually exist in the reaction mixture. This entails calculation from an equation of state. Initially, one would hope to use the virial equation, with initial estimates of mole fractions made as in step 4; however, in the present example, the pseudoreduced conditions are beyond the range of convergence of the virial equation. If the modified Soave-Redlich-Kwong equation is used instead, with a computer program, to calculate the $\hat{\phi}$, the resulting mole fractions are found to be 0.362 for neopentane and 0.638 for $n$-pentane. Thus the Lewis-Randall-rule simplification in this case leads to errors of 3.6 and 2.0 percent, respectively. The degree of accuracy required should dictate whether the simplified approach is sufficient.

### 4.5 ACTIVITIES BASED ON MIXED STANDARD STATES

For the reaction $2 A \rightarrow B+C$ at $573 \mathrm{~K}\left(572^{\circ} \mathrm{F}\right)$, a calculation based on standard states of ideal gas at $101.32 \mathrm{kPa}(1 \mathrm{~atm})$ for $A$ and $B$ and pure liquid at its vapor pressure of $202.65 \mathrm{kPa}(2 \mathrm{~atm})$ for $C$ produces a $\Delta G^{\circ} / R T$ of -5 , with $G$ in calories per gram-mole. Calculate the equilibrium constant based on ratios of final mole fractions at $303.97 \mathrm{kPa}(3 \mathrm{~atm})$, assuming that all three components are ideal gases.

## Calculation Procedure

1. Select the solution method to be employed. This problem may be solved either by setting out the equilibrium-constant equation in terms of the mixed (two) standard states or by first converting the $\Delta G^{\circ}$ to a common standard state. Both methods are shown here.

## 2. Solve the problem by using mixed standard states

a. Calculate the equilibrium constant $K$ in terms of activities based on the given mixed standard states. By definition, $K=\exp \left(-\Delta G^{\circ} / R T\right)=\exp -(-5)=148.41$.
b. Relate the $K$ to compositions. By definition (see previous problem), $K=a_{C} a_{B} / a_{A}^{2}=\left(f_{C} / f_{C}^{\circ}\right)$ $\times\left(f_{B} / f_{B}^{\circ}\right) /\left(f_{A} / f_{A}^{\circ}\right)^{2}$. In the present case, the standard-state fugacities are $f_{A}^{\circ}=f_{B}^{\circ}=1 \mathrm{~atm}$, and $f_{C}^{\circ}=2 \mathrm{~atm}$. Since the gases are assumed to be ideal, $f_{i}=y_{i} P$, where $y$ is mole fraction and $P$ is the system pressure. Therefore

$$
K=148.41=\left[y_{C}(3 \mathrm{~atm}) /(2 \mathrm{~atm})\right]\left[y_{B}(3 \mathrm{~atm}) /(1 \mathrm{~atm})\right] /\left[y_{A}(3 \mathrm{~atm}) /(1 \mathrm{~atm})\right]^{2}
$$

c. Define $K$ in terms of mole fractions and solve for its numerical value. In terms of mole fractions for this reaction, $K=y_{C} y_{B} / y_{A}^{2}$. Rearranging the final equation in the preceding step,

$$
y_{C} y_{B} / y_{A}^{2}=148.41(2 / 3)(1 / 3)(3 / 1)^{2}=296.82=K
$$

## 3. Solve the problem again, this time using uniform standard states

a. Correct $\Delta G^{\circ}$ to 1 atm for all the components. For this reaction, $\Delta G^{\circ}=G_{C}^{\circ}+G_{B}^{\circ}-2 G_{A}^{\circ}$. Now, $G_{B}^{\circ}$ and $G_{A}^{\circ}$ are already based on 1 atm . To correct $G_{C}^{\circ}$ to 1 atm , use the relationship $\Delta G=R T$ $\ln \left(f_{2} / f_{1}\right)$, where $R$ is the gas constant, $T$ is absolute temperature, and $f$ is fugacity. Since we wish to convert from a basis of 2 atm to one of $1 \mathrm{~atm}, f_{1}=2 \mathrm{~atm}$ and $f_{2}=1 \mathrm{~atm}$; therefore,

$$
\Delta G=(1.987)(573)[\ln (1 / 2)]=-789.2 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{~mol})
$$

Thus $G_{C, 1 \mathrm{~atm}}^{\circ}=G_{C, 2 \mathrm{~atm}}^{\circ}-789.2$. Therefore, to correct $\Delta G^{\circ}$ to 1 atm for all components, $789.2 \mathrm{cal} /$ (g. mol) must be subtracted from the $\Delta G^{\circ}$ as given in the statement of the problem; that is, from $-5 R T$. Thus $\Delta G^{\circ}=(-5)(1.987)(573)-789.2=-6481.96$, and $\Delta G^{\circ} / R T$ corrected to 1 atm becomes -5.693 .
b. Solve for $K$, and relate it to compositions and express it in terms of mole fractions. By definition, $K=\exp \left(-\Delta G^{\circ} / R T\right)=\exp -(-5.693)=296.82$. And as in step $2 \mathrm{~b}, K=\left(y_{C} P / f_{C}^{\circ}\right)\left(y_{B} P / f_{B}^{\circ}\right) /$ $\left(y_{A} P / f_{A}^{\circ}\right)^{2}=\left(3 y_{C} / 1\right)\left(3 y_{B} / 1\right) /\left(3 y_{A} / 1\right)^{2}$. Therefore, $y_{C} y_{B} / y_{A}^{2}=K=296.82$, the same result as via the method based on mixed standard states.

Related Calculations. As this example illustrates, one should know the standard state chosen for the Gibbs free energy of formation for each compound (usually, ideal gas at 1 atm ) when considering the relation of mole fractions to $K$ values.

When a solid phase occurs in a reaction, it is often pure; in such a case, its activity may be expressed by

$$
a_{i}=f_{i} / f_{i}^{\circ}=\exp \left[\left(v_{s} / R T\right)\left(P-P^{\circ}\right)\right]
$$

where $v_{s}$ is the molar volume of the solid and $P^{\circ}$ its vapor pressure. This activity is usually close to unity.

If a reaction takes place in the liquid phase, the activity may be expressed by $a_{i}=\gamma_{i} x_{i}$, where $\gamma_{i}$ is the activity coefficient for component $i$ and $x_{i}$ is its mole fraction.

### 4.6 EFFECTS OF TEMPERATURE AND PRESSURE ON EQUILIBRIUM COMPOSITION

The reaction $\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{H}_{2}+1 / 2 \mathrm{O}_{2}$ appears unlikely at $298 \mathrm{~K}\left(77^{\circ} \mathrm{F}\right)$ and $101.3 \mathrm{kPa}(1 \mathrm{~atm})$ because its $\Delta G^{\circ}$ is $2.286 \times 10^{8} \mathrm{~J} /(\mathrm{kg} \cdot \mathrm{mol}$ ) (see Related Calculations under Example 4.3). If one wishes to increase the equilibrium conversion to hydrogen and oxygen, (a) should the temperature be increased or decreased, and (b) should the pressure be increased or decreased?

## Calculation Procedure

1. Calculate $\boldsymbol{\Delta} \boldsymbol{H}^{\circ}$, the heat of reaction. This is done as outlined in Example 4.1. (Actually, since 298 K is a standard temperature, $\Delta H^{\circ}$ for the present example can be read directly from tables.) The value is found to be $2.42 \times 10^{8} \mathrm{~J} /(\mathrm{kg} \cdot \mathrm{mol})\left[1.04 \times 10^{5} \mathrm{Btu} /(\mathrm{lb} \cdot \mathrm{mol})\right]$.
2. Calculate the algebraic sum of the stoichiometric numbers for the reaction $\boldsymbol{\Sigma} \boldsymbol{\nu}_{\boldsymbol{i}}$. As discussed in Example 4.4, stoichiometric numbers for the components in a given reaction are numerically equal to the stoichiometric coefficients, but with the convention that the reactants get minus signs. In the present case, the stoichiometric numbers for $\mathrm{H}_{2} \mathrm{O}, \mathrm{H}_{2}$, and $\mathrm{O}_{2}$ are, respectively, $-1,+1$, and $+1 / 2$. Their sum is $+1 / 2$.
3. Apply rules that pertain to partial derivatives of the reaction-progress variable. As discussed in Example 4.4, the reaction-progress variable $x$ is a measure of the extent to which a reaction has taken place. In the present case, the desired increase in equilibrium conversion to hydrogen and oxygen implies an increase in $x$.

It can be shown that $(\partial x / \partial T)_{P}=$ (a positive number $)\left(\Delta H^{\circ}\right)$ for all reactions. In the present example, $\Delta H^{\circ}$ is positive (i.e., the reaction is endothermic). Therefore, an increase in temperature will increase $x$ and, thus, the conversion to hydrogen and oxygen.

It can also be shown that $(\partial x / \partial P)_{T}=$ (a negative number $)\left(\Sigma v_{i}\right)$ for all reactions. Since $\Sigma v_{i}$ is positive, an increase in pressure will decrease $x$. So, a decrease in pressure will favor the conversion to hydrogen and oxygen.

Related Calculations. While nothing is said above about kinetics, increasing the temperature very frequently changes the reaction rate favorably. Accordingly, in some exothermic-reaction situations, it may be worthwhile to sacrifice some degree of equilibrium conversion in favor of shorter reactor residence time by raising reaction temperature. Similarly, a pressure change may have an effect on kinetics that is contrary to its effect on equilibrium.

The reaction in this example illustrates another point. It happens that (at 1 atm ) water will not appreciably dissociate into hydrogen and oxygen unless the temperature is raised about 1500 K $\left(2240^{\circ} \mathrm{F}\right)$; but at such temperatures, molecules of $\mathrm{H}_{2}$ and $\mathrm{O}_{2}$ may dissociate into atomic H and O and enter into unexpected reactions. The engineer should keep such possibilities in mind when dealing with extreme conditions.

### 4.7 EQUILIBRIUM COMPOSITION FOR SIMULTANEOUS KNOWN CHEMICAL REACTIONS

Given an initial mixture of $1 \mathrm{~g} \cdot \mathrm{~mol}$ each of CO and $\mathrm{H}_{2}$, estimate the equilibrium composition that will result from the following set of simultaneous gas-phase reactions at $900 \mathrm{~K}\left(1160^{\circ} \mathrm{F}\right)$ and 101.3 kPa (1 atm).

$$
\begin{align*}
& \mathrm{CO}+3 \mathrm{H}_{2} \rightarrow \mathrm{CH}_{4}+\mathrm{H}_{2} \mathrm{O}  \tag{4.1}\\
& \mathrm{CO}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{CO}_{2}+\mathrm{H}_{2} \tag{4.2}
\end{align*}
$$

$$
\begin{align*}
\mathrm{CO}_{2}+4 \mathrm{H}_{2} & \rightarrow \mathrm{CH}_{4}+2 \mathrm{H}_{2} \mathrm{O}  \tag{4.3}\\
4 \mathrm{CO}+2 \mathrm{H}_{2} \mathrm{O} & \rightarrow \mathrm{CH}_{4}+3 \mathrm{CO}_{2} \tag{4.4}
\end{align*}
$$

## Calculation Procedure

1. Find the independent chemical reactions. Write equations for the formation of each compound present:

$$
\begin{align*}
\mathrm{C}+1 / 2 \mathrm{O}_{2} & \rightarrow \mathrm{CO}  \tag{4.5}\\
\mathrm{C}+2 \mathrm{H}_{2} & \rightarrow \mathrm{CH}_{4}  \tag{4.6}\\
\mathrm{C}+\mathrm{O}_{2} & \rightarrow \mathrm{CO}_{2}  \tag{4.7}\\
\mathrm{H}_{2}+1 / 2 \mathrm{O}_{2} & \rightarrow \mathrm{H}_{2} \mathrm{O} \tag{4.8}
\end{align*}
$$

Next, algebraically combine these equations to eliminate all elements not present as elements in the system. For instance, eliminate $\mathrm{O}_{2}$ by combining Eqs. 4.5 and 4.7

$$
\begin{equation*}
2 \mathrm{CO} \rightarrow \mathrm{CO}_{2}+\mathrm{C} \tag{4.9}
\end{equation*}
$$

and Eqs. 4.5 and 4.8

$$
\begin{equation*}
\mathrm{C}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{CO}+\mathrm{H}_{2} \tag{4.10}
\end{equation*}
$$

Then eliminate C by combining Eqs. 4.6 and 4.9

$$
\begin{equation*}
2 \mathrm{CO}+2 \mathrm{H}_{2} \rightarrow \mathrm{CO}_{2}+\mathrm{CH}_{4} \tag{4.11}
\end{equation*}
$$

and Eqs. 4.6 and 4.10

$$
\begin{equation*}
\mathrm{CO}+3 \mathrm{H}_{2} \rightarrow \mathrm{H}_{2} \mathrm{O}+\mathrm{CH}_{4} \tag{4.12}
\end{equation*}
$$

The four initial equations are thus reduced into two independent equations, namely, Eqs. 4.11 and 4.12, for which we must find simultaneous equilibria. All components present in the original four equations are contained in Eqs. 4.11 and 4.12.
2. Calculate $\boldsymbol{\Delta} \boldsymbol{G}^{\circ}$ and $\boldsymbol{K}$ for each independent reaction. This may be done as in the relevant examples earlier in this section, with determination of $\Delta G^{\circ}$ as a function of temperature. An easier route, however, is to use the standard Gibbs free-energy change of formation $\Delta G_{f}^{\circ}$ for each compound at the temperature of interest in the relationship

$$
\Delta G^{\circ}=\Sigma \Delta G_{f, \text { products }}^{\circ}-\Sigma \Delta G_{f, \text { reactants }}^{\circ}
$$

Reid et al. [9] give the following values of $\Delta G_{f}^{\circ}$ at 900 K : for $\mathrm{CH}_{4}, 2029 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})$; for CO , $-45,744 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})$; for $\mathrm{CO}_{2},-94,596 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})$; and for $\mathrm{H}_{2} \mathrm{O},-47,352 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})\left(\right.$ since $\mathrm{H}_{2}$ is an element, its $\Delta G_{f}^{\circ}$ is zero).

For Eq. 4.11, $\Delta G^{\circ}=2029+(-94,596)-2(-45,744)=-1079 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})$. For Eq. 4.12, $\Delta G^{\circ}=2029+(-47,352)-(-45,744)=421 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})$.

Finally, since the equilibrium constant $K$ is equal to $\exp \left(-\Delta G^{\circ} / R T\right)$, the value of $K$ for Eq. 4.11 is $\exp [-(-1079) /(1.987)(900)]=1.8283$, and the value of $K$ for Eq. 4.12 is $\exp [-421 /(1.987)(900)]=0.7902$.
3. Express the equilibrium mole fractions in terms of the reaction-progress variables. See Example 4.4 for a discussion of the reaction-progress variable. Let $x_{K}$ and $x_{L}$ be the reaction-progress variables for Reactions 4.11 and 4.12 , respectively. Since Reaction 4.11 has $1 \mathrm{~mol} \mathrm{CO}_{2}$ on the product side, the number of moles of $\mathrm{CO}_{2}$ at equilibrium is $x_{K}$. Since Reactions 4.11 and 4.12 each have $1 \mathrm{~mol} \mathrm{CH}_{4}$ on the product side, the number of moles of $\mathrm{CH}_{4}$ at equilibrium is $x_{K}+x_{L}$. Since Reaction 4.11 has 2 mol CO on the reactant side and Reaction 4.12 has 1 mol , the number of moles of CO at equilibrium is $1-2 x-x$ (because 1 mol CO was originally present). This approach allows us to express the equilibrium mole fractions as follows:

|  | Number of moles |  |  |
| :---: | :---: | :---: | :---: |
| Component | Initially | At equilibrium | Equilibrium mole fraction $y$ |
| $\mathrm{CO}_{2}$ | 0 | $x_{K}$ | $x_{K} / 2\left(1-x_{K}-x_{L}\right)$ |
| $\mathrm{CH}_{4}$ | 0 | $x_{K}+x_{L}$ | $\left(x_{K}+x_{L}\right) / 2\left(1-x_{K}-x_{L}\right)$ |
| CO | 1 | $1-2 x_{K}-x_{L}$ | $\left(1-2 x_{K}-x_{L}\right) / 2\left(1-x_{K}-x_{L}\right)$ |
| $\mathrm{H}_{2}$ | 1 | $1-2 x_{K}-3 x_{L}$ | $\left(1-2 x_{K}-3 x_{L}\right) / 2\left(1-x_{K}-x_{L}\right)$ |
| $\mathrm{H}_{2} \mathrm{O}$ | 0 | $\frac{x_{L}}{2-2 x_{K}-2 x_{L}}$ | $x_{L} / 2\left(1-x_{K}-x_{L}\right)$ |

4. Relate equilibrium mole fractions to the equilibrium constants. By definition, $K=\Pi \hat{a}_{i}^{\nu_{i}}$, where the $\hat{a}_{i}$ are the activities of the components with the mixture, and the $v_{i}$ are the stoichiometric numbers for the reaction (see Example 4.4). The present example is at relatively large reduced temperatures and relatively low reduced pressures, so the activities can be represented by the equilibrium mole fractions $y_{i}$. For Reaction 4.11, $K_{K}=y_{\mathrm{CO}_{2}} y_{\mathrm{CH}_{4}} /\left(y_{\mathrm{CO}}\right)^{2}\left(y_{\mathrm{H}_{2}}\right)^{2}$. Substituting the value for $K$ from step 2 and the values for the $y_{i}$ from the last column of the table in step 3 and algebraically simplifying,

$$
\begin{align*}
1.8283 & =\frac{x_{K}\left(x_{K}+x_{L}\right)\left[2\left(1-x_{K}-x_{L}\right)\right]^{2}}{\left(1-2 x_{K}-x_{L}\right)^{2}\left(1-2 x_{K}-3 x_{L}\right)^{2}}  \tag{4.13}\\
K_{L} & =y_{\mathrm{H}_{2} \mathrm{O}} y_{\mathrm{CH}_{4}} / y_{\mathrm{CO}}\left(y_{\mathrm{H}_{2}}\right)^{3}, \text { or } \\
0.7902 & =\frac{x_{L}\left(x_{K}+x_{L}\right)\left[2\left(1-x_{K}-x_{L}\right)\right]^{2}}{\left(1-2 x_{K}-x_{L}\right)\left(1-2 x_{K}-3 x_{L}\right)^{3}} \tag{4.14}
\end{align*}
$$

And for Reaction 4.12,
5. Solve for the equilibrium conditions. Equations 4.13 and 4.14 in step 4 must be solved simultaneously. These are nonlinear and have more than one set of solutions; however, this complication can be eased by imposing two restrictions to ensure that no more CO or $\mathrm{H}_{2}$ is used than the amount of each that is available ( $1 \mathrm{~g} \cdot \mathrm{~mol}$ ). Thus,

$$
\begin{align*}
& 2 x_{K}+x_{L} \leq 1  \tag{4.15}\\
& 2 x_{K}+3 x_{L} \leq 1 \tag{4.16}
\end{align*}
$$

Even with Restrictions 4.15 and 4.16, the solution to Eqs. 4.13 and 4.14 requires a sophisticated mathematical technique or multiple trial and error calculations, as done most easily on the computer. At the solution, $x_{K}=0.189038$ and $x_{L}=0.0632143$; therefore, $y_{\mathrm{CO}_{2}}=0.1264, y_{\mathrm{CH}_{4}}=0.1687, y_{\mathrm{CO}}=$ $0.37360, y_{\mathrm{H}_{2}}=0.28906$, and $y_{\mathrm{H}_{2} \mathrm{O}}=0.04227$.

Related Calculations. If the gas is not ideal, the fugacity coefficients $\phi_{i}$ will not be unity, so the activities cannot be represented by the mole fractions. If the pressure is sufficient for a nonideal solution to exist in the gas phase, $\hat{\phi}_{i}$ will be a function of $y_{i}$, the solution to the problem. In this case, the $y_{i}$ value obtained for the solution with $\hat{\phi}_{i}=1$ should be used for the next iteration and so on until convergence. Alternatively, one could initially solve the problem using the Lewis-Randall rule for
$\hat{\phi}_{i}\left(\hat{\phi}_{i}=\phi_{i}\right)$; the $y_{i}$ obtained in that solution could be substituted back into $\hat{\phi}_{i}$ for the next estimate. Many times this is done most easily by computer.

### 4.8 EQUILIBRIUM COMPOSITION FOR SIMULTANEOUS UNSPECIFIED CHEMICAL REACTIONS

Given an initial mixture of $1 \mathrm{~g} \cdot \mathrm{~mol} \mathrm{CO}$ and $1 \mathrm{~g} \cdot \mathrm{~mol}_{2}$, determine the equilibrium composition of a final system at $900 \mathrm{~K}\left(1160^{\circ} \mathrm{F}\right)$ and $101.3 \mathrm{kPa}(1 \mathrm{~atm})$ that contains $\mathrm{CO}, \mathrm{CO}_{2}, \mathrm{CH}_{4}, \mathrm{H}_{2}$, and $\mathrm{H}_{2} \mathrm{O}$.

## Calculation Procedure

1. Determine the number of gram-atoms of each atom present in the system. Here $1 \mathrm{~g} \cdot \mathrm{~mol} \mathrm{CO}$ contains $1 \mathrm{~g} \cdot$ atom each of C and O , and $1 \mathrm{~g} \cdot \mathrm{~mol}$ of $\mathrm{H}_{2}$ contains $2 \mathrm{~g} \cdot$ atoms of H . Let $A_{k}$ equal the number of gram-atoms of element $k$ present in the system. Then $A_{\mathrm{C}}=1, A_{\mathrm{O}}=1$, and $A_{\mathrm{H}}=2$.
2. Determine the number of gram-atoms of each element present per gram-mole of each substance. Let $a_{i, k}$ equal the number of gram-atoms of element $k$ per gram-mole of substance $i$. Then the following matrix can be set up:

| $i$ | $a_{i, \mathrm{C}}$ | $a_{i, \mathrm{O}}$ | $a_{i, \mathrm{H}}$ |
| :--- | :---: | :---: | :---: |
| CO | 1 | 1 | 0 |
| $\mathrm{CO}_{2}$ | 1 | 2 | 0 |
| $\mathrm{CH}_{4}$ | 1 | 0 | 4 |
| $\mathrm{H}_{2}$ | 0 | 0 | 2 |
| $\mathrm{H}_{2} \mathrm{O}$ | 0 | 1 | 2 |

3. Determine the Gibbs free energy of formation $\Delta \boldsymbol{G}_{f}^{\circ}$ for each compound at $900 \boldsymbol{K}$. See step 2 of the previous problem. From Reid et al. [9], the values are: for $\mathrm{CH}_{4}, 2029 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})$; for CO , $-45,744 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})$; for $\mathrm{CO}_{2},-94,596 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})$; for $\mathrm{H}_{2} \mathrm{O},-47,352 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{mol})$; and for $\mathrm{H}_{2}$, zero.
4. Write equations for minimization of total Gibbs free energy. This step employs the method of Lagrange undetermined multipliers for minimization under constraint; for a discussion of this method, refer to mathematics handbooks. As for its application to minimization of total Gibbs free energy, see Perry and Chilton [7] and Smith and Van Ness [11].

Write the following equation for each substance $i$ :

$$
\Delta G_{f}^{\circ}+R T \ln \left(y_{i} \hat{\phi}_{i} P / f_{i}^{\circ}\right)+\sum_{k}\left(\lambda_{k} a_{i, k}\right)=0
$$

where $R$ is the gas constant, $T$ is temperature, $y$ is mole fraction, $\hat{\phi}_{i}$ is the fugacity coefficient, $P$ is pressure, $f^{\circ}$ is standard-state fugacity, and $\lambda_{k}$ is the Lagrange undetermined multiplier for element $k$ within substance $i$. Since $T$ is high and $P$ is low, gas ideality is assumed; $\hat{\phi}_{i}=1.0$. Set $f^{\circ}$ at 1 atm . Then the five equations are
For CO: $-45,744+R T \ln y_{\mathrm{CO}}+\lambda_{\mathrm{C}}+\lambda_{\mathrm{O}}=0$
For $\mathrm{CO}_{2}: \quad-94,596+R T \ln y_{\mathrm{CO}_{2}}+\lambda_{\mathrm{C}}+2 \lambda_{\mathrm{O}}=0$
For $\mathrm{CH}_{4}: \quad 2029+R T \ln y_{\mathrm{CH}_{4}}+\lambda_{\mathrm{C}}+4 \lambda_{\mathrm{H}}=0$
For $\mathrm{H}_{2}: \quad R T \ln y_{\mathrm{H}_{2}}+2 \lambda_{\mathrm{H}}=0$

For $\mathrm{H}_{2} \mathrm{O}: \quad-47,352+R T \ln y_{\mathrm{H}_{2} \mathrm{O}}+2 \lambda_{\mathrm{H}}+\lambda_{\mathrm{O}}=0$
[In all cases, $R T=(1.987)(900)$.]
5. Write material-balance and mole-fraction equations. A material-balance equation can be written for each element, based on the values found in steps 1 and 2.

$$
\sum_{i} y_{i} a_{i, k}=A_{k} / n_{T}
$$

where $n_{T}$ is the total number of moles in the system. These three equations are
For O: $\quad y_{\mathrm{CO}}+2 y_{\mathrm{CO}_{2}}+y_{\mathrm{H}_{2} \mathrm{O}}=1 / n_{T}$
For C: $\quad y_{\mathrm{CO}}+y_{\mathrm{CO}_{2}}+y_{\mathrm{CH}_{4}}=1 / n_{T}$
For H: $\quad 4 y_{\mathrm{CH}_{4}}+2 y_{\mathrm{H}_{2}}+2 y_{\mathrm{H}_{2} \mathrm{O}}=2 / n_{T}$
In addition, the requirement that the mole fractions sum to unity yields $y_{\mathrm{CO}}+y_{\mathrm{CO}_{2}}+y_{\mathrm{H}_{4}}+$ $y_{\mathrm{H}_{2}}+y_{\mathrm{H}_{2} \mathrm{O}}=1$.
6. Solve the nine equations from steps 4 and 5 simultaneously, to find $y_{C O}, y_{C O_{2}}, y_{C H_{4}}, y_{H_{2}}, y_{H_{2} O}$, $\boldsymbol{\lambda}_{C}, \boldsymbol{\lambda}_{\boldsymbol{o}}, \boldsymbol{\lambda}_{\boldsymbol{H}}$, and $\boldsymbol{n}_{\boldsymbol{T}}$. This step should, of course, be done on a computer. The Lagrange multipliers have no physical significance and should be eliminated from the solution scheme. The equilibrium composition is thus found to be as follows: $y_{\mathrm{CO}_{2}}=0.122 ; y_{\mathrm{CH}_{4}}=0.166 ; y_{\mathrm{CO}}=0.378 ; y_{\mathrm{H}_{2}}=0.290$; and $y_{\mathrm{H}_{2} \mathrm{O}}=0.044$.

Note that these results closely compare with those found in the previous example, which is based on the same set of reaction conditions.

### 4.9 HETEROGENEOUS CHEMICAL REACTIONS

Estimate the composition of the liquid and vapor phases when $n$-butane isomerizes at $311 \mathrm{~K}\left(100^{\circ} \mathrm{F}\right)$. Assume that the reaction occurs in the vapor phase.

## Calculation Procedure

1. Determine the number of degrees of freedom for the system. Use the phase rule $F=C-$ $P+2-r$, where $F$ is degrees of freedom, $C$ is number of components, $P$ is number of phases, and $r$ is the number of independent reactions. In this case, $C$ is $2, P$ is 2 , and $r$ is 1 (namely, $n-\mathrm{C}_{4} \mathrm{H}_{10} \rightarrow$ iso $-\mathrm{C}_{4} \mathrm{H}_{10}$ ); therefore, $F=1$. This means that we can choose either temperature or pressure alone to specify the system; when the temperature is given ( 311 K in this case), the system pressure is thereby established.
2. Calculate the equilibrium constant at the given temperature. See Example 4.4. $K$ is found to be 2.24 .
3. Relate the equilibrium constant to compositions of the two phases. Let subscripts 1 and 2 refer to $n-\mathrm{C}_{4} \mathrm{H}_{10}$ and iso $-\mathrm{C}_{4} \mathrm{H}_{10}$, respectively. Then $K=a_{2} / a_{1}=\left(\hat{\phi}_{2} y_{2} P / f_{2}^{\circ}\right) /\left(\hat{\phi}_{1} y_{1} P / f_{1}^{\circ}\right)$, where $a$ is activity, $\phi$ is fugacity coefficient, $y$ is mole fraction, $P$ is system pressure, $f$ is fugacity, the caret symbol ${ }^{\wedge}$ denotes the value of $\phi$ in solution, and the superscript ${ }^{\circ}$ denotes the standard state. If $f_{1}^{\circ}$ and $f_{2}^{\circ}$ are both selected to be $1 \mathrm{~atm}(101.3 \mathrm{kPa})$, the expression simplifies to

$$
\begin{equation*}
K=\hat{\phi}_{2} y_{2} P / \hat{\phi}_{1} y_{1} P \tag{4.17}
\end{equation*}
$$

4. Relate the gas phase to the liquid phase. Using phase-equilibrium relationships (see Section 3), the following equation can be set out for each of the two components:

$$
y_{i} \hat{\phi}_{i} P=x_{i} \gamma_{i} P_{i}^{\text {sat }} \phi_{i}^{\text {sat }}
$$

where $x_{i}$ is liquid-phase mole fraction, $\gamma_{i}$ is activity coefficient, $P_{i}^{\text {sat }}$ is vapor pressure, and $\phi_{i}^{\text {sat }}$ is fugacity of pure $i$ in the vapor at the system temperature.

The two butane isomers form an ideal solution in the liquid phase at the system temperature, the molecules being quite similar. Therefore, both activity coefficients can be taken to be unity.

Via relationships discussed in Section 3, $\phi_{i}^{\text {sat }}$ is found to be 0.91 and $\phi_{2}^{\text {sat }}$ to be 0.89 . And from vapor pressure data, $P_{1}^{\text {sat }}$ is 3.53 atm and $P_{2}^{\text {sat }}$ is 4.95 atm .
5. Solve for chemical and phase equilibria simultaneously. Write the equation in step 4 for each component and substitute into Eq. 4.17 while taking into account that $x_{1}+x_{2}=1$. This gives

$$
K=x_{2} P_{2}^{\text {sat }} \phi_{2}^{\text {sat }} /\left(1-x_{2}\right) P_{1}^{\text {sat }} \phi_{1}^{\text {sat }}
$$

Or, substituting the known numerical values,

$$
2.24=x_{2}(4.95)(0.89) /\left(1-x_{2}\right)(3.53)(0.91)
$$

Thus the liquid composition is found to be $x_{2}=0.62$ and $x_{1}=0.38$.
Finding the vapor composition $y_{1}$ and $y_{2}$ first requires trial-and-error solution for $P$ and $\phi_{i}$ in the equations

$$
y_{1} \phi_{1} P=x_{1} P_{1}^{\text {sat }} \phi_{1}^{\text {sat }} \quad \text { and } \quad y_{2} \phi_{2} P=x_{2} P_{2}^{\text {sat }} \phi_{2}^{\text {sat }}
$$

Initially assuming that $\phi_{1}=\phi_{2}=1$ and noting that $y_{1}+y_{2}=1$, we can write a combined expression

$$
\begin{aligned}
P & =x_{1} P_{1}^{\text {sat }} \phi_{1}^{\text {sat }}+x_{2} P_{2}^{\text {sat }} \phi_{2}^{\text {sat }} \\
& =(0.38)(3.53)(0.91)+(0.62)(4.95)(0.89) \\
& =3.95
\end{aligned}
$$

Therefore, $P=3.95 \mathrm{~atm}$.
Using this value of $P$ to estimate the $\phi_{i}$ values (see Section 3), we obtain $\phi_{1}=0.903$ and $\phi_{2}=$ 0.913 . Then we substitute these and solve for a second-round estimate of $P$ in

$$
\begin{align*}
\left(y_{1}+y_{2}\right) & =1=\left(x_{1} P_{1}^{\text {sat }} \phi_{1}^{\text {sat }} / \phi_{1} P\right)+\left(x_{2} P_{2}^{\text {sat }} \phi_{2}^{\text {sat }} / \phi_{2} P\right) \\
& =(0.38)(3.53)(0.91) / 0.903 P+(0.62)(4.95)(0.89) / 0.913 P \tag{4.18}
\end{align*}
$$

Therefore, $P=4.344 \mathrm{~atm}$ in this second-round estimate.
Now, use $P=4.344$ to correct the estimates of the $\phi_{i}$ values, to obtain $\phi_{1}=0.894$ and $\phi_{2}=0.904$.
Substituting in Eq. (4.18) yields $P=4.38 \mathrm{~atm}$, which converges with the previous estimates. Finally, from the relationship $y_{i}=x_{i} P_{i}^{\text {sat }} \phi_{i}^{\text {sat }} / \phi_{i} P, y_{1}=(0.38)(3.53)(0.91) /(0.894)(4.38)=$ 0.31 , and $y_{2}=(0.62)(4.95)(0.89) /(0.904)(4.38)=0.69$.

Thus the liquid composition is $x_{1}=0.38$ and $x_{2}=0.62$, and the vapor composition is $y_{1}=0.31$ and $y_{2}=0.69$. The system pressure at equilibrium is $4.38 \mathrm{~atm}(443.7 \mathrm{kPa})$.

Related Calculations. Most frequently, liquid ideality cannot be assumed, and the engineer must use activity coefficients for the liquid phase. Activity coefficients are strong functions of liquid composition and temperature, so these calculations become trial-and-error, most easily done by computer.

In addition, there are frequently more than two nonideal-liquid components, which requires the use of a multicomponent activity-coefficient equation; see Prausnitz [8]. Often the parameters of the
activity-coefficient equation have not been experimentally determined and must be estimated by a group-contribution technique; see Reid et al. [9].

### 4.10 CALCULATING REACTION CONVERSIONS, SELECTIVITIES, AND YIELDS

Benzene is to be produced from toluene according to the reaction

$$
\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CH}_{3}+\mathrm{H}_{2}=\mathrm{C}_{6} \mathrm{H}_{6}+\mathrm{CH}_{4}
$$

Some of the benzene formed undergoes a secondary reaction in series to an unwanted byproduct, diphenyl, according to the reaction

$$
2 \mathrm{C}_{6} \mathrm{H}_{6}=\mathrm{C}_{12} \mathrm{H}_{10}+\mathrm{H}_{2}
$$

The compositions of the reactor feed and effluent streams appear in the table.

|  | Inlet <br> flow rate, <br> kmol h |
| :--- | :---: | ---: |
| Component |  |$\quad$| Outlet |
| :---: |
| flow rate, |
| $\mathrm{kmol} \mathrm{h}^{-1}$ |,

Calculate the conversion, selectivity, and reactor yield with respect to (a) the toluene feed and (b) the hydrogen feed.

## Calculation Procedure

1. Determine the toluene conversion. The toluene conversion equals (toluene consumed in the reactor)/(toluene fed to the reactor). Thus, toluene conversion $=(372-93) / 372=0.75$.
2. Determine the benzene selectivity from toluene. First, find the relevant stoichiometric factor, namely, the stoichiometeric moles of toluene required per mole of benzene produced. From the reaction to produce benzene from toluene, this stoichiometric factor is seen to equal 1.

Then apply the following relationship:
benzene selectivity from toluene $=$ [(benzene produced in reactor) $/($ toluene consumed in

$$
\text { reactor })][\text { stoichiometric factor }]=[(282-13) /(372-93)][1]=0.96
$$

3. Determine the reactor yield of benzene from toluene. The relationship is as follows:
reactor yield of benzene from toluene $=$ [(benzene produced in reactor) $/($ toluene fed to reactor $)][$ stoichiometric factor $]=[(282-13) / 372][1]=0.72$
4. Determine the hydrogen conversion. Analogously to step 1,
hydrogen conversion $=($ hydrogen consumed in reactor $) /($ hydrogen fed to reactor $)$

$$
=(1858-1583) / 1858=0.15
$$

5. Determine the benzene selectivity from hydrogen. As in step 2, the stoichiometric factor with respect to hydrogen and benzene is, likewise, 1 , from the first reaction in this section.

Then,
benzene selectivity from hydrogen $=$ [(benzene produced in reactor) $/($ hydrogen
consumed in reactor $)][$ stoichiometric factor $]=[(282-13) /(1858-1583)][1]=0.98$
6. Determine reactor yield of benzene from hydrogen. As in step 3,
reactor yield of benzene from hydrogen $=[($ benzene produced in reactor $) /($ hydrogen fed
to reactor $)][$ stoichiometric factor $]=[(282-13) / 1858][1]=0.14$
Related Calculations. Because there are two feeds to this process, the reactor performance can be calculated with respect to both feeds. However, the main concern is the performance with respect to toluene, as it is presumably the more expensive feed.

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## SECTION 5

# REACTION KINETICS AND REACTOR DESIGN* 

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5.1 DETERMINING A RATE EXPRESSION BY INTEGRAL ANALYSIS OF BATCH-REACTOR DATA 5.1
5.2 DETERMINING A RATE EXPRESSION BY DIFFERENTIAL ANALYSIS OF BATCH-REACTOR DATA 5.4
5.3 FINDING REQUIRED VOLUME FOR AN ADIABATIC CONTINUOUS-FLOW STIRRED-TANK REACTOR 5.6
5.4 CALCULATING THE SIZE OF AN ISOTHERMAL PLUG-FLOW REACTOR 5.9
5.5 CALCULATING THE REQUIRED REACTION TIME IN A BATCH REACTOR 5.12
5.6 CALCULATING REACTION RATES FROM CONTINUOUS-FLOW

STIRRED-TANK REACTOR DATA 5.14
5.7 TOTAL SURFACE AREA, ACTIVE SURFACE AREA, POROSITY, AND MEAN PORE RADIUS OF A CATALYST 5.19
5.8 SIZING AND DESIGN OF A SYSTEM OF STIRRED-TANK REACTORS 5.21
5.9 DETERMINATION OF REACTION-RATE EXPRESSIONS FROM PLUG-FLOW-REACTOR DATA 5.24
5.10 REACTION-SEPARATION PROCESSES: OPTIMAL RECYCLE ALTERNATIVES AND MINIMUM REQUIRED SELECTIVITIES 5.28
REFERENCES 5.32

### 5.1 DETERMINING A RATE EXPRESSION BY INTEGRAL ANALYSIS OF BATCH-REACTOR DATA

Saponification of ethyl acetate with sodium hydroxide, that is,

$$
\mathrm{CH}_{3} \mathrm{COOC}_{2} \mathrm{H}_{5}+\mathrm{NaOH} \rightarrow \mathrm{CH}_{3} \mathrm{COONa}+\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}
$$

*Example 5.10 is adapted from Smith, Chemical Process Design, McGraw-Hill.
has been investigated at $298 \mathrm{~K}\left(77^{\circ} \mathrm{F}\right)$ in a well-stirred isothermal batch reactor. The following data were collected:

| Time, $\min$ <br> Concentration of <br> $\mathrm{NaOH}, \mathrm{g} \cdot \mathrm{mol} / \mathrm{L}$ | 5 | 9 | 13 | 20 | 25 | 33 | 37 |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: |

The run began with equimolar $(0.1 \mathrm{~g} \cdot \mathrm{~mol} / \mathrm{L})$ amounts of sodium hydroxide and ethyl acetate as the reactants. Calculate the overall order of the reaction and the value of the reaction rate constant at 298 K , and write the rate expression for the reaction.

## Calculation Procedure

1. Assume a functional form for the rate expression. The rate expression for this reaction may be given by the following equation, which relates the rate of disappearance $r$ of sodium hydroxide to concentrations of reactants and products:

$$
-r_{\mathrm{NaOH}}=k_{1}\left[\mathrm{CH}_{3} \mathrm{COOC}_{2} \mathrm{H}_{5}\right]^{a}[\mathrm{NaOH}]^{b}-k_{-1}\left[\mathrm{CH}_{3} \mathrm{COONa}\right]^{c}\left[\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}\right]^{d}
$$

In this expression, $a, b, c$, and $d$ are the unknown reaction orders, $k_{1}$ and $k_{-1}$ are the forward and reverse rate constants, and the bracketed formulas denote the concentrations of the compounds. Integral analysis of the data requires an assumption as to the functional form of the reaction rate expression (e.g., zero-order, first-order, second-order with regard to a given reactant), which is then inserted into the appropriate reactor material balance. Literature values indicate that the equilibrium constant for this reaction is very large $\left(k_{1} / k_{-1} \rightarrow \infty\right)$. As an initial guess, the reaction may be considered to be first-order in both reactants and irreversible. Thus $-r_{\mathrm{NaOH}}=k[\mathrm{EtAc}]^{1}[\mathrm{NaOH}]^{1}$, where $k$ is the reaction rate constant. Since the reactants are present in equimolar ratio initially, $[\mathrm{EtAc}]=[\mathrm{NaOH}]$ throughout the run (if the initial guess is correct), and the rate expression can therefore be expressed as $-r_{\mathrm{NaOH}}=k[\mathrm{NaOH}]^{2}$.
2. Insert the rate expression into batch-reactor material balance. A transient material balance for the NaOH on an isothermal batch reactor becomes $(\mathrm{NaOH}$ in $)-(\mathrm{NaOH}$ out $)+($ net NaOH generation) $=\mathrm{NaOH}$ accumulation. For this system,

$$
+r_{\mathrm{NaOH}} V=\frac{d N_{\mathrm{NaOH}}}{d t}
$$

where $\quad r=$ rate of generation
$V=$ reactor volume
$N=$ number of moles
$t=$ time

Rearranging, referring to Step 1, and noting that concentration may be given by $N / V$ leads to the expression

$$
\frac{-d[\mathrm{NaOH}]}{d t}=k[\mathrm{NaOH}]^{2}
$$

3. Solve for concentration-versus-time profile. The preceding expression may be separated and integrated to give a concentration-versus-time profile that may be tested against the experimental data. Integrating,

$$
-\int_{\left[\mathrm{NaOH}_{0}\right.}^{[\mathrm{NaOH}]_{t}} \frac{d[\mathrm{NaOH}]}{[\mathrm{NaOH}]^{2}}=k \int_{0}^{t} d t
$$

Carrying out the indicated integrations and simplifying leads to the expression

$$
\frac{1}{[\mathrm{NaOH}]_{0}}-\frac{1}{[\mathrm{NaOH}]}=-k t
$$



FIGURE 5.1 Concentration-versus-time profile (Example 5.1).
4. Plot the data. The assumed model (firstorder in both reactants and irreversible) predicts that if the data are plotted as $\left(1 /[\mathrm{NaOH}]_{0}-\right.$ $1 /[\mathrm{NaOH}])$ versus time, a straight line passing through the origin should be obtained, and the slope of this line will be the reaction rate constant $-k$. A plot of the experimental data according to this model is shown in Fig. 5.1. As may be seen, the data fit the assumed model quite well. The reaction rate constant, as determined by measuring the slope, is found to be

$$
k=6.42 \mathrm{~L} /(\mathrm{g} \cdot \mathrm{~mol})(\mathrm{min})
$$

Thus the rate of saponification of ethyl acetate with sodium hydroxide may be adequately modeled by a rate expression of the form

$$
-r_{\mathrm{NaOH}}=6.42[\mathrm{NaOH}]^{1.0}\left[\mathrm{CH}_{3} \mathrm{COOC}_{2} \mathrm{H}_{5}\right]^{1.0}
$$

Related Calculations. (1) Integral analysis may be used on data from any reactor from which integral reaction rate data have been obtained. The preceding procedure applies equally well to data from an integral tubular-flow reactor, if the tube-flow material balance

$$
+r_{i}=\frac{d C_{i}}{d \tau}
$$

is used rather than the batch-reactor material balance. Here $C_{i}$ is the concentration of species $i$, in moles per volume, and $\tau$ is the residence time. (2) The form of the material balance to be tested depends on the reacting system under investigation and the data available for testing. The preceding analysis was applied because the system was of constant density and the data were in the form of concentration versus time. Data are often presented as fractional conversion $\left(X_{A}\right)$ versus time, where

$$
X_{A}=\frac{C_{A 0}-C_{A}}{C_{A 0}}
$$

### 5.2 DETERMINING A RATE EXPRESSION BY DIFFERENTIAL ANALYSIS OF BATCH-REACTOR DATA

Determine an appropriate rate expression for the gas-phase reaction $A \rightarrow 2 B$ utilizing the following data from a constant-volume batch reactor:

| Time, h | Total pressure, $\mathrm{kPa}(\mathrm{atm})$ |
| :--- | :---: |
| 0 | $132.74(1.31)$ |
| 0.5 | $151.99(1.5)$ |
| 1 | $167.19(1.65)$ |
| 1.5 | $178.33(1.76)$ |
| 2 | $186.44(1.84)$ |
| 2.5 | $192.52(1.90)$ |
| 3 | $197.58(1.95)$ |
| 3.5 | $201.64(1.99)$ |
| 4 | $205.18(2.025)$ |
| 5 | $210.76(2.08)$ |
| 6 | $214.81(2.12)$ |
| 7 | $217.85(2.15)$ |
| 8 | $220.38(2.175)$ |

The reaction mixture consists of $76.94 \%$ A with $23.06 \%$ inerts at 101.325 kPa ( 1 atm ) and 287 K $\left(57.2^{\circ} \mathrm{F}\right)$. The reaction is initiated by dropping the reactor into a constant-temperature bath at 373 K $\left(212^{\circ} \mathrm{F}\right)$. Equilibrium calculations have shown the reaction to be essentially irreversible in this temperature range.

## Calculation Procedure

1. Propose a generalized rate expression for testing the data. Analysis of rate data by the differential method involves utilizing the entire reaction-rate expression to find reaction order and the rate constant. Since the data have been obtained from a batch reactor, a general rate expression of the following form may be used:

$$
\frac{d C_{A}}{d t}=-k C_{A}^{\alpha}
$$

where $k$ and $\alpha$ are the reaction rate constant and reaction order to be determined.
2. Convert the rate expression to units of pressure. Since the data are in the form of total pressure versus time, the rate expression to be tested must also be in the form of total pressure versus time. Assuming ideal-gas behavior, $P V=n R T$, and therefore,

$$
C_{i}=\frac{n_{i}}{V}=\frac{P_{i}}{R T}
$$

where $P_{i}=$ partial pressure of species $i$. Thus the rate expression becomes

$$
\frac{1}{R T} \frac{d P_{A}}{d t}=-\left(\frac{1}{R T}\right)^{\alpha} k P_{A}^{\alpha}
$$

Now, partial pressure of species $A$ must be related to total-system pressure. This may be done easily by a general mole balance on the system, resulting in the following relationships:
a. For any reactant,

$$
P_{R}=P_{R 0}-\frac{r}{\Delta n}\left(\pi-\pi_{0}\right)
$$

b. For any product,

$$
P_{S}=P_{S 0}+\frac{s}{\Delta n}\left(\pi-\pi_{0}\right)
$$

where $P_{R 0}$ and $P_{S 0}$ are initial partial pressures of reactant $R$ and product $S, r$ and $s$ are molar stoichiometric coefficients on $R$ and $P$, $\pi$ is total pressure, $\pi_{0}$ is initial total pressure, and $\Delta n$ is net change in number of moles, equaling total moles of products minus total moles of reactants.

In the present case, $r$ for the reactant $A$ equals $1, s$ for the product $B$ equals 2 , and $\Delta n$ equals $(2-1)=1$. Using the data, and the relationship between partial pressure and total pressure for a reactant, the form of the rate expression to be tested may be derived:

$$
P_{A}=P_{A 0}-\frac{1}{2-1}\left(\pi-\pi_{0}\right)
$$

From the data, $\pi_{0}=132.74 \mathrm{kPa}(1.31 \mathrm{~atm})$, so $P_{A 0}=(132.74)(0.7694)=102.13 \mathrm{kPa}(1.0 \mathrm{~atm})$. Therefore, $P_{A}=102.13-(1 / 1)(\pi-132.74)=234.87-\pi$, with $P_{A}$ and $\pi$ in kilopascals, and $d P_{A} / d t=-d \pi / d t$. Thus the rate expression becomes $d \pi / d t=k^{\prime}(234.87-\pi)^{\alpha}$, where $k^{\prime}=$ $k(R T)^{1-\alpha}$.
3. Linearize the rate expression by taking logs, and plot the data. The proposed rate expression may be linearized by taking logs, resulting in the following expression:

$$
\ln \left(\frac{d \pi}{d t}\right)=\ln k^{\prime}+\alpha \ln (234.87-\pi)
$$

This expression indicates that if $\ln (d \pi / d t)$ is plotted against $\ln (234.87-\pi)$, a straight line should result with slope $\alpha$ and $y$ intercept $\ln k^{\prime}$. Thus, to complete the rate-data analysis, the derivative $d \pi / d t$ must be evaluated.

Three methods are commonly used to estimate this quantity: (1) slopes from a plot of $\pi$ versus $t$, (2) equal-area graphic differentiation, or (3) Taylor series expansion. For details on these, see a mathematics handbook. The derivatives as found by equal-area graphic differentiation and other pertinent data are shown in the following table:

| Time, h | $234.87-\pi, \mathrm{kPa}$ | $d \pi / d t$ |
| :--- | :---: | :---: |
| 0 | 102.13 | 44.5 |
| 0.5 | 82.88 | 34 |
| 1 | 67.68 | 26 |
| 1.5 | 56.54 | 19.5 |
| 2 | 48.43 | 15 |
| 2.5 | 42.35 | 11 |
| 3 | 37.29 | 9 |
| 3.5 | 33.23 | 7.5 |
| 4 | 29.69 | 6.5 |
| 5 | 24.11 | 4.5 |
| 6 | 20.06 | 3.5 |
| 7 | 17.02 | 2.5 |
| 8 | 14.49 | 1.5 |

Plotting $\ln (d \pi / d t)$ versus $\ln (234.87-\pi)$ yields an essentially straight line with a slope of 1.7 and an intercept of 0.0165 . Thus, an appropriate rate expression for this reaction is given by

$$
d \pi / d t=0.0165(234.87-\pi)^{1.7}
$$

or

$$
-d P_{A} / d t=0.0165 P_{A}^{1.7}
$$

Related Calculations. The rate expression derived above may be converted back to concentration units by noting that $C_{A}=P_{A} / R T$ and using $T=373 \mathrm{~K}, R=0.0821(\mathrm{~L})(\mathrm{atm}) /(\mathrm{g} \cdot \mathrm{mol})(\mathrm{K})$.

### 5.3 FINDING REOUIRED VOLUME FOR AN ADIABATIC CONTINUOUS-FLOW STIRRED-TANK REACTOR

Determine the volume required for an adiabatic mixed-flow reactor processing $56.64 \mathrm{~L} / \mathrm{min}\left(2 \mathrm{ft}^{3} / \mathrm{min}\right.$ or $0.05664 \mathrm{~m}^{3} / \mathrm{min}$ ) of a liquid feed containing reactant $R$ and inerts $I$ flowing at a rate of $0.67 \mathrm{~g} \cdot \mathrm{~mol} / \mathrm{min}$ and $0.33 \mathrm{~g} \cdot \mathrm{~mol} / \mathrm{min}$, respectively. In the reactor, $R$ is isomerized to $S$ and $T$ ( 90 percent fractional conversion of $R$ ) by the following elementary reaction: $R \xrightarrow{k_{1}} S+T$. Feed enters the reactor at $300 \mathrm{~K}\left(80.6^{\circ} \mathrm{F}\right)$. Data on the system are as follows:

## Heat Capacities

$$
\begin{aligned}
R & =7 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{~mol})\left({ }^{\circ} \mathrm{C}\right) \\
S & =T=4 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{~mol})\left({ }^{\circ} \mathrm{C}\right) \\
I & =8 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{~mol})\left({ }^{\circ} \mathrm{C}\right)
\end{aligned}
$$

Reaction Rate Constant at 298 K

$$
k_{1}=0.12 \mathrm{~h}^{-1}
$$

## Activation Energy

$$
25,000 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{~mol})
$$

Heat of Reaction at 273 K

$$
\Delta H_{R}=-333 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{~mol}) \text { of } R
$$

## Procedure

1. Write the material- and energy-balance expressions for the reactor. This problem must be solved by simultaneous solution of the material- and energy-balance relationships that describe the reacting system. Since the reactor is well insulated and an exothermic reaction is taking place, the fluid in the reactor will heat up, causing the reaction to take place at some temperature other than where the reaction rate constant and heat of reaction are known.

Assuming a constant-density reacting system, a constant volumetric flow rate through the reactor, and steady-state operation, a material balance on species $R$ gives the expression

$$
v C_{R 0}-v C_{R}+V r_{R}=0
$$

where $C_{R 0}=$ concentration of $R$ in feed
$C_{R}=$ concentration of $R$ in products
$v=$ volumetric flow rate

$$
\begin{aligned}
V & =\text { reactor volume } \\
r_{R} & =\text { net rate of formation of } R
\end{aligned}
$$

This equation can be rearranged into

$$
\frac{C_{R 0}-C_{R}}{-r_{R}}=\tau
$$

where $\tau=$ residence time $(V / v)$.
A first-law energy balance on the continuous-flow stirred-tank reactor gives the expression

$$
Q=\sum_{i=1}^{n} F_{i 0} \hat{C}_{p, i}\left(T-T_{i 0}\right)+X\left[\Delta H^{\circ}+\Delta \hat{C}_{p}\left(T-T^{\circ}\right)\right]
$$

where $Q=$ rate of heat exchange with surroundings
$F_{i}=$ outlet molar flow rate of species $i$
$F_{i 0}=$ inlet molar flow rate of species $i$
$\hat{C}_{p, i}=$ mean heat capacity of species $i$
$T_{i 0}=\operatorname{inlet}$ (feed) temperature of species $i$
$T=$ reactor operating temperature
$X=$ molar conversion rate of species $R\left(=F_{R 0}-F_{R}\right)$
$\Delta H^{\circ}=$ heat of reaction at $T^{\circ}$
$T^{\circ}=$ reference temperature for heat-of-reaction data
$\Delta \hat{C}_{p}=\Sigma v_{i} C_{p, i \text { products }}-\Sigma v_{i} C_{p, i \text { reactants }}$
$v_{i}=$ molar stoichiometric coefficient
2. Calculate the operating temperature in the reactor. Application of the energy balance shown above allows the reaction mass temperature to be calculated, since all quantities in the expression are known except $T$. Pertinent calculations and parameters are as follows:

$$
\begin{aligned}
Q & =0(\text { adiabatic }) \\
F_{R 0} & =0.67 \mathrm{~mol} / \mathrm{min} \\
F_{I 0} & =0.33 \mathrm{~mol} / \mathrm{min} \\
T_{R 0} & =T_{I 0}=300 \mathrm{~K} \\
X & =X_{R} F_{R 0}=(0.90)(0.67)=0.603 \mathrm{~g} \cdot \mathrm{~mol} R \text { per minute } \\
\Delta \hat{C}_{p} & =4+4-7=1 \mathrm{cal} /(\mathrm{g} \cdot \mathrm{~mol})\left({ }^{\circ} \mathrm{C}\right)
\end{aligned}
$$

Substituting into the energy balance,

$$
0=(0.67)(7)(T-300)+(0.33)(8)(T-300)+0.603[-333+(1)(T-273)]
$$

Solving for reactor temperature,

$$
T=323.4 \mathrm{~K}\left(122.7^{\circ} \mathrm{F}\right)
$$

3. Calculate the reaction rate constant at the reactor operating temperature. Since the temperature in the reactor is not $25^{\circ} \mathrm{C}$ (where the value for the reaction rate constant is known), the rate constant must be estimated at the reactor temperature. The Arrhenius form of the rate constant may be used to obtain this estimate:

$$
k=A \exp \left[-E_{A} /(R T)\right]
$$

where $A=$ preexponential factor
$E_{A}=$ activation energy

$$
R=\text { universal gas constant }
$$

$$
T=\text { absolute temperature }
$$

Dividing this Arrhenius equation for $T=T$ by the Arrhenius equation for $T=298 \mathrm{~K}\left(25^{\circ} \mathrm{C}\right)$ and noting that $(1 / T)-(1 / 298)=(298-T) / 298 T$, the following expression can be derived:

$$
k_{T}=k_{298} \exp \left[\frac{-25,000}{1.987}\left(\frac{298-T}{298 T}\right)\right]
$$

Now $k_{298}=0.12 \mathrm{~h}^{-1}$, so when $T=323.4 \mathrm{~K}$ (the reactor operating temperature), the reaction rate constant becomes $k_{323.4}=3.31 \mathrm{~h}^{-1}$.
4. Solve for reactor volume using the material-balance expression. The material balance for the continuous-flow stirred-tank reactor may now be used to calculate the reactor volume required for the isomerization. Inserting the first-order rate expression into the material balance,

$$
\tau=\frac{C_{R 0}-C_{R}}{k C_{R}}=\frac{V}{v}
$$

To apply this material balance, it is first necessary to calculate the inlet and outlet concentrations of species $R$. This may be easily accomplished from the given data and the relationships

$$
C_{i}=\frac{F_{i}}{v} \quad F_{i}=F_{i 0}\left(1-X_{i}\right)
$$

Since $\nu=$ constant, $C_{i}=C_{i 0}\left(1-X_{i}\right)$. In these relationships, $C_{i}$ is the concentration of species $i$, $F_{i}$ is the molar flow rate of species $i, v$ is volumetric flow rate, and $X_{i}$ is fractional conversion of species $i$.

For this example,

$$
C_{R 0}=\frac{F_{R 0}}{v}=\frac{0.67}{56.64}=0.012 \mathrm{~g} \cdot \mathrm{~mol} / \mathrm{L}
$$

and

$$
C_{R}=0.012(1-0.9)=0.0012 \mathrm{~g} \cdot \mathrm{~mol} / \mathrm{L}
$$

Thus the reactor volume may now be directly calculated after converting the volumetric flow rate to an hourly basis:

$$
V=\frac{0.012-0.0012}{(3.31)(0.0012)}(56.64)(60)=9240 \mathrm{~L}\left(326 \mathrm{ft}^{3} \text { or } 9.24 \mathrm{~m}^{3}\right)
$$

Related Calculations. (1) Since the reaction is irreversible, equilibrium considerations do not enter into the calculations. For reversible reactions, the ultimate extent of the reaction should always be checked first, using the procedures outlined in Section 4. If equilibrium calculations show that the required conversion cannot be attained, then either the conditions of the reaction (e.g., temperature) must be changed or the design is not feasible. Higher temperatures should be investigated to increase ultimate conversions for endothermic reactions, while lower temperatures will favor higher conversions for exothermic reactions.
(2) The simultaneous solving of the material- and energy-balance expressions may yield more than one solution. This is especially true for exothermic reactions occurring in continuous stirredtank reactors. The existence of other feasible solutions may be determined by plotting the energybalance and material-balance expressions on molar conversion rate versus temperature coordinates, as shown in Fig. 5.2. In the figure, points $A$ and $C$ represent stable operating points for the reactor, while point $B$ is the metastable, or "ignition," point, where stable operation is difficult. This is due


FIGURE 5.2 Molar conversion rate versus temperature (Example 5.3).
to the relative slopes of the material- and energy-balance lines at $B$. Small positive temperature excursions away from $B$ result in "ignition" of the reaction mass because the rate of heat generation is greater than that of heat removal, and the reactor restabilizes at point $A$. Similarly, a small negative temperature deviation from $B$ causes the reaction mass to "quench," and the reactor restabilizes at point $C$.

### 5.4 CALCULATING THE SIZE OF AN ISOTHERMAL

## PLUG-FLOW REACTOR

Laboratory experiments on the irreversible, homogeneous gas-phase reaction $2 A+B=2 C$ have shown the reaction rate constant to be $1 \times 10^{5}(\mathrm{~g} \cdot \mathrm{~mol} / \mathrm{L})^{-2} \mathrm{~s}^{-1}$ at $500^{\circ} \mathrm{C}\left(932^{\circ} \mathrm{F}\right)$. Analysis of isothermal data from this reaction has indicated that a rate expression of the form $-r_{A}=k C_{A} C_{B}^{2}$ provides an adequate representation for the data at $500^{\circ} \mathrm{C}$ and $101.325 \mathrm{kPa}(1 \mathrm{~atm})$ total pressure. Calculate the volume of an isothermal, isobaric plug-flow reactor that would be required to process $6 \mathrm{~L} / \mathrm{s}$ $\left(0.212 \mathrm{ft}^{3} / \mathrm{s}\right)$ of a feed gas containing $25 \% A, 25 \% B$, and $50 \%$ inserts by volume if a fractional conversion of $90 \%$ is required for component $A$.

## Calculation Procedure

1. Develop a plug-flow-reactor design equation from the material balance. To properly size a reactor for this reaction and feedstock, a relationship between reactor volume, conversion rate of feed, and rate of reaction is needed. This relationship
 is provided by the material balance on the plugflow reactor.

For a single ideal reactor, a component material balance on a differential volume element $d \psi$ (see Fig. 5.3) becomes, for species $A$
FIGURE 5.3 Differential volume element for plug-flow reactor (Example 5.4).

$$
F_{A Z}-F_{A Z+\Delta Z}+r_{A} \Delta \psi=0 \quad \text { or } \quad \frac{d F_{A}}{d \psi}=r_{A}
$$

where $\psi$ is a reactor-size parameter (volume, mass of catalyst, etc.), $F_{A}$ is molar flow rate of $A$, and $r_{A}$ is the rate of generation of $A$ per unit of volume. Upon rearranging and integrating,

$$
\int_{F_{A 0}}^{F_{A}} \frac{d F_{A}}{r_{A}}=\int_{0}^{\psi} d \psi=\psi
$$

In terms of total molar conversion rate of species $A$, designated $X, F_{A}=F_{A 0}-X$, and $d F_{A}=-d X$, where $F_{A 0}$ is molar flow rate of $A$ in feed. Thus the material balance for this homogeneous reaction becomes

$$
\psi=V=-\int_{0}^{X} \frac{d X}{r_{A}}
$$

2. Relate molar flow rates of products and reactants to conversion rate of $\boldsymbol{A}$. To use the mass balance to solve for reactor size $V$, it is necessary to relate the rate of generation $+r_{A}$ of $A$ to the molar conversion rate $X$ of $A$. This is easily done through the rate expression. For this reaction

$$
+r_{A}=-k C_{A} C_{B}^{2}
$$

where $C_{A}$ and $C_{B}$ are molar concentrations of $A$ and $B$. For this gas-phase reaction, the concentrations of $A$ and $B$ may be calculated from the ideal-gas law, so

$$
C_{A}=n_{A} / V=\frac{p_{A}}{R T}=\frac{p_{T} y_{A}}{R T}
$$

where $p_{A}=$ partial pressure of $A$
$V=$ volume
$n_{A}=$ number of moles of $A$
$p_{T}=$ total system pressure
$R=$ universal gas constant
$T=$ absolute temperature
$y_{A}=$ mole fraction of $A$
The rate expression then becomes

$$
+r_{A}=-k\left(\frac{p_{T}}{R T}\right)^{3} y_{A} y_{B}^{2}
$$

Mole fractions for components $A$ and $B$ are computed from a component-by-component mole balance on the reactor, noting that $1 / 2 \mathrm{~mol} B$ and $1 \mathrm{~mol} C$ are involved per mole of $A$ reacted. Thus,

$$
\begin{aligned}
F_{A} & =F_{A 0}-X \\
F_{B} & =F_{B 0}-X / 2 \\
F_{C} & =F_{C 0}+X \\
F_{I} & =F_{I 0} \\
\hline F_{T} & =F_{T 0}-X / 2
\end{aligned}
$$

In this balance, $F_{A}, F_{B}$, and $F_{C}$ are the molar flow rates of species $A, B$, and $C$ at any position in the reactor, $F_{A 0}, F_{B 0}$, and $F_{C 0}$ are the molar flow rates of $A, B$, and $C$ in the feed, and $F_{I}$ and $F_{I 0}$ are the molar flow rates of inerts in product and in the feed.

Now, by definition,

$$
y_{A}=\frac{F_{A}}{F_{T}}=\frac{F_{A 0}-X}{F_{T 0}-X / 2} \quad \text { and } \quad y_{B}=\frac{F_{B}}{F_{T}}=\frac{F_{B 0}-X / 2}{F_{T 0}-X / 2}
$$

and the rate expression in terms of molar conversion rate of $A$ therefore becomes:

$$
+r_{A}=-k\left(\frac{p T}{R T}\right)^{3}\left[\frac{\left(F_{A 0}-X\right)\left(F_{B 0}-X / 2\right)^{2}}{\left(F_{T 0}-X / 2\right)^{3}}\right]
$$

3. Evaluate molar flow rates and integrate the mass balance. Once the known data on molar flow rates are substituted into the mass balance, it can be solved for reactor volume. From step 1, the equation to be solved is

$$
V=\frac{1}{k\left(\frac{p T}{R T}\right)^{3}} \int_{0}^{x} \frac{d X}{\frac{\left(F_{A 0}-X\right)\left(F_{B 0}-X / 2\right)^{2}}{\left(F_{T 0}-X / 2\right)^{3}}}
$$

From the problem statement,

$$
C_{A 0}=\frac{p_{A 0}}{R T}=\frac{0.25(1)}{0.082(773)}=0.004 \mathrm{~g} \cdot \mathrm{~mol} / \mathrm{L}
$$

and

$$
F_{A 0}=v_{0} C_{A 0}=6(0.004)=0.024 \mathrm{~g} \cdot \mathrm{~mol} / \mathrm{L}
$$

and

$$
F_{B 0}=F_{A 0}
$$

Further,

$$
F_{I 0}=F_{I}=0.048 \mathrm{~g} \cdot \mathrm{~mol} / \mathrm{s}, \text { and } F_{T 0}=F_{A 0}+F_{B 0}+F_{I 0}=0.096 \mathrm{~g} \cdot \mathrm{~mol} / \mathrm{s}
$$

For 90 percent fractional conversion of $A$, the upper limit on the integral may be evaluated as

$$
x=X_{A} F_{A 0}=0.9(0.024)=0.022 \mathrm{~g} \cdot \mathrm{~mol} / \mathrm{s}
$$

The integral may now be solved for reactor volume. Since analytical solution is difficult because of the complexity of the integrand, graphic integration (not shown here) may be used to find the required reactor volume.

By graphic integration, the value of the integral is evaluated and reactor volume is calculated as follows: The value of the integral $f(X) d X=91$; then

$$
k\left(\frac{p_{T}}{R T}\right)^{3}=10^{5}\left[\frac{1}{0.082(773)}\right]^{3}=0.393
$$

Therefore,

$$
V=\frac{91}{0.393}=232 \mathrm{~L}\left(8.2 \mathrm{ft}^{3} \text { or } 0.23 \mathrm{~m}^{3}\right)
$$

Related Calculations. (1) The integral may be evaluated more precisely using any of the various numerical integration routines (Euler, Runge-Kutta, for example), which may be readily programmed for computer solution.
(2) If the reaction is reversible instead of irreversible, its ultimate extent must be checked (using methods outlined in the preceding section) to make sure that the required $90 \%$ fractional conversion can be attained. If it cannot, either the problem specification must be altered to allow a lower conversion, or the reactor conditions (i.e., reaction temperature or total pressure) must be changed.

### 5.5 CALCULATING THE REQUIRED REACTION TIME IN A BATCH REACTOR

The heterogeneous gas-phase hydrogenation of acetylene to ethane at $1000 \mathrm{~K}\left(1341^{\circ} \mathrm{F}\right)$, that is,

$$
\mathrm{C}_{2} \mathrm{H}_{2}+2 \mathrm{H}_{2} \rightarrow \mathrm{C}_{2} \mathrm{H}_{6}
$$

has been found to proceed with a reaction rate that may be adequately represented by the rate expression

$$
-r_{\mathrm{C}_{2} \mathrm{H}_{2}}=k C_{\mathrm{H}_{2}}^{2} C_{\mathrm{C}_{2} \mathrm{H}_{2}}
$$

Laboratory experiments at 1000 K indicate that the reaction rate constant is $1 \times 10^{5} \mathrm{~g} \cdot \mathrm{~mol} /(\mathrm{L})(\mathrm{min})$. If a mixture of $75 \mathrm{~mol} \%$ hydrogen and $25 \%$ acetylene is charged to a $1-\mathrm{L}\left(0.035-\mathrm{ft}^{3}\right.$ or $\left.0.001-\mathrm{m}^{3}\right)$ batch reactor and $0.001 \mathrm{~g} \cdot \mathrm{~mol}$ acetylene is present initially in the reactor, calculate the holding time at 1000 K necessary to achieve $90 \%$ fractional conversion of acetylene to ethane. The reactor is to be operated at a constant temperature of 1000 K .

## Calculation Procedure

1. Develop a batch-reactor design equation from the mass balance. To find the required holding time, a relationship between reaction time and the rate of conversion of acetylene must be developed. This may be developed from a mass balance on the batch reactor. Since the molar density of the reacting mixture is not constant (there is a net change in the number of moles due to reaction), the pressure of the reactor will have to change accordingly.

A material balance on component $A$ in a batch reactor gives

$$
\left(\frac{1}{V}\right) \frac{d N_{A}}{d t}=r_{A}
$$

where $r_{A}=$ net rate of generation of species $A$
$V=$ volume
$N_{A}=$ moles of $A$
Since concentration equals $N / V$, the rate of reaction of acetylene is given by

$$
-r_{\mathrm{C}_{2} \mathrm{H}_{2}}=k\left[\frac{N_{\mathrm{H}_{2}}}{V}\right]^{2}\left[\frac{N_{\mathrm{C}_{2} \mathrm{H}_{2}}}{V}\right] \quad \text { or } \quad-r_{\mathrm{C}_{2} \mathrm{H}_{2}}=\frac{k}{V^{3}} N_{\mathrm{H}_{2}}^{2} N_{\mathrm{C}_{2} \mathrm{H}_{2}}
$$

The design equation for the batch reactor thus becomes

$$
\frac{d N_{\mathrm{C}_{2} \mathrm{H}_{2}}}{d t}=-\frac{k}{V^{2}} N_{\mathrm{H}_{2}}^{2} N_{\mathrm{C}_{2} \mathrm{H}_{2}}
$$

This equation may be recast in terms of total moles $X$ of acetylene converted, where $X$ is a function of elapsed time. Since the reaction of 1 mol acetylene involves 2 mol hydrogen and produces 1 mol ethane, the batch reactor will contain at any given time $t$ the following mixture (with subscript 0 referring to the amount initially present):

$$
\begin{aligned}
N_{\mathrm{C}_{2} \mathrm{H}_{2}} & =N_{\mathrm{C}_{2} \mathrm{H}_{2,0}}-X \\
N_{\mathrm{H}_{2}} & =N_{\mathrm{H}_{2,0}}-2 X \\
N_{\mathrm{C}_{2} \mathrm{H}_{6}} & =X
\end{aligned}
$$

The total number of moles is thus the sum of these three equations, or $N_{T, 0}-2 X$. The design equation thus becomes

$$
\frac{-d X}{d t}=\frac{-k}{V^{2}}\left(N_{\mathrm{H}_{2,0}}-2 X\right)^{2}\left(N_{\mathrm{C}_{2} \mathrm{H}_{2,0}}-X\right)
$$

2. Separate and integrate the batch-reactor design equation. The reaction time required for any given initial composition and conversion of reactants may now be calculated directly from the preceding expression, once this expression has been integrated and solved for $t=f(X)$. The appropriate solution method is as follows:
a. Separate the variables.

$$
\int_{0}^{x} \frac{d X}{\left(N_{\mathrm{H}_{2,0}}-2 X\right)^{2}\left(N_{\mathrm{C}_{2} \mathrm{H}_{2,0}}-X\right)}=\frac{k}{V^{2}} \int_{0}^{t} d t
$$

b. Integrate.

$$
\begin{aligned}
\int_{0}^{x} \frac{d X}{\left(N_{\mathrm{H}_{2,0}}-2 X\right)^{2}\left(N_{\mathrm{C}_{2} \mathrm{H}_{2,0}}-X\right)}= & \frac{1}{\left(-N_{\mathrm{H}_{2,0}}+2 N_{\mathrm{C}_{2} \mathrm{H}_{2,0}}\right)} \frac{1}{\left(N_{\mathrm{H}_{2,0}}-2 X\right)} \\
& +\frac{-1}{\left(-N_{\mathrm{H}_{2,0}}+2 N_{\mathrm{C}_{2} \mathrm{H}_{2,0}}\right)} \ln \left(\frac{N_{\mathrm{C}_{2} \mathrm{H}_{2,0}}-X}{N_{\mathrm{H}_{2,0}}-2 X}\right)=\frac{k}{V^{2}} t
\end{aligned}
$$

c. Evaluate between limits. Evaluation of the integral between 0 and $x$ for the left-hand side and between 0 and $t$ for the right-hand side gives the following expression for reaction time as a function of total molar conversion:

$$
\begin{aligned}
& \frac{1}{\left(N_{\mathrm{H}_{2,0}}-2 X\right)\left(2 N_{\mathrm{C}_{2} \mathrm{H}_{2,0}}-N_{\mathrm{H}_{2,0}}\right)}-\frac{1}{N_{\mathrm{H}_{2,0}}\left(2 N_{\mathrm{C}_{2} \mathrm{H}_{2,0}}-N_{\mathrm{H}_{2,0}}\right)} \\
& \quad+\frac{1}{\left(2 N_{\mathrm{C}_{2} \mathrm{H}_{2,0}}-N_{\mathrm{H}_{2,0}}\right)^{2}} \ln \left[\frac{N_{\mathrm{C}_{2} \mathrm{H}_{2,0}} / N_{\mathrm{H}_{2,0}}}{\left(N_{\mathrm{C}_{2} \mathrm{H}_{2,0}}-X\right) /\left(N_{\mathrm{H}_{2,0}}-2 X\right)}\right]=\frac{k}{V^{2}} t
\end{aligned}
$$

3. Solve for reaction time. The total molar conversion of acetylene at $90 \%$ fractional conversion may be found by direct application of the definitions for fractional and total molar conversion. Thus, let $X_{\mathrm{C}_{2} \mathrm{H}_{2}}$ stand for the fractional conversion of acetylene, which is defined as

$$
\frac{N_{\mathrm{C}_{2} \mathrm{H}_{2,0}}-N_{\mathrm{C}_{2} \mathrm{H}_{2}}}{N_{\mathrm{C}_{2} \mathrm{H}_{2,0}}}
$$

According to the problem statement, this equals 0.9 . Since $N_{\mathrm{C}_{2} \mathrm{H}_{2,0}}=0.001 \mathrm{~g} \cdot \mathrm{~mol}, N_{\mathrm{C}_{2} \mathrm{H}_{2}}=0.001-$ $(0.9)(0.001)=0.0001 \mathrm{~g} \cdot \mathrm{~mol}$. Similarly, from step $1, X$ equals total molar conversion of acetylene, defined as $N_{\mathrm{C}_{2} \mathrm{H}_{2,0}}-N_{\mathrm{C}_{2} \mathrm{H}_{2}}$. It is therefore equal to $(0.001-0.0001)=0.0009 \mathrm{~g} \cdot \mathrm{~mol}$.

This value for total molar conversion, along with the initial moles of $\mathrm{C}_{2} \mathrm{H}_{2}$ and $\mathrm{H}_{2}$, now allows reaction time to be calculated. Since the initial mixture is $75 \%$ hydrogen and $25 \%$ acetylene, $N_{\mathrm{H}_{2,0}}=$ $3(0.001)=0.003$. Substituting into the design equation from step 2 ,

$$
\begin{aligned}
& \frac{1}{(0.003-0.0018)(0.002-0.003)}-\frac{1}{0.003(0.002-0.003)} \\
& +\frac{1}{(0.002-0.003)^{2}} \ln \left[\frac{(0.001 / 0.003)}{(0.001-0.0009) /(0.003-0.0018)}\right]=\frac{10^{5}}{1^{2}} t
\end{aligned}
$$

Solving, $t=8.86 \mathrm{~min}$. Thus approximately 9 min is needed to convert $90 \%$ of the acetylene originally charged to the 1-L reactor to ethane.

Related Calculations. (1) The stoichiometry of the chemical reaction strongly influences the final form of the integrated design expression. Different rate expressions will lead to different functional relationships between time and total molar conversion. The preceding example was specific for an irreversible reaction, second-order in hydrogen and first-order in acetylene. If the rate expression had been simply first-order in acetylene (as might be the case with excess hydrogen), the integration of the design expression would yield

$$
-\ln \left(\frac{N_{\mathrm{C}_{2} \mathrm{H}_{2}}-X}{N_{\mathrm{C}_{2} \mathrm{H}_{2}, 0}}\right)=k t
$$

Similarly, other rate expressions yield different forms for the time, molar conversion relationship.
(2) In many cases, analytical integration of the design equation is difficult. The integral may still be evaluated, however, by (a) numerical integration methods, such as Euler or Runge-Kutta, or (b) graphic evaluation of $\int_{0}^{x} f(X) d X$ by plotting $f(X)$ versus $X$ and finding the area under the curve.

### 5.6 CALCULATING REACTION RATES FROM CONTINUOUS-FLOW STIRRED-TANK REACTOR DATA

In a study of the nitration of toluene by mixed acids, the following data were obtained in a continuousflow stirred-tank reactor. It had been previously determined that the reactor was well mixed; the composition within the reactor and in the exit stream can be considered equal. In addition, it had been determined that mass-transfer effects were not limiting the process rate. Thus the rate measured is the true kinetic rate of reaction. Calculate that rate.

| Reactor data: |  |
| :--- | :---: |
| Mixed-acid feed rate, g/h | 325.3 |
| Toluene feed rate, $\mathrm{g} / \mathrm{h}$ | 91.3 |
| Acid-phase leaving, $\mathrm{g} / \mathrm{h}$ | 301.4 |
| Organic-phase leaving, g/h | 117.3 |
| Temperature, ${ }^{\circ} \mathrm{C}\left({ }^{\circ} \mathrm{F}\right)$ | $36.1(97.0)$ |
| Stirrer speed, r/min | 1520 |
| Reactor volume, $\mathrm{cm}^{3}$ | 635 |
| Volume fraction of acid phase in reactor | 0.67 |
| Organic-phase composition: |  |
| Mononitrotoluene, mol \% | 68.1 |
| Toluene, mol \% | 31.1 |
| Sulfuric acid, mol \% | 0.8 |
| Density at $25^{\circ} \mathrm{C}, \mathrm{g} / \mathrm{cm}^{3}$ | 1.0710 |
| Feed acid-phase composition: |  |
| $\mathrm{H}_{2} \mathrm{SO}_{4}$, mol $\%$ | 29.68 |
| $\mathrm{HNO}_{3}$, mol $\%$ | 9.45 |
| $\mathrm{H}_{2} \mathrm{O}$, mol $\%$ | 60.87 |
| ${\text { Density at } 25^{\circ} \mathrm{C}, \mathrm{g} / \mathrm{cm}^{3}}^{3}$ | 1.639 |
| Spent acid composition: $^{\mathrm{H}_{2} \mathrm{SO}_{4}, \mathrm{~mol} \%}$ |  |
| $\mathrm{HNO}_{3}$, mol $\%$ | 29.3 |
| $\mathrm{H}_{2} \mathrm{O}$, mol $\%$ | 0.3 |
| $\mathrm{Density}^{\mathrm{g} / \mathrm{cm}^{3}}$ | 70.4 |

1. Check the elemental material balances. For reference, the molecular weights involved are as follows:

| Component | Molecular weight |
| :--- | :---: |
| Toluene | 92 |
| Mononitrotoluene | 137 |
| Sulfuric acid | 98 |
| Nitric acid | 63 |
| Water | 18 |

The feed consists of $0.0913 \mathrm{~kg} / \mathrm{h}$ of toluene and $0.3253 \mathrm{~kg} / \mathrm{h}$ of mixed acid. The latter stream can be considered as follows:

| Acid <br> component | Mol \% <br> (given) | Kilograms per <br> 100 mol feed | Wt \% | $\mathrm{kg} / \mathrm{h}$ |
| :--- | :---: | :---: | :---: | :---: |
| $\mathrm{H}_{2} \mathrm{SO}_{4}$ | 29.68 | 2908.6 | 63.24 | 0.2057 |
| $\mathrm{HNO}_{3}$ | 9.45 | 595.4 | 12.94 | 0.0421 |
| $\mathrm{H}_{2} \mathrm{O}$ | 60.87 | $\underline{1095.7}$ | $\underline{23.82}$ | $\underline{0.0775}$ |
|  |  | 4599.7 | 100.00 | 0.3253 |

The output consists of $0.1173 \mathrm{~kg} / \mathrm{h}$ of the organic phase and $0.3014 \mathrm{~kg} / \mathrm{h}$ of spent acid. These two streams can be considered as follows:

| Organic-phase <br> component | Mol \% <br> (given) | Kilograms per <br> 100 mol product | Wt \% | $\mathrm{kg} / \mathrm{h}$ |
| :--- | :---: | :---: | :---: | :---: |
| Toluene | 31.1 | $2,861.2$ | 23.32 | 0.0274 |
| Mononitrotoluene | 68.1 | $9,329.7$ | 76.04 | 0.0892 |
| Sulfuric acid | 0.8 | $\underline{78.4}$ | $\underline{0.64}$ | $\underline{0.0007}$ |
|  |  | $12,269.3$ | 100.00 | 0.1173 |


| Spent-acid-phase <br> component | Mol \% <br> (given) | Kilograms per <br> 100 mol acid | $\mathrm{Wt} \%$ | $\mathrm{~kg} / \mathrm{h}$ |
| :---: | :---: | :---: | ---: | :---: |
| $\mathrm{H}_{2} \mathrm{SO}_{4}$ | 29.3 | 2871.4 | 69.07 | 0.2082 |
| $\mathrm{HNO}_{3}$ | 0.3 | 18.9 | 0.45 | 0.0014 |
| $\mathrm{H}_{2} \mathrm{O}$ | $\underline{70.4}$ | $\underline{1267.2}$ | $\underline{30.48}$ | $\underline{0.0918}$ |
|  | 100.0 | 4157.5 | 100.00 | $\underline{0.3014}$ |

The elemental material balances can then be checked. For carbon:

| Component | $\mathrm{kg} / \mathrm{h}$ of C in | $\mathrm{kg} / \mathrm{h}$ of C out |
| :--- | :---: | :---: |
| Toluene | 0.0834 | 0.0250 |
| Mononitrotoluene | $\underline{0.0000}$ | $\underline{0.0547}$ |
|  | 0.0834 | 0.0797 |
| Percent difference in $\mathrm{C}=(100)(0.0834-0.0797) / 0.0834=4.44 \%$ |  |  |

For hydrogen:

| Component | $\mathrm{kg} / \mathrm{h}$ of H in | $\mathrm{kg} / \mathrm{h}$ of H out |
| :--- | :---: | :---: |
| Mononitrotoluene | 0.0000 | 0.0046 |
| Toluene | 0.0079 | 0.0024 |
| $\mathrm{H}_{2} \mathrm{SO}_{4}$ | 0.0042 | 0.0043 |
| $\mathrm{HNO}_{3}$ | 0.0007 | 0.0000 |
| $\mathrm{H}_{2} \mathrm{O}$ | $\underline{0.0086}$ | $\underline{0.0102}$ |
|  | 0.0214 | 0.0215 |

Percent difference in $\mathrm{H}=(100)(0.0215-0.0214) / 0.0214=0.5 \%$

For oxygen:

| Component | $\mathrm{kg} / \mathrm{h}$ of O in | $\mathrm{kg} / \mathrm{h}$ of O out |
| :--- | :---: | :---: |
| Mononitrotoluene | 0.0000 | 0.0208 |
| $\mathrm{H}_{2} \mathrm{SO}_{4}$ | 0.1343 | 0.1364 |
| $\mathrm{HNO}_{3}$ | 0.0321 | 0.0011 |
| $\mathrm{H}_{2} \mathrm{O}$ | $\underline{0.0689}$ | $\underline{0.0816}$ |
|  | 0.2353 | 0.2399 |

Percent difference in $\mathrm{O}=(100)(0.2399-0.2353) / 0.2353=2 \%$

The elemental balances for $\mathrm{C}, \mathrm{H}$, and O suggest that the run is reasonably consistent (because the percent differences between feed and product are small), so there is no need to make material balances for the other elements.
2. Employ the material-balance data to determine the reaction rate. In a continuous-flow stirredtank reactor, the material balance for component $A$ is as follows at steady state:

Rate of input of $A$ - rate of output of $A+$ rate of generation of $A=0$
Thus,

$$
\left(F_{A 0}-F_{A}\right)+r_{A} V=0
$$

where $F_{A 0}, F_{A}=$ inlet and outlet molar flow rates
$r_{A}=$ rate of reaction per unit volume of organic phase
$V=$ volume of the organic phase
Rearranging the material balance,

$$
-r_{A}=\frac{F_{A 0}-F_{A}}{V}=\frac{W_{A 0}-W_{A}}{M V}
$$

where $W_{A 0}$ and $W_{A}$ are mass flow rates, and $M$ is the molecular weight of $A$.
The reaction stoichiometry is as follows:

$$
\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CH}_{3}+\mathrm{HNO}_{3} \xrightarrow[\mathrm{H}_{2} \mathrm{O}]{\mathrm{H}_{2} \mathrm{SO}_{4}} \mathrm{C}_{6} \mathrm{H}_{4}\left(\mathrm{CH}_{3}\right)\left(\mathrm{NO}_{2}\right)+\mathrm{H}_{2} \mathrm{O}
$$

Since the reaction involves 1 mol of each component, $r$ (toluene) $=r\left(\mathrm{HNO}_{3}\right)=-r($ mononitrotoluene $)=-r\left(\mathrm{H}_{2} \mathrm{O}\right)$.

From the reactor data given in the statement of the problem, the organic-phase volume is $0.33(0.635 \mathrm{~L})=0.210 \mathrm{~L}$. Thus, by material balance, the computed rates are

| Component | $r, \mathrm{~kg} \cdot \mathrm{~mol} /(\mathrm{h})(\mathrm{L})$ |
| :--- | :---: |
| Toluene | 0.00331 |
| $\mathrm{HNO}_{3}$ | 0.00308 |
| Mononitrotoluene | 0.00310 |
| Water | 0.00370 |

These can be averaged to give the mean rate of reaction: $0.00330 \pm 0.00021 \mathrm{~kg} \cdot \mathrm{~mol} /(\mathrm{h})(\mathrm{L})$. For a reactant (e.g., toluene), a minus sign should be placed in front of it.

Related Calculations. In this example, it was stated at the outset that mass-transfer effects were not limiting the process rate. In the general case, however, it is important to calculate the effect of mass-transfer resistance on the reaction rate.

Consider, for instance, the gasification of porous carbon pellets in a fixed-bed reactor using steam and oxygen; the reaction rate could be affected both by external-film mass transfer and by porediffusion mass transfer.

The first of these pertains to the stagnant film separating the particle surface from the bulk gas. At steady state, the rate of transport to the surface is given by the standard mass-transfer expression

$$
W=k_{m} A_{p} C\left(Y_{B}-Y_{S}\right)=k_{m} A_{p}\left(C_{B}-C_{S}\right)
$$

where $W=$ transfer rate, in moles per time per weight of solid
$k_{m}=$ mass-transfer coefficient, in length per time
$A_{p}=$ external surface area per weight of solid
$Y_{B}=$ bulk-gas concentration, in mole fraction units
$Y_{S}=$ concentration of gas adjacent to surface, in mole fraction units
$C=$ total gas concentration, in moles per volume
$C_{B}=$ concentration of component in the bulk, in moles per volume
$C_{S}=$ concentration of component adjacent to surface, in moles per volume.
The mass-transfer coefficient $k_{m}$ is a weak function of absolute temperature and velocity. The total concentration $C$ is given approximately by the ideal-gas law $C=P /(R T)$, where $P$ is absolute pressure, $R$ is the gas constant, and $T$ is absolute temperature.

In fixed-bed operation, Satterfield [1] recommends correlations for mass (and heat) transfer coefficients based on the Colburn $j$ factor, defined as follows:

$$
j=\frac{k_{m}}{\left(\rho^{*} V\right)} S c^{2 / 3}
$$

where $j=$ Colburn $j$ factor, dimensionless
$k_{m}=$ mass-transfer coefficient, in moles per unit of time per unit area of particle surface
$\rho^{*}=$ molar density, in moles per volume
$V=$ superficial velocity, based on empty reactor tube
$S c=$ Schmidt number, $\mu / \rho D$, dimensionless
$\mu=$ viscosity
$\rho=$ mass density
$D=$ diffusivity through the film

The $j$ factor depends on the external bed porosity $\epsilon$ and the Reynolds number, $R e=D_{p} V \rho / \mu$, where $D_{p}$ is the particle diameter, as follows:

$$
\epsilon j=\frac{0.357}{R e^{0.359}} \quad 3 \leq R e \leq 2000
$$

The appropriate particle diameter is given as

$$
D_{p}=\frac{6 V_{\mathrm{ex}}}{S_{\mathrm{ex}}}
$$

where $V_{\mathrm{ex}}=$ volume of particle
$S_{\text {ex }}=$ surface area of particle
External mass transfer reduces the concentration of reactant gas close to the particle surface and thus reduces the overall process rate. Thus, consider gasification to be a first-order reaction. Then at steady state, the rate of gasification equals the rate of mass transfer. For a nonporous solid, the surface reaction (whose rate constant is $k^{*}$ ) consumes the diffusing reactant:

$$
k^{*} C_{S}=k_{m} A_{p}\left(C_{B}-C_{S}\right)
$$

Solving for the surface concentration yields

$$
C_{S}=\frac{k_{m} A_{p} C_{B}}{k^{*}+k_{m} A_{p}}
$$

Now, the process rate is given by

$$
-r_{c}=k^{*} C_{S}=\frac{k^{*} k_{m} A_{p} C_{B}}{k^{*}+k_{m} A_{p}}
$$

So, if the mass-transfer rate constant $k_{m}$ is large in comparison to $k^{*}$, the rate reduces to $-r_{c}=k^{*} C_{B}$; that is, the true kinetic rate is based directly on the bulk concentration.

Next, consider the effect of pore diffusion on the reaction rate. The gasification reaction occurs principally within the particle. Except at very high temperatures, reactants must diffuse into the pore to the reacting surface. The average reaction rate within the particle may be related to the rate based on the surface concentration in terms of an effectiveness factor $\eta$ defined as

$$
\eta=\frac{r_{\mathrm{avg}}}{r_{\text {surface }}}
$$

The effectiveness factor is a function of a dimensionless group termed the "Thiele modulus," which depends on the diffusivity in the pore, the rate constant for reaction, pore dimension, and external surface concentration $C_{S}$.

The effectiveness factor for a wide range of reaction kinetic models differs little from that of the first-order case. For an isothermal particle, the first-order reaction effectiveness factor is given as

$$
\eta=\frac{\tanh \phi}{\phi}
$$

where $\phi$ is the Thiele modulus, that is,

$$
\phi=L_{p}\left(\frac{k C_{S}^{m-1}}{V_{p} D}\right)^{1 / 2}
$$

and where $L_{p}=$ effective pore length, $\mathrm{cm}=R / 3$ for spheres ( $R=$ particle radius)
$k=$ reaction rate constant
$C_{S}=$ external surface concentration, in moles per cubic centimeter
$m=$ reaction order (equal to 1 for first-order)
$V_{p}=$ pore volume, in cubic centimeters per gram
$D=$ diffusivity
When porous solids are being used as catalysts or as reactants, the rate constant $k^{*}$ in the global equation is replaced by $\eta k^{*}$. Consequently, this equation applies to porous solids as well as nonporous solids.

When diffusion is fast relative to surface kinetics, $\phi \rightarrow 0, \eta \rightarrow 1$, and $r_{\text {avg }}=r_{\text {surface }}$. Under these conditions, all the pore area is accessible and effective for reaction. When $\phi \rightarrow \infty$, that is, when diffusion is slow relative to kinetics, the reaction occurs exclusively at the particle external surface; reactant gas does not penetrate into the pores.

External mass transport generally becomes dominant at temperatures higher than that at which pore diffusion limits the gasification rate. For small particles, smaller than 20 mesh, mass-transfer limitations generally are not important because these particles have external surface areas that are large compared with their unit volume. Furthermore, mass-transfer coefficients are greater in fluidbed operations owing to the motion of the solid particles. Thus in fluid-bed operations, external mass-transfer limitation in the temperature region below about 900 to $1100^{\circ} \mathrm{C}$ is never important. For fixed-bed operation, however, mass transfer to large particles can be important.

### 5.7 TOTAL SURFACE AREA, ACTIVE SURFACE AREA, POROSITY, AND MEAN PORE RADIUS OF A CATALYST

A catalyst composed of $10 \mathrm{wt} \%$ nickel on $\gamma$-alumina is used to promote the catalytic methanation reaction

$$
\mathrm{CO}+3 \mathrm{H}_{2} \rightarrow \mathrm{CH}_{4}+\mathrm{H}_{2} \mathrm{O}
$$

The important properties of the catalyst for characterization purposes are the total surface area, dispersion of metallic nickel, pore volume, and mean pore radius. Determine each of these, using the experimental data given in the respective calculation steps.

## Calculation Procedure

1. Calculate the total surface area. The weight gain of the catalyst due to the physical adsorption of nitrogen under various nitrogen pressures is a function of, and thus an indicator of, total surface area. The first three columns of Table 5.1 show the weight of adsorbed nitrogen and the corresponding pressure for experimental runs conducted at the atmospheric boiling point of liquid nitrogen.

The most common way of analyzing such data is by using the so-called BET equation. For multilayer adsorption, this equation can be set out in the form

$$
\frac{P}{W\left(P^{*}-P\right)}=\frac{1}{W_{m} C}+\frac{C-1}{C W_{m}} \frac{P}{P^{*}}
$$

where $W$ is weight adsorbed per gram of catalyst at pressure $P, P^{*}$ is the vapor pressure of the adsorbent, $C$ is a parameter related to the heat of adsorption, and $W_{m}$ is the weight for monolayer coverage of the solid.

The last-named variable is the one of interest in the present case, because it represents the weight of adsorbed nitrogen that just covers the entire surface of the catalyst, internal and external. (Because the catalyst is highly porous, most of the area is pore wall and is internal to the solid.)

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TABLE 5.1 BET Calculations for Prototype Catalyst (Example 5.7)

| $W, \mathrm{mg} / \mathrm{g}$ | $P, \mathrm{mmHg}$ | $P, \mathrm{kPa}$ | $\frac{P}{\left(P^{*}-P\right) W} \times 10^{3}$ | $P / P^{*} \times 10^{2}$ |
| :---: | :---: | :---: | :---: | :---: |
| 13 | 6.25 | 0.83 | 0.637 | 0.82 |
| 17 | 15.6 | 2.08 | 1.233 | 2.05 |
| 20 | 25.0 | 3.33 | 1.700 | 3.29 |
| 22 | 34.4 | 4.59 | 2.155 | 4.53 |
| 25 | 56.3 | 7.50 | 3.200 | 7.41 |
| 28 | 84.4 | 11.2 | 4.462 | 11.11 |
| 32 | 163.0 | 21.7 | 8.532 | 21.45 |

$$
\begin{aligned}
\text { Note: } & \text { Let } y=P /\left(P^{*}-P\right) W, X=P / P^{*}, y=S x+I . \text { By least squares, } \\
D & =(\Sigma x)^{2}-n \Sigma x^{2} \\
S & =(\Sigma y \Sigma x-n \Sigma x y) / D \\
I & =\left(\Sigma x \Sigma x y-\Sigma y \Sigma x^{2}\right) / D \\
\Sigma y & =21.92 \times 10^{-3} \\
\Sigma x y & =2.747 \times 10^{-3} \\
\Sigma x^{2} & =0.06747 \\
\Sigma x & =0.5066 \\
n & =7 \\
S & =0.037 \mathrm{mg}^{-1} \\
I & =4.05 \times 10^{-4} \mathrm{mg}^{-1}
\end{aligned}
$$

Now, from the form of the equation, a plot of $P /\left[W\left(P^{*}-P\right)\right]$ against $P / P^{*}$ should yield a straight line. Let $S$ and $I$, respectively, stand for the slope $(C-1) /\left(C W_{m}\right)$ and the intercept $1 /\left(W_{m} C\right)$ of that line. Then, by algebraic rearrangement, $W_{m}=1 /(S+I)$. Since the tests were conducted at the atmospheric boiling point, $P^{*}$ was essentially $760 \mathrm{mmHg}(101.3 \mathrm{kPa})$.

Values for $P /\left[W\left(P^{*}-P\right)\right]$ and $P / P^{*}$ appear in the fourth and fifth columns of Table 5.1. Application of ordinary least-squares regression analysis to the resulting plot (not shown) shows $S$ to be $0.0377 \mathrm{mg}^{-1}$ and $I$ to be $4.05 \times 10^{-4} \mathrm{mg}^{-1}$. Therefore, $W_{m}=26.26 \mathrm{mg}$ nitrogen per gram of catalyst. This equals $0.02626 / 28=9.38 \times 10^{-4} \mathrm{~g} \cdot \mathrm{~mol}$ nitrogen. Employing Avogadro's number, this is $\left(9.38 \times 10^{-4}\right)\left(6.023 \times 10^{23}\right)=5.65 \times 10^{20}$ nitrogen molecules. Finally, the nitrogen molecule can be taken to have a surface area of $15.7 \times 10^{-20} \mathrm{~m}^{2}$. Therefore, the surface area of the catalyst (in intimate contact with the nitrogen monolayer) can be estimated to be $\left(5.65 \times 10^{20}\right)\left(15.7 \times 10^{-20}\right)$, or about $89 \mathrm{~m}^{2} / \mathrm{g}$.
2. Estimate the dispersion of the nickel. Hydrogen dissociatively adsorbs on nickel whereas it does not interact with the catalyst support and is not significantly adsorbed within the nickel crystal lattice. Therefore, the amount of uptake of hydrogen by the catalyst is a measure of how well the nickel has been dispersed when deposited on the support.

At several pressures up to atmospheric, uptake of hydrogen proved to be constant, at $0.256 \mathrm{mg} / \mathrm{g}$ of catalyst, suggesting that the exposed nickel sites were saturated.

Thus, per gram of catalyst, the atoms of hydrogen adsorbed equals $\left(0.256 \times 10^{-3} \mathrm{~g}\right)(1 / 2$ $\mathrm{mol} / \mathrm{g})(2$ atoms $/$ molecule $)\left(6.023 \times 10^{23}\right.$ molecules $\left./ \mathrm{mol}\right)=1.542 \times 10^{20}$ atoms. This can also be taken as the number of surface nickel atoms. Now, since the catalyst consists of $10 \%$ nickel, the total number of nickel atoms per gram of catalyst equals $(0.1 \mathrm{~g})(1 / 58.71 \mathrm{~mol} / \mathrm{g})\left(6.023 \times 10^{23}\right.$ atoms $\left./ \mathrm{mol}\right)=$ $1.0259 \times 10^{21}$ atoms. Therefore, the degree of dispersion of the nickel equals (surface nickel atoms $) /($ total nickel atoms $)=\left(1.542 \times 10^{20}\right) /\left(1.0259 \times 10^{21}\right)=0.15$. Thus only 15 percent of the nickel deposited has been dispersed and is available for catalysis.
3. Calculate the porosity and the mean pore radius. The particle porosity may be readily determined by a helium pycnometer and a mercury porosimeter. In the pycnometer, the solid skeletal volume $V_{S}$ is obtained. The skeletal density $\rho_{S}$ is found from the sample weight $W_{S}$ :

$$
\rho_{S}=\frac{W}{V_{S}}
$$

The total sample volume $V_{A}$, including pores, can be determined by mercury displacement at atmospheric pressure, since mercury will not enter the pores under these conditions. The apparent density $\rho_{A}$, then, is

$$
\rho_{A}=\frac{W}{V_{A}}
$$

And the porosity $\epsilon$ of the solid is given by

$$
\epsilon=1-\rho_{A} / \rho_{S}
$$

For the catalyst in question, the apparent density is $1.3 \mathrm{~kg} / \mathrm{dm}^{3}$ and the skeletal density is $3.0 \mathrm{~kg} / \mathrm{dm}^{3}$. The porosity is therefore $\epsilon=1-1.3 / 3=0.57$.

The pore volume $V_{p}$ equals the porosity divided by the apparent density: $V_{p}=\epsilon / \rho_{A}=0.57 / 1.3=$ $0.44 \mathrm{dm}^{3} / \mathrm{kg}=0.44 \mathrm{~cm}^{3} / \mathrm{g}$. Assuming cylindrical pores of uniform length and radius,

$$
\frac{V_{p}}{A_{p}}=\frac{n \pi R_{p}^{2} L_{p}}{n 2 \pi R_{p} L_{p}}
$$

where $n=$ number of pores
$A_{p}=$ pore surface area (calculated in step 1)
$R_{p}=$ pore radius
$L_{p}=$ pore length
Therefore,

$$
R_{p}=\frac{2 V_{p}}{A_{p}}=\frac{2\left(0.44 \mathrm{~cm}^{3} / \mathrm{g}\right)}{89 \mathrm{~m}^{2} / \mathrm{g}}=99 \times 10^{-10} \mathrm{~m}(99 \AA)
$$

### 5.8 SIZING AND DESIGN OF A SYSTEM OF STIRRED-TANK REACTORS

It is proposed to process $3 \mathrm{~m}^{3} / \mathrm{h}$ of a reaction mixture in either one or two (in series) continuous-flow stirred-tank reactors. The reaction is $A+2 B \rightarrow C$. At $50^{\circ} \mathrm{C}$, the kinetic rate expression is as follows:

$$
-r_{A}=k_{1} C_{A} C_{B} /\left(1+k_{2} C_{A}\right)
$$

where $k_{1}=0.1$ and $k_{2}=0.6$, with concentrations in kilogram-moles per cubic meter and rates in kilogram-moles per cubic meter per hour.

The mixture specific gravity is constant and equal to $1.2 \mathrm{~kg} / \mathrm{dm}^{3}$. The molecular weight of the feed is 40 . The feed contains $10 \mathrm{~mol} \% A, 20 \% \mathrm{~B}$, and $70 \%$ inert solvent $S$. The liquid viscosity is 0.8 $\mathrm{mPa} \cdot \mathrm{s}(\mathrm{cp})$ at reaction temperature.

Determine the reactor volume required for one reactor and that for two equal-sized reactors in series for 80 percent conversion of $A$. And if the capital cost of a continuous-flow stirred-tank reactor unit is given by $200,000(V / 100)^{0.6}$ (where $V$ is reactor volume in $\mathrm{m}^{3}$ ), the life is 20 years with no salvage value, and power costs 3 cents per kilowatt-hour, determine which system has the economic advantage. Assume that overhead, personnel, and other operating costs, except agitation, are constant. The operating year is 340 days. Each reactor is baffled (with a baffle width to tank diameter of $1 / 12$ ) and equipped with an impeller whose diameter is one-third the tank diameter. The impeller is a sixbladed turbine having a width-to-diameter ratio of $1 / 5$. The impeller is located at one-third the liquid depth from the bottom. The tank liquid-depth-to-diameter ratio is unity.

## Calculation Procedure

## 1. Develop the necessary material-balance expressions for a single reactor, and find its volume.

 For a single reactor, the mass-balance design equation is$$
V=\frac{F_{A, 0}-F_{A}}{-r_{A}}=\frac{X}{-r_{A}}
$$

where $V$ is the volume of material within the reactor, $F_{A, 0}$ is inlet molar flow rate of species $A, F_{A}$ is its exit molar flow rate, and $X$ is moles of $A$ reacted per unit of time. As noted, $F_{A}=\left(F_{A, 0}-X\right)$, and since the reaction of $1 \mathrm{~mol} A$ involves $2 \mathrm{~mol} B$ and yields $1 \mathrm{~mol} C$, and since the inlet is $10 \% A$ and $20 \% B, F_{B}=F_{B, 0}-2 X=2\left(F_{A, 0}-X\right)$ and $F_{C}=X$. Because the solvent is inert, $F_{S}=F_{S, 0}$.

Now,

$$
-r_{A}=\frac{K_{1} C_{A} C_{B}}{1+K_{2} C_{A}}=\frac{K_{1}\left(F_{A} / v\right)\left(F_{B} / v\right)}{1+K_{2}\left(F_{A} / v\right)}=\frac{2 K_{1}\left(F_{A} / \nu\right)^{2}}{1+K_{2}\left(F_{A} / v\right)}
$$

where $v$ is the volumetric flow rate at the outlet (which equals the inlet volumetric rate, since the system is of constant density).

Since $80 \%$ conversion of $A$ is specified, $X / F_{A, 0}=0.8$. And since the total inlet molar flow rate $F_{T, 0}$ is $10 \% A$,

$$
F_{A, 0}=0.1 F_{T, 0}=0.1\left(\frac{3 \mathrm{~m}^{3}}{\mathrm{~h}} \times \frac{1.2 \mathrm{~kg}}{\mathrm{dm}^{3}} \times\left(\frac{10 \mathrm{dm}}{\mathrm{~m}}\right)^{3} \times \frac{1 \mathrm{~kg} \cdot \mathrm{~mol}}{40 \mathrm{~kg}}\right)=9 \mathrm{~kg} \cdot \mathrm{~mol} / \mathrm{h}
$$

Therefore, the molar conversion rate $X$ is $0.8(9)=7.2 \mathrm{~kg} \cdot \mathrm{~mol} / \mathrm{h}$. The outlet concentration of $A$ is given by

$$
C_{A}=F_{A} / v=\left(F_{A, 0}-X\right) / v=\frac{9-7.2}{3} \frac{(\mathrm{~kg} \cdot \mathrm{~mol} / \mathrm{h})}{\left(\mathrm{m}^{3} / \mathrm{h}\right)}=0.600 \mathrm{~kg} \cdot \mathrm{~mol} / \mathrm{m}^{3}
$$

Thus the rate at the outlet conditions is given by

$$
-r_{A}=\frac{(2)(0.1)(0.6)^{2}}{1+(0.6)(0.6)}=0.053 \mathrm{~kg} \cdot \mathrm{~mol} /\left(\mathrm{m}^{3}\right)(\mathrm{h})
$$

Finally, the volume is

$$
V=X /-r_{A}=\frac{7.2 \mathrm{~kg} \cdot \mathrm{~mol} / \mathrm{h}}{0.053 \mathrm{~kg} \cdot \mathrm{~mol} /\left(\mathrm{m}^{3}\right)(\mathrm{h})}=136 \mathrm{~m}^{3}\left(4803 \mathrm{ft}^{3}\right)
$$

2. Develop the equations for two reactors in series, and find their volume. For a pair of reactors in series, define $X_{1}$ and $X_{2}$ as the moles of $A$ reacted per unit of time in reactors 1 and 2, respectively. Then,

$$
V=X_{1} /-r_{A 1}=X_{2} /-r_{A 2} \quad \text { and } \quad X_{1}+X_{2}=7.2 \mathrm{~kg} \cdot \mathrm{~mol} / \mathrm{h}
$$

Therefore,

$$
\frac{X_{1}}{7.2-X_{1}}=\frac{-r_{A 1}}{-r_{A 2}}
$$

By material balance,

$$
-r_{A 1}=\frac{2 K_{1}\left(F_{A, 0}-X_{1}\right)^{2} / \nu^{2}}{1+K_{2}\left(F_{A, 0}-X_{1}\right) / v} \quad \text { and } \quad-r_{A 2}=\frac{2 K_{1}\left(F_{A, 0}-X_{1}-X_{2}\right)^{2} / \nu^{2}}{1+K_{2}\left(F_{A, 0}-X_{1}-X_{2}\right) / \nu}
$$

Now, the rate $-r_{A 2}$ is the same as the rate for the single reactor, since $X_{1}+X_{2}=$ overall conversion; therefore, $-r_{A 2}=0.053 \mathrm{~kg} \cdot \mathrm{~mol} /\left(\mathrm{m}^{3}\right)(\mathrm{h})$. Accordingly,

$$
\frac{0.053 X_{1}}{7.2-X_{1}}=\frac{2 K_{1}\left(F_{A, 0}-X_{1}\right)^{2} / \nu^{2}}{1+K_{2}\left(F_{A, 0}-X_{1}\right) / v}=\frac{0.022\left(9-X_{1}\right)^{2}}{1+0.2\left(9-X_{1}\right)}
$$

Solution of this cubic equation (by, for example, Newton's method) gives $X_{1}=5.44$. Therefore, the volume for each reactor is as follows:

$$
V=\frac{X_{2}}{-r_{A 2}}=\frac{7.2-X_{1}}{-r_{A 2}}=\frac{1.76}{0.053}=33.2 \mathrm{~m}^{3}\left(1173 \mathrm{ft}^{3}\right)
$$

3. Conduct an economic analysis and decide between the one- and two-reactor systems. The two costs to be considered are depreciation of capital and power cost for agitation. Using the volumes, 20-year life with no salvage, and the straight-line depreciation method:

| System | Capital cost | Annual depreciation <br> expense |
| :--- | :---: | :---: |
| One reactor, $136 \mathrm{~m}^{3}$ | $\$ 240,520$ | $\$ 12,026$ |
| Two reactors, each $33.2 \mathrm{~m}^{3}$ | 206,415 | 10,321 |

For normal mixing, the Pfaudler agitation-index ( $\gamma$ ) number for this low-viscosity fluid is $2 \mathrm{ft}^{2} / \mathrm{s}^{3}$. Most stirrers are designed for impeller Reynolds numbers of 1000 or greater. For the impeller specified, the power number $\psi_{n}$ is 0.6 at high Reynolds numbers [2].

The required impeller diameter $D_{i}$ may be calculated from the given data. With the liquid height $H_{L}$ equal to the tank diameter $D_{t}$,

$$
V=\frac{\pi D_{t}^{2}}{4}\left(D_{t}\right) \quad D_{i}=1 / 3 D_{t}
$$

For the two cases, the impeller diameters are thus found to be $1.86 \mathrm{~m}(6.10 \mathrm{ft})$ and $1.16 \mathrm{~m}(3.81 \mathrm{ft})$, respectively. In terms of the Pfaudler index, for low-viscosity liquids,

$$
3 \gamma=\frac{4 n^{3} D_{i}^{2}}{\pi} \psi_{n}\left(\frac{D_{i}}{D_{t}}\right)^{2} \frac{D_{i}}{H_{L}}
$$

where $n$ is the mixer revolutions per minute. Solving this equation for $n$, and noting that $\gamma=2 \mathrm{ft}^{2} / \mathrm{s}^{3}=$ $0.186 \mathrm{~m}^{2} / \mathrm{s}^{3}$, the mixer revolutions per minute is given as follows:

$$
n=60 \mathrm{~s} / \mathrm{m}\left[\frac{3 \gamma \pi}{4 D_{i}^{2}} \psi_{n}\left(\frac{D_{t}}{D_{i}}\right)^{3}\right]^{1 / 3}=\frac{162.1}{\left(D_{i}\right)^{2 / 3}} \mathrm{r} / \mathrm{min}
$$

Substituting the impeller diameter in meters gives $107.2 \mathrm{r} / \mathrm{min}$ for the large tank and $146.8 \mathrm{r} / \mathrm{min}$ for each small tank. The Reynolds numbers

$$
R e=\frac{n D_{i}^{2} \rho_{L}}{\mu_{L}}
$$

are $9.27 \times 10^{6}$ for the large and $4.95 \times 10^{6}$ for the small tank, respectively, so the assumption of 0.6 power number is satisfactory.

From the definition of the power number,

$$
\psi_{n}=\frac{P}{\rho_{L} n^{3} D_{i}^{5}}
$$

Therefore,

$$
P=\psi_{n} \rho_{L} n^{3} D_{i}^{5}(\mathrm{~kg})\left(\mathrm{m}^{5}\right) /\left(\mathrm{dm}^{3}\right)\left(\mathrm{s}^{3}\right)
$$

For the two cases, the power consumption is calculated to be $91,417 \mathrm{~N} \cdot \mathrm{~m} / \mathrm{s}$ and $22,150 \mathrm{~N} \cdot \mathrm{~m} / \mathrm{s}$ for a large and small tank, respectively ( 1 watt $=1 \mathrm{~N} \cdot \mathrm{~m} / \mathrm{s}$ ). The power consumption on an annual basis is $745,960 \mathrm{~kW}$ for the large tank and $361,490 \mathrm{~kW}$ for two small tanks. Therefore, the annual cost advantage is as follows:

| System | Depreciation | Power | Total cost |
| :--- | :---: | :---: | :---: |
| 1 tank | $\$ 12,026$ | $\$ 22,379$ | $\$ 34,405$ |
| 2 tanks | 10,321 | 10,845 | 21,166 |

The benefit for the two-tank system is $\$ 13,239$ per year.
For more detail on cost engineering, see Section 18. And for more on mixers, see Section 12.

### 5.9 DETERMINATION OF REACTION-RATE EXPRESSIONS FROM PLUG-FLOW-REACTOR DATA

A $25-\mathrm{cm}$-long by $1-\mathrm{cm}$-diameter plug-flow reactor was used to investigate the homogeneous kinetics of benzene dehydrogenation. The stoichiometric equations are as follows:

Reaction 1: $\quad 2 \mathrm{C}_{6} \mathrm{H}_{6} \rightleftarrows \mathrm{C}_{12} \mathrm{H}_{10}+\mathrm{H}_{2} \quad\left[2 \mathrm{Bz} \rightleftarrows \mathrm{Bi}+\mathrm{H}_{2}\right]$
Reaction 2: $\mathrm{C}_{6} \mathrm{H}_{6}+\mathrm{C}_{12} \mathrm{H}_{10} \rightleftarrows \mathrm{C}_{18} \mathrm{H}_{14}+\mathrm{H}_{2} \quad\left[\mathrm{Bz}+\mathrm{Bi} \rightleftarrows \mathrm{Tri}+\mathrm{H}_{2}\right]$
At $760^{\circ} \mathrm{C}\left(1400^{\circ} \mathrm{F}\right)$ and $101.325 \mathrm{kPa}(1 \mathrm{~atm})$, the data in Table 5.2 were collected. Find rate equations for the production of biphenyl (Bi) and triphenyl (Tri) at $760^{\circ} \mathrm{C}$ by the differential method.

TABLE 5.2 Kinetics of Benzene Dehydrogenation (Example 5.9)

| Residence time |  | Mole fraction in product |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\left(\mathrm{ft}^{3}\right)(\mathrm{h})$ | $\left(\mathrm{dM}^{3}\right)(\mathrm{h})$ |  |  |  |  |
| $\overline{\mathrm{lb} \cdot \mathrm{mol}}$ | $\overline{\mathrm{kg} \cdot \mathrm{mol}}$ | Benzene | Biphenyl | Triphenyl | Hydrogen |
| 0 | 0 | 1.0 | 0 | 0 | 0 |
| 0.01 | 0.129 | 0.941 | 0.0288 | 0.00051 | 0.0298 |
| 0.02 | 0.257 | 0.888 | 0.0534 | 0.00184 | 0.0571 |
| 0.06 | 0.772 | 0.724 | 0.1201 | 0.0119 | 0.1439 |
| 0.12 | 1.543 | 0.583 | 0.163 | 0.0302 | 0.224 |
| 0.22 | 2.829 | 0.477 | 0.179 | 0.0549 | 0.289 |
| 0.30 | 3.858 | 0.448 | 0.175 | 0.0673 | 0.310 |
| $\infty$ | $\infty$ | 0.413 | 0.157 | 0.091 | 0.339 |

## Calculation Procedure

1. Calculate equilibrium constants. From the data, the equilibrium constants for the two reactions, respectively, may be determined as follows (see Section 4):

$$
K_{1}=\frac{a_{\mathrm{Bi}} a_{\mathrm{H}_{2}}}{a_{\mathrm{Bz}}^{2}} \quad K_{2}=\frac{a_{\mathrm{Tr}} a_{\mathrm{H}_{2}}}{a_{\mathrm{Bz}} a_{\mathrm{Bi}}}
$$

where $a_{i}$ is the activity of species $i$. For the standard state being ideal gases at 101.325 kPa and $760^{\circ} \mathrm{C}$, the activity for the Bi component, for example, is

$$
a_{\mathrm{Bi}}=\frac{\hat{f}_{\mathrm{Bi}}}{f_{\mathrm{Bi}}^{\circ}}=\frac{\hat{f}_{\mathrm{Bi}}}{101.325}=\frac{\hat{\phi}_{\mathrm{Bi}} y_{\mathrm{Bi}} P}{101.325}
$$

where $f$ is fugacity, $\phi$ is fugacity coefficient, $y$ is mole fraction, and $P$ is pressure. Assuming that the gases are ideal, $\phi_{\mathrm{Bi}}=1$, so $a_{\mathrm{Bi}}=y_{\mathrm{Bi}}$, and in general, $a_{i}=y_{i}$.

The mole fractions at infinite residence time can be taken as the equilibrium mole fractions. Then, from the preceding data, $K_{1}=a_{\mathrm{Bi}} a_{\mathrm{H}_{2}} / a_{\mathrm{Bz}}^{2}=(0.157)(0.339) /(0.413)^{2}=0.312$, and $K_{2}=a_{\mathrm{Tr}} a_{\mathrm{H}_{2}} / a_{\mathrm{Bz}} a_{\mathrm{Bi}}=(0.091)(0.339) /(0.413)(0.157)=0.476$.
2. Develop the reactor mass balance. Let $x=\mathrm{mol} / \mathrm{h}$ of benzene reacted by reaction 1 and $y=$ $\mathrm{mol} / \mathrm{h}$ of benzene reacted by reaction 2 , and let $F_{i, 0}$ and $F_{i}$ be the moles per hour of species $i$ in the inflow and outflow, respectively. Then, noting that each mole of benzene in reaction 1 involves one-half mole each of biphenyl and hydrogen,

$$
\begin{aligned}
F_{\mathrm{Bz}} & =F_{\mathrm{Bz}, 0}-x-y \\
F_{\mathrm{Bi}} & =F_{\mathrm{Bi}, 0}+x / 2-y \\
F_{\mathrm{H}_{2}} & =F_{\mathrm{H}_{2}, 0}+x / 2+y \\
F_{\mathrm{Tri}} & =F_{\mathrm{Tri}, 0}+y
\end{aligned}
$$

Adding these four equations and letting subscript $t$ stand for moles per hour,

$$
F_{t}=F_{t, 0}=F_{\mathrm{Bz}, 0} \quad \text { and } \quad F_{\mathrm{Bi}, 0}=F_{\mathrm{H}_{2}, 0}=F_{\mathrm{Tr}, 0}=0
$$

Now, for a plug-flow reactor, the material balance is as follows for a differential volume at steady state:
(Rate of $A$ input by flow $)-($ rate of $A$ output by flow $)+($ rate of $A$ generated $)=0$
or

$$
F_{A, 0}-\left(F_{A, 0}+d F_{A}\right)+r_{A} d V=0
$$

where $r_{A}$ is the reaction rate for $A$ and $V$ is the reaction volume. Therefore, $r_{A}=d F_{A} / d V$. In this case, $F_{A}=y_{A} F_{t, 0}$; thus, $d F_{A}=F_{t, 0} d y_{A}$, and the material balance becomes

$$
r_{A}=F_{t, 0} \frac{d y_{A}}{d V}=\frac{d y_{A}}{d\left(V / F_{t, 0}\right)}
$$

where $V / F_{t, 0}$ is residence time in the reactor. Thus the reaction rate is the slope of the concentration-versus-residence-time plot.
3. Calculate reaction rates. For the homogeneous plug-flow reactor, the conversion is a function of residence time. By carrying out a series of experiments at various residence times $\left(V / F_{t, 0}\right)$ in a reactor of fixed volume for a constant feed composition, one obtains the same concentration-versus-residence-time plot as if an infinitely long reactor had been used and the composition had been sampled along the reactor length. Thus the data given can be plotted to give a continuous concentration-versus-residence-time plot that may be differentiated according to the mass-balance equation to give rates of reaction. The concentrations corresponding to those rates are obtained from the data plot at the time for which the rate is evaluated. The differentiation may be accomplished by drawing tangents on the graph at various times to the concentration curves.

The concentration data given can be used to determine net rates of reaction by the material-balance expressions. These rates must be analyzed in terms of the stoichiometry to get the individual rates of reaction. Thus, for the trimer,

$$
\begin{aligned}
& r_{\text {Tri }}=r_{\text {Tri by reaction } 2} \\
& r_{\mathrm{Bi}}=r_{\mathrm{Bi} \text { by reaction } 1}+r_{\mathrm{Bi} \text { by reaction } 2} \\
& r_{\text {Tri by reaction } 2}=-r_{\mathrm{Bi} \text { by reaction } 2}
\end{aligned}
$$

Therefore,

$$
r_{\text {Biby reaction } 1}=r_{\mathrm{Bi}}+r_{\text {Tri by reaction } 2}
$$

The net triphenyl and biphenyl rates $r_{\text {Tri }}$ and $r_{\text {Bi }}$ can be found by plotting the mole fraction of triphenyl and biphenyl versus residence time and taking tangents. Figure 5.4 shows such a plot and Table 5.3 presents the results.

Assume the reactions are elementary, as a first guess. Then, letting $P_{t}$ be total pressure and $k_{i}$ be the specific reaction-rate constant for reaction 1 , the two required equations are

$$
r_{\mathrm{Biby} \text { reaction } 1}=k_{1} P_{t}^{2}\left(y_{\mathrm{Bz}}^{2}-y_{\mathrm{H}_{2}} y_{\mathrm{Bi}} / K_{1}\right)
$$

and

$$
r_{\text {Tri by reaction } 2}=k_{2} P_{t}^{2}\left(y_{\mathrm{Bz}} y_{\mathrm{Bi}}-y_{\mathrm{Tri}} y_{\mathrm{H}_{2}} / K_{2}\right)
$$



FIGURE 5.4 Exit composition as a function of residence time (Example 5.9).

TABLE 5.3 Rates of Reaction for Triphenyl and Biphenyl (Example 5.9)

|  | Rate of reaction, $\mathrm{kg} \cdot \mathrm{mol} /$ <br> $\left(\mathrm{dm}^{3}\right)(\mathrm{h})$ |  |
| :---: | :---: | :---: |
| Residence time $V / F_{t, 0}$, <br> $\left(\mathrm{dm}^{3}\right)(\mathrm{h}) /(\mathrm{kg} \cdot \mathrm{mol})$ | $r_{\text {Tri }}$ | $r_{\mathrm{Bi} \text { (by reaction })}$ |
| 0.129 | 0.00715 | 0.2148 |
| 0.257 | 0.01166 | 0.1893 |
| 0.772 | 0.02916 | 0.1322 |
| 1.543 | 0.02138 | 0.0467 |
| 2.829 | 0.01361 | 0.0194 |

Note: To obtain reaction rate in pound-moles per cubic foot per hour, multiply the preceding rates by 12.86 .

In order to determine $k_{1}$ and $k_{2}$, and to check the suitability of the assumption, plot $r_{\text {Biby reaction } 1}$ against $\left(y_{\mathrm{Bz}}^{2}-y_{\mathrm{H}_{2}} y_{\mathrm{Bi}} / K_{1}\right)$ and plot $r_{\text {Tri }}$ (which equals $r_{\text {Tri by reaction } 2}$ ) against ( $y_{\mathrm{Bz}} y_{\mathrm{Bi}}-y_{\mathrm{Tri}} y_{\mathrm{H}_{2}} / K_{2}$ ). Check to see that the lines are indeed straight, and measure their slope (see Fig. 5.5). Define the slope as $k_{i}^{*}=k_{i} P_{t}^{2}$. Then $k_{1}=k_{1}^{*}=0.2496$ (by measurement of the slope), and $k_{2}=k_{2}^{*}=0.3079$.

With the numerical values for the reaction-rate constants and the equilibrium constants inserted, then,

$$
r_{\text {Bi by reaction } 1}=0.2496\left(y_{\mathrm{Bz}}^{2}-y_{\mathrm{H}_{2}} y_{\mathrm{Bi}} / 0.312\right)
$$



FIGURE 5.5 Rate plots for biphenyl and triphenyl (Example 5.9).
and

$$
r_{\text {Tri by reaction } 2}=0.3079\left(y_{\mathrm{Bz}} y_{\mathrm{Bi}}-y_{\mathrm{Tri}} y_{\mathrm{H}_{2}} / 0.476\right)
$$

Related Calculations. For a batch reactor, the material balance is Rate of accumulation of species $A=$ rate of generation of species $A$, or $d N_{A} / d t=r_{A}$, where $N$ is number of moles at time $t$ and $r$ is rate of reaction (which can be, for example, per unit of catalyst mass in the reactor, in which case it must be multiplied by the number of such units present). The rate at any given time can be found by plotting $N_{A}$ against residence time and measuring the slope, but this technique can lead to large errors. A better approach is to use the Taylor-series interpolation formula (see mathematics handbooks for details).

### 5.10 REACTION-SEPARATION PROCESSES: OPTIMAL RECYCLE ALTERNATIVES AND MINIMUM REQUIRED SELECTIVITIES

Monochlorodecane (MCD) is to be produced from decane (DEC) and chlorine via the reaction

$$
\underset{\text { DEC }}{\mathrm{C}_{10} \mathrm{H}_{22}}+\underset{\text { chlorine }}{\mathrm{Cl}_{2}} \longrightarrow \underset{\text { MCD }}{\mathrm{C}_{10} \mathrm{H}_{21} \mathrm{Cl}}+\underset{\text { hydrogen chloride }}{\mathrm{HCl}}
$$

A side reaction occurs in which dichlorodecane (DCD) is produced:

$$
\underset{\text { MCD }}{\mathrm{C}_{10} \mathrm{H}_{21} \mathrm{Cl}}+\underset{\text { chlorine }}{\mathrm{Cl}_{2}} \longrightarrow \underset{\text { DCD }}{\mathrm{C}_{10} \mathrm{H}_{20} \mathrm{Cl}_{2}}+\underset{\text { hydrogen chloride }}{\mathrm{HCl}}
$$

The byproduct, DCD , is not required for this project. Hydrogen chloride can be sold to a neighboring plant. Assume at this stage that all separations can be carried out by distillation. The normal boiling points are given in the table.

1. Determine alternative recycle structures for the process by assuming different levels of conversion of raw materials and different excesses of reactants.
2. Which structure is most effective in suppressing the side reaction?
3. What is the minimum selectivity of decane that must be achieved for profitable operation? The values of the materials involved together with their molecular weights are given in the table.

| Material | Molecular <br> weight | Normal boiling <br> point $(\mathrm{K})$ | Value <br> $\left(\$ \mathrm{~kg}^{-1}\right)$ |
| :--- | :---: | :---: | :---: |
| Hydrogen chloride | 36 | 188 | 0.35 |
| Chlorine | 71 | 239 | 0.21 |
| Decane | 142 | 447 | 0.27 |
| Monochlorodecane | 176 | 488 | 0.45 |
| Dichlorodecane | 211 | 514 | 0 |

## Calculation Procedure

1. Summarize and assess the alternative recycle structures that are possible. Four possible arrangements can be considered:
I. Complete conversion of both feeds. Figure I shows the most desirable arrangement: complete conversion of the decane and chlorine in the reactor. The absence of reactants in the reactor effluent means that no recycles are needed.


Although the flowsheet shown in Fig. I is very attractive, it is not practical. This would require careful control of the stoichiometric ratio of decane to chlorine, taking into account both the requirements of the primary and byproduct reactions. Even if it were possible to balance out the reactants exactly, a small upset in process conditions would create an excess of either decane or chlorine, and these would then appear as components in the reactor effluent. If these components appear in the reactor effluent of the flowsheet in Fig. I, there are no separators to deal with their presence and no means of recycling unconverted raw materials.

Also, although there are no selectivity data for the reaction, the selectivity losses would be expected to increase with increasing conversion. Complete conversion would tend to produce unacceptable selectivity losses. Finally, the reactor volume required to give a complete conversion would be extremely large.
II. Incomplete conversion of both feeds. If complete conversion is not practical, let us consider incomplete conversion. This is shown in Fig. II. However, in this case, all components are present in the reactor effluent, and one additional separator and a recycle are required. Thus the complexity is somewhat increased compared with complete conversion.
(II)


Note that no attempt has been made to separate the chlorine and decane, since they are remixed after recycling to the reactor.
III. Excess chlorine. Use of excess chlorine in the reactor can force the decane to effectively complete conversion (see Fig. III). Now there is effectively no decane in the reactor effluent, and again, three separators and a recycle are required.

In practice, there is likely to be a trace of decane in the reactor effluent. However, this should not be a problem, since it can either be recycled with the unreacted chlorine or leave with the product, monochlorodecane (providing it can still meet product specifications).

At this stage, how great the excess of chlorine should be for Fig. III to be feasible cannot be specified. Experimental work on the reaction chemistry would be required to establish this. However, the size of the excess does not change the basic structure.

IV. Excess decane. Use of excess decane in the reactor forces the chlorine to effectively complete conversion (see Fig. IV). Now there is effectively no chlorine in the reactor effluent. Again, three separators and a recycle of unconverted raw material are required.


Again, in practice, there is likely to be a trace of chlorine in the reactor effluent. This can be recycled to the reactor with the unreacted decane or allowed to leave with the hydrogen chloride byproduct (providing this meets with the byproduct specification).

It cannot be said at this stage exactly how great an excess of decane would be required to make Fig. IV feasible. This would have to be established experimentally, but the size of the excess does not change the basic structure.

An arrangement is to be chosen to inhibit the side reaction (i.e., give low selectivity losses). The side reaction is suppressed by starving the reactor of either monochlorodecane or chlorine. Since the reactor is designed to produce monochlorodecane, the former option is not practical. However, it is practical to use an excess of decane.

The last of the four flowsheet options generated, which features excess decane in the reactor, is therefore preferred (see Fig. IV).
2. Determine the minimum selectivity of decane needed for profitable operation. The selectivity $S$ is defined by

$$
S=\frac{(\mathrm{MCD} \text { produced in the reactor })}{(\mathrm{DEC} \text { consumed in the reactor })} \times \text { stoichiometric factor }
$$

For more on selectivities, see Section 4 in this book.
In this case, the stoichiometric factor is 1 . This is a measure of the MCD obtained from the DEC consumed. To assess the selectivity losses, the MCD produced in the primary reaction is split into that fraction which will become final product and that which will become the byproduct. Thus the reaction stoichiometry is

$$
\mathrm{C}_{10} \mathrm{H}_{22}+\mathrm{Cl}_{2} \longrightarrow \mathrm{SC}_{10} \mathrm{H}_{12} \mathrm{Cl}+(1-S) \mathrm{C}_{10} \mathrm{H}_{21} \mathrm{Cl}+\mathrm{HCl}
$$

and for the byproduct reaction the stoichiometry is

$$
(1-S) \mathrm{C}_{10} \mathrm{H}_{21} \mathrm{Cl}+(1-S) \mathrm{Cl}_{2} \longrightarrow(1-S) \mathrm{C}_{10} \mathrm{H}_{20} \mathrm{Cl}_{2}+(1-S) \mathrm{HCl}
$$

Adding the two reactions gives overall

$$
\mathrm{C}_{10} \mathrm{H}_{22}+(2-S) \mathrm{Cl}_{2} \longrightarrow S \mathrm{C}_{10} \mathrm{H}_{21} \mathrm{Cl}+(1-S) \mathrm{C}_{10} \mathrm{H}_{20} \mathrm{Cl}_{2}+(2-S) \mathrm{HCl}
$$

Considering raw materials costs only, the economic potential (EP) of the process is defined as

$$
\begin{aligned}
\mathrm{EP}= & \text { value of products }- \text { raw materials cost } \\
= & {[176 \times S \times 0.45+36 \times(2-S) \times 0.35] } \\
& -[142 \times 1 \times 0.27+71 \times(2-S) \times 0.21] \\
= & 79.2 S-2.31(2-S)-38.34\left(\$ \mathrm{kmol}^{-1} \text { decane reacted }\right)
\end{aligned}
$$

The minimum selectivity that can be tolerated is given when the economic potential is just zero:

$$
\begin{aligned}
& 0=79.2 S-2.31(2-S)-38.34 \\
& S=0.53
\end{aligned}
$$

In other words, the process must convert at least 53 percent of the decane that reacts to monochlorodecane rather than to dichlorodecane for the process to be economic. This figure assumes selling the hydrogen chloride to a neighboring process. If this is not the case, there is no value associated with the hydrogen chloride. Assuming that there are no treatment and disposal costs for the now waste hydrogen chloride, the minimum economic potential is given by

$$
\begin{aligned}
0 & =(176 \times S \times 0.45)-[142 \times 1 \times 0.27+71 \times(2-S) \times 0.21] \\
& =79.2 S-14.91(2-S)-38.34 \\
S & =0.72
\end{aligned}
$$

Now the process must convert at least 72 percent of the decane to monochlorodecane.
If the hydrogen chloride cannot be sold, it must be disposed of somehow. Alternatively, it could be converted back to chlorine via the reaction

$$
2 \mathrm{HCl}+\frac{1}{2} \mathrm{O}_{2} \rightleftarrows \mathrm{Cl}_{2}+\mathrm{H}_{2} \mathrm{O}
$$

and then recycled to the MCD reactor. Now the overall stoichiometry changes, since the $(2-S)$ moles of HCl that were being produced as byproduct are now being recycled to substitute fresh
chlorine feed:

$$
(2-S) \mathrm{HCl}+\frac{1}{4}(2-S) \mathrm{O}_{2} \longrightarrow \frac{1}{2}(2-S) \mathrm{Cl}_{2}+\frac{1}{2}(2-S) \mathrm{H}_{2} \mathrm{O}
$$

Thus the overall reaction now becomes

$$
\mathrm{C}_{10} \mathrm{H}_{22}+\frac{1}{2}(2-S) \mathrm{Cl}_{2}+\frac{1}{4}(2-S) \mathrm{O}_{2} \longrightarrow S \mathrm{C}_{10} \mathrm{H}_{21} \mathrm{Cl}+(1-S) \mathrm{C}_{10} \mathrm{H}_{20} \mathrm{Cl}_{2}+\frac{1}{2}(2-S) \mathrm{H}_{2} \mathrm{O}
$$

The economic potential is now given by

$$
\begin{aligned}
0 & =(176 \times S \times 0.45)-\left[142 \times 1 \times 0.27+71 \times \frac{1}{2}(2-S) \times 0.21\right] \\
& =79.2 S-7.455(2-S)-38.34 \\
S & =0.61
\end{aligned}
$$

The minimum selectivity that can now be tolerated becomes 61 percent.
This example is adapted from Smith, Chemical Process Design, McGraw-Hill. For more on calculations and decisions involving recycle streams, see Section 2 in this book.

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## FLOW OF FLUIDS AND SOLIDS*

6.1 BERNOULLI'S THEOREM, AND
EQUATION OF CONTINUITY 6.2
6.2 SPECIFIC GRAVITY AND VISCOSITY
OF LIQUIDS 6.2
6.3 PRESSURE LOSS IN PIPING WITH
LAMINAR FLOW 6.3
6.4 DETERMINING THE PRESSURE LOSS
IN PIPES 6.4
6.5 EQUIVALENT LENGTH OF A
COMPLEX-SERIES PIPELINE 6.9
6.6 HYDRAULIC RADIUS AND LIQUID
VELOCITY IN PIPES 6.9
6.7 FRICTION-HEAD LOSS IN
WATER PIPING OF VARIOUS
MATERIALS 6.10
6.8 RELATIVE CARRYING CAPACITY OF
PIPES 6.12
6.9 FLOW RATE AND PRESSURE LOSS IN
COMPRESSED-AIR AND GAS
PIPING 6.12
6.10 CALCULATIONS FOR PARTIALLY
FILLED PIPES DURING LIQUID
FLOW 6.14
6.11 FRICTION LOSS IN PIPES HANDLING
SOLIDS IN SUSPENSION 6.15
6.12 DETERMINING THE PRESSURE LOSS
IN STEAM PIPING 6.17
6.13 STEAM-TRAP SELECTION FOR
PROCESS APPLICATIONS 6.20
6.14 ORIFICE-METER SELECTION FOR A
STEAM PIPE 6.26
6.15 SELECTION OF A
PRESSURE-REGULATING VALVE FOR
STEAM SERVICE 6.27
6.16 PRESSURE-REDUCING-VALVE
SELECTION FOR WATER PIPING 6.29
6.17 SIMILARITY OR AFFINITY LAWS FOR
CENTRIFUGAL PUMPS 6.30
6.18 SIMILARITY OR AFFINITY LAWS IN
CENTRIFUGAL-PUMP
SELECTION 6.31
6.19 SPECIFIC-SPEED CONSIDERATIONS IN

| 6.1 | BERNOULLI'S THEOREM, AND |
| :--- | :--- |
| EQUATION OF CONTINUITY 6.2 |  |

6.2 SPECIFIC GRAVITY AND VISCOSITY OF LIQUIDS 6.2
6.3 PRESSURE LOSS IN PIPING WITH LAMINAR FLOW 6.3
6.4 DETERMINING THE PRESSURE LOSS IN PIPES 6.4
6.5 EQUIVALENT LENGTH OF A COMPLEX-SERIES PIPELINE 6.9
6.6 HYDRAULIC RADIUS AND LIQUID VELOCITY IN PIPES 6.9
6.7 FRICTION-HEAD LOSS IN MATERIALS 6.10
6.8 RELATIVE CARRYING CAPACITY OF PIPES 6.12
6.9 FLOW RATE AND PRESSURE LOSS IN COMPRESSED-AIR AND GAS PIPING 6.12
6.10 CALCULATIONS FOR PARTIALLY FILLED PIPES DURING LIQUID FLOW 6.14
6.11 FRICTION LOSS IN PIPES HANDLING SOLIDS IN SUSPENSION 6.15
6.12 DETERMINING THE PRESSURE LOSS IN STEAM PIPING 6.17
6.13 STEAM-TRAP SELECTION FOR PROCESS APPLICATIONS 6.20
6.14 ORIFICE-METER SELECTION FOR A STEAM PIPE 6.26
6.15 SELECTION OF A PRESSURE-REGULATING VALVE FOR STEAM SERVICE 6.27
6.16 PRESSURE-REDUCING-VALVE SELECTION FOR WATER PIPING 6.29
6.17 SIMILARITY OR AFFINITY LAWS FOR CENTRIFUGAL PUMPS 6.30
6.18 SIMILARITY OR AFFINITY LAWS IN SELECTION 6.31
6.19 SPECIFIC-SPEED CONSIDERATIONS IN
CENTRIFUGAL-PUMP
SELECTION 6.33
6.20 SELECTING THE BEST OPERATING
SPEED FOR A CENTRIFUGAL
PUMP 6.35
6.21 TOTAL HEAD ON A PUMP HANDLING
VAPOR-FREE LIQUID 6.36
6.22 PUMP SELECTION FOR ANY PUMPING
SYSTEM 6.41
6.23 ANALYSIS OF PUMP AND SYSTEM
CHARACTERISTIC CURVES 6.47
6.24 NET POSITIVE SUCTION HEAD FOR
HOT-LIQUID PUMPS 6.53
6.25 MINIMUM SAFE FLOW FOR A
CENTRIFUGAL PUMP 6.54
6.26 SELECTING A CENTRIFUGAL PUMP
TO HANDLE A VISCOUS LIQUID 6.55
6.27 EFFECT OF LIQUID VISCOSITY ON
REGENERATIVE PUMP
PERFORMANCE 6.57
6.28 EFFECT OF LIQUID VISCOSITY ON
RECEIPROCATING-PUMP
PERFORMANCE 6.59
6.29 EFFECT OF VISCOSITY AND
DSSOLVED GAS ON ROTARY
PUMPS 6.60
6.30 SELECTING FORCED- AND
INDUCED-DRAFT FANS 6.61
6.31 POWER-PLANT FAN SELECTION FROM
CAPACITY TABLES 6.64
6.32 DETERMINATION OF THE MOST
ECONOMICAL FAN CONTROL 6.66
6.33 VACUUM-PUMP SELECTION FOR
HIGH-VACUUM SYSTEMS 6.69
6.34 VACUUM-SYSTEM PUMPING SPEED
AND PIPE SIZE 6.72
6.35 BULK-MATERIAL ELEVATOR AND
CONVEYOR SELECTION 6.73
6.36 SCREW-CONVEYOR POWER INPUT
AND CAPACITY 6.76
REFERENCES 6.78

CENTRIFUGAL-PUMP SELECTION 6.33

SPEED FOR A CENTRIFUGAL
PUMP 6.35
6.21 TOTAL HEAD ON A PUMP HANDLING VAPOR-FREE LIQUID 6.36
6.22 PUMP SELECTION FOR ANY PUMPING SYSTEM 6.41
6.23 ANALYSIS OF PUMP AND SYSTEM CHARACTERISTIC CURVES 6.47
6.24 NET POSITIVE SUCTION HEAD FOR HOT-LIQUID PUMPS 6.53
6.25 MINIMUM SAFE FLOW FOR A CENTRIFUGAL PUMP 6.54
6.26 SELECTING A CENTRIFUGAL PUMP TO HANDLE A VISCOUS LIQUID 6.55
6.27 EFFECT OF LIQUID VISCOSITY ON REGENERATIVE PUMP PERFORMANCE 6.57
6.28 EFFECT OF LIQUID VISCOSITY ON RECEIPROCATING-PUMP PERFORMANCE 6.59
6.29 EFFECT OF VISCOSITY AND DISSOLVED GAS ON ROTARY PUMPS 6.60
6.30 SELECTING FORCED- AND INDUCED-DRAFT FANS 6.61
6.31 POWER-PLANT FAN SELECTION FROM CAPACITY TABLES 6.64
6.32 DETERMINATION OF THE MOST ECONOMICAL FAN CONTROL 6.66
6.33 VACUUM-PUMP SELECTION FOR HIGH-VACUUM SYSTEMS 6.69
6.34 VACUUM-SYSTEM PUMPING SPEED AND PIPE SIZE 6.72
6.35 BULK-MATERIAL ELEVATOR AND CONVEYOR SELECTION 6.73
6.36 SCREW-CONVEYOR POWER INPUT

REFERENCES 6.78

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### 6.1 BERNOULLI'S THEOREM, AND EQUATION OF CONTINUITY

A piping system is conveying $10 \mathrm{ft}^{3} / \mathrm{s}\left(0.28 \mathrm{~m}^{3} / \mathrm{s}\right)$ of ethanol. At a particular cross section of the system, section 1, the pipe diameter is $12 \mathrm{in}(0.30 \mathrm{~m})$, the pressure is $18 \mathrm{lb} / \mathrm{in}^{2}(124 \mathrm{kPa})$, and the elevation is $140 \mathrm{ft}(42.7 \mathrm{~m})$. At another cross section further downstream, section 2, the pipe diameter is $8 \mathrm{in}(0.20 \mathrm{~m})$, and the elevation is $106 \mathrm{ft}(32.3 \mathrm{~m})$. If there is a head loss of $9 \mathrm{ft}(2.74 \mathrm{~m})$ between these sections due to pipe friction, what is the pressure at section 2? Assume that the specific gravity of the ethanol is 0.79 .

## Calculation Procedure

1. Compute the velocity at each section. Use the equation of continuity

$$
Q=A_{1} V_{1}=A_{2} V_{2}
$$

where $Q$ is volumetric rate of flow, $A$ is cross-sectional area, $V$ is velocity, and the subscripts refer to sections 1 and 2 . Now, $A=(\pi / 4) d^{2}$, where $d$ is (inside) pipe diameter, so $A_{1}=(\pi / 4)(1 \mathrm{ft})^{2}=$ $0.785 \mathrm{ft}^{2}$, and $A_{2}=(\pi / 4)(8 / 12 \mathrm{ft})^{2}=0.349 \mathrm{ft}^{2}$; and $Q=10 \mathrm{ft}^{3} / \mathrm{s}$. Therefore, $V_{1}=10 / 0.785=$ $12.7 \mathrm{ft} / \mathrm{s}$, and $V_{2}=10 / 0.349=28.7 \mathrm{ft} / \mathrm{s}$.
2. Compute the pressure at section 2. Use Bernoulli's theorem, which in one form can be written as

$$
\frac{V_{1}^{2}}{2 g}+\frac{p_{1}}{\rho}+z_{1}=\frac{V_{2}^{2}}{2 g}+\frac{p_{2}}{\rho}+z_{2}+h_{L}
$$

where $g$ is the acceleration due to gravity, $32.2 \mathrm{ft} / \mathrm{s}^{2} ; p$ is pressure; $\rho$ is density; $z$ is elevation; and $h_{L}$ is loss of head between two sections. In this case, $\rho=0.79\left(62.4 \mathrm{lb} / \mathrm{ft}^{3}\right)=49.3 \mathrm{lb} / \mathrm{ft}^{3}$. Upon rearranging the equation for Bernoulli's theorem,

$$
\frac{p_{2}-p_{1}}{\rho}=\frac{V_{1}^{2}-V_{2}^{2}}{2 g}+z_{1}-z_{2}-h_{L}
$$

or $\quad\left(p_{2}-p_{1}\right) / 49.3=\left(12.7^{2}-28.7^{2}\right) / 64.4+140-106-9, \quad$ so $\quad\left(p^{2}-p^{1}\right)=725.2 \mathrm{lb} / \mathrm{ft}^{2}, \quad$ or $725.2 / 144=5.0 \mathrm{lb} / \mathrm{in}^{2}$. Therefore, $p_{2}=18+5=23 \mathrm{lb} / \mathrm{in}^{2}(159 \mathrm{kPa})$.

## SPECIFIC GRAVITY AND VISCOSITY OF LIQUIDS

An oil has a specific gravity of 0.8000 and a viscosity of 200 SSU (Saybolt Seconds Universal) at $60^{\circ} \mathrm{F}(289 \mathrm{~K})$. Determine the API gravity and Bé gravity of this oil at $70^{\circ} \mathrm{F}(294 \mathrm{~K})$ and its weight in pounds per gallon. What is the kinematic viscosity in centistokes? What is the absolute viscosity in centipoise?

## Calculation Procedure

1. Determine the API gravity of the liquid. For any oil at $60^{\circ} \mathrm{F}$, its specific gravity $S$, in relation to water at $60^{\circ} \mathrm{F}$, is $S=141.5 /\left(131.5+{ }^{\circ} \mathrm{API}\right)$; or $\mathrm{API}=(141.5-131.5 S) / S$. For this oil, ${ }^{\circ} \mathrm{API}=$ $[141.5-131.5(0.80)] / 0.80=45.4^{\circ}$ API.
2. Determine the Bé gravity of the liquid. For any liquid lighter than water, $S=140 /(130+$ Bé $)$; or Bé $=(140-130 S) / S$. For this oil, Bé $=[140-130(0.80)] / 0.80=45$ Bé.
3. Compute the weight per gallon of liquid. With a specific gravity of $S$, the weight of $1 \mathrm{ft}^{3}$ oil equals $(S)$ (weight of $1 \mathrm{ft}^{3}$ fresh water at $\left.60^{\circ} \mathrm{F}\right)=(0.80)(62.4)=49.92 \mathrm{lb} / \mathrm{ft}^{3}$. Since 1 gal liquid occupies $0.13368 \mathrm{ft}^{3}$, the weight of this oil per gal is $(49.92(0.13368))=6.66 \mathrm{lb} / \mathrm{gal}\left(800 \mathrm{~kg} / \mathrm{m}^{3}\right)$.
4. Compute the kinematic viscosity of the liquid. For any liquid having a viscosity between 32 and 99 SSU, the kinematic viscosity $k=0.226$ SSU $-195 /$ SSU Cst. For this oil, $k=0.226(200)-$ 195/200 $=44.225$ Cst.
5. Convert the kinematic viscosity to absolute viscosity. For any liquid, the absolute viscosity, cP, equals (kinematic viscosity, Cst)(specific gravity). Thus, for this oil, the absolute viscosity $=$ $(44.225)(0.80)=35.38 \mathrm{cP}$.

Related Calculations. For liquids heavier than water, $S=145 /(145-B e ́)$. When the SSU viscosity is greater than $100 \mathrm{~s}, k=0.220 \mathrm{SSU}-135 / \mathrm{SSU}$. Use these relations for any liquid-brine, gasoline, crude oil, kerosene, Bunker C, diesel oil, etc. Consult the Pipe Friction Manual and King and Crocker-Piping Handbook for tabulations of typical viscosities and specific gravities of various liquids.

### 6.3 PRESSURE LOSS IN PIPING WITH LAMINAR FLOW

Fuel oil at $300^{\circ} \mathrm{F}(422 \mathrm{~K})$ and having a specific gravity of 0.850 is pumped through a $30,000-\mathrm{ft}-\mathrm{long}$ 24 -in pipe at the rate of $500 \mathrm{gal} / \mathrm{min}\left(0.032 \mathrm{~m}^{3} / \mathrm{s}\right)$. What is the pressure loss if the viscosity of the oil is 75 cP ?

## Calculation Procedure

1. Determine the type of flow that exists. Flow is laminar (also termed viscous) if the Reynolds number Re for the liquid in the pipe is less than about 2000. Turbulent flow exists if the Reynolds number is greater than about 4000 . Between these values is a zone in which either condition may exist, depending on the roughness of the pipe wall, entrance conditions, and other factors. Avoid sizing a pipe for flow in this critical zone because excessive pressure drops result without a corresponding increase in the pipe discharge.

Compute the Reynolds number from $\operatorname{Re}=3.162 G / k d$, where $G=$ flow rate, gal $/ \mathrm{min}$; $k=$ kinematic viscosity of liquid, $\mathrm{Cst}=$ viscosity $z \mathrm{cP} /$ specific gravity of the liquid $S ; d=$ inside diameter of pipe, in. From a table of pipe properties, $d=22.626 \mathrm{in}$. Also, $k=z / S=75 / 0.85=88.2$ Cst. Then, $\operatorname{Re}=3162(500) /[88.2(22.626)]=792$. Since $\operatorname{Re}<2000$, laminar flow exists in this pipe.
2. Compute the pressure loss using the Poiseuille formula. The Poiseuille formula gives the pressure drop $\rho_{d} \mathrm{lb} / \mathrm{in}^{2}=2.73\left(10^{-4}\right) l u G / d^{4}$, where $l=$ total length of pipe, including equivalent length of fittings, $\mathrm{ft} ; u=$ absolute viscosity of liquid, $\mathrm{cP} ; G=$ flow rate, $\mathrm{gal} / \mathrm{min} ; d=$ inside diameter of pipe, in. For this pipe, $\rho_{d}=2.73\left(10^{-4}\right)(30,000)(75)(500) / 262,078=1.17 \mathrm{lb} / \mathrm{in}^{2}(8.07 \mathrm{kPa})$.

Related Calculations. Use this procedure for any pipe in which there is laminar flow of liquid. Table 6.1 gives a quick summary of various ways in which the Reynolds number can be expressed. The symbols in Table 6.1, in the order of their appearance, are $D=$ inside diameter of pipe, $\mathrm{ft} ; v=$ liquid velocity, $\mathrm{ft} / \mathrm{s} ; \rho=$ liquid density, $\mathrm{lb} / \mathrm{ft}^{3} ; \mu=$ absolute viscosity of liquid, lb mass $/ \mathrm{ft} \cdot \mathrm{s} ; d=$ inside diameter of pipe, in. From a table of pipe properties, $d=22.626$ in. Also, $k=z / S$ liquid flow rate, $\mathrm{lb} / \mathrm{h} ; B=$ liquid flow rate, $\mathrm{bbl} / \mathrm{h} ; k=$ kinematic viscosity of the liquid, Cst; $q=$ liquid flow rate, $\mathrm{ft}^{3} / \mathrm{s} ; Q=$ liquid flow rate, $\mathrm{ft}^{3} / \mathrm{min}$. Use Table 6.1 to find the Reynolds number for any liquid flowing through a pipe.

TABLE 6.1 Reynolds Number

| Reynolds number Re | Numerator |  |  |  | Denominator |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Coefficient | First symbol | Second symbol | Third symbol | Fourth symbol | Fifth symbol |
| Dvp/ $\mu$ | - | ft | $\mathrm{ft} / \mathrm{s}$ | $\mathrm{lb} / \mathrm{ft}^{3}$ | lb mass/ft $\cdot \mathrm{s}$ | - |
| $124 d v \rho / z$ | 124 | in | $\mathrm{ft} / \mathrm{s}$ | $\mathrm{lb} / \mathrm{ft}^{3}$ | cP | - |
| $50.7 \mathrm{G} \rho / \mathrm{dz}$ | 50.7 | $\mathrm{gal} / \mathrm{min}$ | $\mathrm{lb} / \mathrm{ft}^{3}$ | - | in | cP |
| $6.32 \mathrm{~W} / \mathrm{dz}$ | 6.32 | $\mathrm{lb} / \mathrm{h}$ | - | - | in | cP |
| $35.5 \mathrm{~B} \mathrm{\rho} / \mathrm{dz}$ | 35.5 | bbl/h | $\mathrm{lb} / \mathrm{ft}^{3}$ | - | in | cP |
| 7,742dv/k | 7,742 | in | $\mathrm{ft} / \mathrm{s}$ | - | - | cP |
| 3,162G/dk | 3,162 | gal/min | - | - | in | cP |
| 2,214B/dk | 2,214 | bbl/h | - | - | in | cP |
| 22,735q $/ d z$ | 22,735 | $\mathrm{ft}^{3} / \mathrm{s}$ | $\mathrm{lb} / \mathrm{ft}^{3}$ | - | in | cP |
| 378.9Q $/ d z$ | 378.9 | $\mathrm{ft}^{3} / \mathrm{min}$ | $\mathrm{lb} / \mathrm{ft}^{3}$ | - | in | cP |

### 6.4 DETERMINING THE PRESSURE LOSS IN PIPES

What is the pressure drop in a 5000 -ft-long 6-in oil pipe conveying $500 \mathrm{bbl} / \mathrm{h}\left(0.022 \mathrm{~m}^{3} / \mathrm{s}\right)$ kerosene having a specific gravity of 0.813 at $65^{\circ} \mathrm{F}$, which is the temperature of the liquid in the pipe? The pipe is schedule 40 steel.

## Calculation Procedure

1. Determine the kinematic viscosity of the oil. Use Fig. 6.1 and Table 6.2 or the Hydraulic Institute-Pipe Friction Manual kinematic viscosity and Reynolds number chart to determine the kinematic viscosity of the liquid. Enter Table 6.2 at kerosene and find the coordinates as $X=10.2$, $Y=16.9$. Using these coordinates, enter Fig. 6.1 and find the absolute viscosity of kerosene at $65^{\circ} \mathrm{F}$ as 2.4 cP . Using the method of Example 6.2, the kinematic viscosity, in cSt, equals absolute viscosity, $\mathrm{cP} /$ specific gravity of the liquid $=2.4 / 0.813=2.95 \mathrm{cSt}$. This value agrees closely with that given in the Pipe Friction Manual.
2. Determine the Reynolds number of the liquid. The Reynolds number can be found from the Pipe Friction Manual chart mentioned in step 1 or computed from Re $=2214 B / d k=$ $2214(500) /[(6.065)(2.95)]=61,900$.

To use the Pipe Friction Manual chart, compute the velocity of the liquid in the pipe by converting the flow rate to cubic feet per second. Since there are $42 \mathrm{gal} / \mathrm{bbl}$ and $1 \mathrm{gal}=0.13368 \mathrm{ft}^{3}, 1 \mathrm{bbl}$ $=(42)(0.13368)=5.6 \mathrm{ft}^{3}$. With a flow rate of $500 \mathrm{bbl} / \mathrm{h}$, the equivalent flow in $\mathrm{ft}^{3}=(500)(5.6)$ $=2800 \mathrm{ft}^{3} / \mathrm{h}$, or $2800 / 3600 \mathrm{~s} / \mathrm{h}=0.778 \mathrm{ft}^{3} / \mathrm{s}$. Since 6 -in schedule 40 pipe has a cross-sectional area of $0.2006 \mathrm{ft}^{2}$ internally, the liquid velocity, in $\mathrm{ft} / \mathrm{s}$, equals $0.778 / 0.2006=3.88 \mathrm{ft} / \mathrm{s}$. Then, the product $($ velocity, $\mathrm{ft} / \mathrm{s})($ internal diameter, in$)=(3.88)(6.065)=23.75$. In the Pipe Friction Manual, project horizontally from the kerosene specific-gravity curve to the $v d$ product of 23.75 and read the Reynolds number as 61,900 , as before. In general, the Reynolds number can be found faster by computing it using the appropriate relation given in Table 6.1, unless the flow velocity is already known.
3. Determine the friction factor of this pipe. Enter Fig. 6.2 at the Reynolds number value of 61,900 and project to the curve 4 as indicated by Table 6.3. Read the friction factor as 0.0212 at the left. Alternatively, the Pipe Friction Manual friction-factor chart could be used, if desired.

## VISCOSITIES



FIGURE 6.1 Viscosities of liquids at $1 \mathrm{~atm}(101.3 \mathrm{kPa})$. For coordinates, see Table 6.2.
4. Compute the pressure loss in the pipe. Use the Fanning formula $p_{d}=1.06\left(10^{-4}\right) f \rho l B^{2} / d^{5}$. In this formula, $\rho=$ density of the liquid, $\mathrm{lb} / \mathrm{ft}^{3}$. For kerosene, $p=\left(\right.$ density of water, $\left.\mathrm{lb} / \mathrm{ft}^{3}\right)$ $\times($ specific gravity of the kerosene $)=(62.4)(0.813)=50.6 \mathrm{lb} / \mathrm{ft}^{3}$. Then, $p_{d}=1.06\left(10^{-4}\right)$ $(0.0212)(50.6)(5000)(500)^{2} / 8206=17.3 \mathrm{lb} / \mathrm{in}^{2}(119 \mathrm{kPa})$.

Related Calculations. The Fanning formula is popular with oil-pipe designers and can be stated in various ways: (1) with velocity $v$, in $\mathrm{ft} / \mathrm{s}, p_{d}=1.29\left(10^{-3}\right) f \rho v^{2} l / d$; (2) with velocity $V$, in $\mathrm{ft} / \mathrm{min}$, $p_{d}=3.6\left(10^{-7}\right) f \rho V^{2} l / d$; (3) with flow rate $G$, in $\mathrm{gal} / \mathrm{min}, p_{d}=2.15\left(10^{-4}\right) f \rho l G^{2} / d^{2}$; (4) with the flow rate $W$, in lb/h, $p_{d}=3.36\left(10^{-6}\right) \mathrm{fl} W^{2} / d^{5} \rho$.

TABLE 6.2 Viscosities of Liquids (coordinates for use with Fig. 6.1)

| No. | Liquid | $X$ | $Y$ | No. | Liquid | X | $Y$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | Acetaldehyde | 15.2 | 4.8 | 56 | Freon-22 | 17.2 | 4.7 |
|  | Acetic acid: |  |  | 57 | Freon-13 | 12.5 | 11.4 |
| 2 | 100\% | 12.1 | 14.2 |  | Glycerol: |  |  |
| 3 | 70\% | 9.5 | 17.0 | 58 | 100\% | 2.0 | 30.0 |
| 4 | Acetic anhydride | 12.7 | 12.8 | 59 | 50\% | 6.9 | 19.6 |
|  | Acetone: |  |  | 60 | Heptene | 14.1 | 8.4 |
| 5 | 100\% | 14.5 | 7.2 | 61 | Hexane | 14.7 | 7.0 |
| 6 | 35\% | 7.9 | 15.0 | 62 | Hydrochloric acid, 31.5\% | 13.0 | 16.6 |
| 7 | Allyl alcohol | 10.2 | 14.3 | 63 | Isobutyl alcohol | 7.1 | 18.0 |
|  | Ammonia: |  |  | 64 | Isobutyric acid | 12.2 | 14.4 |
| 8 | 100\% | 12.6 | 2.0 | 65 | Isopropyl alcohol | 8.2 | 16.0 |
| 9 | 26\% | 10.1 | 13.9 | 66 | Kerosene | 10.2 | 16.9 |
| 10 | Amyl acetate | 11.8 | 12.5 | 67 | Linseed oil, raw | 7.5 | 27.2 |
| 11 | Amyl alcohol | 7.5 | 18.4 | 68 | Mercury | 18.4 | 16.4 |
| 12 | Aniline | 8.1 | 18.7 |  | Methanol: |  |  |
| 13 | Anisole | 12.3 | 13.5 | 69 | 100\% | 12.4 | 10.5 |
| 14 | Arsenic trichloride | 13.9 | 14.5 | 70 | 90\% | 12.3 | 11.8 |
| 15 | Benzene | 12.5 | 10.9 | 71 | 40\% | 7.8 | 15.5 |
|  | Brine: |  |  | 72 | Methyl acetate | 14.2 | 8.2 |
| 16 | $\mathrm{CaCl}_{2}, 25 \%$ | 6.6 | 15.9 | 73 | Methyl chloride | 15.0 | 3.8 |
| 17 | $\mathrm{NaCl}, 25 \%$ | 10.2 | 16.6 | 74 | Methyl ethyl ketone | 13.9 | 8.6 |
| 18 | Bromine | 14.2 | 13.2 | 75 | Naphthalene | 7.9 | 18.1 |
| 19 | Bromotoluene | 20.0 | 15.9 |  | Nitric acid: |  |  |
| 20 | Butyl acetate | 12.3 | 11.0 | 76 | 95\% | 12.8 | 13.8 |
| 21 | Butyl alcohol | 8.6 | 17.2 | 77 | 60\% | 10.8 | 17.0 |
| 22 | Butyric acid | 12.1 | 15.3 | 78 | Nitrobenzene | 10.6 | 16.2 |
| 23 | Carbon dioxide | 11.6 | 0.3 | 79 | Nitrotoluene | 11.0 | 17.0 |
| 24 | Carbon disulfide | 16.1 | 7.5 | 80 | Octane | 13.7 | 10.0 |
| 25 | Carbon tetrachloride | 12.7 | 13.1 | 81 | Octyl alcohol | 6.6 | 21.1 |
| 26 | Chlorobenzene | 12.3 | 12.4 | 82 | Pentachloroethane | 10.9 | 17.3 |
| 27 | Chloroform | 14.4 | 10.2 | 83 | Pentane | 14.9 | 5.2 |
| 28 | Chlorosulfonic acid | 11.2 | 18.1 | 84 | Phenol | 6.9 | 20.8 |
|  | Chlorotoluene: |  |  | 85 | Phosphorus tribromide | 13.8 | 16.7 |
| 29 | Ortho | 13.0 | 13.3 | 86 | Phosphorus trichloride | 16.2 | 10.9 |
| 30 | Meta | 13.3 | 12.5 | 87 | Propionic acid | 12.8 | 13.8 |
| 31 | Para | 13.3 | 12.5 | 88 | Propyl alcohol | 9.1 | 16.5 |
| 32 | Cresol, meta | 2.5 | 20.8 | 89 | Propyl bromide | 14.5 | 9.6 |
| 33 | Cyclohexanol | 2.9 | 24.3 | 90 | Propyl chloride | 14.4 | 7.5 |
| 34 | Dibromoethane | 12.7 | 15.8 | 91 | Propyl iodide | 14.1 | 11.6 |
| 35 | Dichloroethane | 13.2 | 12.2 | 92 | Sodium | 16.4 | 13.9 |
| 36 | Dichloromethane | 14.6 | 8.9 | 93 | Sodium hydroxide, 50\% | 3.3 | 25.8 |
| 37 | Diethyl oxalate | 11.0 | 16.4 | 94 | Stannic chloride | 13.5 | 12.8 |
| 38 | Dimethyl oxalate | 12.3 | 15.8 | 95 | Sulfur dioxide | 15.2 | 7.1 |
| 39 | Diphenyl | 12.0 | 18.3 |  | Sulfuric acid: |  |  |
| 40 | Dipropyl oxalate | 10.3 | 17.7 | 96 | 110\% | 7.2 | 27.4 |
| 41 | Ethyl acetate | 13.7 | 9.1 | 97 | 98\% | 7.0 | 24.8 |
|  | Ethyl alcohol: |  |  | 98 | 60\% | 10.2 | 21.3 |
| 42 | 100\% | 10.5 | 13.8 | 99 | Sulfuryl chloride | 15.2 | 12.4 |
| 43 | 95\% | 9.8 | 14.3 | 100 | Tetrachloroethane | 11.9 | 15.7 |
| 44 | 40\% | 6.5 | 16.6 | 101 | Tetrachloroethylene | 14.2 | 12.7 |
| 45 | Ethyl benzene | 13.2 | 11.5 | 102 | Titanium tetrachloride | 14.4 | 12.3 |
| 46 | Ethyl bromide | 14.5 | 8.1 | 103 | Toluene | 13.7 | 10.4 |
| 47 | Ethyl chloride | 14.8 | 6.0 | 104 | Trichloroethylene | 14.8 | 10.5 |
| 48 | Ethyl ether | 14.5 | 5.3 | 105 | Turpentine | 11.5 | 14.9 |
| 49 | Ethyl formate |  |  | 106 | Water | 10.2 | 13.0 |
| 50 | Ethyl iodide | 14.7 | 10.3 |  | Xylene: |  |  |
| 51 | Ethylene glycol | 6.0 | 23.6 | 107 | Ortho | 13.5 | 12.1 |
| 52 | Formic acid | 10.7 | 15.8 | 108 | Meta | 13.9 | 10.6 |
| 53 | Freon-11 | 14.4 | 9.0 | 109 | Para | 13.9 | 10.9 |
| 54 | Freon-12 | 16.8 | 5.6 |  |  |  |  |
| 55 | Freon-21 | 15.7 | 7.5 |  |  |  |  |

 FIGURE 6.2 Friction-factor curves. (Mechanical Engineering.)
TABLE 6.3 Data for Fig. 6.2

| Percent roughness | For value of $f$ see curve | Diameter (actual of drawn tubing, nominal of standard-weight pipe) |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | Drawn tubing, brass, tin, lead, glass |  | Clean steel, wrought iron |  | Clean, galvanized |  | Best cast iron |  | Average cast iron |  | Heavy riveted, spiral riveted |  |
|  |  | in | mm | in | mm | in | mm | in | mm | in | mm | in | mm |
| 0.2 | 1 | 0.35 up | 8.89 up | 72 | 1829 | - | - | - | - | - | - | - | - |
| 1.35 | 4 | - | - | 6-12 | 152-305 | 10-24 | 254-610 | 20-48 | 508-1219 | 42-96 | 1067-2438 | 84-204 | 2134-5182 |
| 2.1 | 5 | - | - | 4-5 | 102-127 | 6-8 | 152-203 | 12-16 | 305-406 | 24-36 | 610-914 | 48-72 | 1219-1829 |
| 3.0 | 6 | - | - | 2-3 | 51-76 | 305 | 76-127 | 5-10 | 127-254 | 10-20 | 254-508 | 20-42 | 508-1067 |
| 3.8 | 7 | - | - | $11 / 2$ | 38 | $21 / 2$ | 64 | 3-4 | 76-102 | 6-8 | 152-203 | 16-18 | 406-457 |
| 4.8 | 8 | - | - | $1-11 / 2$ | 25-32 | $11 / 2-2$ | 38-51 | $2-21 / 2$ | 51-64 | 4-5 | 102-127 | 10-14 | 254-356 |
| 6.0 | 9 | - | - | $3 / 4$ | 19 | $11 / 4$ | 32 | $11 / 2$ | 38 | 3 | 76 | 8 | 203 |
| 7.2 | 10 | - | - | 1/2 | 13 | 1 | 25 | $11 / 4$ | 32 | - | - | 5 | 127 |
| 10.5 | 11 | - | - | 3/8 | 9.5 | 3/4 | 19 | 1 | 35 | - | - | 4 | 102 |
| 14.5 | 12 | - | - | 1/4 | 6.4 | 1/2 | 13 | - | - | - | - | 3 | 76 |
| 24.0 | 14 | 0.125 | 3.18 | - | - | 3/8 | 9.5 | - | - | - | - | - | - |
| 31.5 | 16 | - | - | - | - | 1/4 | 6.4 | - | - | - | - | - | - |
| 37.5 | 18 | 0.0625 | 1.588 | - | - | 1/8 | 3.2 | - | - | - | - | - | - |

Use this procedure for any fluid-crude oil, kerosene, benzene, gasoline, naptha, fuel oil, Bunker C, diesel oil toluene, etc. The tables and charts presented here and in the Pipe Friction Manual save computation time.

### 6.5 EQUIVALENT LENGTH OF A COMPLEX-SERIES PIPELINE

Figure 6.3 shows a complex-series pipeline made up of four lengths of different size pipe. Determine the equivalent length of this pipe if each size of pipe has the same friction factor.


FIGURE 6.3 Complex-series pipeline.

## Calculation Procedure

1. Select the pipe size for expressing the equivalent length. The usual procedure when analyzing complex pipelines is to express the equivalent length in terms of the smallest, or next-to-smallest, diameter pipe. Choose the 8 -in size as being suitable for expressing the equivalent length.
2. Find the equivalent length of each pipe. For any complex-series pipeline having equal friction factors in all the pipes, $L_{e}=$ equivalent length, ft , of a section of constant diameter $=$ (actual length of section, ft ) (inside diameter, in, of pipe used to express the equivalent length/inside diameter, in, of section under consideration) ${ }^{5}$.

For the 16 -in pipe, $L_{e}=(1000)(7.981 / 15.000)^{5}=42.6 \mathrm{ft}$. The 12 -in pipe is next; for it, $L_{e}=$ $(3000)(7.981 / 12.00)^{5}=390 \mathrm{ft}$. For the 8 -in pipe, the equivalent length $=$ actual length $=2000 \mathrm{ft}$. For the 4 -in pipe, $L_{e}=(10)(7.981 / 4.026)^{5}=306 \mathrm{ft}$. Then, the total equivalent length of 8 -in pipe $=$ sum of the equivalent lengths $=42.6+390+2000+306=2738.6 \mathrm{ft}$, or rounding off, 2740 ft of 8 -in pipe ( 835 m of $0.2-\mathrm{m}$ pipe) will have a frictional resistance equal to the complex-series pipeline shown in Fig. 6.3. To compute the actual frictional resistance, use the methods given in previous Calculation Procedures.

Related Calculations. Use this general procedure for any complex-series pipeline conveying water, oil, gas, steam, etc. See King and Crocker-Piping Handbook for derivation of the flow equations. Use the tables in King and Crocker to simplify finding the fifth power of the inside diameter of a pipe.

Choosing a flow rate of $1000 \mathrm{gal} / \mathrm{min}$ and using the tables in the Hydraulic Institute Pipe Friction Manual gives an equivalent length of 2770 ft for the 8 -in pipe. This compares favorably with the 2740 ft computed above. The difference of 30 ft is negligible.

The equivalent length is found by summing the friction-head loss for $1000 \mathrm{gal} / \mathrm{min}$ flow for each length of the four pipes-16,12, 8 , and 4 in-and dividing this by the friction-head loss for 1000 $\mathrm{gal} / \mathrm{min}$ flowing through an 8 -in pipe. Be careful to observe the units in which the friction-head loss is stated, because errors are easy to make if the units are ignored.

### 6.6 HYDRAULIC RADIUS AND LIQUID VELOCITY IN PIPES

What is the velocity of $1000 \mathrm{gal} / \mathrm{min}\left(0.064 \mathrm{~m}^{3} / \mathrm{s}\right)$ of water flowing through a 10 -in inside-diameter cast-iron water-main pipe? What is the hydraulic radius of this pipe when it is full of water? When the water depth is 8 in $(0.203 \mathrm{~m})$ ?

## Calculation Procedure

1. Compute the water velocity in the pipe. For any pipe conveying liquid, the liquid velocity, in $\mathrm{ft} / \mathrm{s}$, is $v=(\mathrm{gal} / \mathrm{min}) /\left(2.448 d^{2}\right)$, where $d=$ internal pipe diameter, in. For this pipe, $v=1000 /[2.448(100)]=4.08 \mathrm{ft} / \mathrm{s}$, or $(60)(4.08)=244.8 \mathrm{ft} / \mathrm{min}$.
2. Compute the hydraulic radius for a full pipe. For any pipe, the hydraulic radius is the ratio of the cross-sectional area of the pipe to the wetted perimeter, or $d / 4$. For this pipe, when full of liquid, the hydraulic radius $=10 / 4=2.5$.
3. Compute the hydraulic radius for a partially full pipe. Use the hydraulic radius tables in King and Brater-Handbook of Hydraulics or compute the wetted perimeter using the geometric properties of the pipe, as in step 2. Using the King and Brater table, the hydraulic radius $=F d$, where $F=$ table factor for the ratio of the depth of liquid, in/diameter of channel, in $=8 / 10=0.8$. For this ratio, $F=0.304$. Then, hydraulic radius $=(0.304)(10)=3.04 \mathrm{in}$.

### 6.7 FRICTION-HEAD LOSS IN WATER PIPING OF VARIOUS MATERIALS

Determine the friction-head loss in 2500 ft of clean 10-in new tar-dipped cast-iron pipe when 2000 $\mathrm{gal} / \mathrm{min}\left(0.126 \mathrm{~m}^{3} / \mathrm{s}\right)$ of cold water is flowing. What is the friction-head loss 20 years later? Use the Hazen-Williams and Manning formulas and compare the results.

## Calculation Procedure

1. Compute the friction-head loss using the Hazen-Williams formula. The Hazen-Williams formula is $h_{f}=\left(v / 1.318 C R_{h}^{0.63}\right)^{1.85}$, where $h_{f}=$ friction-head loss per foot of pipe, in feet of water; $v=$ water velocity, in ft/s; $C=$ a constant depending on the condition and kind of pipe; and $R_{h}=$ hydraulic radius of pipe, in ft .

For a water pipe, $v=(\mathrm{gal} / \mathrm{min}) /\left(2.44 d^{2}\right)$; for this pipe, $v=2000 /\left[2.448(10)^{2}\right]=8.18 \mathrm{ft} / \mathrm{s}$. From Table 6.4 or King and Crocker-Piping Handbook, $C$ for new pipe $=120$; for 20-year-old pipe, $C=$ $90 ; R_{h}=d / 4$ for a full-flow pipe $=10 / 4=2.5 \mathrm{in}$, or $2.5 / 12=0.208 \mathrm{ft}$. Then, $h_{f}=(8.18 / 1.318 \times$ $\left.120 \times 0.208^{0.63}\right)^{1.85}=0.0263 \mathrm{ft}$ of water per foot of pipe. For 2500 ft of pipe, the total friction-head loss $=2500(0.0263)=65.9 \mathrm{ft}(20.1 \mathrm{~m})$ of water for the new pipe.

TABLE 6.4 Values of $C$ in Hazen-Williams Formula

| Type of pipe | $C^{*}$ | Type of pipe | $C^{*}$ |
| :--- | ---: | :--- | ---: |
| Cement-asbestos | 140 | Cast iron or wrought iron | 100 |
| Asphalt-lined iron or steel | 140 | Welded or seamless steel | 100 |
| Copper or brass | 130 | Concrete | 100 |
| Lead, tin, or glass | 130 | Corrugated steel | 60 |
| Wood stave | 110 |  |  |

*Values of $C$ commonly used for design. The value of $C$ for pipes made of corrosive materials decreases as the age of the pipe increases; the values given are those which apply at an age of 15 to 20 years. For example, the value of $C$ for cast-iron pipes 30 in in diameter or greater at various ages is approximately as follows: new, 130; 5 years old, 120; 10 years old, 115; 20 years old, 100; 30 years old, $90 ; 40$ years old, 80 ; and 50 years old, 75 . The value of $C$ for smaller-size pipes decreases at a more rapid rate.

TABLE 6.5 Roughness Coefficients (Manning's $n$ ) for Closed Conduits

| Type of conduit |  |  | Manning's $n$ |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  |  | Good construction* | Fair construction* |
| Concrete pipe <br> Corrugated metal pipe or pipe arch, $22 / 3 \times 1 / 2$ in corrugation, riveted: Plain |  |  | 0.013 | 0.015 |
|  |  |  | 0.024 | - |
| Paved invert: <br> Percent of circumference paved |  |  |  |  |
|  | 25 | 50 |  |  |
| Depth of flow: |  |  |  |  |
| Full | 0.021 | 0.018 |  |  |
| $0.8 D$ | 0.021 | 0.016 |  |  |
| 0.6 D | 0.019 | 0.013 |  |  |
| Vitrified clay pipe |  |  | 0.012 | 0.014 |
| Cast-iron pipe, uncoated |  |  | 0.013 | - |
| Steel pipe |  |  | 0.011 | - |
| Brick |  |  | 0.014 | 0.017 |
| Monolithic concrete: |  |  |  |  |
| Wood forms, rough |  |  | 0.015 | 0.017 |
| Wood forms, smooth |  |  | 0.012 | 0.014 |
| Steel forms |  |  | 0.012 | 0.013 |
| Cemented-rubble masonry walls: |  |  |  |  |
| Concrete floor and top |  |  | 0.017 | 0.022 |
| Natural floor |  |  | 0.019 | 0.025 |
| Laminated treated wood |  |  | 0.015 | 0.017 |
| Vitrified-clay liner plates |  |  | 0.015 | - |

*For poor-quality construction, use larger values of $n$.

For 20-year-old pipe using the same formula, except with $C=90, h_{f}=0.0451 \mathrm{ft}$ of water per foot of pipe. For 2500 ft of pipe, the total friction-head loss $=2500(0.0451)=112.9 \mathrm{ft}(34.4 \mathrm{~m})$ of water. Thus the friction-head loss nearly doubles (from 65.9 to 112.9 ft ) in 20 years. This shows that it is wise to design for future friction losses; otherwise, pumping equipment may become overloaded.
2. Compute the friction-head loss using the Manning formula. The Manning formula is $h_{f}=$ $n^{2} v^{2} /\left(2.208 R_{h}^{4 / 3}\right)$, where $n=$ a constant depending on the condition and kind of pipe; other symbols as before.

Using $n=0.011$ for new coated cast-iron pipe from Table 6.5 or King and Crocker-Piping Handbook, $h_{f}=(0.011)^{2}(8.18)^{2} /\left[2.208(0.208)^{4 / 3}\right]=0.0295 \mathrm{ft}$ of water per foot of pipe. For 2500 ft of pipe, the total friction-head loss $=2500(0.0295)=73.8 \mathrm{ft}(22.5 \mathrm{~m})$ of water, as compared with 65.9 ft of water computed with the Hazen-Williams formula.

For coated cast-iron pipe in fair condition, $n=0.013$, and $h_{f}=0.0411 \mathrm{ft}$ of water. For 2500 ft of pipe, the total friction-head loss $=2500(0.0411)=102.8 \mathrm{ft}(31.4 \mathrm{~m})$ of water, as compared with 112.9 ft of water computed with the Hazen-Williams formula. Thus the Manning formula gives results higher than the Hazen-Williams in one case and lower in another. However, the differences in each case are not excessive; $(73.8-65.9) / 65.9=0.12$, or 12 percent higher, and $(112.9-102.8) / 102.8=0.0983$, or 9.83 percent lower. Both these differences are within the normal range of accuracy expected in pipe friction-head calculations.

Related Calculations. The Hazen-Williams and Manning formulas are popular with many piping designers for computing pressure losses in cold-water piping. To simplify calculations, most designers use the precomputed tabulated solutions available in King and Crocker-Piping Handbook, King and Brater-Handbook of Hydraulics, and similar publications. In the rush of daily work these precomputed solutions are also preferred over the more complex Darcy-Weisbach equation used in conjunction with the friction factor $f$, the Reynolds number Re, and the roughness-diameter ratio.

Use the method given here for sewer lines, water-supply pipes for commercial, industrial, or process plants, and all similar applications where cold water at temperatures of 33 to $90^{\circ} \mathrm{F}$ flows through a pipe made of cast iron, riveted steel, welded steel, galvanized iron, brass, glass, wood-stove, concrete, vitrified, common clay, corrugated metal, unlined rock, or enameled steel. Thus either of these formulas, used in conjunction with a suitable constant, gives the friction-head loss for a variety of piping materials. Suitable constants are given in Tables 6.4 and 6.5 and in the preceding references. For the Hazen-Williams formula, the constant $C$ varies from about 70 to 140, while $n$ in the Manning formula varies from about 0.017 for $C=70$ to $n=0.010$ for $C=140$. Values obtained with these formulas have been used for years with satisfactory results.

### 6.8 RELATIVE CARRYING CAPACITY OF PIPES

What is the equivalent steam-carrying capacity of a 24 -in-inside-diameter pipe in terms of a 10 -in-inside-diameter pipe? What is the equivalent water-carrying capacity of a 23 -in-inside-diameter pipe in terms of a 13.25 -in-inside-diameter pipe?

## Calculation Procedure

1. Compute the relative carrying capacity of the steam pipes. For steam, air, or gas pipes, the number $N$ of small pipes of inside diameter $d_{2}$ in equal to one pipe of larger inside diameter $d_{1}$ in is $N=$ $\left(d_{1}^{3} \sqrt{d_{2}+3.6}\right) /\left(d_{2}^{3}+\sqrt{d_{1}+3.6}\right)$. For this piping system, $N=\left(24^{3}+\sqrt{10}+3.6\right) /\left(10^{3}+\sqrt{24}+\right.$ $3.6)=9.69$, say 9.7. Thus a 24 -in-inside-diameter steam pipe has a carrying capacity equivalent to 9.7 pipes having a $10-$ in inside diameter.
2. Compute the relative carrying capacity of the water pipes. For water, $N=\left(d_{2} / d_{1}\right)^{2.5}=$ $(23 / 13.25)^{2.5}=3.97$. Thus one 23-in-inside-diameter pipe can carry as much water as 3.97 pipes of 13.25 in inside diameter.

Related Calculations. King and Crocker-Piping Handbook and certain piping catalogs contain tabulations of relative carrying capacities of pipes of various sizes. Most piping designers use these tables. However, the equations given here are useful for ranges not covered by the tables and when the tables are unavailable.

### 6.9 FLOW RATE AND PRESSURE LOSS IN COMPRESSED-AIR AND GAS PIPING

Dry air at $80^{\circ} \mathrm{F}(300 \mathrm{~K})$ and $150 \mathrm{psia}(1034 \mathrm{kPa})$ flows at the rate of $500 \mathrm{ft}^{3} / \mathrm{min}\left(0.24 \mathrm{~m}^{3} / \mathrm{s}\right)$ through a 4 -in schedule 40 pipe from the discharge of an air compressor. What is the flow rate in pounds per hour and the air velocity in feet per second? Using the Fanning formula, determine the pressure loss if the total equivalent length of the pipe is $500 \mathrm{ft}(153 \mathrm{~m})$.

TABLE 6.6 Gas Constants

|  | $R$ |  | $C$ for critical- <br> Gas |
| :--- | :---: | :---: | :---: |
|  | $\mathrm{ft} \cdot \mathrm{lb} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)$ | $\mathrm{J} /(\mathrm{kg})(\mathrm{K})$ | velocity equation |
| Air | 53.33 | 286.9 | 2870 |
| Ammonia | 89.42 | 481.1 | 2080 |
| Carbon dioxide | 34.87 | 187.6 | 3330 |
| Carbon monoxide | 55.14 | 296.7 | 2820 |
| Ethane | 50.82 | 273.4 |  |
| Ethylene | 54.70 | 294.3 | 2480 |
| Hydrogen | 767.04 | 4126.9 | 750 |
| Hydrogen sulfide | 44.79 | 240.9 |  |
| Isobutane | 25.79 | 138.8 |  |
| Methane | 96.18 | 517.5 | 2030 |
| Natural gas | - | - | $2070-2670$ |
| Nitrogen | 55.13 | 296.6 | 2800 |
| $n$-butane | 25.57 | 137.6 |  |
| Oxygen | 48.24 | 259.5 | 2990 |
| Propane | 34.13 | 183.6 |  |
| Propylene | 36.01 | 193.7 |  |
| Sulfur dioxide | 23.53 | 126.6 | 3870 |

## Calculation Procedure

1. Determine the density of the air or gas in the pipe. For air or a gas, $p V=M R T$, where $p=$ absolute pressure of the gas, in $\mathrm{lb} / \mathrm{ft}^{2} ; V=$ volume of $M \mathrm{lb}$ of gas, in $\mathrm{ft}^{3} ; M=$ weight of gas, in lb ; $R=$ gas constant, in $\mathrm{ft} \cdot \mathrm{lb} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right) ; T=$ absolute temperature of the gas, in R . For this installation, using $1 \mathrm{ft}^{3}$ of air, $M=p V / R T, M=(150)(144) /[(53.33)(80+459.7)]=0.754 \mathrm{lb} / \mathrm{ft}^{3}$. The value of $R$ in this equation was obtained from Table 6.6.
2. Compute the flow rate of the air or gas. For air or a gas, the flow rate $W_{h}$, in $\mathrm{lb} / \mathrm{h},=(60)$ (density, $\left.\mathrm{lb} / \mathrm{ft}^{3}\right)\left(\right.$ flow rate, $\left.\mathrm{ft}^{3} / \mathrm{min}\right)$; or $W_{h}=(60)(0.754)(500)=22,620 \mathrm{lb} / \mathrm{h}$.
3. Compute the velocity of the air or gas in the pipe. For any air or gas pipe, velocity of the moving fluid $v$, in $\mathrm{ft} / \mathrm{s}$, $=183.4 W_{h} /\left(3600 d^{2} \rho\right)$, where $d=$ internal diameter of pipe, in; $\rho=$ density of fluid, $\mathrm{lb} / \mathrm{ft}^{3}$. For this system, $v=(183.4)(22,620) /\left[(3600)(4.026)^{2}(0.754)\right]=95.7 \mathrm{ft} / \mathrm{s}$.
4. Compute the Reynolds number of the air or gas. The viscosity of air at $80^{\circ} \mathrm{F}$ is 0.0186 cP , obtained from King and Crocker-Piping Handbook, Perry et al.-Chemical Engineers' Handbook, or a similar reference. Then, using the Reynolds number relation given in Table 6.1, $\mathrm{Re}=6.32 \mathrm{~W} / \mathrm{dz}=$ $6.32(22,620) /[4.026(0.0186)]=1,910,000$.
5. Compute the pressure loss in the pipe. Using Fig. 6.2 or the Hydraulic Institute Pipe Friction Manual, $f=0.02$ for a 4 -in schedule 40 pipe when the Reynolds number $=$ $1,910,000$. Using the Fanning formula from Example $6.4, p_{d}=3.36\left(10^{-6}\right) f l W^{2} /\left(d^{5} \rho\right)$, or $p_{d}=$ $\left.3.36\left(10^{-6}\right)(0.02)(500)(22,620)^{2} /\left[(4.026)^{5}\right)(0.754)\right]=21.63 \mathrm{lb} / \mathrm{in}^{2}(121 \mathrm{kPa})$.

Related Calculations. Use this procedure to compute the pressure loss, velocity, and flow rate in compressed-air and gas lines of any length. Gases for which this procedure can be used include ammonia, carbon dioxide, carbon monoxide, ethane, ethylene, hydrogen, hydrogen sulfide, isobutane, methane, nitrogen, $n$-butane, oxygen, propane, propylene, and sulfur dioxide.

Alternate relations for computing the velocity of air or gas in a pipe are $v=144 W_{s} /(a \rho) ; v=$ $183.4 W_{s} /\left(d^{2} \rho\right) ; v=0.0509 W_{s} v_{g} / d^{2}$, where $W_{s}=$ flow rate, in $\mathrm{lb} / \mathrm{s} ; a=$ cross-sectional area of pipe, in in ${ }^{2} ; v_{g}=$ specific volume of the air or gas at the operating pressure and temperature, in $\mathrm{ft}^{3} / \mathrm{lb}$.

### 6.10 CALCULATIONS FOR PARTIALLY FILLED PIPES DURING LIQUID FLOW

A horizontal run of 3 in pipe handles $40 \mathrm{gal} / \mathrm{min}$ of water. Determine whether the flow is below or above the minimum needed to keep the pipe sealed (full of liquid). If the pipe instead is only partly filled, determine the height of liquid in it, the velocity of the fluid, and the equivalent diameter of the flooded section.

## Calculation Procedure

1. Calculate the minimum flow required to seal this pipe, and compare it with the flowrate stated for this problem. Use the equation $Q=10.2 D^{2.5}$, where $Q$ is minimum liquid flowrate required for seal flow in gallons per minute and $D$ is the pipe diameter in inches, Thus, $Q=10.2(3)^{2.5}=$ $159 \mathrm{gal} / \mathrm{min}$.

Since the stated flowrate is only $40 \mathrm{gal} / \mathrm{min}$, the pipe is not sealed.
2. Determine the height of liquid in the pipe, $\boldsymbol{H}$. First, calculate the quantity, $Q / D^{2.5}$. It equals $40 /(3)^{2.5}$, or 2.56 . With this value, enter the figure below along its ordinate and, from the abscissa, $\operatorname{read} H / D$ as 0.7 . Therefore, $H=0.7 D=0.7(3)=2.1 \mathrm{in}$.

3. Determine the cross-section area A of the flow. Enter the figure below along its abscissa with an $H / D$ value of 0.7 and, from the ordinate along the right side of the graph, read $A / D^{2}$ as about 0.59 . Therefore, $A=0.59(3)^{2}=5.31 \mathrm{in}^{2}$, or $0.369 \mathrm{ft}^{2}$.

4. Calculate the velocity Vof the fluid flow. The calculation is straightforward:

$$
V=(40 \mathrm{gal} / \mathrm{min})\left(1 \mathrm{ft}^{3} / 7.48 \mathrm{gal}\right)(1 \mathrm{~min} / 60 \mathrm{~s})\left(1 / 0.0369 \mathrm{ft}^{2}\right)=2.42 \mathrm{ft} / \mathrm{s}
$$

5. Determine the equivalent diameter $\boldsymbol{D}_{\boldsymbol{e}}$ for this flow. Enter the figure in step 3 along its abscissa with an $H / D$ value of 0.7 and, from the ordinate along the left side of the graph, read $D_{e} / D$ as about 1.18. Thus, $D_{e}=1.18(3)=3.54 \mathrm{in}$.

### 6.11 FRICTION LOSS IN PIPES HANDLING SOLIDS IN SUSPENSION

What is the friction loss in 800 ft of 6 -in schedule 40 pipe when $400 \mathrm{gal} / \mathrm{min}\left(0.025 \mathrm{~m}^{3} / \mathrm{s}\right)$ of sulfate paper stock is flowing? The consistency of the sulfate stock is 6 percent.

## Calculation Procedure

1. Determine the friction loss in the pipe. There are few general equations for friction loss in pipes conveying liquids having solids in suspension. Therefore, most practicing engineers use plots of friction loss available in engineering handbooks, Cameron Hydraulic Data, Standards of the Hydraulic Institute, and from pump engineering data. Figure 6.4 shows one set of typical friction-loss curves based on work done at the University of Maine on the data of Brecht and Heller of the Technical


FIGURE 6.4 Friction loss of paper stock in 4 -in ( $0.10-\mathrm{m}$ ) steel pipe. (Goulds Pumps, Inc.)

College, Darmstadt, Germany, and published by Goulds Pumps, Inc. There is a similar series of curves for commonly used pipe sizes from 2 through 36 in.

Enter Fig. 6.4 at the pipe flow rate, $400 \mathrm{gal} / \mathrm{min}$, and project vertically upward to the 6 percent consistency curve. From the intersection, project horizontally to the left to read the friction loss as 60 ft of liquid per 100 ft of pipe. Since this pipe is 800 ft long, the total friction-head loss in the pipe is $(800 / 100)(60)=480 \mathrm{ft}(146 \mathrm{~m})$ of liquid flowing.
2. Correct the friction loss for the liquid consistency. Friction-loss factors are usually plotted for one type of liquid, and correction factors are applied to determine the loss for similar, but different, liquids. Thus, with the Goulds charts, a factor of 0.9 is used for soda, sulfate, bleached sulfite, and reclaimed paper stocks. For ground wood, the factor is 1.40 .

When the stock consistency is less than 1.5 percent, water-friction values are used. Below a consistency of 3 percent, the velocity of flow should not exceed $10 \mathrm{ft} / \mathrm{s}$. For suspensions of 3 percent and above, limit the maximum velocity in the pipe to $8 \mathrm{ft} / \mathrm{s}$.

Since the liquid flowing in this pipe is sulfate stock, use the 0.9 correction factor, or the actual total friction head $=(0.9)(480)=432 \mathrm{ft}(132 \mathrm{~m})$ of sulfate liquid. Note that Fig. 6.4 shows that the liquid velocity is less than $8 \mathrm{ft} / \mathrm{s}$.

Related Calculations. Use this procedure for soda, sulfate, bleached sulfite, and reclaimed and ground-wood paper stock. The values obtained are valid for both suction and discharge piping. The same general procedure can be used for sand mixtures, sewage, trash, sludge, foods in suspension in a liquid, and other slurries.

### 6.12 DETERMINING THE PRESSURE LOSS IN STEAM PIPING

Use a suitable pressure-loss chart to determine the pressure loss in 510 ft of 4 -in flanged steel pipe containing two $90^{\circ}$ elbows and four $45^{\circ}$ bends. The schedule 40 piping conveys $13,000 \mathrm{lb} / \mathrm{h}(1.64$ $\mathrm{kg} / \mathrm{s}$ ) of $40-\mathrm{psig} 350^{\circ} \mathrm{F}$ superheated steam. List other methods of determining the pressure loss in steam piping.

## Calculation Procedure

1. Determine the equivalent length of the piping. The equivalent length of a pipe $L_{e}$, in ft , equals length of straight pipe, $\mathrm{ft}+$ equivalent length of fittings, ft . Using data from the Hydraulic Institute, King and Crocker-Piping Handbook, or Fig. 6.5, find the equivalent of a $90^{\circ} 4$-in elbow as 10 ft of straight pipe. Likewise, the equivalent length of a $45^{\circ}$ bend is 5 ft of straight pipe. Substituting in the preceding relation and using the straight lengths and the number of fittings of each type, $L_{e}=510+(2)(10)+4(5)=550 \mathrm{ft}$ of straight pipe.
2. Compute the pressure loss using a suitable chart. Figure 6.6 presents a typical pressure-loss chart for steam piping. Enter the chart at the top left at the superheated steam temperature of $350^{\circ} \mathrm{F}$ and project vertically downward until the 40-psig superheated steam pressure curve is intersected. From here, project horizontally to the right until the outer border of the chart is intersected. Next, project through the steam flow rate, $13,000 \mathrm{lb} / \mathrm{h}$ on scale $B$ of Fig. 6.6 to the pivot scale $C$. From this point, project through $4-$ in $(101.6-\mathrm{mm})$ schedule 40 pipe on scale $D$ of Fig. 6.6. Extend this line to intersect the pressure-drop scale and read the pressure loss as $7.25 \mathrm{lb} / \mathrm{in}^{2}(5 . \mathrm{kPa})$ per $100 \mathrm{ft}(30.4 \mathrm{~m})$ of pipe.

Since the equivalent length of this pipe is $550 \mathrm{ft}(167.6 \mathrm{~m})$, the total pressure loss in the pipe is $(550 / 100)(7.25)=39.875 \mathrm{lb} / \mathrm{m}^{2}(274.9 \mathrm{kPa})$, say $40 \mathrm{lb} / \mathrm{in}^{2}(275.8 \mathrm{kPa})$.
3. List the other methods of computing pressure loss. Numerous pressure-loss equations have been developed to compute the pressure drop in steam piping. Among the better-known equations are those of Unwin, Fritzche, Spitz-glass, Babcock, Gutermuth, and others. These equations are discussed in some detail in King and Crocker-Piping Handbook and in the engineering data published by valve and piping manufacturers.

Most piping designers use a chart to determine the pressure loss in steam piping because a chart saves time and reduces the effort involved. Further, the accuracy obtained is sufficient for all usual design practice.

Figure 6.7 is a popular flowchart for determining steam flow rate, pipe size, steam pressure, or steam velocity in a given pipe. Using this chart, the designer can determine any one of the four variables listed above when the other three are known. In solving a problem on the chart in Fig. 6.7, use the steam-quantity lines to intersect pipe sizes and the steam-pressure lines to intersect steam velocities. Here are two typical applications of this chart.

Example: What size schedule 40 pipe is needed to deliver $8000 \mathrm{lb} / \mathrm{h}(3600 \mathrm{~kg} / \mathrm{h})$ of $120-\mathrm{psig}$ $(827.3-\mathrm{kPa})$ steam at a velocity of $5000 \mathrm{ft} / \mathrm{min}(1524 \mathrm{~m} / \mathrm{min})$ ?

Solution: Enter Fig. 6.7 at the upper left at a velocity of $5000 \mathrm{ft} / \mathrm{min}$ and project along this velocity line until the 120 -psig pressure line is intersected. From this intersection, project horizontally until the $8000 \mathrm{lb} / \mathrm{h}(3600 \mathrm{~kg} / \mathrm{h})$ vertical line is intersected. Read the nearest pipe size as $4 \mathrm{in}(101.6 \mathrm{~mm})$ on the nearest pipe-diameter curve.

Example: What is the steam velocity in a 6-in (152.4-mm) pipe delivering 20,000 lb/h $(9000 \mathrm{~kg} / \mathrm{h})$ of steam at $85 \mathrm{psig}(586 \mathrm{kPa})$ ?

Solution: Enter the bottom of Fig. 6.7 at the flow rate, $20,000 \mathrm{lb} / \mathrm{h}$, and project vertically upward until the 6-in pipe ( $152.4-\mathrm{mm}$ ) curve is intersected. From this point, project horizontally to the $85-\mathrm{psig}$ $(586-\mathrm{kPa})$ curve. At the intersection, read the velocity as $7350 \mathrm{ft} / \mathrm{min}(2240.3 \mathrm{~m} / \mathrm{min})$.


FIGURE 6.5 Equivalent length of pipe fittings and valves. (Crane Co.)

FIGURE 6.6 Pressure loss in steam pipes based on the Fritzche formula. (Power.)


FIGURE 6.7 Spitzglass chart for saturated steam flowing in schedule 40 pipe.

Table 6.7 shows typical steam velocities for various industrial and commercial applications. Use the given values as guides when sizing steam piping.

## STEAM-TRAP SELECTION FOR PROCESS APPLICATIONS

Select steam traps for the following five types of equipment: (1) where the steam directly heats solid materials, as in autoclaves, retorts, and sterilizers; (2) where the steam indirectly heats a liquid through a metallic surface, as in heat exchangers and kettles where the quantity of liquid heated is known and unknown; (3) where the steam indirectly heats a solid through a metallic surface, as in dryers using cylinders or chambers and platen presses; and (4) where the steam indirectly heats air through metallic surfaces, as in unit heaters, pipe coils, and radiators.

## Calculation Procedure

1. Determine the condensate load. The first step in selecting a steam trap for any type of equipment is determination of the condensate load. Use the following general procedure.
a. Solid materials in autoclaves, retorts, and sterilizers. How much condensate is formed when 2000 lb of solid material with a specific heat of 1.0 is processed in 15 min at $240^{\circ} \mathrm{F}$ by 25 -psig steam from an initial temperature of $60^{\circ} \mathrm{F}$ in an insulated steel retort?

TABLE 6.7 Steam Velocities Used in Pipe Design

| Steam <br> condition | Steam pressure |  |  | Steam velocity |  |
| :--- | :--- | :--- | :--- | :--- | :---: |
|  | $\mathrm{lb} / \mathrm{in}^{2}$ | kPa | Steam use |  | $\mathrm{ft} / \mathrm{min}$ |
| Saturated | $0-15$ | $0-103.4$ | Heating | $4000-6000$ | $1219.2-1828.8$ |
| Saturated | $50-150$ | $344.7-1034.1$ | Process | $6000-10,000$ | $1828.8-3048.0$ |
| Superheated | 200 and higher | 1378.8 and higher | Boiler leads | $10,000-15,000$ | $3048.0-4572.0$ |

For this type of equipment, use $C=W s P$, where $C=$ condensate formed, in $\mathrm{lb} / \mathrm{h} ; W=$ weight of material heated, in $\mathrm{lb} ; s=$ specific heat, in $\mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right) ; P=$ factor from Table 6.8. Thus, for this application, $C=(2000)(1.0)(0.193)=386 \mathrm{lb}$ of condensate. Note that $P$ is based on a temperature rise of $240-60=180^{\circ} \mathrm{F}$ and a steam pressure of 25 psig . For the retort, using the specific heat of steel from Table $6.9, C=(4000)(0.12)(0.193)=92.6 \mathrm{lb}$ of condensate, say $93 \mathrm{lb}(41.9 \mathrm{~kg})$. The total weight of condensate formed in $15 \mathrm{~min}=386+93=479 \mathrm{lb}(215.6 \mathrm{~kg})$. In $1 \mathrm{~h}, 479(60 / 15)=$ $1916 \mathrm{lb}(862.2 \mathrm{~kg})$ of condensate is formed.

TABLE 6.8 Factors, $P=(T-t) / L$, to Find Condensate Load

| Pressure |  | Temperature |  |  |
| :---: | :---: | :---: | :---: | :---: |
| psia | kPa | $160^{\circ} \mathrm{F}\left(71.1^{\circ} \mathrm{C}\right)$ | $180^{\circ} \mathrm{F}\left(82.2^{\circ} \mathrm{C}\right)$ | $200^{\circ} \mathrm{F}\left(93.3^{\circ} \mathrm{C}\right)$ |
| 20 | 137.8 | 0.170 | 0.192 | 0.213 |
| 25 | 172.4 | 0.172 | 0.193 | 0.214 |
| 30 | 206.8 | 0.172 | 0.194 | 0.215 |

TABLE 6.9 Use These Specific Heats When Calculating Condensate Load

| Solids | $\mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)$ | $\mathrm{kJ} /(\mathrm{kg})\left({ }^{\circ} \mathrm{C}\right)$ | Liquids | $\mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)$ | $\mathrm{kJ} /(\mathrm{kg})\left({ }^{\circ} \mathrm{C}\right)$ |
| :--- | :---: | :---: | :--- | :---: | :---: |
| Aluminum | 0.23 | 0.96 |  | Alcohol | 0.65 |
| Brass | 0.10 | 0.42 | Carbon tetrachloride | 0.20 | 2.7 |
| Copper | 0.10 | 0.42 | Gasoline | 0.54 |  |
| Glass | 0.20 | 0.84 | Glycerin | 0.58 | 2.22 |
| Iron | 0.13 | 0.54 | Kerosene | 0.47 | 2.43 |
| Steel | 0.12 | 0.50 | Oils | $0.40-0.50$ | $1.67-2.09$ |

A safety factor must be applied to compensate for radiation and other losses. Typical safety factors used in selecting steam traps are

| Steam mains and headers | $2-3$ |
| :--- | ---: |
| Steam heating pipes | $2-6$ |
| Purifiers and separators | $2-3$ |
| Retorts for process | $2-4$ |
| Unit heaters | 3 |
| Submerged pipe coils | $2-4$ |
| Cylinder dryers | $4-10$ |

Using a safety factor of 4 for this process retort, the trap capacity $=(4)(1916)=7664 \mathrm{lb} / \mathrm{h}(3449$ $\mathrm{kg} / \mathrm{h}$ ), say $7700 \mathrm{lb} / \mathrm{h}$ ( $3465 \mathrm{~kg} / \mathrm{h}$ ).
TABLE 6.10 Ordinary Ranges of Overall Coefficients of Heat Transfer

| Type of heat exchanger | State of controlling resistance |  |  |  | Typical fluid | Typical apparatus |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Free convection, $U$ |  | Forced convection, $U$ |  |  |  |
| Liquid to liquid | 25-60 | [141.9-340.7] | 150-300 | [851.7-1703.4] | Water | Liquid-to-liquid heat exchangers |
| Liquid to liquid | 5-10 | [28.4-56.8] | 20-50 | [113.6-283.9] | Oil |  |
| Liquid to gas* | 1-3 | [5.7-17.0] | 2-10 | [11.4-56.8] | - | Hot-water radiators |
| Liquid to boiling liquid | 20-60 | [113.6-340.7] | 50-150 | [283.9-851.7] | Water | Brine coolers |
| Liquid to boiling liquid | 5-20 | [28.4-113.6] | 25-60 | [141.9-340.7] | Oil |  |
| Gas* to liquid | 1-3 | [5.7-17.0] | 2-10 | [11.4-56.8] | - | Air coolers, economizers |
| Gas* to gas | 0.6-2 | [3.4-11.4] | 2-6 | [11.4-34.1] | - | Steam superheaters |
| Gas* to boiling liquid | 1-3 | [5.7-17.0] | 2-10 | [11.4-56.8] | - | Steam boilers |
| Condensing vapor to liquid | 50-200 | [283.9-1136] | 150-800 | [851.7-4542.4] | Steam to water | Liquid heaters and condensers |
| Condensing vapor to liquid | 10-30 | [56.8-170.3] | 20-60 | [113.6-340.7] | Steam to oil |  |
| Condensing vapor to liquid | 40-80 | [227.1-454.2] | 60-150 | [340.7-851.7] | Organic vapor to water |  |
| Condensing vapor to liquid | - | - | 15-300 | [85.2-1703.4] | Steam-gas mixture |  |
| Condensing vapor to gas* | 1-2 | [5.7-11.4] | 2-10 | [11.4-56.8] | - | Steam pipes in air, air heaters |
| Condensing vapor to boiling liquid | 40-100 | [227.1-567.8] | - |  | - | Scale-forming evaporators |
| Condensing vapor to boiling liquid | 300-800 | [1703.4-4542.4] | - |  | Steam to water |  |
| Condensing vapor to boiling liquid | 50-150 | [283.9-851.7] | - |  | Steam to oil |  |

[^5]$\boldsymbol{b}(\mathbf{1})$. Submerged heating surface and a known quantity of liquid. How much condensate forms in the jacket of a kettle when $500 \mathrm{gal}(1892.5 \mathrm{~L})$ of water is heated in 30 min from 72 to $212^{\circ} \mathrm{F}$ ( 22.2 to $100^{\circ} \mathrm{C}$ ) with $50-\mathrm{psig}(344.7-\mathrm{kPa})$ steam?

For this type of equipment, $C=G w s P$, where $G=$ gallons of liquid heated; $w=$ weight of liquid, in lb/gal. Substitute the appropriate values as follows: $C=(500)(8.33)(1.0) \times(0.154)=641 \mathrm{lb}$, or $(641)(60 / 30)=1282 \mathrm{lb} / \mathrm{h}$. Using a safety factor of 3 , the trap capacity $=(3)(1282)=3846 \mathrm{lb} / \mathrm{h}$; say $3900 \mathrm{lb} / \mathrm{h}$.
$\boldsymbol{b}(2)$. Submerged heating surface and an unknown quantity of liquid. How much condensate is formed in a coil submerged in oil when the oil is heated as quickly as possible from 50 to $250^{\circ} \mathrm{F}$ by 25 -psig steam if the coil has an area of $50 \mathrm{ft}^{2}$ and the oil is free to circulate around the coil?

For this condition, $C=U A P$, where $U=$ overall coefficient of heat transfer, in $\mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)$, from Table $6.10 ; A=$ area of heating surface, in $\mathrm{ft}^{2}$. With free convection and a condensing-vapor-toliquid type of heat exchanger, $U=10$ to 30 . Using an average value of $U=20, C=(20)(50)(0.214)$ $=214 \mathrm{lb} / \mathrm{h}$ of condensate. Choosing a safety factor 3, the trap capacity $=(3)(214)=642 \mathrm{lb} / \mathrm{h}$; say $650 \mathrm{lb} / \mathrm{h}$.
$\boldsymbol{b}(3)$. Submerged surfaces having more area then needed to heat a specified quantity of liquid in a given time with condensate withdrawn as rapidly as formed. Use Table 6.11 instead of steps $b(1)$ or $b(2)$. Find the condensation rate by multiplying the submerged area by the appropriate factor from Table 6.11. Use this method for heating water, chemical solutions, oils, and other liquids. Thus, with steam at 100 psig and a temperature of $338^{\circ} \mathrm{F}$ and heating oil from 50 to $226^{\circ} \mathrm{F}$ with a submerged surface having an area of $500 \mathrm{ft}^{2}$, the mean temperature difference equals steam temperature minus the average liquid temperature $=M t d=338-(50+226 / 2)=200^{\circ} \mathrm{F}$. The factor from Table 6.11 for 100 -psig steam and a $200^{\circ} \mathrm{F}$ Mtd is 56.75 . Thus the condensation rate $=(56.75) \times(500)=28,375$ $\mathrm{lb} / \mathrm{h}$. With a safety factor of 2 , the trap capacity $=(2)(28,375)=56,750 \mathrm{lb} / \mathrm{h}$.
c. Solids indirectly heated through a metallic surface. How much condensate is formed in a chamber dryer when 1000 lb of cereal is dried to 750 lb by $10-\mathrm{psig}$ steam? The initial temperature of the cereal is $60^{\circ} \mathrm{F}$ and the final temperature equals that of the steam.

For this condition, $C=970(W-D) / h_{f g}+W P$, where $D=$ dry weight of the material, in lb ; $h_{f g}=$ enthalpy of vaporization of the steam at the trap pressure, in Btu/lb. Using the steam tables and Table $6.8, C=970(1000-750) / 952+(1000)(0.189)=443.5 \mathrm{lb} / \mathrm{h}$ of condensate. With a safety factor of 4, the trap capacity $=(4)(443.5)=1774 \mathrm{lb} / \mathrm{h}$.
d. Indirect heating of air through a metallic surface. How much condensate is formed in a unit heater using 10 -psig steam if the entering-air temperature is $30^{\circ} \mathrm{F}$ and the leaving-air temperature is $130^{\circ} \mathrm{F}$ ? Airflow is $10,000 \mathrm{ft}^{3} / \mathrm{min}$.

Use Table 6.12, entering at a temperature difference of $100^{\circ} \mathrm{F}$ and projecting to a steam pressure of 10 psig. Read the condensate formed as $122 \mathrm{lb} / \mathrm{h}$ per $1000 \mathrm{ft}^{3} / \mathrm{min}$. Since $10,000 \mathrm{ft}^{3} / \mathrm{min}$ of air is being heated, the condensation rate $=(10,000 / 1000)(122)=1220 \mathrm{lb} / \mathrm{h}$. With a safety factor of 3 , the trap capacity $=(3)(1220)=3660 \mathrm{lb} / \mathrm{h}$, say $3700 \mathrm{lb} / \mathrm{h}$.

Table 6.13 shows the condensate formed by radiation from bare iron and steel pipes in still air and with forced-air circulation. Thus, with a steam pressure of 100 psig and an initial air temperature of

TABLE 6.11 Condensate Formed in Submerged Steel* Heating Elements, $\mathrm{lb} /\left(\mathrm{ft}^{2}\right)(\mathrm{h})\left[\mathrm{kg} /\left(\mathrm{m}^{2}\right)(\mathrm{min})\right]$

| $M t d \dagger$ |  | Steam pressure |  |  |  |  |  |  |  |  |  |  |  |
| :--- | ---: | :---: | :---: | :---: | :---: | ---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| ${ }^{\circ} \mathrm{F}$ |  |  |  |  |  |  |  | ${ }^{\circ} \mathrm{C}$ | $75 \mathrm{psia}(517.1 \mathrm{kPa})$ | $100 \mathrm{psia}(689.4 \mathrm{kPa})$ | $150 \mathrm{psia}(1034.1 \mathrm{kPa})$ | Btu/(ft$\left.{ }^{2}\right)(\mathrm{h})$ | $\mathrm{kW} / \mathrm{m}^{2}$ |
| 175 | 97.2 | $44.3(3.6)$ | $45.4(3.7)$ | $46.7(3.8)$ | 40,000 | 126.2 |  |  |  |  |  |  |  |
| 200 | 111.1 | $54.8(4.5)$ | $56.8(4.6)$ | $58.3(4.7)$ | 50,000 | 157.7 |  |  |  |  |  |  |  |
| 250 | 138.9 | $90.0(7.3)$ | $93.1(7.6)$ | $95.7(7.8)$ | 82,000 | 258.6 |  |  |  |  |  |  |  |

[^6]TABLE 6.12 Steam Condensed by Air, $\mathrm{lb} / \mathrm{h}$ at $1000 \mathrm{ft}^{3} / \mathrm{min}\left(\mathrm{kg} / \mathrm{h} \text { at } 28.3 \mathrm{~m}^{3} / \mathrm{min}\right)^{*}$

| Temperature <br> difference |  | Pressure |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| ${ }^{\circ} \mathrm{F}$ |  | ${ }^{\circ} \mathrm{C}$ | $5 \mathrm{psig}(34.5 \mathrm{kPa})$ | $10 \mathrm{psig}(68.9 \mathrm{kPa})$ |  |
| 50 | 27.8 | $61(27.5)$ | $60 \mathrm{psig}(344.7 \mathrm{kPa})$ |  |  |
| 100 | 55.6 | $120(54.0)$ | $122(54.5)$ | $63(28.4)$ |  |
| 150 | 83.3 | $180(81.0)$ | $183(82.4)$ | $126(56.7)$ |  |

${ }^{*}$ Based on $0.0192 \mathrm{Btu}(0.02 \mathrm{~kJ})$ absorbed per cubic foot $\left(0.028 \mathrm{~m}^{3}\right)$ of saturated air per ${ }^{\circ} \mathrm{F}\left(0.556^{\circ} \mathrm{C}\right)$ at $32^{\circ} \mathrm{F}\left(0^{\circ} \mathrm{C}\right)$. For $0^{\circ} \mathrm{F}\left(-17.8^{\circ} \mathrm{C}\right)$, multiply by 1.1 .

TABLE 6.13 Condensate Formed by Radiation from Bare Iron and Steel*, $\mathrm{lb} /\left(\mathrm{ft}^{2}\right)(\mathrm{h})\left[\mathrm{kg} /\left(\mathrm{m}^{2}\right)(\mathrm{h})\right]$

| Air <br> temperature |  | Steam pressure |  |  |  |
| :--- | :---: | :---: | :---: | :---: | :---: |
| ${ }^{\circ} \mathrm{F}$ |  | ${ }^{\circ} \mathrm{C}$ | $50 \mathrm{psig}(344.7 \mathrm{kPa})$ | $75 \mathrm{psig}(517.1 \mathrm{kPa})$ | $100 \mathrm{psig}(689.5 \mathrm{kPa})$ |
| 65 | 18.3 | $0.82(3.97)$ | $150 \mathrm{psig}(1034 \mathrm{kPa})$ |  |  |
| 70 | 21.2 | $0.80(3.87)$ | $0.98(5.84)$ | $1.08(5.23)$ | $1.32(6.39)$ |
| 75 | 23.9 | $0.77(3.73)$ | $0.88(4.26)$ | $1.06(5.13)$ | $1.21(5.86)$ |

*Based on still air; for forced-air circulation, multiply by 5 .
$75^{\circ} \mathrm{F}, 1.05 \mathrm{lb} / \mathrm{h}$ of condensate will be formed per square foot of heating surface in still air. With forced air circulation, the condensate rate is $(5)(1.05)=5.25 \mathrm{lb} / \mathrm{h}$ per square foot of heating surface.

Unit heaters have a standard rating based on 2-psig steam with entering air at $60^{\circ} \mathrm{F}$. If the steam pressure or air temperature is different from these standard conditions, multiply the heater Btu/h capacity rating by the appropriate correction factor from Table 6.14 . Thus a heater rated at 10,000 $\mathrm{Btu} / \mathrm{h}$ with 2-psig steam and $60^{\circ} \mathrm{F}$ air would have an output of $(1.290)(10,000)=12,900 \mathrm{Btu} / \mathrm{h}$ with $40^{\circ} \mathrm{F}$ inlet air and $10-\mathrm{psig}$ steam. Trap manufacturers usually list heater Btu ratings and recommend trap model numbers and sizes in their trap engineering data. This allows easier selection of the correct trap.
2. Select the trap size based on the load and steam pressure. Obtain a chart or tabulation of trap capacities published by the manufacturer whose trap will be used. Figure 6.8 is a capacity chart for one type of bucket trap manufactured by Armstrong Machine Works. Table 6.15 shows typical capacities of impulse traps manufactured by the Yarway Company. Be sure to use up-to-date vendor data.

To select a trap from Fig. 6.8, when the condensation rate is uniform and the pressure across the trap is constant, enter at the left at the condensation rate-say $8000 \mathrm{lb} / \mathrm{h}(3600 \mathrm{~kg} / \mathrm{h})$ (as obtained from step 1) -and project horizontally to the right to the vertical ordinate representing the pressure

TABLE 6.14 Unit-Heater Correction Factors

| Steam pressure |  | Temperature of entering air |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  |  | $20^{\circ} \mathrm{F}$ <br> $\left(-6.7^{\circ} \mathrm{C}\right)$ | $40^{\circ} \mathrm{F}$ <br> $\left(4.4^{\circ} \mathrm{C}\right)$ | $60^{\circ} \mathrm{F}$ <br> $\left(15.6^{\circ} \mathrm{C}\right)$ |
| psig | kPa | 1.370 | 1.206 | 1.050 |
| 5 | 34.5 | 1.460 | 1.290 | 1.131 |
| 10 | 68.9 | 1.525 | 1.335 | 1.194 |
| 15 | 103.4 |  |  |  |

Source: Yarway Corporation; SI values added by Handbook editor.


FIGURE 6.8 Capacities of one type of bucket steam trap. (Armstrong Machine Works.)
across the trap $(=\Delta p=$ steam-line pressure, in psig—return-line pressure with trap valve closed, in psig). Assume $\Delta p=20 \mathrm{psig}(138 \mathrm{kPa})$ for this trap. The intersection of the horizontal $8000 \mathrm{lb} / \mathrm{h}$ $(3600 \mathrm{~kg} / \mathrm{h})$ projection and the vertical $20-\mathrm{psig}(137.9-\mathrm{kPa})$ projection is on the sawtooth capacity curve for a trap having a $9 / 16$-in (14.3-mm) orifice. If these projections intersected beneath this curve, a $9 / 16$-in ( $14.3-\mathrm{mm}$ ) orifice would still be used if the point was between the verticals for this size orifice.

The dashed lines extending downward from the sawtooth curves show the capacity of a trap at reduced $\Delta p$. Thus the capacity of a trap with a $3 / 8-\mathrm{in}(9.53-\mathrm{mm})$ orifice at $\Delta p=30 \mathrm{psig}(207 \mathrm{kPa})$ is $6200 \mathrm{lb} / \mathrm{h}(2790 \mathrm{~kg} / \mathrm{h})$, read at the intersection of the $30-\mathrm{psig}(207-\mathrm{kPa})$ ordinate and the dashed curve extended from the $3 / 8$-in $(9.53-\mathrm{mm})$ solid curve.

To select an impulse trap from Table 6.15, enter the table at the trap inlet pressure-say 125 psig $(862 \mathrm{kPa})$ —and project to the desired capacity—say $8000 \mathrm{lb} / \mathrm{h}(3600 \mathrm{~kg} / \mathrm{h})$, determined from step 1 . Table 6.15 shows that a $2-\mathrm{in}(50.8-\mathrm{mm})$ trap having an $8530 \mathrm{lb} / \mathrm{h}(3839 \mathrm{~kg} / \mathrm{h})$ capacity must be used because the next smallest size has a capacity of $5165 \mathrm{lb} / \mathrm{h}(2324 \mathrm{~kg} / \mathrm{h})$. This capacity is less than that required.

Some trap manufacturers publish capacity tables relating various trap models to specific types of equipment. Such tables simplify trap selection, but the condensation rate must still be computed as given here.

TABLE 6.15 Capacities of Impulse Traps, $\mathrm{lb} / \mathrm{h}(\mathrm{kg} / \mathrm{h})$ [maximum continuous discharge of condensate, based on condensate at $30^{\circ} \mathrm{F}\left(16.7^{\circ} \mathrm{C}\right)$ below steam temperature]

| Pressure at trap inlet |  | Trap nominal size |  |
| :--- | :---: | :---: | :---: |
| psig | kPa | 1.25 in $(38.1 \mathrm{~mm})$ | 2.0 in $(50.8 \mathrm{~mm})$ |
| 125 | 861.8 | $6165(2774)$ | $8530(3839)$ |
| 150 | 1034.1 | $6630(2984)$ | $9075(4084)$ |
| 200 | 1378.8 | $7410(3335)$ | $9950(4478)$ |

Source: Yarway Corporation.

Related Calculations. Use the procedure given here to determine the trap capacity required for any industrial, commercial, or domestic application.

When using a trap-capacity diagram or table, be sure to determine the basis on which it was prepared. Apply any necessary correction factors. Thus cold-water capacity ratings must be corrected for traps operating at higher condensate temperatures. Correction factors are published in trap engineering data. The capacity of a trap is greater at condensate temperatures less than $212^{\circ} \mathrm{F}\left(100^{\circ} \mathrm{C}\right)$, because at or above this temperature condensate forms flash steam when it flows into a pipe or vessel at atmospheric [14.7 psia ( 101.3 kPa )] pressure. At altitudes above sea level, condensate flashes into steam at a lower temperature, depending on the altitude.

The method presented here is the work of L. C. Campbell, Yarway Corporation, as reported in Chemical Engineering.

### 6.14 ORIFICE-METER SELECTION FOR A STEAM PIPE

Steam is metered with an orifice meter in a 10-in boiler lead having an internal diameter of $d_{p}=9.760$ in. Determine the maximum rate of steam flow that can be measured with a steel orifice plate having a diameter of $d_{o}=5.855$ in at $70^{\circ} \mathrm{F}(294 \mathrm{~K})$. The upstream pressure tap is $1 D$ ahead of the orifice, and the downstream tap is $0.5 D$ past the orifice. Steam pressure at the orifice inlet $p_{p}=250 \mathrm{psig}$ ( 1825 kPa ); temperature is $640^{\circ} \mathrm{F}(611 \mathrm{~K})$. A differential gage fitted across the orifice has a maximum range of 120 in of water. What is the steam flow rate when the observed differential pressure is 40 in of water? Use the ASME Research Committee on Fluid Meters method in analyzing the meter. Atmospheric pressure is 14.696 psia.

## Calculation Procedure

1. Determine the diameter ratio and steam density. For any orifice meter, diameter ratio $=\beta=$ meter orifice diameter, in/pipe internal diameter, in $=5.855 / 9.760=0.5999$.

Determine the density of the steam by entering the superheated steam table at $250+14.696=$ 264.696 psia and $640^{\circ} \mathrm{F}$ and reading the specific volume as $2.387 \mathrm{ft}^{3} / \mathrm{lb}$. For steam, the density $=$ $1 /$ specific volume $=d_{s}=1 / 2.387=0.4193 \mathrm{lb} / \mathrm{ft}^{3}$.
2. Determine the steam viscosity and meter flow coefficient. From the ASME publication Fluid Meters-Their Theory and Application, the steam viscosity $g u_{1}$ for a steam system operating at $640^{\circ} \mathrm{F}$ is $g u_{1}=0.0000141 \mathrm{in} \cdot \mathrm{lb} /\left({ }^{\circ} \mathrm{F}\right)(\mathrm{s})\left(\mathrm{ft}^{2}\right)$.

Find the flow coefficient $K$ from the same ASME source by entering the 10 -in nominal pipe diameter table at $\beta=0.5999$ and projecting to the appropriate Reynolds number column. Assume that the Reynolds number $=10^{7}$, approximately, for the flow conditions in this pipe. Then, $K=$ 0.6486. Since the Reynolds number for steam pressures above $100 \mathrm{lb} / \mathrm{in}^{2}$ ranges from $10^{6}$ to $10^{7}$, this assumption is safe because the value of $K$ does not vary appreciably in this Reynolds number range. Also, the Reynolds number cannot be computed yet because the flow rate is unknown. Therefore, assumption of the Reynolds number is necessary. The assumption will be checked later.
3. Determine the expansion factor and the meter area factor. Since steam is a compressible fluid, the expansion factor $Y_{1}$ must be determined. For superheated steam, the ratio of the specific heat at constant pressure $c_{p}$ to the specific heat at constant volume $c_{v}$ is $k=c_{p} / c_{v}=1.3$. Also, the ratio of the differential maximum pressure reading $h_{w}$, in in of water, to the maximum pressure in the pipe, in psia, equals $120 / 246.7=0.454$. Using the expansion-factor curve in the ASME Fluid Meters, $Y_{1}=$ 0.994 for $\beta=0.5999$, and the pressure ratio $=0.454$. And, from the same reference, the meter area factor $F_{a}=1.0084$ for a steel meter operating at $640^{\circ} \mathrm{F}$.
4. Compute the rate of steam flow. For square-edged orifices, the flow rate, in $\mathrm{lb} / \mathrm{s}$, is $w=0.0997 F_{a} K d^{2} Y_{1}\left(h_{w} d_{s}\right)^{0.5}=(0.0997)(1.0084)(0.6468)(5.855)^{2}(0.994)(120 \times 0.4188)^{0.5}=$ $15.75 \mathrm{lb} / \mathrm{s}$.
5. Compute the Reynolds number for the actual flow rate. For any steam pipe, the Reynolds number $\operatorname{Re}=48 w / d_{p} g u_{1}=48(15.75) /[3.1416(0.760)(0.0000141)]=1,750,000$.
6. Adjust the flow coefficient for the actual Reynolds number. In step $2, \mathrm{Re}=10^{7}$ was assumed and $K=0.6486$. For $\operatorname{Re}=1,750,000, K=0.6489$, from ASME Fluid Meters, by interpolation. Then, the actual flow rate $w_{h}=$ (computed flow rate) (ratio of flow coefficients based on assumed and actual Reynolds numbers $)=(15.75)(0.6489 / 0.6486)(3600)=56,700 \mathrm{lb} / \mathrm{h}$, closely, where the value 3600 is a conversion factor for changing $\mathrm{lb} / \mathrm{s}$ to $\mathrm{lb} / \mathrm{h}$.
7. Compute the flow rate for a specific differential gage deflection. For a $40-\mathrm{in} \mathrm{H}_{2} \mathrm{O}$ deflection, $F_{a}$ is unchanged and equals 1.0084. The expansion factor changes because $h_{w} / p_{p}=40 / 264.7=0.151$. Using the ASME Fluid Meters, $Y_{1}=0.998$. Assuming again that $\operatorname{Re}=10^{7}, K=0.6486$, as before; then $w=0.0997(1.0084)(0.6486)(5.855)^{2}(0.998)(40 \times 0.4188)^{0.5}=9.132 \mathrm{lb} / \mathrm{s}$. Computing the Reynolds number as before, $\operatorname{Re}=40(0.132) /[3.1416(0.76)(0.0000141)]=1,014,000$. The value of $K$ corresponding to this value, as before, is from ASME Fluid Meters; $K=0.6497$. Therefore, the flow rate for a 40 -in $\mathrm{H}_{2} \mathrm{O}$ reading, in $\mathrm{lb} / \mathrm{h}$, is $w_{h}=0.132(0.6497 / 0.6486)(3600)=32,940 \mathrm{lb} / \mathrm{h}$ $(4.15 \mathrm{~kg} / \mathrm{s})$.

Related Calculations. Use these steps and the ASME Fluid Meters or comprehensive meter engineering tables giving similar data to select or check an orifice meter used in any type of steam pipe-main, auxiliary, process, industrial, marine, heating, or commercial-conveying wet, saturated, or superheated steam.

### 6.15 SELECTION OF A PRESSURE-REGULATING VALVE FOR STEAM SERVICE

Select a single-seat spring-loaded diaphragm-actuated pressure-reducing valve to deliver $350 \mathrm{lb} / \mathrm{h}$ $(0.044 \mathrm{~kg} / \mathrm{s})$ of steam at 50 psig when the initial pressure is 225 psig . Also select an integral pilotcontrolled piston-operated single-seat pressure-regulating valve to deliver $30,000 \mathrm{lb} / \mathrm{h}(3.78 \mathrm{~kg} / \mathrm{s})$ of steam at 40 psig with an initial pressure of 225 psig saturated. What size pipe must be used on the downstream side of the valve to produce a velocity of $10,000 \mathrm{ft} / \mathrm{min}(50.8 \mathrm{~m} / \mathrm{s})$ ? How large should the pressure-regulating valve be if the steam entering the valve is at 225 psig and $600^{\circ} \mathrm{F}(589 \mathrm{~K})$ ?

## Calculation Procedure

1. Compute the maximum flow for the diaphragm-actuated valve. For best results in service, pressure-reducing valves are selected so that they operate 60 to 70 percent open at normal load. To obtain a valve sized for this opening, divide the desired delivery, in lb/h, by 0.7 to obtain the maximum flow expected. For this valve, then, the maximum flow is $350 / 0.7=500 \mathrm{lb} / \mathrm{h}$.
2. Select the diaphragm-actuated valve size. Using a manufacturer's engineering data for an acceptable valve, enter the appropriate valve-capacity table at the valve inlet steam pressure, 225 psig, and project to a capacity of $500 \mathrm{lb} / \mathrm{h}$, as in Table 6.16 . Read the valve size as $3 / 4$ in at the top of the capacity column.

TABLE 6.16 Pressure-Reducing-Valve Capacity, $\mathrm{lb} / \mathrm{h}(\mathrm{kg} / \mathrm{h})$

| Inlet pressure |  | Valve size |  |  |
| :--- | :---: | :---: | :---: | :---: |
| psig | kPa | $1 / 2$ in $(12.7 \mathrm{~mm})$ | $3 / 4$ in $(19.1 \mathrm{~mm})$ | 1 in $(25.4 \mathrm{~mm})$ |
| 200 | 1379 | $420(189)$ | $460(207)$ | $560(252)$ |
| 225 | 1551 | $450(203)$ | $500(225)$ | $600(270)$ |
| 250 | 1724 | $485(218)$ | $560(252)$ | $650(293)$ |

Source: Clark-Reliance Corporation.
3. Select the size of the pilot-controlled pressure-regulating valve. Enter the capacity table in the engineering data of an acceptable pilot-controlled pressure-regulating valve, similar to Table 6.17, at the required capacity, $30,000 \mathrm{lb} / \mathrm{h}$, and project across until the correct inlet steam pressure column, 225 psig , is intercepted, and read the required valve size as 4 in .

Note that it is not necessary to compute the maximum capacity before entering the table, as in step 1 , for the pressure-reducing valve. Also note that a capacity table such as Table 6.17 can be used only for valves conveying saturated steam, unless the table notes state that the values listed are valid for other steam conditions.
4. Determine the size of the downstream pipe. Enter Table 6.17 at the required capacity, 30,000 $\mathrm{lb} / \mathrm{h}(13,500 \mathrm{~kg} / \mathrm{h})$, and project across to the valve outlet pressure, $40 \mathrm{psig}(275.8 \mathrm{kPa})$, and read the required pipe size as 8 in ( 203.2 mm ) for a velocity of $10,000 \mathrm{ft} / \mathrm{min}(3048 \mathrm{~m} / \mathrm{min})$. Thus the pipe immediately downstream from the valve must be enlarged from the valve size, 4 in ( 101.6 mm ), to the required pipe size, 8 in ( 203.2 mm ), to obtain the desired steam velocity.
5. Determine the size of the valve handling superheated steam. To determine the correct size of a pilot-controlled pressure regulating valve handling superheated steam, a correction must be applied. Either a factor may be used or a tabulation of corrected pressures, such as Table 6.18. To use Table 6.18, enter at the valve inlet pressure, $225 \mathrm{psig}(1551.2 \mathrm{kPa})$, and project across to the total temperature, $600^{\circ} \mathrm{F}\left(316^{\circ} \mathrm{C}\right)$, to read the corrected pressure, $165 \mathrm{psig}(1137.5 \mathrm{kPa})$. Enter Table 6.17 at the next highest saturated steam pressure, 175 psig , and project down to the required capacity, $30,000 \mathrm{lb} / \mathrm{h}$ $(13,500 \mathrm{~kg} / \mathrm{h})$, and read the required valve size as 5 in $(127 \mathrm{~mm})$.

Related Calculations. To simplify pressure-reducing and pressure-regulating valve selection, become familiar with two or three acceptable valve manufacturers' engineering data. Use the procedures given in the engineering data or those given here to select valves for industrial, marine, utility, heating, process, laundry, kitchen, or hospital service with a saturated or superheated steam supply.

Do not oversize reducing or regulating valves. Oversizing causes chatter and excessive wear.
When an anticipated load on the downstream side will not develop for several months after installation of a valve, fit to the valve a reduced-area disk sized to handle the present load. When the load increases, install a full-size disk. Size the valve for the ultimate load, not the reduced load.

Where there is a wide variation in demand for steam at the reduced pressure, consider installing two regulators piped in parallel. Size the smaller regulator to handle light loads and the larger regulator to

TABLE 6.17 Pressure-Regulating-Valve Capacity

| Steam capacity |  | Initital steam pressure, saturated |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{lb} / \mathrm{h}$ | $\mathrm{kg} / \mathrm{h}$ | $40 \mathrm{psig}(276 \mathrm{kPa})$ | $175 \mathrm{psig}(1206 \mathrm{kPa})$ | $225 \mathrm{psig}(1551 \mathrm{kPa})$ | $300 \mathrm{psig}(2068 \mathrm{kPa})$ |  |
| 20,000 | 9,000 | $6^{*}(152.4)$ | $4(101.6)$ | $4(101.6)$ | $3(76.2)$ |  |
| 30,000 | 13,500 | $8(203.2)$ | $5(127.0)$ | $4(101.6)$ | $4(101.6)$ |  |
| 40,000 | 18,000 | - | - | $5(127.0)$ | $5(127.0)$ |  |

[^7]Any use is subject to the Terms of Use as given at the website.

TABLE 6.18 Equivalent Saturated Steam Values for Superheated Steam at Various Pressures and Temperatures

|  |  | Total temperature |  |  |  |  |  |  |  |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | ---: |
|  | Steam pressure |  | Steam temp. |  | $500^{\circ} \mathrm{F}$ | $600^{\circ} \mathrm{F}$ | $700^{\circ} \mathrm{F}$ | $260.0^{\circ} \mathrm{C}$ | $315.6^{\circ} \mathrm{C}$ |
| $371.1^{\circ} \mathrm{C}$ |  |  |  |  |  |  |  |  |  |
| psig | kPa | ${ }^{\circ} \mathrm{F}$ | ${ }^{\circ} \mathrm{C}$ | Steam values, psig |  | Steam values, kPa |  |  |  |
| 205 | 1413.3 | 389 | 198 | 171 | 149 | 133 | 1178.9 | 1027.2 | 916.9 |
| 225 | 1551.2 | 397 | 203 | 190 | 165 | 147 | 1309.9 | 1137.5 | 1013.4 |
| 265 | 1826.9 | 411 | 211 | 227 | 200 | 177 | 1564.9 | 1378.8 | 1220.2 |

Source: Clark-Reliance Corporation.
handle the difference between 60 percent of the light load and the maximum heavy load. Set the larger regulator to open when the minimum allowable reduced pressure is reached. Then both regulators will be open to handle the heavy load. Be certain to use the actual regulator inlet pressure and not the boiler pressure when sizing the valve if this is different from the inlet pressure. Data in this calculation procedure are based on valves built by the Clark-Reliance Corporation, Cleveland, Ohio.

Some valve manufacturers use the valve-flow coefficient $C_{v}$ for valve sizing. This coefficient is defined as the flow rate, in $\mathrm{lb} / \mathrm{h}$, through a valve of given size when the pressure loss across the valve is $1 \mathrm{lb} / \mathrm{in}^{2}$. Tabulations such as Tables 6.16 and 6.17 incorporate this flow coefficient and are somewhat, easier to use. These tables make the necessary allowances for downstream pressures less than the critical pressure ( $=0.55 \times$ absolute upstream pressure, in $\mathrm{lb} / \mathrm{in}^{2}$, for superheated steam and hydrocarbon vapors, and $0.58 \times$ absolute upstream pressure, in $1 \mathrm{lb} / \mathrm{in}^{2}$, for saturated steam). The accuracy of these tabulations equals that of valve size determined by using the flow coefficient.

### 6.16 PRESSURE-REDUCING-VALVE SELECTION FOR WATER PIPING

What size pressure-reducing valve should be used to deliver $1200 \mathrm{gal} / \mathrm{h}(1.26 \mathrm{~L} / \mathrm{s})$ of water at $40 \mathrm{lb} / \mathrm{in}^{2}$ $(275.8 \mathrm{kPa})$ if the inlet pressure is $140 \mathrm{lb} / \mathrm{in}^{2}(965.2 \mathrm{kPa})$ ?

## Calculation Procedure

1. Determine the valve capacity required. Pressure-reducing valves in water systems operate best when the nominal load is 60 to 70 percent of the maximum load. Using 60 percent, the maximum load for this valve $=1200 / 0.6=2000 \mathrm{gal} / \mathrm{h}(2.1 \mathrm{~L} / \mathrm{s})$.
2. Determine the valve size required. Enter a valve-capacity table in suitable valve engineering data at the valve inlet pressure and project to the exact, or next higher, valve capacity. Thus, enter Table $6.19 \mathrm{at} 140 \mathrm{lb} / \mathrm{in}^{2}(965.2 \mathrm{kPa})$ and project to the next higher capacity, $2200 \mathrm{gal} / \mathrm{h}(2.3 \mathrm{~L} / \mathrm{s})$, since

TABLE 6.19 Maximum Capacities of Water Pressure-Reducing Valves, gal/h (L/h)

| Inlet pressure |  | Valve size |  |  |
| :---: | :---: | :---: | :---: | :---: |
| psig | kPa | $3 / 4$ in $(19.1 \mathrm{~mm})$ | 1 in $(25.4 \mathrm{~mm})$ | $11 / 4$ in $(31.8 \mathrm{~mm})$ |
| 120 | 827.3 | $1550(5867)$ | $2000(7570$ | $4500(17,033)$ |
| 140 | 965.2 | $1700(6435)$ | $2200(8327)$ | $5000(18,925)$ |
| 160 | 1103.0 | $1850(7002)$ | $2400(9084)$ | $5500(20,818)$ |

Source: Clark-Reliance Corporation.


FIGURE 6.9 Pressure-reducing valve flow capacity. (Foster Engineering Co.)
a capacity of $2000 \mathrm{gal} / \mathrm{h}(2.1 \mathrm{~L} / \mathrm{s})$ is not tabulated. Read at the top of the column the required valve size as 1 in ( 25.4 mm ).

Some valve manufacturers present the capacity of their valves in graphic instead of tabular form. One popular chart, Fig. 6.9, is entered at the difference between the inlet and outlet pressures on the abscissa, or $140-40=100 \mathrm{lb} / \mathrm{in}^{2}(689.4 \mathrm{kPa})$. Project vertically to the flow rate of $2000 / 60=33.3$ $\mathrm{gal} / \mathrm{min}(2.1 \mathrm{~L} / \mathrm{s})$. Read the valve size on the intersecting valve-capacity curve, or on the next curve if there is no intersection with the curve. Figure 6.9 shows that a 1 -in valve should be used. This agrees with the tabulated capacity.

Related Calculations. Use this method for pressure-reducing valves in any type of water pipingprocess, domestic, commercial-where the water temperature is $100^{\circ} \mathrm{F}\left(37.8^{\circ} \mathrm{C}\right)$ or less. Table 6.19 is from data prepared by the Clark-Reliance Corporation; Figure 6.9 is from Foster Engineering Company data. Be sure to use up-to-date vendor data.

Some valve manufacturers use the valve-flow coefficient $C_{v}$ for valve sizing. This coefficient is defined as the flow rate, in gal/min, through a valve of given size when the pressure loss across the valve is $1 \mathrm{lb} / \mathrm{in}^{2}$. Tabulations such as Table 6.19 and flowcharts such as Fig. 6.9 incorporate this flow coefficient and are somewhat easier to use. Their accuracy equals that of the flow-coefficient method.

### 6.17 SIMILARITY OR AFFINITY LAWS FOR CENTRIFUGAL PUMPS

A centrifugal pump designed for an 1800-r/min operation and a head of $200 \mathrm{ft}(61 \mathrm{~m})$ has a capacity of $3000 \mathrm{gal} / \mathrm{min}\left(0.19 \mathrm{~m}^{3} / \mathrm{s}\right)$ with a power input of 175 hp . What effect will a speed reduction to 1200 $\mathrm{r} / \mathrm{min}$ have on the head, capacity, and power input of the pump? What will be the change in these variables if the impeller diameter is reduced from 12 to 10 in while the speed is held constant at $1800 \mathrm{r} / \mathrm{min}$ ?

## Calculation Procedure

1. Compute the effect of a change in pump speed. For any centrifugal pump in which the effects of fluid viscosity are negligible or are neglected, the similarity or affinity laws can be used to determine the effect of a speed, power, or head change. For a constant impeller diameter, these laws are $Q_{1} / Q_{2}=N_{1} / N_{2} ; H_{1} / H_{2}=\left(N_{1} / N_{2}\right)^{2} ; P_{1} / P_{2}=\left(N_{1} / N_{2}\right)^{3}$. For a constant speed, $Q_{1} / Q_{2}=D_{1} / D_{2} ; H_{1} / H_{2}=\left(D_{1} / D_{2}\right)^{2} ; P_{1} / P_{2}=\left(D_{1} / D_{2}\right)^{3}$. In both sets of laws, $Q=$ capacity, in gal $/ \mathrm{min} ; N=$ impeller $\mathrm{r} / \mathrm{min} ; D=$ impeller diameter, in in; $H=$ total head, in ft of liquid; $P=$ bhp input. The subscripts 1 and 2 refer to the initial and changed conditions, respectively.

For this pump, with a constant impeller diameter, $Q_{1} / Q_{2}=N_{1} / N_{2} ; 3000 / Q_{2}=1800 / 1200$; $Q_{2}=2000 \mathrm{gal} / \mathrm{min}\left(0.13 \mathrm{~m}^{3} / \mathrm{s}\right)$. And, $H_{1} / H_{2}=\left(N_{1} / N_{2}\right)^{2}=200 / H_{2}=(1800 / 1200)^{2} ; H_{2}=$ $88.9 \mathrm{ft}(27.1 \mathrm{~m})$. Also, $P_{1} / P_{2}=\left(N_{1} / N_{2}\right)^{3}=175 / P_{2}=(1800 / 1200)^{3} ; P_{2}=51.8 \mathrm{bhp}$.
2. Compute the effect of a change in impeller diameter. With the speed constant, use the second set of laws. Or for this pump, $Q_{1} / Q_{2}=D_{1} / D_{2} ; 3000 / Q_{2}={ }^{12} / 10 ; Q_{2}=2500 \mathrm{gal} / \mathrm{min}$ $\left(0.016 \mathrm{~m}^{3} / \mathrm{s}\right)$. And, $H_{1} / H_{2}=\left(D_{1} / D_{2}\right)^{2} ; 200 / H_{2}=(12 / 10)^{2} ; H^{2}=138.8 \mathrm{ft}(42.3 \mathrm{~m})$. Also, $P_{1} / P_{2}=$ $\left(D_{1} / D_{2}\right)^{3} ; 175 / P_{2}=(12 / 10)^{3} ; P_{2}=101.2$ bhp.

Related Calculations. Use the similarity laws to extend or change the data obtained from centrifugalpump characteristic curves. These laws are also useful in field calculations when the pump head, capacity, speed, or impeller diameter is changed.

The similarity laws are most accurate when the efficiency of the pump remains nearly constant. Results obtained when the laws are applied to a pump having a constant impeller diameter are somewhat more accurate than for a pump at constant speed with a changed impeller diameter. The latter laws are more accurate when applied to pumps having a low specific speed.

If the similarity laws are applied to a pump whose impeller diameter is increased, be certain to consider the effect of the higher velocity in the pump suction line. Use the similarity laws for any liquid whose viscosity remains constant during passage through the pump. However, the accuracy of the similarity laws decreases as the liquid viscosity increases.

### 6.18 SIMILARITY OR AFFINITY LAWS IN CENTRIFUGAL-PUMP SELECTION

A test-model pump delivers, at its best efficiency point, $500 \mathrm{gal} / \mathrm{min}\left(0.03 \mathrm{~m}^{3} / \mathrm{s}\right)$ at a $350-\mathrm{ft}(107-\mathrm{m})$ head with a required net positive suction head (NPSH) of $10 \mathrm{ft}(3.05 \mathrm{~m})$ and a power input of 55 hp $(41 \mathrm{~kW})$ at $3500 \mathrm{r} / \mathrm{min}$, when using a $10.5-\mathrm{in}$-diameter impeller. Determine the performance of the model at $1750 \mathrm{r} / \mathrm{min}$. What is the performance of a full-scale prototype pump with a 20 -in impeller operating at $1170 \mathrm{r} / \mathrm{min}$ ? What are the specific speeds and the suction specific speeds of the test-model and prototype pumps?

## Calculation Procedure

1. Compute the pump performance at the new speed. The similarity or affinity laws can be stated in general terms, with subscripts $p$ and $m$ for prototype and model, respectively, as $Q_{p}=$ $K_{d}^{3} K_{n} Q_{m} ; H_{p}=K_{d}^{2} K_{n}^{2} H_{m} ; \mathrm{NPSH}_{p}=K_{2}^{2} K_{n}^{2} \mathrm{NPSH}_{m} ; P_{p}=K_{d}^{5} K_{n}^{5} P_{m}$, where $K_{d}=$ size factor $=$ prototype dimension/model dimension. The usual dimension used for the size factor is the impeller diameter. Both dimensions should be in the same units of measure. Also, $K_{n}=$ prototype speed, $\mathrm{r} / \mathrm{min} / \mathrm{model}$ speed, $\mathrm{r} / \mathrm{min}$. Other symbols are the same as in the previous example.

When the model speed is reduced from 3500 to $1750 \mathrm{r} / \mathrm{min}$, the pump dimensions remain the same and $K_{d}=1.0 ; K_{n}=1750 / 3500=0.5$. Then $Q=(1.0)(0.5)(500)=250 \mathrm{r} / \mathrm{min}$; $H=(1.0)^{2}(0.5)^{2}(350)=87.5 \mathrm{ft}(26.7 \mathrm{~m}) ; \mathrm{NPSH}=(1.0)^{2}(0.5)^{2}(10)=2.5 \mathrm{ft}(0.76 \mathrm{~m}) ; P=$
$(1.0)^{5}(0.5)^{3}(55)=6.9 \mathrm{hp}$. In this computation, the subscripts were omitted from the equation because the same pump, the test model, was being considered.
2. Compute performance of the prototype pump. First, $K_{d}$ and $K_{n}$ must be found. $K_{d}=$ $20 / 10.5=1.905 ; K_{n}=1170 / 3500=0.335$. Then, $Q_{p}=(1.905)^{3}(0.335)(500)=1158 \mathrm{gal} / \mathrm{min}$ $\left(0.073 \mathrm{~m}^{3} / \mathrm{s}\right) ; H_{p}=(1.905)^{2}(0.335)^{2}(350)=142.5 \mathrm{ft}(43.4 \mathrm{~m}) ; \mathrm{NPSH}_{p}=(1.905)^{2}(0.335)^{2}(10)=$ $4.06 \mathrm{ft} ; P_{p}=(1.905)^{5}(0.335)^{3}(55)=51.8 \mathrm{hp}$.
3. Compute the specific speed and suction specific speed. The specific speed or, as Horwitz [2] says, "more correctly, discharge specific speed," $N_{S}=N(Q)^{0.5} /(H)^{0.75}$, while the suction specific speed $S=N(Q)^{0.5} / \mathrm{NPSH}^{0.75}$, where all values are taken at the best efficiency point of the pump.


FIGURE 6.10 Upper limits of specific speeds of single-stage single- and double-suction centrifugal pumps handling clear water at $85^{\circ} \mathrm{F}\left(29^{\circ} \mathrm{C}\right)$ at sea level. (Hydraulic Institute.)

For the model, $N_{S}=3500(500)^{0.5} / 350^{0.75}=965 ; S=3500(500)^{0.5} / 10^{0.75}=13,900$. For the prototype, $N_{S}=1170(1158)^{0.5} / 142.5^{0.75}=965 ; S=1170(1156)^{0.5} / 4.06^{0.75}=13,900$. The specific speed and suction specific speed of the model and prototype are equal because these units are geometrically similar or homologous pumps and both speeds are mathematically derived from the similarity laws.

Related Calculations. Use the procedure given here for any type of centrifugal pump where the similarity laws apply. When the term "model" is used, it can apply to a production test pump or to a standard unit ready for installation. The procedure presented here is the work of R. P. Horwitz, as reported in Power magazine [2].

### 6.19 SPECIFIC-SPEED CONSIDERATIONS IN CENTRIFUGAL-PUMP SELECTION

What is the upper limit of specific speed and capacity of a $1750-\mathrm{r} / \mathrm{min}$ single-stage double-suction centrifugal pump having a shaft that passes through the impeller eye if it handles clear water at $85^{\circ} \mathrm{F}$ $(302 \mathrm{~K})$ at sea level at a total head of 280 ft with a $10-\mathrm{ft}$ suction lift? What is the efficiency of the pump and its approximate impeller shape?

## Calculation Procedure

1. Determine the upper limit of specific speed. Use the Hydraulic Institute upper-specific-speed curve, Fig. 6.10, for centrifugal pumps or a similar curve, Fig. 6.11, for mixed- and axial-flow


FIGURE 6.11 Upper limits of specific speeds of single-suction mixed-flow and axial-flow pumps. (Hydraulic Institute.)


FIGURE 6.12 Approximate relative impeller shapes and efficiency variations for various specific speeds of centrifugal pumps. (Worthington Corp.)
pumps. Enter Fig. 6.10 at the bottom at $280-\mathrm{ft}$ total head and project vertically upward until the $10-\mathrm{ft}$ suction-lift curve is intersected. From here, project horizontally to the right to read the specific speed $N_{S}=2000$. Figure 6.11 is used in a similar manner.
2. Compute the maximum pump capacity. For any centrifugal, mixed- or axial-flow pump, $N_{S}=$ $(\mathrm{gal} / \mathrm{min})^{0.5}(\mathrm{r} / \mathrm{min}) / \mathrm{H}_{t}^{0.75}$, where $H_{t}=$ total head on the pump, in ft of liquid. Solving for the maximum capacity, gal $/ \min =\left[N_{S} H_{t}^{0.75} /(\mathrm{r} / \mathrm{min})\right]^{2}=\left(2000 \times 280^{0.75} / 1750\right)^{2}=6040 \mathrm{gal} / \mathrm{min}$.
3. Determine the pump efficiency and impeller shape. Figure 6.12 shows the general relation between impeller shape, specific speed, pump capacity, efficiency, and characteristic curves. At $N_{S}=2000$, efficiency $=87$ percent. The impeller, as shown in Fig. 6.12, is moderately short and has a relatively large discharge area. A cross section of the impeller appears directly under the $N_{S}=2000$ ordinate .

Related Calculations. Use the method given here for any type of pump whose variables are included in the Hydraulic Institute curves (Figs. 6.10 and 6.11) and in similar curves available from the same source. Operating specific speed, computed as above, is sometimes plotted on the performance curve of a centrifugal pump so that the characteristics of the unit can be better understood. Type specific speed is the operating specific speed giving maximum efficiency for a given pump and is a number used
to identify a pump. Specific speed is important in cavitation and suction-lift studies. The Hydraulic Institute curves (Figs. 6.10 and 6.11) give upper limits of speed, head, capacity, and suction lift for cavitation-free operation. When making actual pump analyses, be certain to use the curves (Figs. 6.10 and 6.11 herewith) in the latest edition of the Standards of the Hydraulic Institute.

### 6.20 SELECTING THE BEST OPERATING SPEED FOR A CENTRIFUGAL PUMP

A single-suction centrifugal pump is driven by a $60-\mathrm{Hz}$ ac motor. The pump delivers $10,000 \mathrm{gal} / \mathrm{min}$ $\left(0.63 \mathrm{~m}^{3} / \mathrm{s}\right)$ of water at a $100-\mathrm{ft}(30.5-\mathrm{m})$ head. The available net positive suction head is 32 ft $(9.75 \mathrm{~m})$ of water. What is the best operating speed for this pump if the pump operates at its best efficiency point?

## Calculation Procedure

1. Determine the specific speed and suction specific speed. Alternating-current motors can operate at a variety of speeds, depending on the number of poles. Assume that the motor driving this pump might operate at $870,1160,1750$, or $3500 \mathrm{r} / \mathrm{min}$. Compute the specific speed $N_{S}=N(Q)^{0.5} / H^{0.75}=N(10,000)^{0.5} / 100^{0.75}=3.14 N$, and the suction specific speed $S=$ $N(Q)^{0.5} / \mathrm{NPSH}^{0.75}=N(10,000)^{0.5} / 32^{0.75}=7.43 N$ for each of the assumed speeds, and tabulate the results as follows:

| Operating speed, <br> r/min | Required specific <br> speed | Required suction <br> specific speed |
| :---: | :---: | :---: |
| 870 | 2,740 | 6,460 |
| 1,160 | 3,640 | 8,620 |
| 1,750 | 5,500 | 13,000 |
| 3,500 | 11,000 | 26,000 |

2. Choose the best speed for the pump. Analyze the specific speed and suction specific speed at each of the various operating speeds using the data in Tables 6.20 and 6.21. These tables show that at 870 and $1160 \mathrm{r} / \mathrm{min}$, the suction specific-speed rating is poor. At $1750 \mathrm{r} / \mathrm{min}$, the suction specific-speed rating is excellent, and a turbine or mixed-flow type of pump will be suitable. Operation at $3500 \mathrm{r} / \mathrm{min}$ is unfeasible because a suction specific speed of 26,000 is beyond the range of conventional pumps.

Related Calculations. Use this procedure for any type of centrifugal pump handling water for plant services, cooling, process, fire protection, and similar requirements. This procedure is the work of R. P. Horwitz, Hydrodynamics Division, Peerless Pump, FMC Corporation, as reported in Power magazine.

TABLE 6.20 Pump Types Listed by Specific Speed

| Specific speed range | Type of pump |
| :---: | :--- |
| Below 2,000 | Volute, diffuser |
| $2,000-5,000$ | Turbine |
| $4,000-10,000$ | Mixed-flow |
| $9,000-15,000$ | Axial-flow |

Source: Peerless Pump Division, FMC Corporation.

TABLE 6.21 Suction Specific-Speed Ratings

| Single-suction <br> pump | Double-suction <br> pump | Rating |
| :--- | :---: | :--- |
| Above 11,000 | Above 14,000 | Excellent |
| $9,000-11,000$ | $11,000-14,000$ | Good |
| $7,000-9,000$ | $9,000-11,000$ | Average |
| $5,000-7,000$ | $7,000-9,000$ | Poor |
| Below 5,000 | Below 7,000 | Very poor |

Source: Peerless Pump Division, FMC Corporation.

### 6.21 TOTAL HEAD ON A PUMP HANDLING VAPOR-FREE LIQUID

Sketch three typical pump piping arrangements with static suction lift and submerged, free, and varying discharge head. Prepare similar sketches for the same pump with static suction head. Label the various heads. Compute the total head on each pump if the elevations are as shown in Fig. 6.13 and the pump discharges a maximum of $2000 \mathrm{gal} / \mathrm{min}\left(0.126 \mathrm{~m}^{3} / \mathrm{s}\right)$ of water through 8 -in schedule 40 pipe. What horsepower is required to drive the pump? A swing check valve is used on the pump suction line and a gate valve on the discharge line.

## Calculation Procedure

1. Sketch the possible piping arrangements. Figure 6.13 shows the six possible piping arrangements for the stated conditions of the installation. Label the total static head-i.e., the vertical distance from the surface of the source of the liquid supply to the free surface of the liquid in the discharge receiver, or to the point of free discharge from the discharge pipe. When both the suction and discharge surfaces are open to the atmosphere, the total static head equals the vertical difference in elevation. Use the free-surface elevations that cause the maximum suction lift and discharge head-i.e., the lowest possible level in the supply tank and the highest possible level in the discharge tank or pipe. When the supply source is below the pump centerline, the vertical distance is called the "static suction lift." With the supply above the pump centerline, the vertical distance is called "static suction head." With variable static suction head, use the lowest liquid level in the supply tank when computing total static head. Label the diagrams as shown in Fig. 6.13.
2. Compute the total static head on the pump. The total static head, in feet, is $H_{t s}=$ static suction lift, in feet, $h_{s l}+$ static discharge head, in feet, $h_{s d}$, where the pump has a suction lift, $s$ in Fig. 6.13a, $b$, and $c$. In these installations, $H_{t s}=10+100=110 \mathrm{ft}$. Note that the static discharge head is computed between the pump centerline and the water level with an underwater discharge (Fig. 6.13a), to the pipe outlet with a free discharge (Fig. 6.13b), and to the maximum water level in the discharge tank (Fig. 6.13c). When a pump is discharging into a closed compression tank, the total discharge head equals the static discharge head plus the head equivalent, in feet of liquid, of the internal pressure in the tank, or $2.31 \times$ tank pressure, in $\mathrm{lb} / \mathrm{in}^{2}$.

Where the pump has a static suction head, as in Fig. 6.13d, e, and $f$, the total static head, in feet, is $H_{t s}=h_{s d}$ - static suction head, in feet, $h_{s h}$. In these installations, $H_{t}=100-15=85 \mathrm{ft}$.

The total static head, as computed above, refers to the head on the pump without liquid flow. To determine the total head on the pump, the friction losses in the piping system during liquid flow must also be determined.
3. Compute the piping friction losses. Mark the length of each piece of straight pipe on the piping drawing. Thus, in Fig. $6.13 a$, the total length of straight pipe $L_{t}$, in feet, is $8+10+5+102+5=$


FIGURE 6.13 Typical pump suction and discharge piping arrangements.

130 ft , starting at the suction tank and adding each length until the discharge tank is reached. To the total length of straight pipe must be added the equivalent length of the pipe fittings. In Fig. 6.13a there are four long-radius elbows, one swing check valve, and one globe valve. In addition, there is a minor head loss at the pipe inlet and at the pipe outlet.

The equivalent length of one 8 -in-long-radius elbow is 14 ft of pipe, from Table 6.22 . Since the pipe contains four elbows, the total equivalent length is $4(14)=56 \mathrm{ft}$ of straight pipe. The open gate valve has an equivalent resistance of 4.5 ft , and the open swing check valve has an equivalent resistance of 53 ft .

The entrance loss $h_{e}$, in feet, assuming a basket-type strainer is used at the suction-pipe inlet, is $K v^{2} /(2 g)$, where $K=$ a constant from Fig. 6.14; $v=$ liquid velocity, in $\mathrm{ft} / \mathrm{s}$; and $g=32.2 \mathrm{ft} / \mathrm{s}^{2}$. The exit loss occurs when the liquid passes through a sudden enlargement, as from a pipe to a tank. Where the area of the tank is large, causing a final velocity that is zero, $h_{e x}=v^{2} / 2 g$.

The velocity $v$, in feet per second, in a pipe is $(\mathrm{gal} / \mathrm{min}) /\left(2.448 d^{2}\right)$. For this pipe, $v=$ $2000 /\left[2.448(7.98)^{2}\right]=12.82 \mathrm{ft} / \mathrm{s}$. Then, $h_{e}=0.74(12.82)^{2} /[2(32.2)]=1.89 \mathrm{ft}$, and $h_{e x}=$ $(12.82)^{2} /[2(32.2)]=2.56 \mathrm{ft}(0.78 \mathrm{~m})$. Hence the total length of the piping system in Fig. $6.13 a$ is $130+56+4.5+53+1.89+2.56=247.95 \mathrm{ft}(75.6 \mathrm{~m})$, say $248 \mathrm{ft}(75.6 \mathrm{~m})$.


FIGURE 6.14 Resistance coefficients of pipe fittings. (Hydraulic Institute.)

TABLE 6.23 Pipe Friction Loss for Water (wrought-iron or steel schedule 40 pipe in good condition)

| Diameter |  | Flow |  | Velocity |  | Velocity head |  | Friction loss/ 100 ft ( 30.5 m ) pipe |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| in | mm | gal/min | L/s | $\mathrm{ft} / \mathrm{s}$ | m/s | ft water | $m$ water | ft water | m water |
| 6 | 152.4 | 1000 | 63.1 | 11.1 | 3.4 | 1.92 | 0.59 | 6.17 | 1.88 |
| 6 | 152.4 | 2000 | 126.2 | 22.2 | 6.8 | 7.67 | 2.3 | 23.8 | 7.25 |
| 6 | 152.4 | 4000 | 252.4 | 44.4 | 13.5 | 30.7 | 9.4 | 93.1 | 28.4 |
| 8 | 203.2 | 1000 | 63.1 | 6.41 | 1.9 | 0.639 | 0.195 | 1.56 | 0.475 |
| 8 | 203.2 | 2000 | 126.2 | 12.8 | 3.9 | 2.56 | 0.78 | 5.86 | 1.786 |
| 8 | 203.2 | 4000 | 252.4 | 25.7 | 7.8 | 10.2 | 3.1 | 22.6 | 6.888 |
| 10 | 254.0 | 1000 | 63.1 | 3.93 | 1.2 | 0.240 | 0.07 | 0.497 | 0.151 |
| 10 | 254.0 | 3000 | 189.3 | 11.8 | 3.6 | 2.16 | 0.658 | 4.00 | 1.219 |
| 10 | 254.0 | 5000 | 315.5 | 19.6 | 5.9 | 5.99 | 1.82 | 10.8 | 3.292 |

Use a suitable head-loss equation, or Table 6.23 , to compute the head loss for the pipe and fittings. Enter Table 6.23 at an 8 -in ( $203.2-\mathrm{mm}$ ) pipe size and project horizontally across to $2000 \mathrm{gal} / \mathrm{min}$ $(126.2 \mathrm{~L} / \mathrm{s})$ and read the head loss as 5.86 ft of water per $100 \mathrm{ft}(1.8 \mathrm{~m} / 30.5 \mathrm{~m})$ of pipe.

The total length of pipe and fittings computed above is $288 \mathrm{ft}(87.8 \mathrm{~m})$. Then, total friction-head loss with a $2000-\mathrm{gal} / \mathrm{min}(126.2 \mathrm{~L} / \mathrm{s})$ flow is $H_{f}=(5.86)(248 / 100)=14.53 \mathrm{ft}(4.5 \mathrm{~m})$.
4. Compute the total head on the pump. The total head on the pump $H_{t}=H_{t s}+H_{f}$. For the pump in Fig. $6.13 a, H_{t}=110+14.53=124.53 \mathrm{ft}(38.0 \mathrm{~m})$, say $125 \mathrm{ft}(38.0 \mathrm{~m})$. The total head on the pump in Fig. $6.13 b$ and $c$ would be the same. Some engineers term the total head on a pump the "total dyamic head" to distinguish between static head (no-flow vertical head) and operating head (rated flow through the pump).

The total head on the pumps in Fig. 6.13d, $c$, and $f$ is computed in the same way as described above, except that the total static head is less because the pump has a static suction head-that is, the elevation of the liquid on the suction side reduces the total distance through which the pump must discharge liquid; thus the total static head is less. The static suction head is subtracted from the static discharge head to determine the total static head on the pump.
5. Compute the horsepower required to drive the pump. The brake horsepower input to a pump equals $(\mathrm{gal} / \mathrm{min})\left(H_{t}\right)(s) / 3960 e$, where $s=$ specific gravity of the liquid handled, and $e=$ hydraulic efficiency of the pump, expressed as a decimal. The usual hydraulic efficiency of a centrifugal pump is 60 to 80 percent; reciprocating pumps, 55 to 90 percent; rotary pumps, 50 to 90 percent. For each class of pump, the hydraulic efficiency decreases as the liquid viscosity increases.

Assume that the hydraulic efficiency of the pump in this system is 70 percent and the specific gravity of the liquid handled is 1.0 . Then, input brake horsepower equals $(2000)(125)(1.0) /[3960(0.70)]=$ $90.2 \mathrm{hp}(67.4 \mathrm{~kW})$.

The theoretical or hydraulic horsepower equals $(\mathrm{gal} / \mathrm{min})\left(H_{t}\right)(s) / 3960=(2000)(125)(1.0) /$ $3900=64.1 \mathrm{hp}(47.8 \mathrm{~kW})$.

Related Calculations. Use this procedure for any liquid-water, oil, chemical, sludge, etc.-whose specific gravity is known. When liquids other than water are being pumped, the specific gravity and viscosity of the liquid must be taken into consideration. The procedure given here can be used for any class of pump-centrifugal, rotary, or reciprocating.

Note that Fig. 6.14 can be used to determine the equivalent length of a variety of pipe fittings. To use Fig. 6.14, simply substitute the appropriate $K$ value in the relation $h=K v^{2} / 2 g$, where $h=$ equivalent length of straight pipe; other symbols as before.

### 6.22 PUMP SELECTION FOR ANY PUMPING SYSTEM

Give a step-by-step procedure for choosing the class, type, capacity, drive, and materials for a pump that will be used in an industrial pumping system.

## Calculation Procedure

1. Sketch the proposed piping layout. Use a single-line diagram (Fig. 6.15) of the piping system. Base the sketch on the actual job conditions. Show all the piping, fittings, valves, equipment, and other units in the system. Mark the actual and equivalent pipe length (see the previous example) on the sketch. Be certain to include all vertical lifts, sharp bends, sudden enlargements, storage tanks, and similar equipment in the proposed system.
2. Determine the required capacity of the pump. The required capacity is the flow rate that must be handled in $\mathrm{gal} / \mathrm{min}$, million gal $/$ day, $\mathrm{ft}^{3} / \mathrm{s}$, gal/h, $\mathrm{bbl} / \mathrm{day}$, $\mathrm{lb} / \mathrm{h}$, acre- $\mathrm{ft} /$ day, mil $/ \mathrm{h}$, or some similar measure. Obtain the required flow rate from the process conditions-for example, boiler feed rate,


FIGURE 6.15 (a) Single-line diagrams for an industrial pipeline; (b) single-line diagram of a boiler feed system. (Worthington Corp.)
cooling-water flow rate, chemical feed rate, etc. The required flow rate for any process unit is usually given by the manufacturer.

Once the required flow rate is determined, apply a suitable factor of safety. The value of this factor of safety can vary from a low of 5 percent of the required flow to a high of 50 percent or more, depending on the application. Typical safety factors are in the 10 percent range. With flow rates up to $1000 \mathrm{gal} / \mathrm{min}$, and in the selection of process pumps, it is common practice to round off a computed required flow rate to the next highest round-number capacity. Thus, with a required flow rate of 450 $\mathrm{gal} / \mathrm{min}$ and a 10 percent safety factor, the flow of $450+0.10(450)=495 \mathrm{gal} / \mathrm{min}$ would be rounded off to $500 \mathrm{gal} / \mathrm{min}$ before selecting the pump. A pump of $500 \mathrm{gal} / \mathrm{min}$, or larger, capacity would be selected.

## Summary of Essential Data Required in Selection of Centrifugal Pumps

## 1. Number of Units Required

2. Nature of the Liquid to Be Pumped Is the liquid:
a. Fresh or salt water, acid or alkali, oil, gasoline, slurry, or paper stock?
b. Cold or hot and if hot, at what temperature? What is the vapor pressure of the liquid at the pumping temperature?
c. What is its specific gravity?
d. Is it viscous or nonviscous?
e. Clear and free from suspended foreign matter or dirty and gritty? If the latter, what is the size and nature of the solids, and are they abrasive? If the liquid is of a pulpy nature, what is the consistency expressed either in percentage or in lb per cu ft of liquid? What is the suspended material?
f. What is the chemical analysis, pH value, etc.? What are the expected variations of this analysis? If corrosive, what has been the past experience, both with successful materials and with unsatisfactory materials?
3. Capacity

What is the required capacity as well as the minimum and maximum amount of liquid the pump will ever be called upon to deliver?
4. Suction Conditions

Is there:
a. A suction lift?
b. Or a suction head?
c. What are the length and diameter of the suction pipe?
5. Discharge Conditions
a. What is the static head? Is it constant or variable?
b. What is the friction head?
c. What is the maximum discharge pressure against which the pump must deliver the liquid?
6. Total Head

Variations in items 4 and 5 will cause variations in the total head.
7. Is the service continuous or intermittent?
8. Is the pump to be installed in a horizontal or vertical position? If the latter,
a. In a wet pit?
b. In a dry pit?
9. What type of power is available to drive the pump and what are the characteristics of this power?
10. What space, weight, or transportation limitations are involved?
11. Location of installation
a. Geographical location
b. Elevation above sea level
c. Indoor or outdoor installation
d. Range of ambient temperatures
12. Are there any special requirements or marked preferences with respect to the design, construction, or performance of the pump?

FIGURE 6.16 Typical selection chart for centrifugal pumps. (Worthington Corp.)
3. Compute the total head on the pump. Use the steps given in the previous example to compute the total head on the pump. Express the result in feet of water-this is the most common way of expressing the head on a pump. Be certain to use the exact specific gravity of the liquid handled when expressing the head in feet of water. A specific gravity less than 1.00 reduces the total head when expressed in feet of water, whereas a specific gravity greater than 1.00 increases the total head when expressed in feet of water. Note that variations in the suction and discharge conditions can affect the total head on the pump.
4. Analyze the liquid conditions. Obtain complete data on the liquid pumped. These data should include the name and chemical formula of the liquid, maximum and minimum pumping temperature, corresponding vapor pressure at these temperatures, specific gravity, viscosity at the pumping temperature, pH , flash point, ignition temperature, unusual characteristics (such as tendency to foam, curd, crystallize, become gelatinous or tacky), solids content, type of solids and their size, and variation in the chemical analysis of the liquid.

Enter the liquid conditions on a pump-selection form such as that in Fig. 6.16. Such forms are available from many pump manufacturers or can be prepared to meet special job conditions.
5. Select the class and type of pump. Three classes of pumps are used today-centrifugal, rotary, and reciprocating (Fig. 6.17). Note that these terms apply only to the mechanics of moving the liquidnot to the service for which the pump was designed. Each class of pump is further subdivided into a number of types (Fig. 6.17).

Use Table 6.24 as a general guide to the class and type of pump to be used. For example, when a large capacity at moderate pressure is required. Table 6.24 shows that a centrifugal pump would probably be best. Table 6.24 also shows the typical characteristics of various classes and types of pumps used in industrial process work.

Consider the liquid properties when choosing the class and type of pump, because exceptionally severe conditions may rule out one or another class of pump at the start. Thus, screw- and gear-type rotary pumps are suitable for handling viscous, nonabrasive liquid (Table 6.24). When an abrasive liquid must be handled, either another class of pump or another type of rotary pump must be used.


FIGURE 6.17 Pump classes and types.

TABLE 6.24 Characteristics of Modern Pumps

|  | Centrifugal |  | Rotary | Reciprocating |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Volute and diffuser | Axial flow | Screw and gear | Direct acting steam | Double acting power | Triplex |
| Discharge flow Usual maximum suction lift, ft (m) | Steady $15 \text { (4.6) }$ | Steady $15 \text { (4.6) }$ | Steady $22 \text { (6.7) }$ | Pulsating $22 \text { (6.7) }$ | Pulsating $22 \text { (6.7) }$ | Pulsating 22 (6.7) |
| Liquids handled | Clean, clear; dirty, abrasive; liquids with high solids content |  | Viscous, nonabrasive | Clean and clear |  |  |
| Discharge pressure range | Low to high |  | Medium | Low to highest produced |  |  |
| Usual capacity range | Small to largest available |  | Small to medium | Relatively small |  |  |
| How increased head affects: Capacity Power input | Decrease <br> Depends on specific speed |  | None Increase | Decrease Increase | None Increase | None Increase |
| How decreased head affects: Capacity Power input | Increase <br> Depends on specific speed |  | None <br> Decrease | Small increase Decrease | None <br> Decrease | None <br> Decrease |

Also consider all the operating factors related to the particular pump. These factors include the type of service (continuous or intermittent), operating-speed preferences, future load expected and its effect on pump head and capacity, maintenance facilities available, possibility of parallel or series hookup, and other conditions peculiar to a given job.

Once the class and type of pump are selected, consult a rating table (Table 6.25) or rating chart (Fig. 6.18) to determine if a suitable pump is available from the manufacturer whose unit will be used. When the hydraulic requirements fall between two standard pump models, it is usual practice to choose the next larger size of pump, unless there is some reason why an exact head and capacity are required for the unit. When one manufacturer does not have the desired unit, refer to the engineering data of other manufacturers. Also keep in mind that some pumps are custom-built for a given job when precise head and capacity requirements must be met.

Other pump data included in manufacturer's engineering information include characteristic curves for various diameter impellers in the same casing (Fig. 6.19) and variable-speed head-capacity curves for an impeller of given diameter (Fig. 6.20). Note that the required power input is given in Figs. 6.18 and 6.19 and may also be given in Fig. 6.20. Use of Table 6.25 is explained in the table.

Performance data for rotary pumps is given in several forms. Figure 6.21 shows a typical plot of the head and capacity ranges of different types of rotary pumps. Reciprocating-pump capacity data are often tabulated, as in Table 6.26.
6. Evaluate the pump chosen for the installation. Check the specific speed of a centrifugal pump using the method given in Example 6.20. Once the specific speed is known, the impeller type and approximate operating efficiency can be found from Fig. 6.12.

TABLE 6.25 Typical Centrifugal-Pump Rating Table

| Size |  | Total head |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{gal} / \mathrm{min}$ | $\mathrm{L} / \mathrm{s}$ | $20 \mathrm{ft}, \mathrm{r} / \mathrm{min}-\mathrm{hp}$ | $6.1 \mathrm{~m}, \mathrm{r} / \mathrm{min}-\mathrm{kW}$ | $25 \mathrm{ft}, \mathrm{r} / \mathrm{min}-\mathrm{hp}$ | $7.6 \mathrm{~m}, \mathrm{r} / \mathrm{min}-\mathrm{kW}$ |
| $3 \mathrm{CL}:$ |  |  |  |  |  |
| 200 | 12.6 | $910-1.3$ | $910-0.97$ | $1010-1.6$ | $1010-1.19$ |
| 300 | 18.9 | $1000-1.9$ | $1000-1.41$ | $1100-2.4$ | $1100-1.79$ |
| 400 | 25.2 | $1200-3.1$ | $1200-2.31$ | $1230-3.7$ | $1230-2.76$ |
| 500 | 31.5 | - | - | - | - |
| 4 C: |  |  | $940-1.79$ | $1040-3$ | $1040-2.24$ |
| 400 | 25.2 | $940-2.4$ | $1080-2.98$ | $1170-4.6$ | $1170-3.43$ |
| 600 | 37.9 | $1080-4$ | - | - | - |
| 800 | 50.5 | - |  |  |  |

Example: 1080-4 indicates pump speed is $1080 \mathrm{r} / \mathrm{min}$; actual input required to operate the pump is 4 hp ( 2.98 kW ).

Source: Condensed from data of Goulds Pumps, Inc.; SI values added by Handbook editor.


FIGURE 6.18 Composite rating chart for a typical centrifugal pump. (Goulds Pumps, Inc.)

Check the piping system, using the method of Example 6.20, to see if the available net positive suction head equals, or is greater than, the required net positive suction head of the pump.

Determine whether a vertical or horizontal pump is more desirable. From the standpoint of floor space occupied, required NPSH, priming, and flexibility in changing the pump use, vertical pumps may be preferable to horizontal designs in some installations. But where headroom, corrosion, abrasion, and ease of maintenance are important factors, horizontal pumps may be preferable.


FIGURE 6.19 Pump characteristics when impeller diameter is varied within the same casing.


FIGURE 6.20 Variable-speed head-capacity curves for a centrifugal pump.

As a general guide, single-suction centrifugal pumps handle up to $50 \mathrm{gal} / \mathrm{min}\left(0.0032 \mathrm{~m}^{3} / \mathrm{s}\right)$ at total heads up to $50 \mathrm{ft}(15 \mathrm{~m})$; either single- or double-suction pumps are used for the flow rates to $1000 \mathrm{gal} / \mathrm{min}\left(0.063 \mathrm{~m}^{3} / \mathrm{s}\right)$ and total heads to $300 \mathrm{ft}(91 \mathrm{~m})$; beyond these capacities and heads, double-suction or multistage pumps are generally used.

Mechanical seals have fully established themselves for all types of centrifugal pumps in a variety of services. Though more costly than packing, the mechanical seal reduces pump maintenance costs.

Related Calculations. Use the procedure given here to select any class of pump-centrifugal, rotary, or reciprocating-for any type of service-power plant, atomic energy, petroleum processing, chemical manufacture, paper mills, textile mills, rubber factories, food processing, water supply, sewage and sump service, air conditioning and heating, irrigation and flood control, mining and construction, marine services, industrial hydraulics, iron and steel manufacture, etc.


FIGURE 6.21 Capacity ranges of some rotary pumps. (Worthington Corp.)

TABLE 6.26 Capacities of Typical Horizontal Duplex Plunger Pumps

| Size |  | Cold-water pressure service |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| in | cm | gal/min |  | L/s | Piston speed |  |  |
|  |  |  |  | $\mathrm{ft} / \mathrm{min}$ | $\mathrm{m} / \mathrm{min}$ |  |
| $6 \times 31 / 2 \times 6$ | $15.2 \times 8.9 \times 15.2$ |  | 60 |  | 3.8 | 60 | 18.3 |  |
| $71 / 2 \times 41 / 2 \times 10$ | $19.1 \times 11.4 \times 25.4$ |  | 124 | 7.8 | 75 | 22.9 |  |
| $9 \times 5 \times 10$ | $22.9 \times 12.7 \times 25.4$ |  | 153 | 9.7 | 75 | 22.9 |  |
| $10 \times 6 \times 12$ | $25.4 \times 15.2 \times 30.5$ |  | 235 | 14.8 | 80 | 24.4 |  |
| $12 \times 7 \times 12$ | $30.5 \times 17.8 \times 30.5$ |  | 320 | 20.2 | 80 | 24.4 |  |
| Size |  | Boiler-feed service |  |  |  |  |  |
|  | cm | gal/min | L/s | Boiler |  | Piston speed |  |
| in |  |  |  | hp | kW | $\mathrm{ft} / \mathrm{min}$ | $\mathrm{m} / \mathrm{min}$ |
| $6 \times 31 / 2 \times 6$ | $15.2 \times 8.9 \times 15.2$ | 36 | 2.3 | 475 | 354.4 | 36 | 10.9 |
| $71 / 2 \times 41 / 2 \times 10$ | $19.1 \times 11.4 \times 25.4$ | 74 | 4.7 | 975 | 727.4 | 45 | 13.7 |
| $9 \times 5 \times 10$ | $22.9 \times 12.7 \times 25.4$ | 92 | 5.8 | 1210 | 902.7 | 45 | 13.7 |
| $10 \times 6 \times 12$ | $25.4 \times 15.2 \times 30.5$ | 141 | 8.9 | 1860 | 1387.6 | 48 | 14.6 |
| $12 \times 7 \times 12$ | $30.5 \times 17.8 \times 30.5$ | 192 | 12.1 | 2530 | 1887.4 | 48 | 14.6 |

Source: Courtesy of Worthington Corporation.

### 6.23 ANALYSIS OF PUMP AND SYSTEM CHARACTERISTIC CURVES

Analyze a set of pump and system characteristic curves for the following conditions: friction losses without static head, friction losses with static head, pump without lift, system with little friction and much static head, system with gravity head, system with different pipe sizes, system with two discharge heads, system with diverted flow, and effect of pump wear on characteristic curve.

## Calculation Procedure

1. Plot the system-friction curve. Without static head, the system friction curve passes through the origin $(0,0)$ (Fig. 6.22), because when no head is developed by the pump, flow through the piping is zero. For most piping systems, the friction-head loss varies as the square of the liquid flow rate in the system. Hence, a system-friction curve, also called


FIGURE 6.22 Typical system-friction curve. a "friction-head curve," is parabolic-the friction head increasing as the flow rate or capacity of the system increases. Draw the curve as shown in Fig. 6.22.
2. Plot the piping system and system-head curve. Figure $6.23 a$ shows a typical piping system with a pump operating against a static discharge head. Indicate the total static head (Fig. 6.23b) by a dashed line-in this installation $H_{t s}=110 \mathrm{ft}$. Since static head is a physical dimension, it does not vary with flow rate and is a constant for all flow rates. Draw the dashed line parallel to the abscissa (Fig. 6.23b).
From the point of no flow-zero capacity-plot the friction-head loss at various flow rates-100, $200,300 \mathrm{gal} / \mathrm{min}$, etc. Determine the friction-head loss by computing it as shown in Example 6.7. Draw a curve through the points obtained. This is called the "system-head curve."

(a)

(b)

FIGURE 6.23 (a) Significant friction loss and lift; (b) system-head curve superimposed on pump head-capacity curve. (Peerless Pumps.)



FIGURE 6.24 No lift; all friction head. (Peerless Pumps.)

Plot the pump head-capacity $(H-Q)$ curve of the pump on Fig. 6.23b. The $H-Q$ curve can be obtained from the pump manufacturer or from a tabulation of $H$ and $Q$ values for the pump being considered. The point of intersection, $A$, between the $H-Q$ and system-head curves is the operating point of the pump.

Changing the resistance of a given piping system by partially closing a valve or making some other change in the friction alters the position of the system-head curve and pump operating point. Compute the frictional resistance as before and plot the artificial system-head curve as shown. Where this curve intersects the $H-Q$ curve is the new operating point of the pump. System-head curves are valuable for analyzing the suitability of a given pump for a particular application.
3. Plot the no-lift system-head curve and compute the losses. With no static head or lift, the system-head curve passes through the origin $(0,0)$ (Fig. 6.24). For a flow of $900 \mathrm{gal} / \mathrm{min}(56.8 \mathrm{~L} / \mathrm{s})$, in this system, compute the friction loss as follows using the Hydraulic Institute-Pipe Friction Manual tables or the method of Example 6.7:

|  | ft | m |
| :--- | ---: | ---: |
| Entrance loss from tank into 10-in (254-mm) suction pipe, $0.5 v^{2} / 2 g$ | 0.10 | 0.03 |
| Friction loss in 2 $\mathrm{ft}(0.61 \mathrm{~m})$ of suction pipe | 0.02 | 0.01 |
| Loss in 10-in (254-mm) $90^{\circ}$ elbow at pump | 0.20 | 0.06 |
| Friction loss in 3000 $\mathrm{ft}(914.4 \mathrm{~m})$ of 8-in (203.2-mm) discharge pipe | 74.50 | 22.71 |
| Loss in fully open 8-in (203.2-mm) gate valve | 0.12 | 0.04 |
| Exit loss from 8-in (203.2-mm) pipe into tank, $v^{2} / 2 g$ | $\underline{0.52}$ | $\underline{0.16}$ |
| Total friction loss | 75.46 | 23.01 |

Compute the friction loss at other flow rates in a similar manner and plot the system-head curve (Fig. 6.24). Note that if all losses in this system except the friction in the discharge pipe are ignored, the total head would not change appreciably. However, for the purposes of accuracy, all losses should always be computed.
4. Plot the low-friction, high-head system-head curve. The system-head curve for the vertical pump installation in Fig. 6.25 starts at the total static head, $15 \mathrm{ft}(4.6 \mathrm{~m})$, and zero flow. Compute the friction head for $15,000 \mathrm{gal} / \mathrm{min}(946.4 \mathrm{~L} / \mathrm{s})$ as follows:

|  | ft | m |
| :--- | :---: | :---: |
| Friction in 20 ft (6.1 m) of 24-in pipe | 0.40 | 0.12 |
| Exit loss from 24-in pipe into tank, $v^{2} / 2 g$ | 1.60 | 0.49 |
| Total friction loss | 2.00 | 0.61 |



FIGURE 6.25 Mostly lift; little friction head. (Peerless Pumps.)


FIGURE 6.26 Negative lift (gravity head). (Peerless Pumps.)

Hence, almost 90 percent of the total head of $15+2=17 \mathrm{ft}$ at $15,000 \mathrm{gal} / \mathrm{min}(946.4-\mathrm{L} / \mathrm{s}$ ) flow is static head. But neglect of the pipe friction and exit losses could cause appreciable error during selection of a pump for the job.
5. Plot the gravity-head system-head curve. In a system with gravity head (also called "negative lift"), fluid flow will continue until the system friction loss equals the available gravity head. In Fig. 6.26 the available gravity head is $50 \mathrm{ft}(15.2 \mathrm{~m})$. Flows up to $7200 \mathrm{gal} / \mathrm{min}(454.3 \mathrm{~L} / \mathrm{s})$ are obtained by gravity head alone. To obtain larger flow rates, a pump is needed to overcome the friction in the piping between the tanks. Compute the friction loss for several flow rates as follows:

|  | ft | m |
| :--- | ---: | ---: |
| At $5000 \mathrm{gal} / \mathrm{min}(315.5 \mathrm{~L} / \mathrm{s})$ friction loss in $1000 \mathrm{ft}(305 \mathrm{~m})$ of 16 -in pipe | 25 | 7.6 |
| At $7200 \mathrm{gal} / \mathrm{min}(454.3 \mathrm{~L} / \mathrm{s})$ friction loss = available gravity head | 50 | 15.2 |
| At $13,000 \mathrm{gal} / \mathrm{min}(820.2 \mathrm{~L} / \mathrm{s})$ friction loss | 150 | 45.7 |

Using these three flow rates, plot the system-head curve (Fig. 6.26).
6. Plot the system-head curves for different pipe sizes. When different diameter pipes are used, the friction-loss-vs.-flow rate is plotted independently for the two pipe sizes. At a given flow rate, the total friction loss for the system is the sum of the loss for the two pipes. Thus the combined system-head curve represents the sum of the static head and the friction losses for all portions of the pipe.


FIGURE 6.27 System with two different pipe sizes. (Peerless Pumps.)

Figure 6.27 shows a system with two different pipe sizes. Compute the friction losses as follows:

|  | ft | m |
| :--- | ---: | ---: |
| At $150 \mathrm{gal} / \mathrm{min}(9.5 \mathrm{~L} / \mathrm{s})$, friction loss in $200 \mathrm{ft}(60.9 \mathrm{~m})$ of 4-in $(102-\mathrm{mm})$ pipe | 5 | 1.52 |
| At $150 \mathrm{gal} / \mathrm{min}(9.5 \mathrm{~L} / \mathrm{s})$, friction loss in $200 \mathrm{ft}(60.9 \mathrm{~m})$ of 3-in $(76.2-\mathrm{mm})$ pipe | 19 | 5.79 |
| Total static head for 3- $(76.2-\mathrm{mm})$ and 4-in $(102-\mathrm{mm})$ pipes | $\frac{10}{3.05}$ | $\underline{34}$ |
| Total head at $150-\mathrm{gal} / \mathrm{min}(9.5 \mathrm{~L} / \mathrm{s})$ flow | $\mathbf{1 0 . 3 6}$ |  |

Compute the total head at other flow rates and plot the system-head curve as shown in Fig. 6.27.
7. Plot the system-head curve for two discharge heads. Figure 6.28 shows a typical pumping system having two different discharge heads. Plot separate system-head curves when the discharge heads are different. Add the flow rates for the two pipes at the same head to find points on the combined system-head curve (Fig. 6.28). Thus,

|  | ft | m |
| :--- | :---: | :---: |
| At $550 \mathrm{gal} / \mathrm{min}(34.7 \mathrm{~L} / \mathrm{s})$, friction loss in $1000 \mathrm{ft}(305 \mathrm{~m})$ of 8-in pipe | $=10$ | 3.05 |
| At $1150 \mathrm{gal} / \mathrm{min}(72.6 \mathrm{~L} / \mathrm{s})$, friction | $=38$ | 11.6 |
| At $1150 \mathrm{gal} / \mathrm{min}(72.6 \mathrm{~L} / \mathrm{s})$, friction + lift in pipe $1=38+50$ | $=88$ | 26.8 |
| At $550 \mathrm{gal} / \mathrm{min}(34.7 \mathrm{~L} / \mathrm{s})$, friction + lift in pipe $2=10+78$ | $=88$ | 26.8 |

The flow rate for the combined system at a head of 88 ft is $1150+550=1700 \mathrm{gal} / \mathrm{min}(107.3 \mathrm{~L} / \mathrm{s})$. To produce a flow of $1700 \mathrm{gal} / \mathrm{min}(107.3 \mathrm{~L} / \mathrm{s})$ through this system, a pump capable of developing an 88 - $\mathrm{ft}(26.8-\mathrm{m})$ head is required.
8. Plot the system-head curve for diverted flow. To analyze a system with diverted flow, assume that a constant quantity of liquid is tapped off at the intermediate point. Plot the friction-loss-vs.-flow rate in the normal manner for pipe 1 (Fig. 6.29). Move the curve for pipe 3 to the right at zero head by an amount equal to $Q_{2}$, since this represents the quantity passing through pipes 1 and 2 but not through pipe 3. Plot the combined system-head curve by adding, at a given flow rate, the head losses for pipes 1 and 3 . With $Q=300 \mathrm{gal} / \mathrm{min}(18.9 \mathrm{~L} / \mathrm{s})$, pipe $1=500 \mathrm{ft}(152.4 \mathrm{~m})$ of $10-\mathrm{in}(254-\mathrm{mm})$



FIGURE 6.28 System with two different discharge heads. (Peerless Pumps.)


FIGURE 6.29 Part of the fluid flow diverted from the main pipe. (Peerless Pumps.)
pipe, and pipe $3=50 \mathrm{ft}(15.2 \mathrm{~m})$ of $6-\mathrm{in}(152.4-\mathrm{mm})$ pipe:

|  | ft | m |
| :--- | :---: | :---: |
| At $1500 \mathrm{gal} / \mathrm{min}(94.6 \mathrm{~L} / \mathrm{s})$ through pipe 1 , friction loss | $=11$ | 3.35 |
| Friction loss for pipe $3(1500-300=1200 \mathrm{gal} / \mathrm{min})(75.7 \mathrm{~L} / \mathrm{s})$ | $=8$ | $\underline{2.44}$ |
| Total friction loss at $1500-\mathrm{gal} / \mathrm{min}(94.6-\mathrm{L} / \mathrm{s})$ delivery | $=19$ | 5.79 |

9. Plot the effect of pump wear. When a pump wears, there is a loss in capacity and efficiency. The amount of loss depends, however, on the shape of the system-head curve. For a centrifugal pump (Fig. 6.30), the capacity loss is greater for a given amount of wear if the system-head curve is flat, as compared with a steep system-head curve.

Determine the capacity loss for a worn pump by plotting its $H-Q$ curve. Find this curve by testing the pump at different capacities and plotting the corresponding head. On the same chart, plot the $H-Q$ curve for a new pump of the same size (Fig. 6.30). Plot the system-head curve and determine the capacity loss as shown in Fig. 6.30.

Related Calculations. Use the techniques given here for any type of pump-centrifugal, reciprocating, or rotary-handling any type of liquid-oil, water, chemicals, etc. The methods given here are the work of Melvin Mann, as reported in Chemical Engineering, and Peerless Pump Div. of FMC Corp.


FIGURE 6.30 Effect of pump wear on pump capacity. (Peerless Pumps.)

### 6.24 NET POSITIVE SUCTION HEAD FOR HOT-LIQUID PUMPS

What is the maximum capacity of a double-suction condensate pump operating at $1750 \mathrm{r} / \mathrm{min}$ if it handles $100^{\circ} \mathrm{F}(311 \mathrm{~K})$ water from a hot well in a condenser having an absolute pressure of 2.0 in Hg $(6.8 \mathrm{kPa})$ if the pump centerline is $10 \mathrm{ft}(3.05 \mathrm{~m})$ below the hot-well liquid level and the friction-head loss in the suction piping and fitting is $5 \mathrm{ft}(1.5 \mathrm{~m})$ of water?

## Calculation Procedure

1. Compute the net positive suction head on the pump. The net positive suction head $h_{n}$ on a pump when the liquid supply is above the pump inlet equals pressure on liquid surface + static suction head-friction-head loss in suction piping and pump inlet-vapor pressure of the liquid, all expressed in feet absolute of liquid handled. When the liquid supply is below the pump centerline-i.e., there is a static suction lift-the vertical distance of the lift is subtracted from the pressure on the liquid surface instead of added as in the preceding relation.

The density of $100^{\circ} \mathrm{F}$ water is $62.0 \mathrm{lb} / \mathrm{ft}^{3}$. The pressure on the liquid surface, in absolute feet of liquid, is $(2.0 \mathrm{inHg})(1.133)(62.4 / 62.0)=2.24 \mathrm{ft}$. In this calculation, $1.133=\mathrm{ft}$ of $39.2^{\circ} \mathrm{F}$ water $=1$ inHg; $62.4=\mathrm{lb} / \mathrm{ft}^{3}$ of $39.2^{\circ} \mathrm{F}$ water. The temperature of $39.2^{\circ} \mathrm{F}$ is used because at this temperature water has its maximum density. Thus, to convert inches of mercury to feet of absolute of water, find the product of $(\mathrm{inHg})(1.133)\left(\right.$ water density at $\left.39.2^{\circ} \mathrm{F}\right) /($ water density at operating temperature). Express both density values in the same unit, usually $\mathrm{lb} / \mathrm{ft}^{3}$.

The static suction head is a physical dimension that is measured in feet of liquid at the operating temperature. In this installation, $h_{s h}=10 \mathrm{ft}$ absolute.

The friction-head loss is 5 ft of water at maximum density. To convert to feet absolute, multiply by the ratio of water densities at $39.2^{\circ} \mathrm{F}$ and the operating temperature or $(5)(62.4 / 62.0)=5.03 \mathrm{ft}$.

The vapor pressure of water at $100^{\circ} \mathrm{F}$ is 0.949 psia , from the steam tables. Convert any vapor pressure to feet absolute by finding the result of (vapor pressure, psia$)\left(144 \mathrm{in}^{2} / \mathrm{ft}^{2}\right) /$ liquid density at operating temperature, or $(0.949)(144) / 62.0=2.204 \mathrm{ft}$ absolute.

With all the heads known, the net positive suction head is $h_{n}=2.24+10-5.03-2.204=$ $5.01 \mathrm{ft}(1.53 \mathrm{~m})$ absolute.
2. Determine the capacity of the condensate pump. Use the Hydraulic Institute curve (Fig. 6.31) to determine the maximum capacity of the pump. Enter at the left of Fig. 6.31 at a net positive suction head of 5.01 ft and project horizontally to the right until the $3500-\mathrm{r} / \mathrm{min}$ curve is intersected. At the top, read the capacity as $278 \mathrm{gal} / \mathrm{min}\left(0.0175 \mathrm{~m}^{3} / \mathrm{s}\right)$.

Related Calculations. Use this procedure for any condensate or boiler-feed pump handling water at an elevated temperature. Consult the Standards of the Hydraulic Institute for capacity curves of

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FIGURE 6.31 Capacity and speed limitations of condensate pumps with the shaft through the impeller eye. (Hydraulic Institute.)
pumps having different types of construction. In general, pump manufacturers who are members of the Hydraulic Institute rate their pumps in accordance with the Standards, and a pump chosen from a catalog capacity table or curve will deliver the stated capacity. A similar procedure is used for computing the capacity of pumps handling volatile petroleum liquids. When using this procedure, be certain to refer to the latest edition of the Standards.

### 6.25 MINIMUM SAFE FLOW FOR A CENTRIFUGAL PUMP

A centrifugal pump handles $220^{\circ} \mathrm{F}$ ( 377 K ) water and has a shutoff head (with closed discharge valve) of $3200 \mathrm{ft}(975 \mathrm{~m})$. At shutoff, the pump efficiency is 17 percent and the input brake horsepower is 210. What is the minimum safe flow through this pump to prevent overheating at shutoff? Determine
the minimum safe flow if the NPSH is $18.8 \mathrm{ft}(5.73 \mathrm{~m})$ of water and the liquid specific gravity is 0.995 . If the pump contains $500 \mathrm{lb}(227 \mathrm{~kg})$ of water, determine the rate of the temperature rise at shutoff.

## Calculation Procedure

1. Compute the temperature rise in the pump. With the discharge valve closed, the power input to the pump is converted to heat in the casing and causes the liquid temperature to rise. The temperature rise $t=(1-e) \times H_{s} / 778 e$, where $t$ is temperature rise during shutoff, ${ }^{\circ} \mathrm{F}$; $e$ is pump efficiency, expressed as a decimal; $H_{s}$ is shutoff head, ft. For this pump, $t=(1-0.17)(3200) /[778(0.17)]=$ $20.4^{\circ} \mathrm{F}\left(11.3^{\circ} \mathrm{C}\right)$.
2. Compute the minimum safe liquid flow. For general-service pumps, the minimum safe flow $M$, in $\mathrm{gal} / \mathrm{min}$, is $6.0\left(\mathrm{bhp}\right.$ input at shutoff) $/ t$. Or, $M=6.0(210) / 20.4=62.7 \mathrm{gal} / \mathrm{min}\left(0.00396 \mathrm{~m}^{3} / \mathrm{s}\right)$. This equation includes a 20 percent safety factor.

Centrifugal boiler-feed pumps usually have a maximum allowable temperature rise of $15^{\circ} \mathrm{F}$. The minimum allowable flow through the pump to prevent the water temperature from rising more than $15^{\circ} \mathrm{F}$ is $30 \mathrm{gal} / \mathrm{min}$ for each 100 bhp input at shutoff.
3. Compute the temperature rise for the operating NPSH. An NPSH of 18.8 ft is equivalent to a pressure of $18.8(0.433)(0.995)=7.78$ psia at $220^{\circ} \mathrm{F}$, where the factor 0.433 converts feet of water to pounds per square inch. At $220^{\circ} \mathrm{F}$, the vapor pressure of the water is 17.19 psia , from the steam tables. Thus the total vapor pressure the water can develop before flashing occurs equals NPSH pressure + vapor pressure at operating temperature $=7.78+17.19=24.97$ psia. Enter the steam tables at this pressure and read the corresponding temperature as $240^{\circ} \mathrm{F}$. The allowable temperature rise of the water is then $240-220=20^{\circ} \mathrm{F}$. Using the safe-flow relation of step 2, the minimum safe flow is $62.9 \mathrm{gal} / \mathrm{min}\left(0.00397 \mathrm{~m}^{3} / \mathrm{s}\right)$.
4. Compute the rate of temperature rise. In any centrifugal pump, the rate of temperature rise $t_{r}$, in ${ }^{\circ} \mathrm{F}$ per minute, is 42.4 (bhp input at shutoff) $/ w c$, where $w$ is weight of liquid in the pump, lb; $c$ is specific heat of the liquid in the pump, $\mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)$. For this pump containing 500 lb of water with a specific heat $c$ of $1.0, t_{r}=42.4(210) /[500(1.0)]=17.8^{\circ} \mathrm{F} / \mathrm{min}(0.16 \mathrm{~K} / \mathrm{s})$. This is a very rapid temperature rise and could lead to overheating in a few minutes.

Related Calculations. Use this procedure for any centrifugal pump handling any liquid in any service-power, process, marine, industrial, or commercial. Pump manufacturers can supply a temperature-rise curve for a given model pump if it is requested. This curve is superimposed on the pump characteristic curve and shows the temperature rise accompanying a specific flow through the pump.

### 6.26 SELECTING A CENTRIFUGAL PUMP TO HANDLE A VISCOUS LIQUID

Select a centrifugal pump to deliver $750 \mathrm{gal} / \mathrm{min}\left(0.047 \mathrm{~m}^{3} / \mathrm{s}\right)$ of $1000-\mathrm{SSU}$ oil at a total head of 100 $\mathrm{ft}(30.5 \mathrm{~m})$. The oil has a specific gravity of 0.90 at the pumping temperature. Show how to plot the characteristic curves when the pump is handling the viscous liquid.

## Calculation Procedure

1. Determine the required correction factors. A centrifugal pump handling a viscous liquid usually must develop a greater capacity and head, and it requires a larger power input than the same pump


FIGURE 6.32 Correction factors for viscous liquids handled by centrifugal pumps. (Hydraulic Institute.)
handling water. With the water performance of the pump known-either from the pump characteristic curves or a tabulation of pump performance parameters-Fig. 6.32, prepared by the Hydraulic Institute, can be used to find suitable correction factors. Use this chart only within its scale limits; do not extrapolate. Do not use the chart for mixed-flow or axial-flow pumps or for pumps of special design. Use the chart only for pumps handling uniform liquids; slurries, gels, paper stock, etc. may cause incorrect results. In using the chart, the available net positive suction head is assumed adequate for the pump.

To use Fig. 6.32, enter at the bottom at the required capacity, $750 \mathrm{gal} / \mathrm{min}$, and project vertically to intersect the $100-\mathrm{ft}$ head curve, the required head. From here project horizontally to the $1000-$ SSU viscosity curve and then vertically upward to the correction-factor curves. Read $C_{E}=0.635$; $C_{Q}=0.95 ; C_{H}=0.92$ for $1.0 Q_{N W}$. The subscripts $E, Q$, and $H$ refer to correction factors for efficiency, capacity, and head, respectively, and $N W$ refers to the water capacity at a particular efficiency. At maximum efficiency, the water capacity is given as $1.0 Q_{N W}$; other efficiencies, expressed by numbers equal to or less than unity, give different capacities.
2. Compute the water characteristics required. The water capacity required for the pump $Q_{w}=$ $Q_{v} / C_{Q}$, where $Q_{v}$ is viscous capacity, gal $/ \mathrm{min}$. For this pump, $Q_{w}=750 / 0.95=790 \mathrm{gal} / \mathrm{min}$. Likewise, water head $H_{w}=H_{v} / C_{H}$, where $H_{v}$ is viscous head. Or, $H_{w}=100 / 0.92=108.8$, say 109 ft water.

Choose a pump to deliver $790 \mathrm{gal} / \mathrm{min}$ of water at $109-\mathrm{ft}$ head of water and the required viscous head and capacity will be obtained. Pick the pump so that it is operating at or near its maximum efficiency on water. If the water efficiency $E_{w}=81$ percent at $790 \mathrm{gal} / \mathrm{min}$ for this pump, the efficiency when handling the viscous liquid $E_{w}=E_{w} C_{E}$. Or, $E_{v}=0.81(0.635)=0.515$, or 51.5 percent.

The power input to the pump when handling viscous liquids is given by $P_{v}=Q_{v} H_{v} s /\left(3960 E_{v}\right)$, where $s$ is specific gravity of the viscous liquid. For this pump, $P_{v}=(750)(100)(0.90) /$ $[3960(0.515)]=33.1 \mathrm{hp}(24.7 \mathrm{~kW})$.
3. Plot the characteristic curves for viscous-liquid pumping. Follow these eight steps to plot the complete characteristic curves of a centrifugal pump handling a viscous liquid when the water characteristics are known: (a) Secure a complete set of characteristic curves $(H, Q, P, E)$ for the pump to be used. (b) Locate the point of maximum efficiency for the pump when handling water. (c) Read the pump capacity, $Q \mathrm{gal} / \mathrm{min}$, at this point. (d) Compute the values of $0.6 Q, 0.8 Q$, and $1.2 Q$ at the maximum efficiency, ( $e$ ) Using Fig. 6.32, determine the correction factors at the capacities in steps $c$ and $d$. Where a multistage pump is being considered, use the head per stage ( = total pump head, $\mathrm{ft} /$ number of stages), when entering Fig. 6.32. (f) Correct the head, capacity, and efficiency for each of the flow rates in $c$ and $d$ using the correction factors from Fig. 6.32. (g) Plot the corrected head and efficiency against the corrected capacity, as in Fig. 6.33. (h) Compute the power input at each flow rate and plot. Draw smooth curves through the points obtained (Fig. 6.33).

Related Calculations. Use the method given here for any uniform viscous liquid-oil, gasoline, kerosene, mercury, etc.-handled by a centrifugal pump. Be careful to use Fig. 6.32 only within its scale limits; do not extrapolate. The method presented here is that developed by the Hydraulic Institute. For new developments in the method, be certain to consult the latest edition of the Hydraulic Institute-Standards.

### 6.27 EFFECT OF LIOUID VISCOSITY ON REGENERATIVE PUMP PERFORMANCE

A regenerative (turbine) pump has the water head-capacity and power-input characteristics shown in Fig. 6.34. Determine the head-capacity and power-input characteristics for four different viscosity oils to be handled by the pump-400, 600, 900 , and 1000 SSU. What effect does increased viscosity have on the performance of the pump?


FIGURE 6.33 Characteristic curves for water (solid line) and oil (dashed line). (Hydraulic Institute.)

## Calculation Procedure

1. Plot the water characteristics of the pump. Obtain a tabulation or plot of the water characteristics of the pump from the manufacturer or from the engineering data. With a tabulation of the characteristics, enter the various capacity and power points given and draw a smooth curve through them (Fig. 6.34).


FIGURE 6.34 Regenerative pump performance when handling water and oil. (Aurora Pump Division, The New York Air Brake Co.)
2. Plot the viscous-liquid characteristics of the pump. The viscous-liquid characteristics of regenerative-type pumps are obtained by test of the actual unit. Hence the only source of this information is the pump manufacturer. Obtain these characteristics from the pump manufacturer or the test data and plot them on Fig. 6.34, as shown, for each oil or other liquid handled.
3. Evaluate the effect of viscosity on pump performance. Study Fig. 6.34 to determine the effect of increased liquid viscosity on the performance of the pump. Thus at a given head-say 100 ft -the capacity of the pump decreases as the liquid viscosity increases. At $100-\mathrm{ft}$ head, this pump has a water capacity of $43.5 \mathrm{gal} / \mathrm{min}$ (Fig. 6.34). The pump capacity for the various oils at $100-\mathrm{ft}$ head is $36 \mathrm{gal} / \mathrm{min}$ for $400 \mathrm{SSU}, 32 \mathrm{gal} / \mathrm{min}$ for $600 \mathrm{SSU}, 28 \mathrm{gal} / \mathrm{min}$ for 900 SSU , and $26 \mathrm{gal} / \mathrm{min}$ for 1000 SSU, respectively. There is a similar reduction in capacity of the pump at the other heads plotted in Fig. 6.34. Thus, as a general rule, it can be stated that the capacity of a regenerative pump decreases with an increase in liquid viscosity at constant head. Or conversely, at constant capacity, the head developed decreases as the liquid viscosity increases.

Plots of the power input to this pump show that the input power increases as the liquid viscosity increases.

Related Calculations. Use this procedure for a regenerative-type pump handling any liquid-water, oil, kerosene, gasoline, etc. A decrease in the viscosity of a liquid-as compared with the viscosity of water-will produce the opposite effect from that of increased viscosity.

### 6.28 EFFECT OF LIQUID VISCOSITY ON RECIPROCATING-PUMP PERFORMANCE

A direct-acting steam-driven reciprocating pump delivers $100 \mathrm{gal} / \mathrm{min}\left(0.0063 \mathrm{~m}^{3} / \mathrm{s}\right)$ of $70^{\circ} \mathrm{F}(294 \mathrm{~K})$ water when operating at 50 strokes $/ \mathrm{min}$. How much 2000-SSU crude oil will this pump deliver? How much $125^{\circ} \mathrm{F}(325 \mathrm{~K})$ water will this pump deliver?

## Calculation Procedure

1. Determine the recommended change in the pump performance. Reciprocating pumps of any type-direct-acting or power-having any number of liquid-handling cylinders-1 to 5, or more-are usually rated for maximum delivery when handling 250-SSU liquids or $70^{\circ} \mathrm{F}\left(21^{\circ} \mathrm{C}\right)$ water. At higher liquid viscosities or water temperatures, the speed-strokes or revolutions per minute-is reduced. Table 6.27 shows typical recommended speed-correction factors for reciprocating pumps for various

TABLE 6.27 Speed-Correction Factors

|  |  | $\begin{array}{c}\text { Water } \\ \text { Liquid viscosity, } \\ \text { SSU }\end{array}$ |  |
| :---: | :---: | :---: | :---: |
| temperature |  |  |  |\(\left.\quad \begin{array}{c}Speed <br>

reduction, \%\end{array}\right)\)

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liquid viscosities and water temperatures. This table shows that with a liquid viscosity of 2000 SSU, the pump speed should be reduced 20 percent. When handling $125^{\circ} \mathrm{F}\left(51.7^{\circ} \mathrm{C}\right)$ water, the pump speed should be reduced 25 percent, as shown in Table 6.27.
2. Compute the delivery of the pump. The delivery capacity of any reciprocating pump is directly proportional to the number of strokes per minute it makes or to its revolutions per minute.

When handling 2000-SSU oil, the pump strokes/min must be reduced 20 percent, or $(50)(0.20)$ $=10$ strokes $/ \mathrm{min}$. Hence the pump speed will be $50-10=40$ strokes $/ \mathrm{min}$. Since the delivery is directly proportional to speed, the delivery of $2000-\mathrm{SSU}$ oil is $(40 / 50)(100)=80 \mathrm{gal} / \mathrm{min}(5.1 \mathrm{~L} / \mathrm{s})$.

When handling $125^{\circ} \mathrm{F}\left(51.7^{\circ} \mathrm{C}\right)$ water, the pump strokes per minute must be reduced 25 percent, or $(50)(0.5)=12.5$ strokes $/ \mathrm{min}$. Hence the pump speed will be $50.0-12.5=37.5$ strokes $/ \mathrm{min}$. Since the delivery is directly proportional to speed, the delivery of $125^{\circ} \mathrm{F}\left(51.7^{\circ} \mathrm{C}\right)$ water is $(37.5 / 50)(100)=$ $75 \mathrm{gal} / \mathrm{min}(4.7 \mathrm{~L} / \mathrm{s})$.

Related Calculations. Use this procedure for any type of reciprocating pump handling liquids falling within the range of Table 6.27. Such liquids include oil, kerosene, gasoline, brine, water, etc.

### 6.29 EFFECT OF VISCOSITY AND DISSOLVED GAS ON ROTARY PUMPS

A rotary pump handles 8000 -SSU liquid containing 5\% entrained gas and $10 \%$ dissolved gas at a $20-\mathrm{in}(508-\mathrm{mm}) \mathrm{Hg}$ pump inlet vacuum. The pump is rated at $1000 \mathrm{gal} / \mathrm{min}(63.1 \mathrm{~L} / \mathrm{s})$ when handling gas-free liquids at viscosities less than 600 SSU. What is the output of this pump without slip? With 10 percent slip?

## Calculation Procedure

1. Compute the required speed reduction of the pump. When the liquid viscosity exceeds 600 SSU, many pump manufacturers recommend that the speed of a rotary pump be reduced to permit operation without excessive noise or vibration. The speed reduction ususally recommended is shown in Table 6.28.

TABLE 6.28 Rotary-Pump Speed Reduction for Various
Liquid Viscosities

| Liquid viscosity, SSU | Speed reduction, <br> percent of rated <br> pump speed |
| :---: | :---: |
| 600 | 2 |
| 800 | 6 |
| 1,000 | 10 |
| 1,500 | 12 |
| 2,000 | 14 |
| 4,000 | 20 |
| 6,000 | 30 |
| 8,000 | 40 |
| 10,000 | 50 |
| 20,000 | 55 |
| 30,000 | 57 |
| 40,000 | 60 |

With this pump handling 8000-SSU liquid, a speed reduction of 40 percent is necessary, as shown in Table 6.28 . Since the capacity of a rotary pump varies directly with its speed, the output of this pump when handling 8000 -SSU liquid is $(1000 \mathrm{gal} / \mathrm{min}) \times(1.0-0.40)=600 \mathrm{gal} / \mathrm{min}(37.9 \mathrm{~L} / \mathrm{s})$.
2. Compute the effect of gas on the pump output. Entrained or dissolved gas reduces the output of a rotary pump, as shown in Table 6.29. The gas in the liquid expands when the inlet pressure of the pump is below atmospheric and the gas occupies part of the pump chamber, reducing the liquid capacity.

With a $20-\mathrm{in}(508-\mathrm{mm}) \mathrm{Hg}$ inlet vacuum, $5 \%$ entrained gas, and $10 \%$ dissolved gas, Table 6.29 shows that the liquid displacement is 74 percent of the rated displacement. Thus, the output of the pump when handling this viscous, gas-containing liquid will be $(600 \mathrm{gal} / \mathrm{min})(0.74)=444 \mathrm{gal} / \mathrm{min}$ ( $28.0 \mathrm{~L} / \mathrm{s}$ ) without slip.
3. Compute the effect of slip on the pump output. Slip reduces rotary-pump output in direct proportion to the slip. Thus, with 10 percent slip, the output of this pump is $(444 \mathrm{gal} / \mathrm{min})(1.0-$ $0.10)=399.6 \mathrm{gal} / \mathrm{min}(25 \mathrm{~L} / \mathrm{s})$.

Related Calculations. Use this procedure for any type of rotary pump-gear, lobe, screw, swingingvane, sliding-vane, or shuttle-block-handling any clear, viscous liquid. Where the liquid is gas-free, apply only the viscosity correction. Where the liquid viscosity is less than 600 SSU but the liquid contains gas or air, apply the entrained or dissolved gas correction, or both corrections.

### 6.30 SELECTING FORCED- AND INDUCED-DRAFT FANS

Combustion calculations show that an oil-fired watertube boiler requires $200,000 \mathrm{lb} / \mathrm{h}(25.2 \mathrm{~kg} / \mathrm{s})$ for air of combustion at maximum load. Select forced- and induced-draft fans for this boiler if the average temperature of the inlet air is $75^{\circ} \mathrm{F}(297 \mathrm{~K})$ and the average temperature of the combustion gas leaving the air heater is $350^{\circ} \mathrm{F}(450 \mathrm{~K})$ with an ambient barometric pressure of 29.9 inHg . Pressure losses on the air-inlet side are, in $\mathrm{inH}_{2} \mathrm{O}$ : air heater, 1.5 ; air supply ducts, 0.75 ; boiler windbox, 1.75 ; burners, 1.25. Draft losses in the boiler and related equipment are, in $\mathrm{inH}_{2} \mathrm{O}$ : furnace pressure, 0.20 ; boiler, 3.0 ; superheater, 1.0 ; economizer, 1.50 ; air heater, 2.00 ; uptake ducts and dampers, 1.25 . Determine the fan discharge pressure and horsepower input. The boiler burns $18,000 \mathrm{lb} / \mathrm{h}(2.27 \mathrm{~kg} / \mathrm{s})$ of oil at full load.

## Calculation Procedure

1. Compute the quantity of air required for combustion. The combustion calculations show that $200,000 \mathrm{lb} / \mathrm{h}$ of air is theoretically required for combustion in this boiler. To this theoretical requirement must be added allowances for excess air at the burner and leakage out of the air heater and furnace. Allow 25 percent excess air for this boiler. The exact allowance for a given installation depends on the type of fuel burned. However, a 25 percent excess-air allowance is an average used by power-plant designers for coal, oil, and gas firing. Using this allowance, the required excess air is 200,000(0.25) $=50,000 \mathrm{lb} / \mathrm{h}$.

Air-heater air leakage varies from about 1 to 2 percent of the theoretically required airflow. Using 2 percent, the air-heater leakage allowance is $200,000(0.02)=4,000 \mathrm{lb} / \mathrm{h}$.

Furnace air leakage ranges from 5 to 10 percent of the theoretically required airflow. Using 7.5 percent, the furnace leakage allowance is $200,000(0.075)=15,000 \mathrm{lb} / \mathrm{h}$.

The total airflow required is the sum of the theoretical requirement, excess air, and leakage, or $200,000+50,000+4000+15,000=269,000 \mathrm{lb} / \mathrm{h}$. The forced-draft fan must supply at least this quantity of air to the boiler. Usual practice is to allow a 10 to 20 percent safety factor for fan capacity

| Vacuum at pump inlet, $\mathrm{inHg}(\mathrm{mmHg})$ | Gas entrainment |  |  |  |  | Gas solubility |  |  |  |  | Gas entrainment and gas solubility combined |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 1\% | 2\% | 3\% | 4\% | 5\% | 2\% | 4\% | 6\% | 8\% | 10\% | $\begin{aligned} & 1 \% \\ & 2 \% \end{aligned}$ | $\begin{aligned} & 2 \% \\ & 4 \% \end{aligned}$ | $\begin{aligned} & 3 \% \\ & 6 \% \end{aligned}$ | $\begin{aligned} & 4 \% \\ & 8 \% \end{aligned}$ | $\begin{gathered} 5 \% \\ 10 \% \end{gathered}$ |
| 5 (127) | 99 | 971/2 | 961/2 | 95 | 931/2 | 991/2 | 99 | 981/2 | 97 | 971/2 | 981/2 | 961/2 | 96 | 92 | 91 |
| 10 (254) | 981/2 | 971/4 | 951/2 | 94 | 92 | 99 | 971/2 | 97 | 95 | 95 | 971/2 | 95 | 90 | 90 | $88^{1 / 4}$ |
| 15 (381) | 98 | 961/2 | 941/2 | 921/2 | 901/2 | 97 | 96 | 94 | 92 | 901/2 | 96 | 93 | $89^{1 / 2}$ | $861 / 2$ | $831 / 4$ |
| 20 (508) | 971/2 | 941/2 | 92 | 89 | 861/2 | 96 | 92 | 89 | 86 | 83 | 94 | 88 | 83 | 78 | 74 |
| 25 (635) | 94 | 89 | 84 | 79 | $751 / 2$ | 90 | 83 | $761 / 2$ | 71 | 66 | 851/2 | $751 / 2$ | 68 | 61 | 55 |

For example: with 5 percent gas entrainment at 15 in $\mathrm{Hg}(381 \mathrm{mmHg})$ vacuum, the liquid displacement will be $90^{1} / 2$ percent of the pump displacement neglecting slip or with 10 percent
dissolved gas liquid displacement will be $90^{1} / 2$ percent of pump displacement, and with 5 percent entrained gas combined with 10 percent dissolved gas, the liquid displacement will be $83^{1 / 4}$
Source: Courtesy of Kinney Mfg. Div., The New York Air Brake Co.
to ensure an adequate air supply at all operating conditions. This factor of safety is applied to the total airflow required. Using a 10 percent factor of safety, fan capacity is $269,000+269,000(0.1)=$ $295,000 \mathrm{lb} / \mathrm{h}$. Round this off to $296,000 \mathrm{lb} / \mathrm{h}(37.3 \mathrm{~kg} / \mathrm{s})$ fan capacity.
2. Express the required airflow in cubic feet per minute. Convert the required flow in pounds per hour to cubic feet per minute. To do this, apply a factor of safety to the ambient air temperature to ensure an adequate air supply during times of high ambient temperature. At such times, the density of the air is lower and the fan discharges less air to the boiler. The usual practice is to apply a factor of safety of 20 to 25 percent to the known ambient air temperature. Using 20 percent, the ambient temperature for fan selection is $75+75(0.20)=90^{\circ} \mathrm{F}$. The density of air at $90^{\circ} \mathrm{F}$ is $0.0717 \mathrm{lb} / \mathrm{ft}^{3}$, found in Baumeister—Standard Handbook for Mechanical Engineers. Converting, $\mathrm{ft}^{3} / \mathrm{min}=\mathrm{lb} / \mathrm{h} / 60\left(\mathrm{lb} / \mathrm{ft}^{3}\right)=$ $296,000 / 60(0.0717)=69,400 \mathrm{ft}^{3} / \mathrm{min}$. This is the minimum capacity the forced-draft fan may have.
3. Determine the forced-draft discharge pressure. The total resistance between the forced-draft fan outlet and furnace is the sum of the losses in the air heater, air-supply ducts, boiler windbox, and burners. For this boiler, the total resistance, in inH2 O , is $1.5+0.75+1.75+1.25=5.25 \mathrm{inH}_{2} \mathrm{O}$. Apply a 15 to 30 percent factor of safety to the required discharge pressure to ensure adequate airflow at all times. Or fan discharge pressure, using a 20 percent factor of safety, is $5.25+5.25(0.20)=6.30$ $\mathrm{inH}_{2} \mathrm{O}$. The fan must therefore deliver at least $69,400 \mathrm{ft}^{3} / \mathrm{min}\left(32.7 \mathrm{~m}^{3} / \mathrm{s}\right)$ at $6.30 \mathrm{inH}_{2} \mathrm{O}$.
4. Compute the power required to drive the forced-draft fan. The air horsepower for any fan is $0.0001753 H_{f} C$, where $H_{f}$ is total head developed by fan, in $\mathrm{inH}_{2} \mathrm{O} ; C$ is airflow, in $\mathrm{ft}^{3} / \mathrm{min}$. For this fan, air $\mathrm{hp}=0.0001753(6.3)(69,400),=76.5 \mathrm{hp}$. Assume or obtain the fan and fan-driver efficiencies at the rated capacity $\left(69,400 \mathrm{ft}^{3} / \mathrm{min}\right)$ and pressure $\left(6.30 \mathrm{inH}_{2} \mathrm{O}\right)$. With a fan efficiency of 75 percent and assuming the fan is driven by an electric motor having an efficiency of 90 percent, the overall efficiency of the fan-motor combination is $(0.75)(0.90)=0.675$, or 67.5 percent. Then the motor horsepower required equals air horsepower/overall efficiency $=76.5 / 0.675=113.2 \mathrm{hp}(84.4 \mathrm{~kW})$. A 125-hp motor would be chosen because it is the nearest, next larger, unit readily available. Usual practice is to choose a larger driver capacity when the computed capacity is lower than a standard capacity. The next larger standard capacity is generally chosen, except for extremely large fans where a special motor may be ordered.
5. Compute the quantity of flue gas handled. The quantity of gas reaching the induced draft fan is the sum of the actual air required for combustion from step 1, air leakage in the boiler and furnace, and the weight of fuel burned. With an air leakage of 10 percent in the boiler and furnace (this is a typical leakage factor applied in practice), the gas flow is as follows:

|  | $\mathrm{lb} / \mathrm{h}$ | $\mathrm{kg} / \mathrm{s}$ |
| :--- | ---: | ---: |
| Actual airflow required | 296,000 | 37.3 |
| Air leakage in boiler and furnace | 29,600 | 3.7 |
| Weight of oil burned | 18,000 | $\underline{2.3}$ |
| Total | 343,600 | 43.3 |

Determine from combustion calculations for the boiler the density of the flue gas. Assume that the combustion calculations for this boiler show that the flue-gas density is $0.045 \mathrm{lb} / \mathrm{ft}^{3}\left(0.72 \mathrm{~kg} / \mathrm{m}^{3}\right)$ at the exit-gas temperature. To determine the exit-gas temperature, apply a 10 percent factor of safety to the given exit temperature, $350^{\circ} \mathrm{F}\left(176.6^{\circ} \mathrm{C}\right)$. Hence exit-gas temperature is $350+350(0.10)=$ $385^{\circ} \mathrm{F}\left(196.1^{\circ} \mathrm{C}\right)$. Then, flue-gas flow, in $\mathrm{ft}^{3} / \mathrm{min}$, is (flue-gas flow, $\left.\mathrm{lb} / \mathrm{h}\right) /(60)$ (flue-gas density, $\mathrm{lb} / \mathrm{ft}^{3}$ ) $=343,600 /[(60)(0.045)]=127,000 \mathrm{ft}^{3} / \mathrm{min}\left(59.9 \mathrm{~m}^{3} / \mathrm{s}\right)$. Apply a 10 to 25 percent factor of safety to the flue-gas quantity to allow for increased gas flow. Using a 20 percent factor of safety, the actual flue-gas flow the fan must handle is $127,000+127,000(0.20)=152,400 \mathrm{ft}^{3} / \mathrm{min}\left(71.8 \mathrm{~m}^{3} / \mathrm{s}\right)$, say $152,500 \mathrm{ft}^{3} / \mathrm{min}$ for fan-selection purposes.
6. Compute the induced-draft fan discharge pressure. Find the sum of the draft losses from the burner outlet to the induced-draft inlet. These losses are, for this boiler:

|  | $\mathrm{inH}_{2} \mathrm{O}$ | kPa |
| :--- | :---: | :---: |
| Furnace draft loss | 0.20 | 0.05 |
| Boiler draft loss | 3.00 | 0.75 |
| Superheater draft loss | 1.00 | 0.25 |
| Economizer draft loss | 1.50 | 0.37 |
| Air heater draft loss | 2.00 | 0.50 |
| Uptake ducts and damper draft loss | $\underline{1.25}$ | $\underline{0.31}$ |
| Total draft loss | 8.95 | 2.23 |

Allow a 10 to 25 percent factor of safety to ensure adequate pressure during all boiler loads and furnace conditions. Using a 20 percent factor of safety for this fan, the total actual pressure loss is $8.95+$ $8.95(0.20)=10.74 \mathrm{inH}_{2} \mathrm{O}(2.7 \mathrm{kPa})$. Round this off to $11.0 \mathrm{inH}_{2} \mathrm{O}(2.7 \mathrm{kPa})$ for fan-selection purposes.
7. Compute the power required to drive the induced-draft fan. As with the forced-draft fan, air horsepower is $0.0001753 H_{f} C=0.0001753(11.0)(127,000)=245 \mathrm{hp}(182.7 \mathrm{~kW})$. If the combined efficiency of the fan and its driver, assumed to be an electric motor, is 68 percent, the motor horsepower required is $245 / 0.68=360.5 \mathrm{hp}(268.8 \mathrm{~kW})$. A $375-\mathrm{hp}(279.6-\mathrm{kW})$ motor would be chosen for the fan driver.
8. Choose the fans from a manufacturer's engineering data. Use Example 6.31 to select the fans from the engineering data of an acceptable manufacturer. For larger boiler units, the forceddraft fan is usually a backward-curved blade centrifugal-type unit. Where two fans are chosen to operate in parallel, the pressure curve of each fan should decrease at the same rate near shutoff so that the fans divide the load equally. Be certain that forced-draft fans are heavy-duty units designed for continuous operation with well-balanced rotors. Choose high-efficiency units with self-limiting power characteristics to prevent overloading the driving motor. Airflow is usually controlled by dampers on the fan discharge.

Induced-draft fans handle hot, dusty combustion products. For this reason, extreme care must be used to choose units specifically designed for induced-draft service. The usual choice for large boilers is a centrifugal-type unit with forward- or backward-curved, or flat blades, depending on the type of gas handled. Flat blades are popular when the flue gas contains large quantities of dust. Fan bearings are generally water-cooled.

Related Calculations. Use this procedure for selecting draft fans for all types of boilers-fire-tube, packaged, portable, marine, and stationary. Obtain draft losses from the boiler manufacturer. Compute duct pressure losses using the methods given in later Procedures in this Handbook.

## POWER-PLANT FAN SELECTION FROM CAPACITY TABLES

Choose a forced-draft fan to handle $69,400 \mathrm{ft}^{3} / \mathrm{min}\left(32.7 \mathrm{~m}^{3} / \mathrm{s}\right)$ of $90^{\circ} \mathrm{F}(305 \mathrm{~K})$ air at $6.30 \mathrm{inH}_{2} \mathrm{O}$ static pressure and an induced-draft fan to handle $152,500 \mathrm{ft}^{3} / \mathrm{min}\left(71.9 \mathrm{~m}^{3} / \mathrm{s}\right)$ of $385^{\circ} \mathrm{F}(469 \mathrm{~K})$ gas at $11.0 \mathrm{inH}_{2} \mathrm{O}$ static pressure. The boiler that these fans serve is installed at an elevation of 5000 ft $(1524 \mathrm{~m})$ above sea level. Use commercially available capacity tables for making the fan choice. The flue-gas density is $0.045 \mathrm{lb} / \mathrm{ft}^{3}\left(0.72 \mathrm{~kg} / \mathrm{m}^{3}\right)$ at $385^{\circ} \mathrm{F}(469 \mathrm{~K})$.

## Calculation Procedure

1. Compute the correction factors for the forced-draft fan. Commercial fan-capacity tables are based on fans handling standard air at $70^{\circ} \mathrm{F}$ at a barometric pressure of 29.92 inHg and having a density

TABLE 6.30 Fan Correction Factors

| Temperature |  | Correction <br> factor |  | Altitude |  |
| ---: | ---: | ---: | :---: | :---: | :---: |

of $0.075 \mathrm{lb} / \mathrm{ft}^{3}$. Where different conditions exist, the fan flow rate must be corrected for temperature and altitude.

Obtain the engineering data for commercially available forced-draft fans and turn to the temperature and altitude correction-factor tables. Pick the appropriate correction factors from these tables for the prevailing temperature and altitude of the installation. Thus, in Table 6.30, select the correction factors for $90^{\circ} \mathrm{F}$ air and 5000-ft altitude. These correction factors are $C_{T}=1.018$ for $90^{\circ} \mathrm{F}$ air and $C_{A}=1.095$ for 5000 -ft altitude.

Find the composite correction factor CCF by taking the product of the temperature and altitude correction factors, or CCF $=C_{T} C_{A}=1.018(1.095)=1.1147$. Now divide the given $\mathrm{ft}^{3} / \mathrm{min}$ by the composite correction factor to find the capacity-table $\mathrm{ft}^{3} / \mathrm{min}$. Or, capacity-table $\mathrm{ft}^{3} / \mathrm{min}$ is $69,400 / 1.1147=62,250 \mathrm{ft}^{3} / \mathrm{min}$.
2. Choose the fan size from the capacity table. Turn to the fan-capacity table in the engineering data and look for a fan delivering $62,250 \mathrm{ft}^{3} / \mathrm{min}$ at $6.3 \mathrm{inH}_{2} \mathrm{O}$ static pressure. Inspection of the table shows that the capacities are tabulated for pressures of 6.0 and $6.5 \mathrm{inH}_{2} \mathrm{O}$ static pressure. There is no tabulation for $6.3 \mathrm{inH}_{2} \mathrm{O}$. The fan must therefore be selected for $6.5 \mathrm{inH}_{2} \mathrm{O}$ static pressure.

Enter the table at the nearest capacity to that required, $62,250 \mathrm{ft}^{3} / \mathrm{min}$, as shown in Table 6.31. This table, excerpted with permission from the American Standard Inc. engineering data, shows that the nearest capacity of this particular type of fan is $62,595 \mathrm{ft}^{3} / \mathrm{min}$. The difference, or $62,595-62,250$ $=345 \mathrm{ft}^{3} / \mathrm{min}$, is only $345 / 62,250=0.0055$, or 0.55 percent. This is a negligible difference, and the $62,595-\mathrm{ft}^{3} / \mathrm{min}$ fan is well suited for its intended use. The extra static pressure, $6.5-6.3=0.2$ $\mathrm{inH}_{2} \mathrm{O}$, is desirable in a forced-draft fan because furnace or duct resistance may increase during the life of the boiler. Also, the extra static pressure is so small that it will not markedly increase the fan power consumption.
3. Compute the fan speed and power input. Multiply the capacity-table $\mathrm{r} / \mathrm{min}$ and bhp by the composite correction factor to determine the actual $\mathrm{r} / \mathrm{min}$ and bhp. Thus, using data from Table 6.31, the actual $\mathrm{r} / \mathrm{min}$ is $(1096)(1.1147)=1221.7 \mathrm{r} / \mathrm{min}$. Actual bhp is $(99.08)(1.1147)=110.5 \mathrm{hp}$. This is the horsepower input required to drive the fan and is close to the 113.2 hp computed in the previous example. The actual motor horsepower would be the same in each case because a standard-size motor

TABLE 6.31 Typical Fan Capacities

| Capacity |  | Outlet velocity |  | Outlet velocity <br> pressure |  | Ratings at $6.5 \mathrm{inH}_{2} \mathrm{O}$ |  |  |
| :--- | :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $(1.6 \mathrm{kPa})$ | static pressure |  |  |  |  |  |  |  |
| $\mathrm{ft}^{3} / \mathrm{min}$ | $\mathrm{m}^{3} / \mathrm{s}$ | $\mathrm{ft} / \mathrm{min}$ | $\mathrm{m} / \mathrm{s}$ | $\mathrm{inH}_{2} \mathrm{O}$ | kPa | $\mathrm{r} / \mathrm{min}$ | bhp | kW |
| 61,204 | 28.9 | 4400 | 22.4 | 1.210 | 0.3011 | 1083 | 95.45 | 71.2 |
| 62,595 | 29.5 | 4500 | 22.9 | 1.266 | 0.3150 | 1096 | 99.08 | 73.9 |
| 63,975 | 30.2 | 4600 | 23.4 | 1.323 | 0.3212 | 1109 | 103.0 | 76.8 |

would be chosen. The difference of $113.2-110.5=2.7 \mathrm{hp}$ results from the assumed efficiencies that depart from the actual values. Also, a sea-level altitude was assumed in the previous example. However, the two methods used show how accurately fan capacity and horsepower input can be estimated by judicious evaluation of variables.
4. Compute the correction factors for the induced-draft fan. The flue-gas density is $0.045 \mathrm{lb} / \mathrm{ft}^{3}$ at $385^{\circ} \mathrm{F}$. Interpolate in the temperature correction-factor table because a value of $385^{\circ} \mathrm{F}$ is not tabulated. Find the correction factor for $385^{\circ} \mathrm{F}$ thus: (Actual temperature - lower temperature)/(higher temperature - lower temperature $) \times$ (higher temperature-correction factor - lower temperaturecorrection factor) + lower-temperature-correction factor. Or, $[(385-375) /(400-375)](1.273-$ $1.255)+1.255=1.262$.

The altitude-correction factor is 1.095 for an elevation of 5000 ft , as shown in Table 6.30. As for the forced-draft fan, $\mathrm{CCF}=C_{T} C_{A}=(1.262)(1.095)=1.3819$. Use the CCF to find the capacitytable $\mathrm{ft}^{3} / \mathrm{min}$ in the same manner as for the forced-draft fan. Or, capacity-table $\mathrm{ft}^{3} / \mathrm{min}$ is (given $\left.\mathrm{ft}^{3} / \mathrm{min}\right) / \mathrm{CCF}=152,500 / 1.3819=110,355 \mathrm{ft}^{3} / \mathrm{min}$.
5. Choose the fan size from the capacity table. Check the capacity table to be sure that it lists fans suitable for induced-draft (elevated temperature) service. Turn to the 11-in static-pressure-capacity table and find a capacity equal to $110,355 \mathrm{ft}^{3} / \mathrm{min}$. In the engineering data used for this fan, the nearest capacity at 11 -in static pressure is $110,467 \mathrm{ft}^{3} / \mathrm{min}$, with an outlet velocity of $4400 \mathrm{ft}^{3} / \mathrm{min}$, an outlet velocity pressure of $1.210 \mathrm{inH}_{2} \mathrm{O}$, a speed of $1222 \mathrm{r} / \mathrm{min}$, and an input horsepower of 255.5 bhp . The tabulation of these quantities is of the same form as that given for the forced-draft fan (step 2). The selected capacity of $110,467 \mathrm{ft}^{3} / \mathrm{min}$ is entirely satisfactory because it is only $(110,467-110,355) / 110,355=0.00101$, or 0.1 percent, higher than the desired capacity.
6. Compute the fan speed and power input. Multiply the capacity-table $\mathrm{r} / \mathrm{min}$ and brake horsepower by the CCF to determine the actual $\mathrm{r} / \mathrm{min}$ and brake horsepower. Thus, the actual $\mathrm{r} / \mathrm{min}$ is $(1222)(1.3819)=1690 \mathrm{r} / \mathrm{min}$. Actual brake horsepower is $(255.5)(1.3819)=353.5 \mathrm{bhp}(263.7 \mathrm{~kW})$. This is the horsepower input required to drive the fan and is close to the 360.5 hp computed in the previous example. The actual motor horsepower would be the same in each case because a standardsize motor would be chosen. The difference in horsepower of $360.5-353.5=7.0 \mathrm{hp}$ results from the same factors discussed in step 3.

Note: The static pressure is normally used in most fan-selection procedures because this is the pressure value used in computing pressure and draft losses in boilers, economizers, air heaters, and ducts. In any fan system, the total air pressure equals static pressure + velocity pressure. However, the velocity pressure at the fan discharge is not considered in draft calculations unless there are factors requiring its evaluation. These requirements are generally related to pressure losses in the fan-control devices.

## DETERMINATION OF THE MOST ECONOMICAL N CONTROL

Determine the most economical fan control for a forced- or induced-draft fan designed to deliver $140,000 \mathrm{ft}^{3} / \mathrm{min}\left(66.03 \mathrm{~m}^{3} / \mathrm{s}\right)$ at $14 \mathrm{inH}_{2} \mathrm{O}(3.5 \mathrm{kPa})$ at full load. Plot the power-consumption curve for each type of control device considered.

## Calculation Procedure

1. Determine the types of controls to consider. There are five types of controls used for forced- and induced-draft fans: (a) a damper in the duct with constant-speed fan drive, (b) two-speed fan driver, (c) inlet vanes or inlet louvres with a constant-speed fan drive, $(d)$ multiple-step variable-speed fan drive, and $(e)$ hydraulic or electric coupling with constant-speed driver giving wide control over fan speed.

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2. Evaluate each type of fan control. Tabulate the selection factors influencing the control decision as follows, using the control letters in step 1:

| Control type | Control cost | Required power <br> input | Advantages (A), and <br> disadvantages (D) |
| :---: | :--- | :--- | :--- |
| $a$ | Low | High | (A) Simplicity; (D) <br> High power input |
| $b$ | Moderate | Moderate | (A) Lower input <br> power; (D) Higher cost <br> $c$ |
| Low | Moderate | (A) Simplicity; (D) ID <br> fan erosion |  |
| $d$ | Moderate | Moderate | (D) Complex; also <br> needs dampers |
| $e$ | High | Low | (A) Simple; no dampers <br> needed |

3. Plot the control characteristics for the fans. Draw the fan head-capacity curve for the airflow or gasflow range considered (Fig. 6.35). This plot shows the maximum capacity of $140,000 \mathrm{ft}^{3} / \mathrm{min}$ and required static head of $14 \mathrm{inH}_{2} \mathrm{O}$, point $P$.

Plot the power-input curve $A B C D$ for a constant-speed motor or turbine drive with damper control-type $a$, listed above-after obtaining from the fan manufacturer or damper builder the input power required at various static pressures and capacities. Plotting these values gives curve $A B C D$. Fan speed is $1200 \mathrm{r} / \mathrm{min}$.

Plot the power-input curve $G H K$ for a two-speed drive, type $b$. This drive might be a motor with an additional winding, or it might be a second motor for use at reduced boiler capacities. With either arrangement, the fan speed at lower boiler capacities is $900 \mathrm{r} / \mathrm{min}$.

Plot the power-input curve $A F E D$ for inlet-vane control on the forced-draft fan or inlet-louvre control on induced-draft fans. The data for plotting this curve can be obtained from the fan manufacturer.

Multiple-step variable-speed fan control, type $d$, is best applied with steam-turbine drives. In a plant with ac auxiliary motor drives, slip-ring motors with damper integration must be used between steps, making the installation expensive. Although dc motor drives would be less costly, few power plants other than marine propulsion plants have direct current available. And since marine units normally operate at full load 90 percent or more of the time, part-load operating economics are unimportant. If steam-turbine drive will be used for the fans, plot the power-input curve $L M D$, using data from the fan manufacturer.

A hydraulic coupling or electric magnetic coupling, type $e$, with a constant-speed motor drive would have the power-input curve $D E J$.

Study of the power-input curves shows that the hydraulic and electric couplings have the smallest power input. Their first cost, however, is usually greater than any other types of power-saving devices. To determine the return on any extra investment in power-saving devices, an economic study, including a load-duration analysis of the boiler load, must be made.
4. Compare the return on the extra investment. Compute and tabulate the total cost of each type of control system. Then determine the extra investment for each of the more costly systems by subtracting the cost of type $a$ from the cost of each of the other types. With the extra investment known, compute the lifetime savings in power input for each of the more efficient control methods. With the extra investment and savings resulting from it known, compute the percentage return on the extra investment. Tabulate the findings as in Table 6.32.

In Table 6.32, considering control type $c$, the extra cost of type $c$ over type $b$ is $\$ 75,000-50,000=$ $\$ 25,000$. The total power saving of $\$ 6500$ is computed on the basis of the cost of energy in the plant for the life of the control. The return on the extra investment then is $\$ 6500 / \$ 25,000=0.26$, or 26 percent. Type $e$ control provides the highest percentage return on the extra investment. It would probably be


FIGURE 6.35 Power requirements for a fan fitted with different types of controls. (American Standard Inc.)
chosen if the only measure of investment desirability is the return on the extra investment. However, if other criteria are used-such as a minimum rate of return on the extra investment-one of the other control types might be chosen. This is easily determined by studying the tabulation in conjunction with the investment requirement. For more on investment decisions, see Section 18.

Related Calculations. The procedure used here can be applied to heating, power, marine, and portable boilers of all types. Follow the same steps given above, changing the values to suit the existing conditions. Work closely with the fan and drive manufacturer when analyzing drive power input and costs.

TABLE 6.32 Fan Control Comparison

|  | Type of control used |  |  |  |  |
| :--- | :---: | ---: | ---: | ---: | ---: |
|  | $a$ | $b$ | $c$ | $d$ | $e$ |
| Total cost, \$ | 30,000 | 50,000 | 75,000 | 89,500 | 98,000 |
| Extra cost, \$ | - | 20,000 | 25,000 | 14,500 | 8,500 |
| Total power saving, \$ | - | 8,000 | 6,500 | 3,000 | 6,300 |
| Return on extra investment, \% | - | 40 | 26 | 20.7 | 74.2 |

### 6.33 VACUUM-PUMP SELECTION FOR HIGH-VACUUM SYSTEMS

Choose a mechanical vacuum pump for use in a laboratory fitted with a vacuum system having a total volume, including the piping, of $12,000 \mathrm{ft}^{3}\left(340 \mathrm{~m}^{3}\right)$. The operating pressure of the system is 0.10 torr, and the optimum pump-down time is 150 min . (Note: 1 torr $=1 \mathrm{mmHg}$.)

## Calculation Procedure

1. Make a tentative choice of pump type. Mechanical vacuum pumps of the reciprocating type are well suited for system pressures in the 0.0001- to 760-torr range. Hence, this type of pump will be considered first to see if it meets the desired pump-down time.
2. Obtain the pump characteristic curves. Many manufacturers publish pump-down factor curves such as those in Fig. 6.36a and $b$. These curves are usually published as part of the engineering data for a given line of pumps. Obtain the curves from the manufacturers whose pumps are being considered.
3. Compute the pump-down time for the pumps being considered. Three reciprocating pumps can serve this system: (a) a single-stage pump, (b) a compound or two-stage pump, or $(c)$ a combination of a mechanical booster and a single-stage backing or roughing-down pump. Figure 6.36 gives the pump-down factor for each type of pump.

To use the pump-down factor, apply this relation: $t=V F / d$, where $t$ is pump-down time, min; $V$ is system volume, $\mathrm{ft}^{3} ; F$ is pump-down factor for the pump; $d$ is pump displacement, $\mathrm{ft}^{3} / \mathrm{min}$.

Thus, for a single-stage pump, Fig. $6.36 a$ shows that $F=10.8$ for a pressure of 0.10 torr. Assuming a pump displacement of $1000 \mathrm{ft}^{3} / \mathrm{min}, t=12,000(10.8) / 1000=129.6 \mathrm{~min}$; say 130 min .

For a compound pump, $F=9.5$ from Fig. 6.36a. Hence, a compound pump having the same displacement, or $1000 \mathrm{ft}^{3} / \mathrm{min}$, will require $t=12,000(9.5) / 1000=114.0 \mathrm{~min}$.

With a combination arrangement, the backing or roughing pump, a $130-\mathrm{ft}^{3} / \mathrm{min}$ unit, reduces the system pressure from atmospheric, 760 torr, to the economical transition pressure, 15 torr (Fig. 6.36b). Then the single-stage mechanical booster pump, a $1200-\mathrm{ft}^{3} / \mathrm{min}$ unit, takes over and in combination with the backing pump reduces the pressure to the desired level, or 0.10 torr. During this part of the cycle, the unit operates as a two-stage pump. Hence the total pump-down time consists of the sum of the backing-pump and booster-pump times. The pump-down factors are, respectively, 4.2 for the backing pump at 15 torr and 6.9 for the booster pump at 0.10 torr. Hence the respective pump-down times are $t_{1}=12,000(4.2) / 130=388 \mathrm{~min} ; t_{2}=12,000(6.9) / 1200=69 \mathrm{~min}$. The total time is thus $388+69=457 \mathrm{~min}$.

The pump-down time with the combination arrangement is greater than the optimum 150 min . Where a future lower operating pressure is anticipated, making the combination arrangement desirable, an additional large-capacity single-stage roughing pump can be used to assist the $130-\mathrm{ft}^{3} / \mathrm{min}$ unit. This large-capacity unit is operated until the transition pressure is reached and roughing down is finished. The pump is then shut off and the balance of the pumping down is carried on by the combination unit. This keeps the power consumption at a minimum.

Thus, if a $1200-\mathrm{ft}^{3} / \mathrm{min}$ single-stage roughing pump were used to reduce the pressure to 15 torr, its pump-down time would be $t=12,000(4.0) / 1200=40 \mathrm{~min}$. The total pump-down time for the combination would then be $40+69=109 \mathrm{~min}$, using the time computed above for the two pumps in combination.
4. Apply the respective system factors. Studies and experience show that the calculated pumpdown time for a vacuum system must be corrected by an appropriate system factor. This factor makes allowance for the normal outgassing of surfaces exposed to atmospheric air. It also provides a basis for judging whether a system is pumping down normally or whether some problem exists that must be corrected. Table 6.33 lists typical system factors that have proven reliable in many tests. To use the system factor for any pump, apply it this way: $t_{a}=t S$, where $t_{a}$ is actual pump-down time, in min; $t$ is computed pump-down time from step 3 , in $\min ; S$ is system factor for the type of pump being considered.

(a)

(b)

FIGURE 6.36 (a) Pump-down factor for single-stage and compound vacuum pumps; (b) pump-down factor for mechanical booster and backing pump. (After Kinney Vacuum Division, The New York Air Brake Co., and Van Atta.)

TABLE 6.33 Recommended System Factors

| Pressure range |  | System factors |  |  |
| :---: | :---: | :---: | :---: | :---: |
| torr | Pa | Single-stage <br> mechanical pump | Compound <br> mechanical pump | Mechanical booster <br> pump* |
| $760-20$ | $115.6 \mathrm{kPa}-3000$ | 1.0 | 1.0 | - |
| $20-1$ | $3000-150$ | 1.1 | 1.1 | 1.15 |
| $1-0.5$ | $150-76$ | 1.25 | 1.25 | 1.15 |
| $0.5-0.1$ | $76-15$ | 1.5 | 1.25 | 1.35 |
| $0.1-0.02$ | $15-3$ | - | 1.25 | 1.35 |
| $0.02-0.001$ | $3-0.15$ | - | - | 2.0 |

[^8]Thus, using the appropriate system factor for each pump, the actual pump-down time for the singlestage mechanical pump is $t_{a}=130(1.5)=195 \mathrm{~min}$. For the compound mechanical pump, $t_{a}=$ $114(1.25)=142.5 \mathrm{~min}$. For the combination mechanical booster pump, $t_{a}=109(1.35)=147 \mathrm{~min}$.
5. Choose the pump to use. Based on the actual pump-down time, either the compound mechanical pump or the combination mechanical booster pump can be used. The final choice of the pump should take other factors into consideration-first cost, operating cost, maintenance cost, reliability, and probable future pressure requirements in the system. Where future lower pressure requirements are not expected, the compound mechanical pump would be a good choice. However, if lower operating pressures are anticipated in the future, the combination mechanical booster pump would probably be a better choice.

Van Atta [4] gives the following typical examples of pumps chosen for vacuum systems:

| Pressure range, torr | Typical pump choice |
| :--- | :---: |
| Down to $50(7.6 \mathrm{kPa})$ | Single-stage oil-sealed rotary; large water or <br> vapor load may require use of refrigerated traps |
| 0.05 to $0.01(7.6$ to 1.5 Pa$)$ | Single-stage or compound oil-sealed pump plus <br> refrigerated traps, particularly at the lower <br> pressure limit |
| 0.01 to $0.005(1.5$ to 0.76 Pa$)$ | Compound oil-sealed plus refrigerated traps, or <br> single-stage pumps backing diffusion pumps if <br> a continuous large evolution of gas is expected <br> Mechanical booster and backing pump <br> combination with interstage refrigerated <br> condenser and cooled vapor trap at the |
|  | high-vacuum inlet for extreme freedom from <br> vapor contamination |
| 0.0005 and lower (0.076 Pa and lower) | Single-stage pumps backing diffusion pumps, <br> with refrigerated traps on the high-vacuum side <br> of the diffusion pumps and possibly between |
| the single-stage and diffusion pumps if |  |
| evolution of condensable vapor is expected |  |

### 6.34 VACUUM-SYSTEM PUMPING SPEED AND PIPE SIZE


#### Abstract

A laboratory vacuum system has a volume of $500 \mathrm{ft}^{3}\left(14 \mathrm{~m}^{3}\right)$. Leakage into the system is expected at the rate of $0.00035 \mathrm{ft}^{3} / \mathrm{min}$. What backing pump speed, i.e., displacement, should an oil-sealed vacuum pump serving this system have if the pump blocking pressure is 0.150 mmHg and the desired operating pressure is 0.0002 mmHg ? What should the speed of the diffusion pump be? What pump size is needed for the connecting pipe of the backing pump if it has a displacement or pumping speed of $388 \mathrm{ft}^{3} / \mathrm{min}\left(0.18 \mathrm{~m}^{3} / \mathrm{s}\right)$ at 0.150 mmHg and a length of $15 \mathrm{ft}(4.6 \mathrm{~m})$ ?


## Calculation Procedure

1. Compute the required backing pump speed. Use the relation $d_{b}=G / P_{b}$, where $d_{b}$ is backing pump speed or pump displacement, in $\mathrm{ft}^{3} / \mathrm{min}$; $G$ is gas leakage or flow rate, in $\mathrm{mm} /\left(\mathrm{ft}^{3} / \mathrm{min}\right)$. To convert the gas or leakage flow rate to $\mathrm{mm} /\left(\mathrm{ft}^{3} / \mathrm{min}\right)$, multiply the $\mathrm{ft}^{3} / \mathrm{min}$ by 760 mm , the standard atmospheric pressure, in mmHg. Thus, $d_{b}=760(0.00035) / 0.150=1.775 \mathrm{ft}^{3} / \mathrm{min}$.
2. Select the actual backing pump speed. For practical purposes, since gas leakage and outgassing are impossible to calculate accurately, a backing pump speed or displacement of at least twice the computed value, or $2(1.775)=3.550 \mathrm{ft}^{3} / \mathrm{min}$ —say $4 \mathrm{ft}^{3} / \mathrm{min}\left(0.002 \mathrm{~m}^{3} / \mathrm{s}\right)$-would probably be used.

If this backing pump is to be used for pumping down the system, compute the pump-down time as shown in the previous example. Should the pump-down time be excessive, increase the pump displacement until a suitable pump-down time is obtained.
3. Compute the diffusion pump speed. The diffusion pump reduces the system pressure from the blocking point, 0.150 mmHg , to the system operating pressure of 0.0002 mmHg . (Note: 1 torr $=$ 1 mmHg .) Compute the diffusion pump speed from $d_{d}=G / P_{d}$, where $d$ is diffusion pump speed, in $\mathrm{ft}^{3} / \mathrm{min} ; P_{d}$ is diffusion-pump operating pressure, mmHg . Or $d_{d}=760(0.00035) / 0.0002=1330$ $\mathrm{ft}^{3} / \mathrm{min}\left(0.627 \mathrm{~m}^{3} / \mathrm{s}\right)$. To allow for excessive leaks, outgassing, and manifold pressure loss, a $3000-$ or $4000-\mathrm{ft}^{3} / \mathrm{min}$ diffusion pump would be chosen. To ensure reliability of service, two diffusion pumps would be chosen so that one could operate while the other was being overhauled.
4. Compute the size of the connection pipe. In usual vacuum-pump practice, the pressure drop in pipes serving mechanical pumps is not allowed to exceed 20 percent of the inlet pressure prevailing under steady operating conditions. A correctly designed vacuum system, where this pressure loss is not exceeded, will have a pump-down time which closely approximates that obtained under ideal conditions.

Compute the pressure drop in the high-pressure region of vacuum pumps from $p_{d}=1.9 d_{b} L / d^{4}$, where $p_{d}$ is pipe pressure drop, in $\mu ; d_{b}$ is backing pump displacement or speed, in $\mathrm{ft}^{3} / \mathrm{min}$; $L$ is pipe length, in ft ; $d$ is inside diameter of pipe, in in. Since the pressure drop should not exceed 20 percent of the inlet or system operating pressure, the drop for a backing pump is based on its blocking pressure, or 0.150 mmHg , or $150 \mu$. Hence $p_{d}=0.20(150)=30 \mu$. Then, $30=1.9(380)(15) / d^{4}$, and $d=4.35$ in $(0.110 \mathrm{~m})$. Use a 5 -in-diameter pipe.

In the low-pressure region, the diameter of the converting pipe should equal, or be larger than, the pump inlet connection. Whenever the size of a pump is increased, the diameter of the pipe should also be increased to conform with the above guide.

Related Calculations. Use the general procedures given here for laboratory- and production-type high-vacuum systems.

### 6.35 BULK-MATERIAL ELEVATOR AND CONVEYOR SELECTION

Choose a bucket elevator to handle 150 tons $/ \mathrm{h}\left(136.1\right.$ tonnes $/ \mathrm{h}$ ) of abrasive material weighing $50 \mathrm{lb} / \mathrm{ft}^{3}$ $\left(800.5 \mathrm{~kg} / \mathrm{m}^{3}\right)$ through a vertical distance of $75 \mathrm{ft}(22.9 \mathrm{~m})$ at a speed of $100 \mathrm{ft} / \mathrm{min}(30.5 \mathrm{~m} / \mathrm{min})$. What horsepower input is required to drive the elevator? The bucket elevator discharges onto a horizontal conveyor which must transport the material $1400 \mathrm{ft}(426.7 \mathrm{~m})$. Choose the type of conveyor to use and determine the required power input needed to drive it.

## Calculation Procedure

1. Select the type of elevator to use. Table 6.34 summarizes the various characteristics of bucket elevators used to transport bulk materials vertically. This table shows that a continuous bucket elevator would be a good choice, because it is a recommended type for abrasive materials. The second choice would be a pivoted bucket elevator. However, the continuous bucket type is popular and will be chosen for this application.
2. Compute the elevator height. To allow for satisfactory loading of the bulk material, the elevator length is usually increased by about $5 \mathrm{ft}(1.5 \mathrm{~m})$ more than the vertical lift. Hence the elevator height is $75+5=80 \mathrm{ft}(24.4 \mathrm{~m})$.
3. Compute the required power input to the elevator. Use the relation $h p=2 C H / 1000$, where $C$ is elevator capacity, in tons $/ \mathrm{h} ; H$ is elevator height, in ft . Thus, for this elevator, $h p=$ $2(150)(80) / 1000=24.9 \mathrm{hp}(17.9 \mathrm{~kW})$.

The power input relation given above is valid for continuous bucket, centrifugal-discharge, perfectdischarge, and supercapacity elevators. A $25-\mathrm{hp}$ (18.7-kW) motor would probably be chosen for this elevator.
4. Select the type of conveyor to use. Since the elevator discharges onto the conveyor, the capacity of the conveyor should be the same, per unit time, as the elevator. Table 6.35 lists the characteristics

TABLE 6.34 Bucket Elevators

|  | Centrifugal discharge | Perfect discharge | Continuous bucket | Gravity discharge | Pivoted bucket |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Carrying paths | Vertical | Vertical to inclination $15^{\circ}$ from vertical | Vertical to inclination $15^{\circ}$ from vertical | Vertical and horizontal | Vertical and horizontal |
| $\begin{aligned} & \text { Capacity range, } \\ & \text { tons/h (tonnes } / \mathrm{h} \text { ), } \\ & \text { material weighing } \\ & 50 \mathrm{lb} / \mathrm{ft}^{3}(800.5 \\ & \left.\mathrm{kg} / \mathrm{m}^{3}\right) \end{aligned}$ | 78 (70.8) | 34 (30.8) | 345 (312.9) | 191 (173.3) | 255 (231.3) |
| Speed range, $\mathrm{ft} / \mathrm{min}$ ( $\mathrm{m} / \mathrm{min}$ ) | 306 (93.3) | 120 (36.6) | 100 (30.5) | 100 (30.5) | 80 (24.4) |
| Location of loading point | Boot | Boot | Boot | On lower horizontal run | On lower horizontal run |
| Location of discharge point | Over head wheel | Over head wheel | Over head wheel | On horizontal run | On horizontal run |
| Handling abrasive materials | Not preferred | Not preferred | Recommended | Not recommended | Recommended |

Source: Link-Belt Div. of FMC Corp.
TABLE 6.35 Conveyor Characteristics

|  | Belt conveyor | Apron conveyor | Flight conveyor | Drag chain | En masse conveyor | Screw conveyor | Vibratory conveyor |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| Carrying paths | Horizontal to $18^{\circ}$ | Horizontal to $25^{\circ}$ | Horizontal to $45^{\circ}$ | Horizontal or <br> slight incline, | Horizontal to $90^{\circ}$ | Horizontal to <br> $15^{\circ} ;$ may be <br> used up to <br> $90^{\circ}$ <br> but capacity <br> falls off rapidly | Horizontal or <br> slight incline, <br> $5^{\circ}$ above or <br> below <br> horizontal |
| $100(90.7)$ |  |  |  |  |  |  |  |

[^9]

FIGURE 6.37 Power required to move an empty conveyor belt at $100 \mathrm{ft} / \mathrm{min}(0.508 \mathrm{~m} / \mathrm{s})$.
of various types of conveyors. Study of the tabulation shows that a belt conveyor would probably be best for this application, based on the speed, capacity, and type of material it can handle, hence, it will be chosen for this installation.
5. Compute the required power input to the conveyor. The power input to a conveyor is composed of two portions: $(a)$ the power required to move the empty belt conveyor, and $(b)$ the power required to move the load horizontally.

Determine from Fig. 6.37 the power required to move the empty belt conveyor, after choosing the required belt width. Determine the belt width from Table 6.36.

Thus, for this conveyor, Table 6.36 shows that a belt width of 42 in $(106.7 \mathrm{~cm})$ is required to transport up to 150 tons $/ \mathrm{h}(136.1$ tonnes $/ \mathrm{h}$ ) at a belt speed of $100 \mathrm{ft} / \mathrm{min}(30.5 \mathrm{~m} / \mathrm{min})$. (Note that the next larger capacity, 162 tons/h ( 146.9 tonnes/h), is used when the exact capacity required is not tabulated.) Find the horsepower required to drive the empty belt by entering Fig. 6.37 at the belt distance between centers, $1400 \mathrm{ft}(426.7 \mathrm{~m})$, and projecting vertically upward to the belt width, 42 in $(106.7 \mathrm{~cm})$. At the left, read the required power input as $7.2 \mathrm{hp}(5.4 \mathrm{~kW})$.

TABLE 6.36 Capacities of Troughed Rest [tons/h (tonnes/h) with belt speed of $100 \mathrm{ft} / \mathrm{min}(30.5 \mathrm{~m} / \mathrm{min})$ ]

| Belt width, in <br> $(\mathrm{cm})$ | Weight of material, $\mathrm{lb} / \mathrm{ft}^{3}\left(\mathrm{~kg} / \mathrm{m}^{3}\right)$ |  |  |  |
| :---: | ---: | ---: | ---: | ---: |
|  | $(400.3)$ | $50(800.5)$ | $100(1601)$ | $150(2402)$ |
| $30(9.1)$ | $47(42.6)$ | $79(71.7)$ | $158(143.3)$ | $237(214.9)$ |
| $36(10.9)$ | $69(62.6)$ | $114(103.4)$ | $228(206.8)$ | $342(310.2)$ |
| $42(12.8)$ | $97(87.9)$ | $162(146.9)$ | $324(293.9)$ | $486(440.9)$ |
| $48(14.6)$ | $130(117.9)$ | $215(195.0)$ | $430(390.1)$ | $645(585.1)$ |
| $60(18.3)$ | $207(187.8)$ | $345(312.9)$ | $690(625.9)$ | $1035(938.9)$ |

Source: United States Rubber Co.

TABLE 6.37 Minimum Belt Width for Lumps

| Belt width, in (mm) | $24(609.6)$ | $36(914.4)$ | $42(1066.8)$ | $48(1219.2)$ |
| :--- | ---: | ---: | :--- | :--- |
| Sized materials, in (mm) | $41 / 2(114.3)$ | $8(203.2)$ | $10(254)$ | $12(304.9)$ |
| Unsized material, in (mm) | $8(203.2)$ | $14(355.6)$ | $20(508)$ | $35(889)$ |

TABLE 6.38 Maximum Belt Speeds for Various Materials

|  | Width of belt | Light or free-flowing <br> materials, grains <br> dry sand, etc. |  | Moderately free-flowing <br> sand, gravel, fine <br> stone, etc. |  | Lump coal, coarse <br> stone, crushed ore | Heavy sharp lumpy <br> materials, heavy <br> ores, lump coke |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| in | mm | $\mathrm{ft} / \mathrm{min}$ | $\mathrm{m} / \mathrm{min}$ | $\mathrm{ft} / \mathrm{min}$ | $\mathrm{m} / \mathrm{min}$ | $\mathrm{ft} / \mathrm{min}$ | $\mathrm{m} / \mathrm{min}$ | $\mathrm{ft} / \mathrm{min}$ | $\mathrm{m} / \mathrm{min}$ |
| $12-14$ | $305-356$ | 400 | 122 | 250 | 76 | - | - | - | - |
| $16-18$ | $406-457$ | 500 | 152 | 300 | 91 | 250 | 76 | - | - |
| $20-24$ | $508-610$ | 600 | 183 | 400 | 122 | 350 | 107 | 250 | 76 |
| $30-36$ | $762-914$ | 750 | 229 | 500 | 152 | 400 | 122 | 300 | 91 |

Compute the power required to move the load horizontally from $h p=(C / 100)(0.4+0.00345 L)$, where $L$ is distance between conveyor centers, in ft ; other symbols as before. For this conveyor, $h p=(150 / 100)(0.4+0.00325 \times 1400)=6.83 \mathrm{hp}(5.1 \mathrm{~kW})$. Hence the total horsepower to drive this horizontal conveyor is $7.2+6.83=14.03 \mathrm{hp}(10.5 \mathrm{~kW})$.

The total horsepower input to this conveyor installation is the sum of the elevator and conveyor belt horsepowers, or $14.03+24.0=38.03 \mathrm{hp}(28.4 \mathrm{~kW})$.

Related Calculations. This procedure is valid for conveyors using rubber belts reinforced with cotton duck, open-mesh fabric, cords, or steel wires. It is also valid for stitched-canvas belts, balata belts, and flat-steel belts. The required horsepower input includes any power absorbed by idler pulleys.

Table 6.37 shows the minimum recommended belt widths for lumpy materials of various sizes. Maximum recommended belt speeds for various materials are shown in Table 6.38.

When a conveyor belt is equipped with a tripper, the belt must rise about $5 \mathrm{ft}(1.5 \mathrm{~m})$ above its horizontal plane of travel.

This rise must be included in the vertical lift power input computation. When the tripper is driven by the belt, allow $1 \mathrm{hp}(0.75 \mathrm{~kW})$ for a 16-in ( $406.4-\mathrm{mm}$ ) belt, $3 \mathrm{hp}(2.2 \mathrm{~kW})$ for a $36-\mathrm{in}(914.4-\mathrm{mm})$ belt, and $7 \mathrm{hp}(5.2 \mathrm{~kW})$ for a $60-\mathrm{in}(1524-\mathrm{mm})$ belt. Where a rotary cleaning brush is driven by the conveyor shaft, allow about the same power input to the brush for belts of various widths.

## SCREW-CONVEYOR POWER INPUT AND CAPACITY

What is the required input for a $100-\mathrm{ft}(30.5-\mathrm{m})$ long screw conveyor handling dry coal ashes having a maximum density of $40 \mathrm{lb} / \mathrm{ft}^{3}$ if the conveyor capacity is 30 tons $/ \mathrm{h}$ ( 27.2 tonnes $/ \mathrm{h}$ )?

## Calculation Procedure

1. Select the conveyor diameter and speed. Refer to a manufacturer's engineering data or Table 6.39 for a listing of recommended screw-conveyor diameters and speeds for various types of materials. Dry coal ashes are commonly rated as group 3 materials (Table 6.40)-i.e., materials with small mixed lumps with fines.

To determine a suitable screw diameter, assume two typical values and obtain the recommended $\mathrm{r} / \mathrm{min}$ from the sources listed above or Table 6.39. Thus the maximum $\mathrm{r} / \mathrm{min}$ recommended for a

TABLE 6.39 Screw-Conveyor Capacities and Speeds

| Material <br> group | Max material density, <br> $\mathrm{lb} / \mathrm{ft}^{3}\left(\mathrm{~kg} / \mathrm{m}^{3}\right)$ | Max r/min for diameters of |  |
| :---: | :---: | :---: | :---: |
| 1 | $50(801)$ | 170 | 20 in $(152 \mathrm{~mm})$ |

TABLE 6.40 Material Factors for Screw Conveyors

| Material group | Material type | Material factor |
| :---: | :---: | :---: |
| 1 | Lightweight: |  |
|  | Barley, beans, flour, oats, pulverized coal, etc. | 0.5 |
| 2 | Fines and granular: |  |
|  | Coal-slack or fines | 0.9 |
|  | Sawdust, soda ash | 0.7 |
|  | Flyash | 0.4 |
| 3 | Small lumps and fines: |  |
|  | Ashes, dry alum | 4.0 |
|  | Salt | 1.4 |
| 4 | Semiabrasives; small lumps: |  |
|  | Phosphate, cement | 1.4 |
|  | Clay, limestone; | 2.0 |
|  | Sugar, white lead | 1.0 |
| 5 | Abrasive lumps: |  |
|  | Wet ashes | 5.0 |
|  | Sewage sludge | 6.0 |
|  | Flue dust | 4.0 |

6 -in ( $152.4-\mathrm{mm}$ ) screw when handling group 3 material is 90 , as shown in Table 6.39 ; for a 20 -in ( $508.0-\mathrm{mm}$ ) screw, $60 \mathrm{r} / \mathrm{min}$. Assume a 6-in ( $152.4-\mathrm{mm}$ ) screw as a trial diameter.
2. Determine the material factor for the conveyor. A material factor is used in the screw conveyor power input computation to allow for the character of the substance handled. Table 6.40 lists the material factor for dry ashes as $F=4.0$. Standard references show that the average weight of dry coal ashes is 35 to $40 \mathrm{lb} / \mathrm{ft}^{3}\left(640.4 \mathrm{~kg} / \mathrm{m}^{3}\right)$.
3. Determine the conveyor size factor. A size factor that is a function of the conveyor diameter is also used in the power input computation. Table 6.41 shows that for a 6-in diameter conveyor the size factor $A=54$.

TABLE 6.41 Screw Conveyor Size Factors

| Conveyor diameter, <br> in $(\mathrm{mm})$ | Size factor | Conveyor diameter, <br> in $(\mathrm{mm})$ | Size factor |
| :---: | :---: | :---: | :---: |
| $6(152.4)$ | 54 | $16(406.4)$ | 336 |
| $9(228.6)$ | 96 | $18(457.2)$ | 414 |
| $10(254)$ | 114 | $20(508)$ | 510 |
| $12(304.8)$ | 171 | $24(609.6)$ | 690 |

4. Compute the required power input to the conveyor. Use the relation $h p=10^{-6}(A L N+$ $C W L F$ ), where $h p$ is hp input to the screw conveyor head shaft; $A$ is size factor from step $3 ; L$ is conveyor length, in ft ; $N$ is conveyor $\mathrm{r} / \mathrm{min}$; $C$ is quantity of material handled, $\mathrm{in}^{\mathrm{ft}} / \mathrm{h} ; W$ is density of material, in $\mathrm{lb} / \mathrm{ft}^{3} ; F$ is material factor from step 2 . For this conveyor, using the data listed above $h p=10^{-6}(54 \times 100 \times 60+1500 \times 40 \times 100 \times 4.0)=24.3 \mathrm{hp}(18.1 \mathrm{~kW})$. With a 90 percent motor efficiency, the required motor rating would be $24.3 / 0.90=27 \mathrm{hp}(20.1 \mathrm{~kW})$. A $30-\mathrm{hp}$ (22.4kW ) motor would be chosen to drive this conveyor. Since this is not an excessive power input, the 6 -in ( $152.4-\mathrm{mm}$ ) conveyor is suitable for this application.

If the calculation indicates that an excessively large power input—say $50 \mathrm{hp}(37.3 \mathrm{~kW})$ or more-is required, the larger-diameter conveyor should be analyzed. In general, a higher initial investment in conveyor size that reduces the power input will be more than recovered by the savings in power costs.

Related Calculations. Use this procedure for screw or spiral conveyors and feeders handling any material that will flow. The usual screw or spiral conveyor is suitable for conveying materials for distances up to about $200 \mathrm{ft}(60 \mathrm{~m})$, although special designs can be built for greater distances. Conveyors of this type can be sloped upward to angles of $35^{\circ}$ with the horizontal. However, the capacity of the conveyor decreases as the angle of inclination is increased. Thus the reduction in capacity at a $10^{\circ}$ inclination is 10 percent over the horizontal capacity; at $35^{\circ}$ the reduction is 78 percent.

The capacities of screw and spiral conveyors are generally stated in $\mathrm{ft}^{3} / \mathrm{h}$ of various classes of materials at the maximum recommended shaft $\mathrm{r} / \mathrm{min}$. As the size of the lumps in the material conveyed increases, the recommended shaft $\mathrm{r} / \mathrm{min}$ decreases. The capacity of a screw or spiral conveyor at a lower speed is found from (capacity at given speed, in $\mathrm{ft}^{3} / \mathrm{h}$ ) (lower speed, $\mathrm{r} / \mathrm{min} /$ higher speed, $\mathrm{r} / \mathrm{min}$ ). Table 6.39 shows typical screw conveyor capacities at usual operating speeds.

Various types of screws are used for modern conveyors. These include short-pitch, variable-pitch, cut flights, ribbon, and paddle screws. The Procedure given above also applies to these screws.

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## SECTION 7

HEAT TRANSFER*

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7.1 SPECIFYING RADIATION SHIELDING ..... 7.2
7.2 RADIANT INTERCHANGE INSIDE A BLACK-SURFACED ENCLOSURE 7.4
7.3 EFFECT OF SOLAR HEAT ON A STORAGE TANK ..... 7.7
7.4 HEAT LOSS FROM AN UNINSULATED SURFACE TO AIR 7.9
7.5 HEAT LOSS FROM AN INSULATED SURFACE TO AIR 7.10
7.6 HEAT LOSS FROM A BURIED LINE 7.11
7.7 CONDUCTION OF HEAT IN THEUNSTEADY STATE: COOLINGTIME 7.12
7.8 CONDUCTION OF HEAT IN THE UNSTEADY STATE: TEMPERATURE 7.13
7.9 CONDUCTION OF HEAT IN THE UNSTEADY STATE: TEMPERATURE DISTRIBUTION 7.15
7.10 CONDUCTION OF HEAT FROM A BELTCOOLER 7.16
7.11 SIZING A BELT COOLER ..... 7.19
7.12 BATCH HEATING: INTERNAL COIL,ISOTHERMAL HEATINGMEDIUM 7.19
7.13 BATCH COOLING: INTERNAL COIL,NONISOTHERMAL COOLINGMEDIUM 7.20
7.14 BATCH COOLING: EXTERNAL HEATEXCHANGER (COUNTERFLOW),NONISOTHERMAL COOLINGMEDIUM7.21
7.15 BATCH COOLING: EXTERNAL HEATEXCHANGER (1-2 MULTIPASS),

NONISOTHERMAL COOLING MEDIUM 7.22
7.16 HEAT TRANSFER IN AGITATED VESSELS 7.23
7.17 NATURAL-CONVECTION HEAT TRANSFER 7.24
7.18 HEAT-TRANSFER COEFFICIENTS FOR FLUIDS FLOWING INSIDE TUBES: FORCED CONVECTION, SENSIBLE HEAT 7.26
7.19 HEAT-TRANSFER COEFFICIENTS FOR FLUIDS FLOWING INSIDE HELICAL COILS 7.28
7.20 HEAT-TRANSFER COEFFICIENTS: FLUIDS FLOWING ACROSS BANKS OF TUBES; FORCED CONVECTION, SENSIBLE HEAT 7.28
7.21 MEAN TEMPERATURE DIFFERENCE FOR HEAT EXCHANGERS 7.31
7.22 OVERALL HEAT-TRANSFER COEFFICIENT FOR SHELL-AND-TUBE HEAT EXCHANGER 7.35
7.23 OUTLET TEMPERATURES FOR COUNTERCURRENT HEAT EXCHANGER 7.38
7.24 OUTLET TEMPERATURES FOR 1-2 MULTIPASS HEAT EXCHANGER 7.40
7.25 CONDENSATION FOR VERTICAL TUBES 7.41
7.26 CONDENSATION INSIDE HORIZONTAL TUBES 7.45
7.27 CONDENSATION OUTSIDE HORIZONTAL TUBES 7.49
7.28 CONDENSATION IN THE PRESENCE OF NONCONDENSABLES
7.53

[^10]7.29 MAXIMUM VAPOR VELOCITY FOR CONDENSERS WITH UPFLOW VAPOR 7.56
7.30 NUCLEATE-BOILING HEAT TRANSFER 7.57
7.31 MINIMUM TEMPERATURE DIFFERENCE TO ACHIEVE NUCLEATE BOILING 7.58
7.32 MAXIMUM HEAT FLUX FOR KETTLE-TYPE REBOILER 7.60

### 7.33 DOUBLE-PIPE HEAT EXCHANGERS WITH BARE TUBES 7.61

7.34 DOUBLE-PIPE HEAT EXCHANGERS WITH LONGITUDINALLY FINNED TUBES 7.62
7.35 HEAT TRANSFER FOR LOW-FIN TUBES 7.64
7.36 HEAT TRANSFER FOR BANKS OFFINNED TUBES 7.67
7.37 AIR-COOLED HEATEXCHANGERS 7.70
7.38 PRESSURE DROP FOR FLOW INSIDETUBES: SINGLE-PHASE FLUIDS 7.737.39 PRESSURE DROP FOR FLOW INSIDETUBES: TWO-PHASE FLUIDS 7.76
7.40 PRESSURE DROP FOR FLOW ACROSSTUBE BANKS: SINGLE-PHASEFLUIDS 7.79
7.41 PRESSURE DROP FOR FLOW ACROSSTUBE BUNDLES: TWO-PHASEFLOW 7.84
7.42 CONDENSER-SUBCOOLER TESTDATA 7.87
7.43 HEAT EXCHANGER
NETWORKING 7.91
REFERENCES 7.94

### 7.1 SPECIFYING RADIATION SHIELDING

A furnace is to be located next to a dense complex of cryogenic propane piping. To protect the cold equipment from excessive heat loads, reflective aluminum radiation shielding sheets are to be placed between the piping and the $400^{\circ} \mathrm{F}(477 \mathrm{~K})$ furnace wall. The space between the furnace wall and the cold surface is $2 \mathrm{ft}(0.61 \mathrm{~m})$. The facing surfaces of the furnace and the piping array are each $25 \times 40 \mathrm{ft}$ $(7.6 \times 12.2 \mathrm{~m})$. With the ice-covered surface of the cold equipment at an average temperature of $35^{\circ} \mathrm{F}$ ( 275 K ), how many $25 \times 40 \mathrm{ft}$ aluminum sheets must be installed between the two faces to keep the last sheet at or below $90^{\circ} \mathrm{F}(305 \mathrm{~K})$ ? Emittances of the furnace wall and cryogenic equipment are 0.90 and 0.65 , respectively; that of the aluminum shields is 0.1 .

## Calculation Procedure

1. Analyze the arrangement to assess the type(s) of heat transfer involved. The distance separating the hot and cold surfaces is small compared with the size of the surfaces. The approximation can thus be made that the furnace wall, the dense network of cryogenic piping, and the radiation shields are all infinitely extended parallel planes. This is a conservative assumption, since the effect of proximity to an edge is to introduce a source of moderate temperature, thus allowing the hot wall to cool off. Convection is omitted with the same justification. So the problem can be treated as pure radiation.

Radiant heat transfer between two parallel, infinite plates is given by

$$
\frac{q_{1-2}}{A}=\frac{\sigma\left(T_{1}^{4}-T_{2}^{4}\right)}{\left(1 / \epsilon_{1}\right)+\left(1 / \epsilon_{2}\right)-1}
$$

where $q_{1-2} / A$ is the heat flux between hotter surface 1 and colder surface $2, \sigma$ is the Stefan-Boltzmann constant, $0.1713 \times 10^{-8} \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{R}^{4}\right), T_{1}$ and $T_{2}$ are absolute temperatures of the hotter and colder surfaces, and $\epsilon_{1}$ and $\epsilon_{2}$ are the emittances of the two surfaces. Emittance is the ratio of radiant energy emitted by a given real surface to the radiant energy that would be emitted by a theoretical, perfectly radiating black surface. Emittances of several materials are given in Table 7.1. The variations indicated between values of $\epsilon$ for apparently similar surfaces are not unusual, and they indicate the advisability of using measured data whenever available.

TABLE 7.1 Emittances of Some Real Surfaces

| Material | Theoretical emittance $\epsilon_{t h}$ |
| :--- | :---: |
| Aluminum foil, bright, foil, at $700^{\circ} \mathrm{F}(644 \mathrm{~K})$ | 0.04 |
| Aluminum alloy $6061 \mathrm{~T} 6 \mathrm{H}_{2} \mathrm{CrO} 4$ anodized, $300^{\circ} \mathrm{F}(422 \mathrm{~K})$ | 0.17 |
| Aluminum alloy $6061 \mathrm{~T} 6, \mathrm{H}_{2} \mathrm{SO}_{4}$ anodized, $300^{\circ} \mathrm{F}(422 \mathrm{~K})$ | 0.80 |
| Cast iron, polished, at $392^{\circ} \mathrm{F}(473 \mathrm{~K})$ | 0.21 |
| Cast iron, oxidized, at $390^{\circ} \mathrm{F}(472 \mathrm{~K})$ | 0.64 |
| Black lacquer on iron at $76^{\circ} \mathrm{F}(298 \mathrm{~K})$ | 0.88 |
| White enamel on iron at $66^{\circ} \mathrm{F}(292 \mathrm{~K})$ | 0.90 |
| Lampblack on iron at $68^{\circ} \mathrm{F}(293 \mathrm{~K})$ | 0.97 |
| Firebrick at $1832^{\circ} \mathrm{F}(1273 \mathrm{~K})$ | 0.75 |
| Roofing paper at $69^{\circ} \mathrm{F}(294 \mathrm{~K})$ | 0.91 |

Source: Chapman [7].

Note that the numerator expresses a potential and the denominator a resistance. If a series of $n$ radiation shields with emittance $\epsilon_{s}$ is interspersed between the two infinite parallel plates, the equivalent resistance can be shown to be

$$
\left[\frac{1}{\epsilon_{1}}+\frac{1}{\epsilon_{2}}-1\right]+n\left[\frac{2}{\epsilon_{s}}-1\right]
$$

2. Set up an equation for heat flux from the furnace to the cold equipment, expressed in terms of $n$. Substituting into the equation in step 1,

$$
\frac{q}{A}=\frac{\left(0.1713 \times 10^{-8}\right)\left[(400+460)^{4}-(35+460)^{4}\right]}{[(1 / 0.9)+(1 / 0.65)-1]+n[(2 / 0.1)-1]}=834.19 /(1.65+19 n)
$$

3. Set up an equation for heat flux from the furnace to the last shield, expressed in terms of $\boldsymbol{n}$. In this case, the heat flows through $n-1$ shields en route to the last shield, whose temperature is to be kept at or below $90^{\circ} \mathrm{F}$ and whose emittance (like that of the other shields) is 0.1 . Substituting again into the equation in step 1 ,

$$
\begin{aligned}
\frac{q}{A} & =\frac{\left(0.1713 \times 10^{-8}\right)\left[(400+460)^{4}-(90+460)^{4}\right]}{[(1 / 0.9)+(1 / 0.1)-1]+(n-1)[(2 / 0.1)-1]} \\
& =\frac{780.27}{10.11+(n-1)(19)} \\
& =\frac{780.27}{(-8.89+19 n)}
\end{aligned}
$$

4. Solve for $n$. Since all the heat must pass through all shields, the expressions of steps 2 and 3 are equal. Setting them equal to each other and solving for $n$, it is found to be 8.499 . Rounding off, we specify 9 shields.
5. Check the answer by back-calculating the temperature of the last shield. Substituting 9 for $n$ in the equation in step 2 , the heat transferred is

$$
\begin{aligned}
\frac{q}{A} & =\frac{\left(0.1713 \times 10^{-8}\right)\left(860^{4}-495^{4}\right)}{[(1 / 0.9)+1 /(0.65)-1]+9[(2 / 0.1)-1]} \\
& =4.83 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)
\end{aligned}
$$

Next, let $T_{2}$ in the equation in step 3 , that is, $(90+460)$, become an unknown, while substituting 9 for $n$ and 4.83 for $q / A$. Thus, $4.83=\left(0.1713 \times 10^{8}\right)\left(860^{4}-T^{4}\right) /\{[(1 / 0.9)+(1 / 0.1)-1]+$ $[9-1][(2 / 0.1)-1]\}$. Solving for $T_{2}$, we find it to be $547.6^{\circ} \mathrm{R}$ (or $\left.87.6^{\circ} \mathrm{F}\right)$, thus satisfying the requirement of the problem.

### 7.2 RADIANT INTERCHANGE INSIDE A BLACK-SURFACED ENCLOSURE

A furnace firebox is $20 \mathrm{ft}(6.1 \mathrm{~m})$ long, $10 \mathrm{ft}(3.05 \mathrm{~m})$ wide, and $5 \mathrm{ft}(1.5 \mathrm{~m})$ high. Because of a rich fuel-air mixture, all surfaces have become coated with lampblack, so that they all act as black-body surfaces with virtually complete absorption and emittance of radiant energy; emittance $\epsilon$ is 0.97 . The furnace is overfired; i.e., its cold surface is the floor, composed of closely spaced tubes flowing water at $250^{\circ} \mathrm{F}(394 \mathrm{~K})$. When the furnace is operating, its roof is at $1150^{\circ} \mathrm{F}(894 \mathrm{~K})$, the sidewalls are at $920^{\circ} \mathrm{F}(766 \mathrm{~K})$, and the end walls at around $800^{\circ} \mathrm{F}(700 \mathrm{~K})$. A plant emergency suddenly shuts the furnace down. Determine the initial rate of heat transfer from each interior surface if the water in the tubes remains at $250^{\circ} \mathrm{F}$. Assume that the tube surface is at the water temperature.

## Calculation Procedure

1. Analyze the situation to determine the type(s) of heat transfer involved. The temperatures are relatively high and the problem does not involve material flow; it is safe to treat it as a radiation problem. In view of the high emittance, consider the entire enclosure black in a radiation sense. Since all surfaces are black, they absorb all radiation incident upon them, with no reflection. Therefore, the radiant-interchange factors depend only on the geometric relationships among the surfaces. A radiantinterchange factor is the proportionality constant that indicates the fraction of radiant-energy-transfer potential between two surfaces, as measured by Boltzmann's constant times the difference between the fourth powers of their absolute temperatures, that shows up as actual heat flux between them. Thus, $\mathcal{J}_{1-2}$ is the radiant interchange factor in the equation $q / A=\sigma \mathcal{J}_{1-2}\left(T_{1}^{4}-T_{2}^{4}\right)$, where $q / A$ is heat flux, $\sigma$ is Boltzmann's constant, and $T_{i}$ is the absolute temperature of surface $i$. In Example 7.1, $\mathcal{J}_{1-2}$ is given by $1 /\left\{\left[\left(1 / \epsilon_{1}\right)+\left(1 / \epsilon_{2}\right)-1\right]+n\left[\left(2 / \epsilon_{s}\right)-1\right]\right\}$.

In particular, for any two Lambertian surfaces (surfaces that emit or reflect with an intensity independent of angle, a condition approximately satisfied by most nonmetallic, tarnished, oxidized, or rough surfaces), the fraction $F_{1-2}$ of total energy from one of them, designated 1 , that is intercepted by the other, designated 2 , is given by

$$
F_{1-2}=\frac{1}{A_{1}} \int_{A_{1}} \int_{A_{2}}\left(\frac{\cos \theta_{1} \cos \theta_{2}}{\pi r_{1,2}^{2}}\right) d A_{2} d A_{1}
$$

where $A_{1}$ and $\mathrm{A}_{2}$ are the areas of the emitting and receiving surfaces, $r_{1,2}$ is the distance between the surfaces, and $\theta_{1}$ and $\theta_{2}$ are the angles between line $r_{1,2}$ and the normals to the two surfaces.

For black surfaces, the purely geometrically derived factor $F_{1-2}$ is an acceptable substitute for the radiant interchange factor, evaluation of which requires one to consider the emittances of all surfaces and is beyond the scope of this book. For instance, in Example 7.1 the expression for $\mathcal{J}_{1-2}$ reduces to unity if $\epsilon_{1}=\epsilon_{2}=\epsilon_{s}=1.0$, which is equal to the solution for $F_{1-2}$ for closely spaced parallel rectangles.
$F_{1-2}$ is called the "configuration factor," "the geometric factor," or "the shape factor." This has been integrated for many common configurations, two of which are plotted in Figs. 7.1 and 7.2. Other figures are presented in the literature, particularly Krieth [2], Chapman [7], and Siegel and Howell [9].

For configurations not presented specifically, geometric relationships exist whereby existing data can be combined to yield the required data. These relationships are called "shape-factor algebra" and are summarized as follows:


FIGURE 7.1 Configuration factors for two rectangular figures with a common edge, at right angles [7].


FIGURE 7.2 Configuration factors for two parallel rectangular figures [7].

1. Reciprocity: For two areas 1 and 2 ,

$$
A_{1} F_{1-2}=A_{2} F_{2-1}
$$

2. Addition: If a surface $i$ is subdivided into any number $n$ of subsurfaces, $i 1, i 2, \ldots$, in,

$$
A_{i} F_{i-j}=\sum_{n} A_{i n} F_{i n}-j
$$

3. Enclosure: If a surface $i$ is completely enclosed by $n$ other surfaces, the sum of all configuration

## HEAT TRANSFER*

factors from $i$ to the other surfaces is 1 :

$$
\sum_{j=1}^{n} F_{i-j}=1.0
$$

The enclosure property also serves as a check to determine whether all the separately determined configuration factors are correct.


FIGURE 7.3 Sketch of furnace for Example 7.2.
2. Evaluate the configuration factors. The furnace can be sketched as in Fig. 7.3. Each of its six faces has a roman numeral and (for convenience later in the problem) the temperature of that face is shown. Since heat radiated from each face will impinge on every other face, there are $6(6-1)=30$ configuration factors to be determined. However, because of the reciprocity property and symmetry, fewer calculation steps will be needed.

1. $A_{I} F_{I-V I}$ : Refer to Fig. 7.1. Here, $D=10, L=20$, and $W=5$. Then $R_{1}=L / D=2.0$ and $R_{2}=$ $W / D=0.5$. From the graph, $F_{\mathrm{I}-\mathrm{VI}}=0.08$. Now, $A_{\mathrm{I}}=10 \times 20=200 \mathrm{ft}^{2}$, so $A_{\mathrm{I}} F_{\mathrm{I}-\mathrm{VI}}=16 \mathrm{ft}^{2}$. By reciprocity, $A_{\mathrm{VI}} F_{\mathrm{VI}-\mathrm{I}}=16 \mathrm{ft}^{2}$ also. And by symmetry, $F_{\mathrm{I}-\mathrm{VI}}=F_{\mathrm{I}-\mathrm{IV}}$, so $A_{\mathrm{I}} F_{\mathrm{I}-\mathrm{IV}}=A_{\mathrm{IV}} F_{\mathrm{IV}-\mathrm{I}}=$ $16 \mathrm{ft}^{2}$ as well.
2. $A_{I I} F_{I I-I I I}$ : See Fig. 7.2. Here, $D=10, L=20$, and $W=5$. Then $R_{1}=2.0$ and $R_{2}=0.5$. From the graph, $F_{\text {II-III }}=F_{\text {III-II }}=0.167$. Now, $A_{\text {II }}=100 \mathrm{ft}^{2}$, so $A_{\text {II }} F_{\text {II-III }}=16.7 \mathrm{ft}^{2}=A_{\text {III }} F_{\text {III-II }}$
3. $A_{I V} F_{I V-V}: D=10, L=5, \quad$ and $\quad W=20 . R_{1}=0.5, R_{2}=0.25, \quad$ and $\quad F_{\mathrm{IV}-\mathrm{V}}=0.31 . A_{\mathrm{IV}}=$ $50 \mathrm{ft}^{2}$, so $A_{\mathrm{IV}} F_{\mathrm{IV}-\mathrm{V}}=15.5 \mathrm{ft}^{2}=A_{\mathrm{V}} F_{\mathrm{V}-\mathrm{IV}}=A_{\mathrm{VI}} F_{\mathrm{VI}-\mathrm{V}}=A_{\mathrm{V}} F_{\mathrm{V}-\mathrm{VI}}$.
4. $A_{I} F_{I-I I I}: D=20, L=10$, and $W=5 . R_{1}=L / D=0.50, R_{2}=W / D=0.25$, and $F_{\text {I-III }}=$ 0.168. $A_{\mathrm{I}}=200 \mathrm{ft}^{2}$, so $A_{\mathrm{I}} F_{\mathrm{I}-\mathrm{III}}=33.60 \mathrm{ft}^{2}=A_{\mathrm{I}} F_{\mathrm{I}-\mathrm{II}}=A_{\mathrm{III}} F_{\mathrm{III}-\mathrm{I}}=A_{\mathrm{II}} F_{\mathrm{II}-\mathrm{I}}$.
5. $A_{I} F_{I-V}: D=5, L=20$, and $W=10 . R_{1}=4.0, R_{2}=2.0$, and $F_{\mathrm{I}-\mathrm{V}}=0.508 . A_{\mathrm{I}}=200 \mathrm{ft}^{2}$, so $A_{\mathrm{I}} F_{\mathrm{I}-\mathrm{V}}=116 \mathrm{ft}^{2}=A_{\mathrm{V}} F_{\mathrm{V}-\mathrm{I}}$.
6. $A_{I I} F_{I I-I V}: D=5, L=20, W=10 . R_{1}=4.0, R_{2}=2.0$, and $F_{\text {II-IV }}=0.085 . A_{\text {II }}=100 \mathrm{ft}^{2}$, so $A_{\mathrm{II}} F_{\mathrm{II}-\mathrm{IV}}=8.5 \quad \mathrm{ft}^{2}=A_{\mathrm{IV}} F_{\mathrm{IV}-\mathrm{II}}=A_{\mathrm{II}} F_{\mathrm{II}-\mathrm{VI}}=A_{\mathrm{VI}} F_{\mathrm{VI}-\mathrm{II}} . \quad$ And $\quad$ by $\quad$ symmetry,$\quad A_{\mathrm{III}} F_{\mathrm{III}-\mathrm{IV}}=$ $A_{\mathrm{IV}} F_{\mathrm{IV}-\mathrm{III}}=A_{\mathrm{III}} F_{\mathrm{III}-\mathrm{VI}}=A_{\mathrm{VI}} F_{\mathrm{VI}-\mathrm{III}}=8.5 \mathrm{ft}^{2}$.
7. $A_{I I} F_{I I-V}: D=20, L=5$, and $W=10 . R_{1}=0.25, R_{2}=0.5$, and $F_{I I-\mathrm{V}}=0.33 . A_{\mathrm{II}}=100 \mathrm{ft}^{2}$, so $A_{\mathrm{II}} F_{\mathrm{II}-\mathrm{V}}=33 \mathrm{ft}^{2}=A_{\mathrm{V}} F_{\mathrm{V}-\mathrm{II}}=A_{\mathrm{III}} F_{\mathrm{III}-\mathrm{V}}=A_{\mathrm{V}} F_{\mathrm{V}-\mathrm{III}}$.
8. $A_{I V} F_{I V-V I}: D=20, L=10$, and $W=5 . R_{1}=0.5, R_{2}=0.25, F_{\mathrm{IV}-\mathrm{VI}}=0.038$. $A_{\mathrm{IV}}=50 \mathrm{ft}^{2}$, so $A_{\mathrm{IV}} F_{\mathrm{IV}-\mathrm{VI}}=1.90 \mathrm{ft}^{2}=A_{\mathrm{VI}} F_{\mathrm{VI}-\mathrm{IV}}$.
Throughout, $F_{i, j}$ is found by dividing $A_{i} F_{i, j}$ by $A_{i}$, if $F_{i, j}$ is not already explicit.
9. Check the accuracy of all configuration factors. Use the enclosure principle described in step 1. For surface I, $F_{\mathrm{I}-\mathrm{II}}+F_{\mathrm{I}-\mathrm{III}}+F_{\mathrm{I}-\mathrm{IV}}+F_{\mathrm{I}-\mathrm{V}}+F_{\mathrm{I}-\mathrm{VI}}=0.168+0.168+0.08+0.508+0.08=$ 1.004, which is close enough to 1.0 .

For surface II, the sum of the configuration factors is $\left(A_{\mathrm{II}} F_{\mathrm{II}-\mathrm{I}} / A_{\mathrm{II}}\right)+F_{\mathrm{II}-\mathrm{III}}+F_{\mathrm{II}-\mathrm{IV}}+F_{\mathrm{II}-\mathrm{V}}+$ $F_{\text {II-VI }}=33.6 / 100+0.167+0.085+0.33+0.085=1.003$. Close enough. The sums of the configuration factors for the other four surfaces are calculated similarly.
4. Calculate heat transfer from each surface. Let $q_{i}$ equal the heat emitted by surface $i$, and $q_{i, j}$ the heat emitted by surface $i$ that impinges on surface $j$. Then, $q_{i}=\sum_{j} q_{i, j}$. For surface I,

$$
\begin{aligned}
q_{\mathrm{I}}= & q_{\mathrm{I}-\mathrm{II}}+q_{\mathrm{I}-\mathrm{III}}+q_{\mathrm{I}-\mathrm{IV}}+q_{\mathrm{I}-\mathrm{V}}+q_{\mathrm{I}-\mathrm{VI}}=\sigma A_{\mathrm{I}}\left[F_{\mathrm{I}-\mathrm{II}}\left(T_{\mathrm{I}}^{4}-T_{\mathrm{II}}^{4}\right)+F_{\mathrm{I}-\mathrm{III}}\left(T_{\mathrm{I}}^{4}-T_{\mathrm{III}}^{4}\right)\right. \\
& \left.+F_{\mathrm{I}-\mathrm{IV}}\left(T_{\mathrm{I}}^{4}-T_{\mathrm{IV}}^{4}\right)+F_{\mathrm{I}-\mathrm{V}}\left(T_{\mathrm{I}}^{4}-T_{\mathrm{V}}^{4}\right)+F_{\mathrm{I}-\mathrm{VI}}\left(T_{\mathrm{I}}^{4}-T_{\mathrm{VI}}^{4}\right)\right]
\end{aligned}
$$

This can be simplified by considering symmetry; thus,

$$
q_{\mathrm{I}}=\sigma A_{\mathrm{I}}\left[2 F_{\mathrm{I}-\mathrm{II}}\left(T_{\mathrm{I}}^{4}-T_{\mathrm{II}}^{4}\right)+2 F_{\mathrm{I}-\mathrm{IV}}\left(T_{\mathrm{I}}^{4}-T_{\mathrm{IV}}^{4}\right)+F_{\mathrm{I}-\mathrm{V}}\left(T_{\mathrm{I}}^{4}-T_{\mathrm{V}}^{4}\right)\right]
$$

where $\sigma$ is the Boltzmann constant and $T$ is absolute temperature. Thus,

$$
\begin{aligned}
q_{\mathrm{I}}= & \left(0.1713 \times 10^{-8}\right)(200)\left[2(0.168)\left(1610^{4}-1380^{4}\right)+2(0.08)\left(1610^{4}-1260^{4}\right)\right. \\
& \left.+0.508\left(1610^{4}-710^{4}\right)\right]=171.1 \times 10^{4} \mathrm{Btu} / \mathrm{h}(496 \mathrm{~kW})
\end{aligned}
$$

Similarly, for the other five surfaces: $q_{\text {II }}=4.489 \times 10^{4} \mathrm{Btu} / \mathrm{h}(13 \mathrm{~kW})=q_{\mathrm{III}} ; q_{\mathrm{IV}}=-8.711 \times 10^{4}$ $\mathrm{Btu} / \mathrm{h}(-25.3 \mathrm{~kW})=q_{\mathrm{VI}}$; and $q_{\mathrm{V}}=-162.7 \times 10^{4} \mathrm{Btu} / \mathrm{h}(-472 \mathrm{~kW})$.
5. Check the results. Since the system as a whole neither gains nor loses heat, the sum of the heat transferred should algebraically be zero. Now, $171.1+2(4.489)+2(-8.711)+(-162.7)=0$, so the results do check.

Related Calculations. If the six surfaces are not black but gray (in the radiation sense), it is nominally necessary to set up and solve six simultaneous equations in six unknowns. In practice, however, the network can be simplified by combining two or more surfaces (the two smaller end walls, for instance) into one node. Once this is done and the configuration factors are calculated, the next step is to construct a radiosity network (since each surface is assumed diffuse, all energy leaving it is equally distributed directionally and can therefore be taken as the radiosity of the surface rather than its emissive power). Then, using standard mathematical network-solution techniques, create and solve an equivalent network with direct connections between nodes representing the surfaces. For details, see Oppenheim [8].

### 7.3 EFFECT OF SOLAR HEAT ON A STORAGE TANK

A flat-topped, nitrogen-blanketed atmospheric-pressure tank in a plant at Texas City, Texas, has a diameter of 30 ft and a height of $20 \mathrm{ft}(9.1 \mathrm{~m}$ diameter and 6.1 m high $)$ and is half full of ethanol at $85^{\circ} \mathrm{F}(302 \mathrm{~K})$. As a first step in calculating nitrogen flow rates into and out of the tank during operations, calculate the solar heating of the tank and the tank skin temperature in the ullage space at a maximum-temperature condition. The tank has a coating of white zinc oxide paint, whose solar absorptance is 0.18 . The latitude of Texas City is about $\mathrm{N} 29^{\circ} 20^{\prime}$. For the maximum-temperature condition, select noon on June 20, the summer solstice, when the solar declination is $23.5^{\circ}$. Assume that the solar constant (the solar flux on a surface perpendicular to the solar vector) is $343 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)$ ( $1080 \mathrm{~W} / \mathrm{m}^{2}$ ), the air temperature is $90^{\circ} \mathrm{F}(305 \mathrm{~K})$, and the effective sky temperature is $5^{\circ} \mathrm{F}(258 \mathrm{~K})$. Also assume that surrounding structural and other elements (such as hot pipes) are at $105^{\circ} \mathrm{F}$ ( 314 K ) and have a radiant interchange factor of 0.2 with the tank and that the effective film coefficients for convection heat transfer between (1) the air and the outside of the tank and (2) the inside of the tank and the contained material are 0.72 and $0.75 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)$ [4.08 and $\left.4.25 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$, respectively.

## Calculation Procedure

1. Calculate the solar-heat input to the tank. Since the sun, although an extremely powerful emitter, subtends a very small solid angle, it has an only minute radiant interchange factor with objects on earth. The earth's orbital distance from the sun is nearly constant throughout the year. Therefore, it is a valid simplification to consider solar radiation simply as a heat source independent of the radiation environment and governed solely by the solar absorptance of each surface and the angular relationship of the surface to the solar vector.

TABLE 7.2 Representative Values of Solar Constant and Sky Temperature

| Conditions for total normal incident solar radiation | Solar constant |  | Effective sky temp., ${ }^{\circ} \mathrm{F}$ | $\begin{gathered} \text { Effective sky } \\ \text { temp., K } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: |
|  | Btu/(h)(ft ${ }^{2}$ ) | $\mathrm{kJ} /(\mathrm{s})\left(\mathrm{m}^{2}\right)$ |  |  |
| Southwestern United States, June, 6:00 A.M., extreme | 252.3 | 0.797 | -30 to - 22 | 239 to 243 |
| Southwestern United States, June, 12:00 m., extreme | 385.1 | 1.216 | -30 to - 22 | 239 to 243 |
| Southwestern United States, December, 9:00 A.M., extreme | 307.7 | 0.972 | -30 to -22 | 239 to 243 |
| Southwestern United States, December, 12:00 м., extreme | 396.2 | 1.251 | -30 to -22 | 239 to 243 |
| NASA recommended high design value, $12: 00 \mathrm{~m}$. | 363.0 | 1.146 | - | - |
| NASA recommended low design value, $12: 00 \mathrm{~m}$. | 75.0 | 0.237 | - | - |
| Southern United States, maximum for extremely bad weather | 111.0 | 0.350 | - | - |
| Southern United States desert, maximum for extremely bad weather | 177.0 | 0.559 | - | - |

Source: Daniels [13].

The magnitude of the solar heating is indicated by the so-called solar constant. In space, at the radius of the earth's orbit, the solar constant is about $443 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left(1396 \mathrm{~W} / \mathrm{m}^{2}\right)$. However, solar radiation is attenuated by passage through the atmosphere; it is also reflected diffusely by the atmosphere, which itself varies greatly in composition. Table 7.2 provides representative values of the solar constant for use at ground level, as well as of the apparent daytime temperature of the sky for radiation purposes.

Since the solar constant $G_{n}$ is a measure of total solar radiation perpendicular to the solar vector, it is necessary to also factor in the actual angle which the solar vector makes with the surface(s) being heated. This takes into account the geographic location, the time of year, the time of day, and the geometry of the surface and gives a corrected solar constant $G_{i}$.

For a horizontal surface, such as the tank roof, $G_{i}=G_{n} \cos Z$, where $Z=\cos ^{-1}\left(\sin \phi \sin \delta_{s}+\right.$ $\left.\cos \phi \cos \delta_{s} \cos h\right), \phi$ is the latitude, $\delta_{s}$ is the solar declination, and $h$ the hour angle, measured from $0^{\circ}$ at high noon. In the present case, $Z=\cos ^{-1}\left(\sin 29^{\circ} 20^{\prime} \sin 23.5^{\circ}+\cos 29^{\circ} 20^{\prime} \cos 23.5^{\circ} \cos 0^{\circ}\right)=$ $\cos ^{-1} 0.995=5^{\circ} 50^{\prime}$, and $G_{i}=343(0.995)=341.2 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)$.

For a surface that is tilted $\psi^{\circ}$ from horizontal and whose surface normal has an azimuth of $\alpha^{\circ}$ from due south (westward being positive), $G_{i}=G_{n}(\cos |Z-\psi|-\sin Z \sin \psi+\sin Z \sin \psi \cos |A-\alpha|)$, where $A=\sin ^{-1}\left\{\cos \delta_{s} \sin h /[\cos (90-Z)]\right\}$. In the present case, $A=0^{\circ}$ because $\sin h=0$.

Because the solar effect is distributed around the vertical surface of the tank to a varying degree (the effect being strongest from the south, since the sun is in the south), select wall segments $30^{\circ}$ apart and calculate each separately. In the $G_{i}$ equation, $\alpha$ will thus assume values ranging from $-90^{\circ}$ (facing due east) to $+90^{\circ}$ (due west); the northern half of the tank will be in shadow. Because the wall is vertical, $\psi=90^{\circ}$.

It is also necessary to take sky radiation into account, that is, sunlight scattered by the atmosphere and reflected diffusely and which reaches all surfaces of the tank, including those not hit by direct sunlight because they are in shadow. This diffuse radiation $G_{s}$ varies greatly but is generally small, between about $2.2 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left(6.93 \mathrm{~W} / \mathrm{m}^{2}\right)$ on a clear day and $44.2 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left(139 \mathrm{~W} / \mathrm{m}^{2}\right)$ on a cloudy day. For the day as described, assume that $G_{s}$ is $25 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)$. This value must be added to all surfaces, including those in shadow.

Finally, take the solar absorptance of the paint $\alpha_{s}$ into account. Thus, the solar heat absorbed $q_{s}$ equals $\alpha_{s}\left(G_{i}+G_{s}\right)$. The calculations can be summarized as follows:

|  | Roof | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Segment (azimuth) |  | -90 | -60 | -30 | 0 | 30 | 60 | 90 |
| $G_{i}$ | 341.2 | 0 | 17.4 | 30.2 | 34.9 | 30.2 | 17.4 | 0 |
| $G_{i}+G_{s}$ | 366.2 | 25 | 42.4 | 55.2 | 59.9 | 55.2 | 42.4 | 25 |
| $q_{s} / A, \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)$ | 65.92 | 4.50 | 7.63 | 9.94 | 10.8 | 9.94 | 7.63 | 4.50 |
| $q_{s} / A, \mathrm{~W} / \mathrm{m}^{2}$ | 208 | 14.2 | 24.0 | 31.3 | 34.0 | 31.3 | 24.0 | 14.2 |

Since this calculation procedure treats the tank as if it had 12 flat sides, the calculated $\mathrm{G}_{i}$ for segments 1 and 7 is zero. Of course, $G_{i}$ is also zero for the shaded half of the tank [and $q_{s} / A=$ 4.5 Btu/(h)(ft $\left.\left.{ }^{2}\right)\right]$.
2. Calculate the equilibrium temperature of each of the tank surfaces. It can be shown that conduction between the segments is negligible. Then, at equilibrium, each segment must satisfy the heat-balance equation, that is, solar-heat absorption + net heat input by radiation + heat transferred in by outside convection + heat transferred in by inside convection $=0$, or

$$
q_{s} / A+\sigma \mathcal{J}_{o}\left(T_{o}^{4}-T_{w}^{4}\right)+\sigma \mathcal{J}_{R}\left(T_{R}^{4}--T_{w}^{4}\right)+h_{a}\left(T_{a}-T_{w}\right)+h_{i}\left(T_{i}-T_{w}\right)=0
$$

where $T_{w}$ is the tank-wall temperature; subscript $o$ refers to surrounding structural and other elements having a radiant interchange factor $\mathcal{J}_{o}$ with the segments; subscript $R$ refers to the atmosphere, having an equivalent radiation temperature $T_{R}$ and a radiant interchange factor $\mathcal{J}_{R}$; subscript $a$ refers to the air surrounding the tank, and subscript $i$ refers to the gas inside the tank. The heat balance for the roof is solved as follows (similar calculations can be made for each segment of the tank wall):

Now, $q_{s} / A=65.92 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right), T_{o}=105^{\circ} \mathrm{F}=565^{\circ} \mathrm{R}$ (due to hot pipes and other equipment in the vicinity), $\mathcal{J}_{o}=0.2, T_{R}=5^{\circ} \mathrm{F}=465^{\circ} \mathrm{R}$, a good assumption for $\mathcal{J}_{R}$ is $0.75, h_{a}=0.72$, and $h_{i}=0.75$. Therefore,

$$
\begin{aligned}
& 65.92+\left(0.1713 \times 10^{-8}\right)(0.2)\left(565^{4}-T_{w}^{4}\right)+\left(0.1713 \times 10^{-8}\right)(0.75)\left(465^{4}-T_{w}^{4}\right) \\
& +0.72\left(90+460-T_{w}\right)+0.75\left(85+460-T_{w}\right)=0 \\
& 65.92+34.91-\left(3.426 \times 10^{-10}+12.848 \times 10^{-10}\right) T_{w}^{4}+60.07+396 \\
& -(0.72+0.75) T_{w}+408=0 \\
& 1.6274 \times 10^{-9} T_{w}^{4}+1.47 T_{w}=965
\end{aligned}
$$

This is solved by trial and error, to yield $T_{w}=553^{\circ} \mathrm{R}=93^{\circ} \mathrm{F}(307 \mathrm{~K})$. Note that if the paint had been black, $\alpha_{s}$ might have been 0.97 instead of 0.18 . In that case, the temperature would have been about $200^{\circ} \mathrm{F}(366 \mathrm{~K})$.

The same procedure is then applied to each of the other tank segments.

### 7.4 HEAT LOSS FROM AN UNINSULATED SURFACE TO AIR

A steam line with a diameter of $3.5 \mathrm{in}(0.089 \mathrm{~m})$ and a length of $50 \mathrm{ft}(15.2 \mathrm{~m})$ transports steam at $320^{\circ} \mathrm{F}(433 \mathrm{~K})$. The carbon steel pipe [thermal conductivity of $25 \mathrm{Btu} /(\mathrm{h})(\mathrm{ft})\left({ }^{\circ} \mathrm{F}\right)$ or $142 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})$ ] is not insulated. Its emissivity is 0.8 . Calculate the heat loss for calm air and also for a wind velocity of $15 \mathrm{mi} / \mathrm{h}(24 \mathrm{~km} / \mathrm{h})$, if the air temperature is $68^{\circ} \mathrm{F}(293 \mathrm{~K})$.

## Calculation Procedure

1. Calculate the heat loss due to radiation. Because the coefficient for heat transfer from the outside of the pipe as a result of radiation and convection is much less than all other heat-transfer coefficients involved in this example, the surface temperature of the pipe can be assumed to be that of the steam. To calculate the heat loss, use the straightforward radiation formula

$$
\frac{Q}{A}=0.1713 \epsilon\left[\left(\frac{T_{s}}{100}\right)^{4}-\left(\frac{T_{s}}{100}\right)^{4}\right]
$$

where $Q$ is heat loss in British thermal units per hour, $A$ is heat-transfer area in square feet, $T_{s}$ is absolute temperature of the surface in degrees Rankine, $T_{a}$ is absolute temperature of the air, and $\epsilon$ is the emissivity of the pipe. (Note that in this version of the formula, the $10^{-8}$ portion of the Stefan-Boltzmann constant is built into the temperature terms.)

Thus,

$$
\frac{Q}{A}=0.1713(0.8)\left[\left(\frac{460+320}{100}\right)^{4}-\left(\frac{460+68}{100}\right)^{4}\right]=401 \mathrm{Btu} /(\mathrm{h})(\mathrm{ft})^{2}\left(1264 \mathrm{~W} / \mathrm{m}^{2}\right)
$$

2. Calculate the heat loss as a result of natural convection in calm air. Use the formula

$$
\frac{Q}{A}=\frac{0.27 \Delta T^{1.25}}{D^{0.25}}
$$

where $\Delta T=T_{s}-T_{a}$ in degrees Fahrenheit and $D$ is pipe diameter in feet. Thus,

$$
\frac{Q}{A}=\frac{0.27(320-68)^{1.25}}{(3.5 / 12)^{0.25}}=369 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left(1164 \mathrm{~W} / \mathrm{m}^{2}\right)
$$

3. Calculate the total heat loss for the pipe in calm air. Now, $Q=(Q / A) A$, and $A=\pi(3.5 / 12)$ $\times 50=45.81 \mathrm{ft}^{2}\left(4.26 \mathrm{~m}^{2}\right)$, so $Q=(401+369)(45.81)=35,270 \mathrm{Btu} / \mathrm{h}(10,330 \mathrm{~W})$.
4. Calculate the heat loss by convection for a wind velocity of $15 \mathrm{mi} / \mathrm{h}$. First, determine the mass velocity $G$ of the air: $G=\rho v$, where $\rho$ is density and $v$ is linear velocity. For air, $\rho=0.075$ $\mathrm{lb} / \mathrm{ft}^{3}\left(1.20 \mathrm{~kg} / \mathrm{m}^{3}\right)$. In this problem, $v=15 \mathrm{mi} / \mathrm{h}(5280 \mathrm{ft} / \mathrm{mi})=79,200 \mathrm{ft} / \mathrm{h}(24,140 \mathrm{~m} / \mathrm{h})$, so $G=$ $0.075(79,200)=5940 \mathrm{lb} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left[29,000 \mathrm{~kg} /(\mathrm{h})\left(\mathrm{m}^{2}\right)\right]$.

Next, determine the heat-transfer coefficient, using the formula $h=0.11 c G^{0.6} / D^{0.4}$, where $h$ is heat-transfer coefficient in British thermal units per hour per square foot per degree Fahrenheit, $c$ is specific heat in British thermal units per pound per degree Fahrenheit ( 0.24 for air), $G$ is mass velocity in pounds per hour per square foot, and $D$ is diameter in feet. Thus, $h=$ $0.11(0.24)(5940)^{0.6} /(3.5 / 12)^{0.4}=7.94 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[45.05 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.

Finally, use this coefficient to determine the heat loss due to convection via the formula $Q / A=$ $h\left(T_{s}-T_{a}\right)$. Thus, $Q / A=7.94(320-68)=2000.9 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left(6307 \mathrm{~W} / \mathrm{m}^{2}\right)$.
5. Calculate the total heat loss for the pipe when the wind velocity is $15 \mathrm{mi} / \mathrm{h}$. As in step 3, $Q=(401+2000.9)(45.81)=110,030 \mathrm{Btu} / \mathrm{h}(32,240 \mathrm{~W})$.

### 7.5 HEAT LOSS FROM AN INSULATED SURFACE TO AIR

Calculate the heat loss from the steam line in Example 7.4 if it has insulation 2 in $(0.050 \mathrm{~m})$ thick having a thermal conductivity of $0.05 \mathrm{Btu} /(\mathrm{h})(\mathrm{ft})\left({ }^{\circ} \mathrm{F}\right)[0.086 \mathrm{~W} /(\mathrm{m})(\mathrm{K})]$. The inside diameter of the pipe is 3 in $(0.076 \mathrm{~m})$, and the heat-transfer coefficient from the condensing steam to the pipe wall
is $1500 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[8500 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$. Assume that the wind velocity is $15 \mathrm{mi} / \mathrm{h}(24 \mathrm{~km} / \mathrm{h})$. The pipe is illustrated in Fig. 7.4.

## Calculation Procedure

1. Set out the appropriate overall heat-transfer equation. The heat loss can be calculated from the equation $Q=U A_{o}\left(T_{s}-T_{a}\right)$, where $Q$ is heat loss, $U$ is overall heat-transfer coefficient, $A_{o}$ is area of the outside surface of the insulation ( $=$


$$
\begin{aligned}
& r_{1}=3.0 / 2 \mathrm{in}=1.5 \mathrm{in}=0.125 \mathrm{ft}(0.0381 \mathrm{~m}) \\
& r_{2}=3.5 / 2 \mathrm{in}=1.75 \mathrm{in}=0.1458 \mathrm{ft}(0.0445 \mathrm{~m}) \\
& r_{3}=7.5 / 2 \mathrm{in}=3.75 \mathrm{in}=0.3125 \mathrm{ft}(0.0953 \mathrm{~m})
\end{aligned}
$$

FIGURE 7.4 Cross section of insulated pipe in Example 7.5. $2 \pi L r_{3}$; see Fig. 7.4), $T_{s}$ is steam temperature, and $T_{a}$ is air temperature. The overall heat-transfer coefficient can be calculated with the equation

$$
U=\frac{1}{\frac{r_{3}}{r_{1} h_{i}}+\frac{r_{3} \ln \left(r_{2} / r_{1}\right)}{k_{1}}+\frac{r_{3} \ln \left(r_{3} / r_{2}\right)}{k_{2}}+\frac{1}{h_{o}}}
$$

where the $r_{i}$ are as described in Fig. 7.4, $k_{1}$ is the thermal conductivity of the pipe, $k_{2}$ is that of the insulation, and $h_{o}$ and $h_{i}$ are the outside and inside heat-transfer coefficients, respectively.
2. Calculate $\boldsymbol{h}_{\boldsymbol{o}}$. The outside heat-transfer coefficient $h_{o}$ is the sum of the heat-transfer coefficient for convection to the wind $h_{c}$ and the transfer of heat as a result of radiation $h_{r}$. The latter is approximately $1.0 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)$ $\left[5.68 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$, and we will use that value here. From step 4 of Example 7.4, $h_{c}=7.94$. Thus, $h_{o}=h_{c}+h_{r}=7.94+1.0=8.94 \mathrm{Btu} /$ $(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[50.78 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.
3. Calculate $\boldsymbol{U}$. Substituting into the equation in step 1 ,

$$
\begin{aligned}
U & =\frac{1}{\frac{0.3125}{(0.125)(1500)}+\frac{0.3125 \ln (1.75 / 1.5)}{25}+\frac{0.3125 \ln (3.75 / 1.75)}{0.05}+\frac{1}{8.94}} \\
& =0.205 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[1.16 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]
\end{aligned}
$$

4. Calculate the heat loss. From step $1, Q=0.205(2 \pi)(50)(0.3125)(320-68)=5070 \mathrm{Btu} / \mathrm{h}$ (1486 W).

### 7.6 HEAT LOSS FROM A BURIED LINE

A steam line with a diameter of $12.75 \mathrm{in}(0.3239 \mathrm{~m})$ is buried with its center $6 \mathrm{ft}(1.829 \mathrm{~m})$ below the surface in soil having an average thermal conductivity of $0.3 \mathrm{Btu} /(\mathrm{h})(\mathrm{ft})\left({ }^{\circ} \mathrm{F}\right)[0.52 \mathrm{~W} /(\mathrm{m})(\mathrm{K})]$. Calculate the heat loss if the pipe is $200 \mathrm{ft}(60.96 \mathrm{~m})$ long, the steam is saturated at a temperature of $320^{\circ} \mathrm{F}(433 \mathrm{~K})$, and the surface of the soil is at a temperature of $40^{\circ} \mathrm{F}(277 \mathrm{~K})$.

## Calculation Procedure

1. Select the appropriate heat-transfer equation. The heat loss can be calculated from the equation

$$
Q=S k\left(T_{1}-T_{2}\right)
$$

where $Q$ is heat loss, $k$ is thermal conductivity of the soil, $T_{1}$ is surface temperature of the pipe, $T_{2}$ is surface temperature of the soil, and $S$ is a shape factor.
2. Determine the shape factor. Use the equation $S=2 \pi L / \cosh ^{-1}(2 z / D)$ (when $z$ is much less than $L$ ), where $L$ is length, $z$ is distance from ground surface to the center of the pipe, and $D$ is diameter. Now,

$$
\cosh ^{-1}(2 z / D)=\ln \left\{(2 z / D)+\left[(2 z / D)^{2}-1\right]^{1 / 2}\right\}
$$

For this example, $2 z / D=2(6) /(12.75 / 12)=11.294$, and $\cosh ^{-1}(2 z / D)=\ln \left[11.294+\left(11.294^{2}-\right.\right.$ $\left.1)^{1 / 2}\right]=3.116$. Thus, $S=2 \pi 200 / 3.116=403.29 \mathrm{ft}(122.92 \mathrm{~m})$.
3. Calculate the heat loss. Because the heat-transfer resistance through the soil is much greater than all other resistances to heat transfer, the surface of the pipe can be assumed to be at the temperature of the steam. Thus, $Q=403.29(0.3)(320-40)=33,876 \mathrm{Btu} / \mathrm{h}(9926 \mathrm{~W})$.

Related Calculations. This approach can be used for any geometry for which shape factors can be evaluated. Shape factors for many other geometries are presented in several of the references, including Krieth [2] and Holman [4].

### 7.7 CONDUCTION OF HEAT IN THE UNSTEADY STATE: COOLING TIME

A steel sphere with a radius of 0.5 in $(0.0127 \mathrm{~m})$ at a temperature of $500^{\circ} \mathrm{F}(533 \mathrm{~K})$ is suddenly immersed in a water bath. The water temperature is $68^{\circ} \mathrm{F}(293 \mathrm{~K})$ and the heat-transfer coefficient from the steel surface to the water is $200 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[1130 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$. Calculate the time required for the center of the sphere to reach a temperature of $250^{\circ} \mathrm{F}(394 \mathrm{~K})$. The thermal diffusivity $\alpha$ of the steel is $0.45 \mathrm{ft}^{2} / \mathrm{h}\left(0.0418 \mathrm{~m}^{2} / \mathrm{h}\right)$, and the thermal conductivity is $25 \mathrm{Btu} /(\mathrm{h})(\mathrm{ft})\left({ }^{\circ} \mathrm{F}\right)$ [43 W/(m)(K)].

## Procedure

1. Referring to the curves in Fig. 7.5, calculate $k /\left(h r_{o}\right)$

$$
\frac{k}{h r_{o}}=\frac{25}{200(0.5 / 12)}=3.0
$$

2. Calculate $\alpha \tau / r_{o}^{2}$

$$
\frac{\theta_{o}}{\theta_{i}}=\frac{250-68}{500-68}=0.421
$$

3. Determine $\boldsymbol{\alpha} \boldsymbol{\tau} / \boldsymbol{r}_{\boldsymbol{o}}^{\mathbf{2}}$. From Fig. 7.5, with $k /\left(h r_{o}\right)=3.0$ and $\theta_{o} / \theta_{i}=0.421, \alpha r / r_{o}^{2}=1.1$.


FIGURE 7.5 Center temperature for a sphere of radius $r_{o}$.
4. Calculate the time required. Now, $\alpha \tau / r_{o}^{2}=1.1$, so

$$
\begin{aligned}
\tau & =\frac{\left(1.1 r_{o}^{2}\right)}{\alpha} \\
& =\frac{1.1(0.5 / 12)^{2}}{0.45} \\
& =0.0042 \mathrm{~h} \\
& =15.3 \mathrm{~s}
\end{aligned}
$$

### 7.8 CONDUCTION OF HEAT IN THE UNSTEADY STATE: TEMPERATURE

For the sphere described in the preceding example, calculate the temperature at the center of the sphere after a period of 1 min .

## Calculation Procedure

1. Referring to the curves in Fig. 7.5, calculate $\boldsymbol{\alpha} \boldsymbol{\tau} / \boldsymbol{r}_{o}^{\mathbf{2}}$. Here, $\alpha \tau / r_{o}^{2}=0.45(1 / 60) /(0.5 / 12)^{2}=$ 4.32.
2. Determine $\boldsymbol{\theta}_{\boldsymbol{o}} / \boldsymbol{\theta}_{\boldsymbol{i}}$. From Fig. 7.5, with $\alpha \tau / r_{o}^{2}=4.32$ and $k /\left(h r_{o}\right)=3.0, \theta_{o} / \theta_{i}=0.02$.


FIGURE 7.6 Axis temperature for a cylinder of radius $r_{o}$.


FIGURE 7.7 Midplane temperature for a plate of thickness $2 L$.
3. Calculate the temperature after a period of 1 min. Now, $\theta_{o} / \theta_{i}=\left(T-T_{\infty}\right) /\left(T_{i}-T_{\infty}\right)=0.02$, SO

$$
\begin{aligned}
T & =T_{\infty}+0.02\left(T_{i}-T_{\infty}\right) \\
& =68+0.02(500-68) \\
& =76.6^{\circ} \mathrm{F}(298 \mathrm{~K})
\end{aligned}
$$

Related Calculations. The procedure outlined in these two problems can also be used for geometries other than spheres. Figure 7.6 can be used for cylinders, and Fig. 7.7 can be used for slabs.

### 7.9 CONDUCTION OF HEAT IN THE UNSTEADY STATE: TEMPERATURE DISTRIBUTION

Calculate the temperature distribution in a steel cylinder 1 min after the surrounding temperature is suddenly changed. Conditions are as follows:
$\mathrm{D}_{o}=$ outside diameter $=2$ in $(0.05 \mathrm{~m})$
$k=$ thermal conductivity $=25 \mathrm{Btu} /(\mathrm{h})(\mathrm{ft})\left({ }^{\circ} \mathrm{F}\right)[43 \mathrm{~W} /(\mathrm{m})(\mathrm{K})]$
$\alpha=$ thermal diffusivity $=0.45 \mathrm{ft}^{2} / \mathrm{h}\left(0.0418 \mathrm{~m}^{2} / \mathrm{h}\right)$
$h=$ heat-transfer coefficient $=300 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[1700 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$
$T_{1}=$ initial cylinder temperature $=68^{\circ} \mathrm{F}(293 \mathrm{~K})$
$T_{\infty}=$ surrounding temperature $=1000^{\circ} \mathrm{F}(811 \mathrm{~K})$

## Calculation Procedure

1. With regard to the curves in Figs. 7.6 and 7.9 , calculate $k /\left(h r_{o}\right)$. Now, $k /\left(h r_{o}\right)=$ $25 / 300(1 / 12)=1.0$.
2. Calculate $\alpha \tau / \boldsymbol{r}_{\boldsymbol{o}}^{\mathbf{2}}$. Now, $\alpha \tau / r_{o}^{2}=0.45(1 / 60) /(1 / 12)^{2}=1.08$.
3. Determine $\boldsymbol{\theta}_{\boldsymbol{o}} / \boldsymbol{\theta}_{\boldsymbol{i}}$. From Fig. 7.6, for $k /\left(h r_{o}\right)=1.0$ and $\alpha \tau / r_{o}^{2}=1.08, \theta_{o} / \theta_{i}=0.20$.
4. Determine $\boldsymbol{\theta}_{\boldsymbol{o}}$. $\quad$ Since $\theta_{o} / \theta_{i}=0.2=\left(T-T_{\infty}\right) /\left(T_{i}-T_{\infty}\right), \theta_{o}=0.2(68-1000)=-186.4^{\circ} \mathrm{F}$.
5. Determine $\boldsymbol{\theta}_{\boldsymbol{o}} / \boldsymbol{\theta}_{\boldsymbol{i}}$ as a function of radius. From Fig. 7.9, for $k /\left(h r_{o}\right)=1.0$, the following parameters are obtained and the following values of $\theta$ calculated:

| $r / r_{o}$ | $\theta / \theta_{o}$ | $\theta=\left(\theta / \theta_{o}\right)(-186.4)$ |
| :--- | :--- | :---: |
| 0 | 1.0 | $-186.4^{\circ} \mathrm{F}$ |
| 0.2 | 0.98 | -182.7 |
| 0.4 | 0.93 | -173.4 |
| 0.6 | 0.86 | -160.3 |
| 0.8 | 0.75 | -139.8 |
| 1.0 | 0.64 | -119.3 |


$r_{0}=$ outside radius
$r=$ radius
$k=$ thermal conductivity
$h=$ heat-transfer coefficient
$\theta=T-T_{\infty}=$ temperature at r minus surrounding temperature
$\theta_{0}=T_{i}-T_{\infty}=$ center temperature minus surrounding temperature
FIGURE 7.8 Temperature as a function of center temperature for a sphere.
6. Determine temperature as a function of radius. Since $T=T_{\infty}+\theta=1000+\theta$, the following temperatures are found:

| $r / r_{o}$ | $T,{ }^{\circ} \mathrm{F}$ | $T, \mathrm{~K}$ |
| :--- | :---: | :---: |
| 0 | 813.6 | 707.2 |
| 0.2 | 817.3 | 709.3 |
| 0.4 | 826.6 | 714.4 |
| 0.6 | 839.7 | 721.7 |
| 0.8 | 860.2 | 733.1 |
| 1.0 | 880.7 | 744.5 |

Related Calculations. The procedure outlined here can also be used for solids with other geometries. Figures 7.5 and 7.8 can be used for spheres, and Figs. 7.7 and 7.10 with slabs.

### 7.10 CONDUCTION OF HEAT FROM A BELT COOLER

A stainless steel belt cooler with a width of $3 \mathrm{ft}(0.914 \mathrm{~m})$, a thickness of $1 / 8$ in $(3.175 \mathrm{~mm})$, and a length of $100 \mathrm{ft}(30.48 \mathrm{~m})$ is to be used to cool $10,000 \mathrm{lb} / \mathrm{h}(4535.9 \mathrm{~kg} / \mathrm{h})$ of material with the physical properties listed below. The bottom of the belt is sprayed with water at $86^{\circ} \mathrm{F}(303 \mathrm{~K})$, and

$r=$ rodius
$r_{0}=$ outside radius
$k=$ thermal conductivity
$h=$ heat-transfer coefficient
$\theta=T-T_{\infty}=$ temperature at $r$ minus surrounding temperature
$\theta_{0}=T-T_{\infty}=$ axis temperature minus surrounding temperature
FIGURE 7.9 Temperature as a function of axis temperature in a cylinder.
the heat-transfer coefficient $h$ from the belt to the water is $500 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[2835 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$. Calculate the surface temperature of the material as it leaves the belt if the material is placed on the belt at a temperature of $400^{\circ} \mathrm{F}(477 \mathrm{~K})$ and the belt moves at a speed of $150 \mathrm{ft} / \mathrm{min}(45.72 \mathrm{~m} / \mathrm{min})$.

## Physical Properties of the Material

$\rho=$ density $=60 \mathrm{lb} / \mathrm{ft}^{3}\left(961.1 \mathrm{~kg} / \mathrm{m}^{3}\right)$
$k=$ thermal conductivity $=0.10 \mathrm{Btu} /(\mathrm{h})(\mathrm{ft})\left({ }^{\circ} \mathrm{F}\right)[0.17 \mathrm{~W} /(\mathrm{m})(\mathrm{K})]$
$\alpha=$ thermal diffusivity $=0.0042 \mathrm{ft}^{2} / \mathrm{h}\left(3.871 \mathrm{~cm}^{3} / \mathrm{h}\right)$
$c=$ specific heat $=0.4 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)[1.7 \mathrm{~kJ} /(\mathrm{kg})(\mathrm{K})]$
Physical Properties of the Belt
$\rho=$ density $=500 \mathrm{lb} / \mathrm{ft}^{3}\left(8009.2 \mathrm{~kg} / \mathrm{m}^{3}\right)$
$k=$ thermal conductivity $=10 \mathrm{Btu} /(\mathrm{h})(\mathrm{ft})\left({ }^{\circ} \mathrm{F}\right)[17 \mathrm{~W} /(\mathrm{m})(\mathrm{K})]$
$c=$ specific heat $=0.11 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)[0.46 \mathrm{~kJ} /(\mathrm{kg})(\mathrm{K})]$
$\alpha=$ thermal diffusivity $=0.182 \mathrm{ft}^{2} / \mathrm{h}\left(0.169 \mathrm{~m}^{2} / \mathrm{h}\right)$

## Calculation Procedure

1. Calculate the thickness of the material on the belt. By dimensional analysis, ( $\mathrm{lb} / \mathrm{h}$ ) $\left(\mathrm{ft}^{3} / \mathrm{lb}\right)(\mathrm{min} / \mathrm{ft}$ belt $)(\mathrm{h} / \mathrm{min})(1 / \mathrm{ft}$ belt $)=\mathrm{ft}$, so $(10,000)(1 / 60)(1 / 150)(1 / 60)(1 / 3)=0.00617 \mathrm{ft}(1.881$ mm ).

$x=$ distance
$L=$ half slab thickness
$k=$ thermol conductivity
$h=$ heat-transfer coefficient
$\theta=T-T_{\infty}=$ temperature of $x$ minus surrounding temperature
$\theta_{0}=T_{i}-T_{\infty}=$ center temperature minus surrounding temperature
FIGURE 7.10 Temperature as a function of center temperature for a plate.
2. Calculate the time the material is in contact with the cooled belt. $H \mathrm{He},(\mathrm{ft})(\mathrm{min} / \mathrm{ft})(\mathrm{h} / \mathrm{min})=\mathrm{h}$, so $100(1 / 150)(1 / 60)=0.0111 \mathrm{~h}$.
3. Calculate $\alpha \boldsymbol{\tau} / \boldsymbol{L}^{\mathbf{2}}$ for the belt. Use the curves in Fig. 7.7. Assume that the water flow rate is high enough to neglect the temperature rise as the water removes heat from the material. Then, $\alpha \tau / L^{2}=0.182(0.0111) /(0.125 / 12)^{2}=18.62$.
4. Calculate $\boldsymbol{k} /(\boldsymbol{h} \boldsymbol{L})$ for the belt. $\quad \mathrm{Now}, k /(h L)=10 /[500(0.125 / 12)]=1.92$.
5. Determine $\boldsymbol{\theta}_{\boldsymbol{o}} / \boldsymbol{\theta}_{\boldsymbol{i}}$ for the belt. From Fig. 7.7, for $\alpha \tau / L^{2}=18.62$ and $k /(h L)=1.92, \theta_{o} / \theta_{i}$ is less than 0.001 . Therefore, pending the outcome of steps 6 through 8 , the conduction of heat through the belt will presumably be negligible compared with the conduction of heat through the material to be cooled.
6. Calculate $\boldsymbol{\alpha} \boldsymbol{\tau} / \boldsymbol{L}^{\mathbf{2}}$ for the material. $\quad$ Now, $\alpha \tau / L^{2}=0.0042(0.0111) / 0.00617^{2}=1.225$.
7. Calculate $\boldsymbol{k} /(\boldsymbol{h} \boldsymbol{L})$ for the material. $\quad$ Now, $k /(h L)=0.10 /[500(0.00617)]=0.0324$.
8. Determine $\boldsymbol{\theta}_{\boldsymbol{o}} / \boldsymbol{\theta}_{\boldsymbol{i}}$. From Fig. 7.7, for $\alpha \tau / L^{2}=1.225$ and $k /(h L)=0.0324, \theta_{o} / \theta_{i}=0.075$.
9. Determine the final surface temperature of the material. Now, $\theta_{o} / \theta_{i}=\left(T-T_{\infty}\right) /\left(T_{i}-T_{\infty}\right)$, where $T$ is the temperature at the end of the belt, $T_{i}$ is the initial material temperature, and $T_{\infty}$ is the water temperature. So, $\theta_{o} / \theta_{i}=(T-86) /(400-86)=0.075$, and $T=109.6^{\circ} \mathrm{F}(316.3 \mathrm{~K})$.

### 7.11 SIZING A BELT COOLER

For the conditions in the preceding example, calculate the length of belt required if the belt speed is reduced to $100 \mathrm{ft} / \mathrm{min}(30.48 \mathrm{~m} / \mathrm{min})$ and an outlet temperature of $125^{\circ} \mathrm{F}(324.8 \mathrm{~K})$ is acceptable.

## Calculation Procedure

The curves in Fig. 7.7 will be used.

1. Calculate the thickness of the material on the belt. By dimensional analysis, ( $\mathrm{lb} / \mathrm{h}$ ) $\left(\mathrm{ft}{ }^{3} / \mathrm{lb}\right)$ $(\mathrm{min} / \mathrm{ft}$ belt $)(\mathrm{h} / \mathrm{min})(1 / \mathrm{ft}$ belt $)=\mathrm{ft}$, so $(10,000)(1 / 60)(1 / 100)(1 / 60)(1 / 3)=0.0093 \mathrm{ft}(2.82 \mathrm{~mm})$.
2. Calculate $\boldsymbol{k} /(\boldsymbol{h} \boldsymbol{L})$ for the material. $\quad$ Now, $k /(h L)=0.10 /[500(0.0093)]=0.0215$.
3. Calculate $\boldsymbol{\theta}_{\boldsymbol{o}} / \boldsymbol{\theta}_{\boldsymbol{i}}$. Thus, $\theta_{o} / \theta_{i}=(125-86) /(400-86)=0.1242$.
4. Determine $\boldsymbol{\alpha} \boldsymbol{\tau} / \boldsymbol{L}^{\mathbf{2}}$. From Fig. 7.7, for $\theta_{o} / \theta_{i}=0.1242$ and $k /(h L)=0.0215, \alpha \tau / L^{2}=1.0$.
5. Determine the time required for contact with the water. Since $\alpha \tau / L^{2}=1.0=0.0042 \tau$ / $0.0093^{2}, \tau=0.0206 \mathrm{~h}$.
6. Calculate the length of belt required. Now, $\tau=\mathrm{h}=\mathrm{ft}(\mathrm{min} / \mathrm{ft})(\mathrm{h} / \mathrm{min})=0.0206$, which is feet of belt $(1 / 100)(1 / 60)$, so the length of belt is $(0.0206)(100)(60)=123.6 \mathrm{ft}(37.67 \mathrm{~m})$.

### 7.12 BATCH HEATING: INTERNAL COIL, ISOTHERMAL HEATING MEDIUM

A tank containing $50,000 \mathrm{lb}(22,679.5 \mathrm{~kg})$ of material with a specific heat of $0.5 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)[2.1 \mathrm{~kJ} /$ $(\mathrm{kg})(\mathrm{K})]$ is to be heated from $68^{\circ} \mathrm{F}(293 \mathrm{~K})$ to $257^{\circ} \mathrm{F}(398 \mathrm{~K})$. The tank contains a heating coil with a heat-transfer surface of $100 \mathrm{ft}^{2}\left(9.29 \mathrm{~m}^{2}\right)$, and the overall heat-transfer coefficient from the coil to the tank contents is $150 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[850 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$. Calculate the time required to heat the tank contents with steam condensing at $320^{\circ} \mathrm{F}(433 \mathrm{~K})$.

## Calculation Procedure

1. Select and apply the appropriate heat-transfer formula. When heating a batch with an internal coil with an isothermal heating medium, the following equation applies:

$$
\ln \left(\frac{T_{1}-t_{1}}{T_{1}-t_{2}}\right)=\left(\frac{U A}{M c}\right) \theta
$$

where $T_{1}=$ heating-medium temperature
$t_{1}=$ initial batch temperature
$t_{2}=$ final batch temperature
$U=$ overall heat-transfer coefficient
$A=$ heat-transfer surface
$M=$ weight of batch
$c=$ specific heat of batch
$\theta=$ time
For this problem, $\ln [(320-68) /(320-257)]=\{150(100) /[50,000(0.5)]\} \theta$, so $\theta=2.31 \mathrm{~h}$.

Related Calculations. This procedure can also be used for batch cooling with internal coils and isothermal cooling media. The equation in such cases is

$$
\ln \left(\frac{T_{1}-t_{1}}{T_{2}-t_{1}}\right)=\left(\frac{U A}{M c}\right) \theta
$$

where $T_{1}=$ initial batch temperature
$T_{2}=$ final batch temperature
$t_{1}=$ cooling-medium temperature

### 7.13 BATCH COOLING: INTERNAL COIL, NONISOTHERMAL COOLING MEDIUM

For the tank described in the preceding example, calculate the time required to cool the batch from $257^{\circ} \mathrm{F}(398 \mathrm{~K})$ to $104^{\circ} \mathrm{F}(313 \mathrm{~K})$ if cooling water is available at a temperature of $86^{\circ} \mathrm{F}(303 \mathrm{~K})$ and a flow rate of $10,000 \mathrm{lb} / \mathrm{h}(4535.9 \mathrm{~kg} / \mathrm{h})$.

## Calculation Procedure

1. Select and apply the appropriate heat-transfer formula. When cooling a batch with an internal coil and a nonisothermal cooling medium, the following equation applies:

$$
\ln \left(\frac{T_{1}-t_{1}}{T_{2}-t_{1}}\right)=\frac{w_{c} c_{c}}{M c}\left(K_{2}-1\right)\left(\frac{1}{K_{2}}\right) \theta
$$

where $K_{2}=e^{U A / w_{c} c_{c}}$
$T_{1}=$ initial batch temperature
$T_{2}=$ final batch temperature
$t_{1}=$ initial coolant temperature
$w_{c}=$ coolant flow rate
$c_{c}=$ coolant specific heat
$U=$ overall heat-transfer coefficient
$A=$ heat-transfer surface
$M=$ weight of batch
$c=$ specific heat of batch
$\theta=$ time
For this problem, $K_{2}=\exp 150(100) /[10,000(1.0)]=4.4817$, so

$$
\ln \frac{257-86}{104-86}=\frac{(10,000) 1.0}{(50,000) 0.5} \frac{4.4817-1}{4.4817} \theta
$$

Therefore, $\theta=7.245 \mathrm{~h}$.
Related Calculations. This procedure can also be used for batch heating with internal coils and isothermal heating media. The equations in such cases are

$$
\ln \frac{T_{1}-t_{1}}{T_{1}-t_{2}}=\frac{W_{h} c_{h}}{M c}\left(K_{3}-1\right) \frac{1}{K_{3}} \theta \quad \text { and } \quad K_{3}=\exp \frac{U A}{W_{h} c_{h}}
$$

where $T_{1}=$ heating-medium temperature
$t_{1}=$ initial batch temperature
$t_{2}=$ final batch temperature
$W_{h}=$ heating-medium flow rate
$c_{h}=$ heating-medium specific heat

### 7.14 BATCH COOLING: EXTERNAL HEAT EXCHANGER (COUNTERFLOW), NONISOTHERMAL COOLING MEDIUM

Calculate the time required to cool the batch described in the preceding example if an external heat exchanger with a heat-transfer surface of $200 \mathrm{ft}^{2}\left(18.58 \mathrm{~m}^{2}\right)$ is available. The batch material is circulated through the exchanger at the rate of $25,000 \mathrm{lb} / \mathrm{h}(11,339.8 \mathrm{~kg} / \mathrm{h})$. The overall heat-transfer coefficient in the heat exchanger is $200 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[1134 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.

## Calculation Procedure

1. Select and apply the appropriate heat-transfer formula. When cooling a batch with an external heat exchanger and a nonisothermal cooling medium, the following equations apply:

$$
\ln \frac{T_{1}-t_{1}}{T_{2}-t_{1}}=\frac{K_{4}-1}{M} \frac{W_{b} w_{c} c_{c}}{K_{4} w_{c} c_{c}-W_{b} c} \theta \quad \text { and } \quad K_{4}=\exp U A\left(\frac{1}{W_{b} c}-\frac{1}{w_{c} c_{c}}\right)
$$

where $T_{1}=$ initial batch temperature
$T_{2}=$ final batch temperature
$t_{1}=$ initial coolant temperature
$w_{c}=$ coolant flow rate
$c_{c}=$ coolant specific heat
$W_{b}=$ batch flow rate
$c=$ batch specific heat
$M=$ weight of batch
$U=$ overall heat-transfer coefficient
$A=$ heat transfer surface
$\theta=$ time

For this problem,

$$
K_{4}=\exp (200)(200)\left[\frac{1}{(25,000) 0.5}-\frac{1}{(10,000) 1.0}\right]=0.4493
$$

So,

$$
\ln \frac{257-86}{104-86}=\frac{0.4493-1}{50,000} \frac{25,000(10,000)(1.0)}{[0.4493(10,000)(1.0)-25,000(0.5)]} \theta
$$

Therefore, $\theta=6.547 \mathrm{~h}$.

Related Calculations. This procedure can also be used for batch heating with external heat exchangers and nonisothermal heating media. The equations in such cases are

$$
\ln \frac{T_{1}-t_{1}}{T_{1}-t_{2}}=\frac{K_{5}-1}{M} \frac{W_{b} W_{h} c_{h}}{K_{5} W_{h} c_{h}-W_{b} c} \theta \quad \text { and } \quad K_{5}=\exp U A\left(\frac{1}{W_{b} c}-\frac{1}{W_{h} c_{h}}\right)
$$

where $T_{1}=$ heating-medium initial temperature
$t_{1}=$ initial batch temperature
$t_{2}=$ final batch temperature
$W_{h}=$ heating-medium flow rate
$c_{h}=$ specific heat of heating medium

### 7.15 BATCH COOLING: EXTERNAL HEAT EXCHANGER

 (1-2 MULTIPASS), NONISOTHERMAL COOLING MEDIUMCalculate the time required to cool the batch described in the preceding example if the external heat exchanger is a $1-2$ multipass unit rather than counterflow.

## Calculation Procedure

1. Select and apply the appropriate heat-transfer formula. When cooling a batch with an external 1-2 multipass heat exchanger and a nonisothermal cooling medium, the following equations apply:

$$
\ln \frac{T_{1}-t_{1}}{T_{2}-t_{1}}=S \frac{w_{c} c_{c}}{M c} \theta
$$

and

$$
S=\frac{2\left(K_{7}-1\right)}{K_{7}\left[R+1+\left(R^{2}+1\right)^{1 / 2}\right]-\left[R+1-\left(R^{2}+1\right)^{1 / 2}\right]}
$$

$$
\text { where } K_{7}=\exp \frac{U A}{w_{c} c_{c}}\left(R^{2}+1\right)^{1 / 2}
$$

$R=\frac{w_{c} c_{c}}{W_{b} c}$
$T_{1}=$ initial batch temperature
$T_{2}=$ final batch temperature
$t_{1}=$ initial coolant temperature
$w_{c}=$ coolant flow rate
$c_{c}=$ coolant specific heat
$M=$ weight of batch
$W_{b}=$ batch flow rate
$c=$ specific heat of batch
$\theta=$ time required to cool the batch
$U=$ overall heat-transfer coefficient
$A=$ heat-transfer surface

For the problem here, $R=10,000(1.0) /[25,000(0.5)]=0.80$, so

$$
\begin{aligned}
K_{7} & =\exp \frac{200(200)}{10,000(1.0)}\left(0.80^{2}+1\right)^{1 / 2} \\
& =167.75
\end{aligned}
$$

and

$$
\begin{aligned}
S & =\frac{2(167.75-1)}{167.75\left[0.80+1+\left(0.8^{2}+1\right)^{1 / 2}\right]-\left[0.8+1-\left(0.8^{2}+1\right)^{1 / 2}\right]} \\
& =0.646
\end{aligned}
$$

Therefore,

$$
\ln \frac{257-86}{104-86}=\frac{0.646(10,000)(1.0)}{50,000(0.5)} \theta
$$

and $\theta=8.713 \mathrm{~h}$

Related Calculations. This procedure can also be used for batch heating with external 1-2 multipass heat exchangers and nonisothermal heating media. The equation in such a case is

$$
\ln \frac{T_{1}-t_{1}}{T_{1}-t_{2}}=\frac{S W_{h}}{M} \theta
$$

where $S$ is defined by the preceding equation, and

$$
\begin{aligned}
R & =\frac{W_{b} c}{W_{h} c_{h}} \\
K_{7} & =\exp \frac{U A}{W_{b} c}\left(R^{2}+1\right)^{1 / 2} \\
T_{1} & =\text { initial temperature of heating medium } \\
t_{1} & =\text { initial temperature of batch } \\
t_{2} & =\text { final batch temperature } \\
W_{h} & =\text { heating-medium flow rate } \\
c_{h} & =\text { specific heat of heating medium }
\end{aligned}
$$

Calculate the heat-transfer coefficient from a coil immersed in an agitated vessel with a diameter of $8 \mathrm{ft}(2.44 \mathrm{~m})$. The agitator is a turbine $3 \mathrm{ft}(0.91 \mathrm{~m})$ in diameter and turns at $150 \mathrm{r} / \mathrm{min}$. The fluid has these properties:

$$
\begin{aligned}
\rho & =\text { density }=45 \mathrm{lb} / \mathrm{ft}^{3}\left(720.8 \mathrm{~kg} / \mathrm{m}^{3}\right) \\
\mu & =\text { viscosity }=10 \mathrm{lb} /(\mathrm{ft})(\mathrm{h})(4.13 \mathrm{cP}) \\
c & =\text { specific heat }=0.7 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)[2.9 \mathrm{~kJ} /(\mathrm{kg})(\mathrm{K})] \\
k & =\text { thermal conductivity }=0.10 \mathrm{Btu} /(\mathrm{h})(\mathrm{ft})\left({ }^{\circ} \mathrm{F}\right)[0.17 \mathrm{~W} /(\mathrm{m})(\mathrm{K})]
\end{aligned}
$$

The viscosity may be assumed to be constant with temperature.

## Calculation Procedure

1. Select and apply the appropriate heat-transfer formula. The following equation can be used to predict heat-transfer coefficients from coils or tank walls in agitated tanks:

$$
\frac{h D_{j}}{k}=a\left(\frac{L^{2} N \rho}{\mu}\right)^{2 / 3}\left(\frac{c \mu}{k}\right)^{1 / 3}\left(\frac{\mu_{b}}{\mu_{w}}\right)^{0.14}
$$

The term $a$ has these values:

| Agitator | Surface | $a$ |
| :--- | :--- | :---: |
| Turbine | Jacket | 0.62 |
| Turbine | Coil | 1.50 |
| Paddle | Jacket | 0.36 |
| Paddle | Coil | 0.87 |
| Anchor | Jacket | 0.46 |
| Propeller | Jacket | 0.54 |
| Propeller | Coil | 0.83 |

The other variables in the equation are
$h=$ heat-transfer coefficient
$D_{j}=$ diameter of vessel
$k=$ thermal conductivity
$L=$ diameter of agitator
$N=$ speed of agitator in revolutions per hour
$\rho=$ density
$\mu=$ viscosity
$c=$ specific heat
$\mu_{b}=$ viscosity at bulk fluid temperature
$\mu_{w}=$ viscosity at surface temperature
Therefore, $h=1.50\left(k / D_{j}\right)\left(L^{2} N \rho / \mu\right)^{2 / 3}(c \mu / k)^{1 / 3}\left(\mu_{b} / \mu_{w}\right)^{0.14}$. As noted above, assume that $\left(\mu_{b} / \mu_{w}\right)^{0.14}=1.0$. Then,

$$
\begin{align*}
h & =1.50(0.10 / 8)\left[\frac{3^{2}(150)(60)(45)}{10}\right]^{2 / 3}\left[\frac{0.7(10)}{0.1}\right]^{1.3}(1.0)  \tag{1.0}\\
& =394 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[2238 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]
\end{align*}
$$

## NATURAL-CONVECTION HEAT TRANSFER

Calculate the heat-transfer coefficient from a coil immersed in water with the physical properties listed below. The coil has a diameter of 1 in $(0.025 \mathrm{~m})$, and the temperature difference between the surface of the coil and the fluid is $10^{\circ} \mathrm{F}(5.56 \mathrm{~K})$. The properties of the water are
$c=$ specific heat $=1.0 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)[4.19 \mathrm{~kJ} /(\mathrm{kg})(\mathrm{K})]$
$\rho=$ liquid density $=60 \mathrm{lb} / \mathrm{ft}^{3}\left(961.1 \mathrm{~kg} / \mathrm{m}^{3}\right)$
$k=$ thermal conductivity $=0.395 \mathrm{Btu} /(\mathrm{h})(\mathrm{ft})\left({ }^{\circ} \mathrm{F}\right)[0.683 \mathrm{~W} /(\mathrm{m})(\mathrm{K})]$
$\mu=$ viscosity $=0.72 \mathrm{lb} /(\mathrm{ft})(\mathrm{h})(0.298 \mathrm{cP})$
$\beta=$ coefficient of expansion $=0.0004^{\circ} \mathrm{F}^{-1}\left(0.00022 \mathrm{~K}^{-1}\right)$

## Calculation Procedure

1. Consider the natural-convection equations available. Heat-transfer coefficients for natural convection may be calculated using the equations presented below. These equations are also valid for horizontal plates or discs. For horizontal plates facing upward which are heated or for plates facing downward which are cooled, the equations are applicable directly. For heated plates facing downward or cooled plates facing upward, the heat-transfer coefficients obtained should be multiplied by 0.5 .

| Vertical surfaces | Horizontal cylinders |
| :---: | :---: |
| For Reynolds numbers greater than $10,000:$ |  |
| $[h /(c G)](c \mu / k)^{2 / 3}=0.13 /(L G / \mu)^{1 / 3}$ | $=0.13 /(D G / \mu)^{1 / 3}$ |

For Reynolds numbers from 100 to 10,000 :

$$
[h /(c G)](c \mu / k)^{3 / 4}=0.59 /(L G / \mu)^{1 / 2} \quad=0.53 /(D G / \mu)^{1 / 2}
$$

For Reynolds numbers less than 100 :

$$
[h /(c G)](c \mu / k)^{5 / 6}=1.36 /(L G / \mu)^{2 / 3} \quad=1.09 /(D G / \mu)^{2 / 3}
$$

In these equations, $G$ is mass velocity, that is, $\left(g \beta \Delta T \rho^{2} L\right)^{1 / 2}$ for vertical surfaces or $\left(g \beta \Delta \rho^{2} D\right)^{1 / 2}$ for horizontal cylinders, and,
$h=$ heat-transfer coefficient
$c=$ specific heat
$L=$ length
$D=$ diameter
$\mu=$ viscosity
$g=$ acceleration of gravity $\left(4.18 \times 10^{8} \mathrm{ft} / \mathrm{h}^{2}\right)$
$\beta=$ coefficient of expansion
$\Delta T=$ temperature difference between surface and fluid
$\rho=$ density
$k=$ thermal conductivity
2. Calculate mass velocity. Thus, $G=\left(g \beta \Delta T \rho^{2} D\right)^{1 / 2}=\left[\left(4.18 \times 10^{8}\right)(0.0004)(10) 60^{2}(1 /\right.$ $12)]^{1 / 2}=22,396.4 \mathrm{lb} /\left(\mathrm{ft}^{2}\right)(\mathrm{h})$.
3. Calculate the Reynolds number $\boldsymbol{D G} / \boldsymbol{\mu}$. Thus, $D G / \mu=(1 / 12)(22,396.4) / 0.72=2592.2$.
4. Calculate the heat-transfer coefficient h. Thus, $h=0.53 c G /\left[(c \mu / k)^{3 / 4}(D G / \mu)^{1 / 2}\right]=$ $0.53(1.0)(22,396.4) /\left\{[1.0(0.72) / 0.395]^{3 / 4}(2592.2)^{1 / 2}\right\}=148.6 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[844 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.

Related Calculations. The equations presented above can be simplified for natural-convection heat transfer in air. The usual cases yield the following equations: For vertical surfaces,

$$
h=0.29(\Delta T / L)^{1 / 4}
$$

for horizontal cylinders,

$$
h=0.27(\Delta T / D)^{1 / 4}
$$

In these, $h$ is in $\mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right), \Delta T$ is in ${ }^{\circ} \mathrm{F}$, and $L$ and $D$ are in feet.

### 7.18 HEAT-TRANSFER COEFFICIENTS FOR FLUIDS FLOWING INSIDE TUBES: FORCED CONVECTION, SENSIBLE HEAT

Calculate the heat-transfer coefficient for a fluid with the properties listed below flowing through a tube $20 \mathrm{ft}(6.1 \mathrm{~m})$ long and of 0.62 -in $(0.016-\mathrm{m})$ inside diameter. The bulk fluid temperature is $212^{\circ} \mathrm{F}$ $(373 \mathrm{~K})$, and the tube surface temperature is $122^{\circ} \mathrm{F}(323 \mathrm{~K})$. Calculate the heat-transfer coefficient if the fluid is flowing at a rate of $2000 \mathrm{lb} / \mathrm{h}(907.2 \mathrm{~kg} / \mathrm{h})$. Also calculate the heat-transfer coefficient if the flow rate is reduced to $100 \mathrm{lb} / \mathrm{h}(45.36 \mathrm{~kg} / \mathrm{h})$.

## Physical Properties of the Fluid

$$
c=\text { specific heat }=0.65 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)[2.72 \mathrm{~kJ} /(\mathrm{kg})(\mathrm{K})]
$$

$k=$ thermal conductivity $=0.085 \mathrm{Btu} /(\mathrm{h})(\mathrm{ft})\left({ }^{\circ} \mathrm{F}\right)[0.147 \mathrm{~W} /(\mathrm{m})(\mathrm{K})]$
$\mu_{w}=$ viscosity at $122^{\circ} \mathrm{F}=4.0 \mathrm{lb} /(\mathrm{ft})(\mathrm{h})(1.65 \mathrm{cP})$
$\mu_{b}=$ viscosity at $212^{\circ} \mathrm{F}=1.95 \mathrm{lb} /(\mathrm{ft})(\mathrm{h})(0.806 \mathrm{cP})$

## Calculation Procedure

1. Select the appropriate heat-transfer coefficient equation. Heat-transfer coefficients for fluids flowing inside tubes or ducts can be calculated using these equations:
a. For Reynolds numbers $(D G / \mu)$ greater than 8000 ,

$$
\frac{h}{c G}=\frac{0.023}{(c \mu / k)^{2 / 3}\left(D_{i} G / \mu\right)^{0.2}\left(\mu_{w} / \mu_{b}\right)^{0.14}}
$$

b. For Reynolds numbers $(D G / \mu)$ less than 2100 ,

$$
\frac{h}{c G}=\frac{1.86}{(c \mu / k)^{2 / 3}\left(D_{i} G / \mu\right)^{2 / 3}\left(L / D_{i}\right)^{1 / 3}\left(\mu_{w} / \mu_{b}\right)^{0.14}}
$$

In these equations,
$h=$ heat-transfer coefficient
$c=$ specific heat
$G=$ mass velocity (mass flow rate divided by cross-sectional area)
$\mu=$ viscosity
$\mu_{w}=$ viscosity at the surface temperature
$\mu_{b}=$ viscosity at the bulk fluid temperature
$k=$ thermal conductivity
$D_{i}=$ inside diameter
$L=$ length
2. Calculate $D_{i} G / \mu$ for a 2000 lb/h flow rate.

$$
\begin{aligned}
\frac{D_{i} G}{\mu} & =\frac{0.62}{12} \frac{2000}{(0.62 / 12)^{2}(\pi / 4)} \frac{1}{1.95} \\
& =25,275
\end{aligned}
$$

3. Calculate $\boldsymbol{h}$ for the $2000 \mathbf{l b} / \mathbf{h}$ flow rate. Because $D G / \mu$ is greater than 8000 ,

$$
\begin{aligned}
\frac{h}{c G} & =\frac{0.023}{(c \mu / k)^{2 / 3}\left(D_{i} G / \mu\right)^{0.2}\left(\mu_{w} / \mu_{b}\right)^{0.14}} \\
& =\frac{0.023(0.65)\left[2000 /(0.62 / 12)^{2}(\pi / 4)\right]}{[0.65(1.95) / 0.085]^{2 / 3} 25,275^{0.2}(4.0 / 1.95)^{0.14}} \\
& =280.3 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)(\mathrm{K})\left[1592 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]
\end{aligned}
$$

## 4. Calculate $D G / \mu$ for a $100 \mathrm{lb} / \mathrm{h}$ flow rate.

$$
D_{i} G / \mu=25,275(100 / 2000)=1263.8
$$

5. Calculate $\boldsymbol{h}$ for the $\mathbf{1 0 0} \boldsymbol{l b} / \boldsymbol{h}$ flow rate. Because $D G / \mu$ is less than 2100 ,

$$
\begin{aligned}
\frac{h}{c G} & =\frac{1.86}{(c \mu / k)^{2 / 3}(D G / \mu)^{2 / 3}(L / D)^{1 / 3}\left(\mu_{w} / \mu_{b}\right)^{0.14}} \\
& =\frac{1.86(0.65)\left\{100 /\left[(0.62 / 12)^{2}(\pi / 4)\right]\right\}}{\left[\frac{0.65(1.95)}{0.085}\right]^{2 / 3} 1263.8^{2 / 3}\left[\frac{20}{(0.62 / 12)}\right]^{1 / 3}\left(\frac{4.0}{1.95}\right)^{0.14}} \\
& =10.1 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[57.4 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]
\end{aligned}
$$

Related Calculations. Heat transfer for fluids with Reynolds numbers between 2100 and 8000 is not stable, and the heat-transfer coefficients in this region cannot be predicted with certainty. Equations have been presented in many of the references. The heat-transfer coefficients in this region can be bracketed by calculating the values using both the preceding equations for the Reynolds number in question.

The equations presented here can also be used to predict heat-transfer coefficients for the shell side of shell-and-tube heat exchangers in which the baffles have been designed to produce flow parallel to the axis of the tube. For such cases, the diameter that should be used is the equivalent diameter

$$
D_{e}=\frac{4 a}{P}
$$

where $a=$ flow area
$P=$ wetted perimeter
Here, $a=\left(D_{s}^{2}-n D_{o}^{2}\right)(\pi / 4)$, where $D_{s}$ is the shell inside diameter, $D_{o}$ is the tube outside diameter, and $n$ is the number of tubes; and $P=\pi\left(D_{s}+n D_{o}\right)$.

For shells with triple or double segmental baffles, the heat-transfer coefficient calculated for turbulent flow ( $D G / \mu$ greater than 8000 ) should be multiplied by a value of 1.3.

For gases, the equation for heat transfer in the turbulent region ( $D G / \mu$ greater than 8000 ) can be simplified because the Prandtl number $(c \mu / k)$ and the viscosity for most gases are approximately constant. Assigning the values $c \mu / k=0.78$ and $\mu=0.0426 \mathrm{lb} /(\mathrm{h})(\mathrm{ft})(0.0176 \mathrm{cP})$ results in the
following equation for gases:

$$
h=0.0144 \frac{c G^{0.8}}{D_{i}^{0.2}}
$$

with the variables defined in English units.

### 7.19 HEAT-TRANSFER COEFFICIENTS FOR FLUIDS FLOWING INSIDE HELICAL COILS

Calculate the heat-transfer coefficient for a fluid with a flow rate of $100 \mathrm{lb} / \mathrm{h}(45.36 \mathrm{~kg} / \mathrm{h})$ and the physical properties outlined in Example 7.18. The inside diameter of the tube is 0.62 in ( 0.016 m ), and the tube is fabricated into a helical coil with a helix diameter of 24 in $(0.61 \mathrm{~m})$.

## Calculation Procedure

1. Select the appropriate heat-transfer coefficient equation. Heat-transfer coefficients for fluids flowing inside helical coils can be calculated with modifications of the equations for straight tubes. The equations presented in Example 7.18 should be multiplied by the factor $1+3.5 D_{i} / D_{c}$, where $D_{i}$ is the inside diameter and $D_{c}$ is the diameter of the helix or coil. In addition, for laminar flow, the term $\left(D_{c} / D_{i}\right)^{1 / 6}$ should be substituted for the term $(L / D)^{1 / 3}$. The Reynolds number required for turbulent flow is $2100\left[1+12\left(D_{i} / D_{c}\right)^{1 / 2}\right]$.
2. Calculate the minimum Reynolds number for turbulent flow. Now,

$$
\begin{aligned}
D G / \mu)_{\min } & =2100\left[1+12\left(D_{i} / D_{c}\right)^{1 / 2}\right] \\
& =2100\left[1+12(0.62 / 24)^{1 / 2}\right] \\
& =6150
\end{aligned}
$$

3. Calculate $\boldsymbol{h}$. From the preceding calculations, $D G / \mu=1263.8$ at a flow rate of of $100 \mathrm{lb} / \mathrm{h}$. Therefore,

$$
\begin{aligned}
h & =\frac{1.86 c G\left(1+3.5 D_{i} / D_{c}\right)}{(c \mu / k)^{2 / 3}(D G / \mu)^{2 / 3}\left(D_{c} / D_{i}\right)^{1 / 6}\left(\mu_{w} / \mu_{b}\right)^{0.14}} \\
& =\frac{1.86(0.65)\left\{100 /\left[(0.62 / 12)^{2}(\pi / 4)\right]\right\}[1+3.5(0.62 / 24)]}{[0.65(1.95) / 0.085]^{2 / 3} 1263.8^{2 / 3}(24 / 0.62)^{1 / 6}(4.0 / 1.95)^{0.14}} \\
& =43.7 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[248 \mathrm{~W} /\left(\mathrm{M}^{2}\right)(\mathrm{K})\right]
\end{aligned}
$$

### 7.20 HEAT-TRANSFER COEFFICIENTS: FLUIDS FLOWING ACROSS BANKS OF TUBES; FORCED CONVECTION, SENSIBLE HEAT

Calculate the heat-transfer coefficient for a fluid with the properties listed in Example 7.18 if the fluid is flowing across a tube bundle with the following geometry. The fluid flows at a rate of $50,000 \mathrm{lb} / \mathrm{h}(22,679.5 \mathrm{~kg} / \mathrm{h})$. Calculate the heat-transfer coefficient for both clean and fouled conditions.

## Tube Bundle Geometry

$D_{s}=$ shell diameter $=25 \mathrm{in}(2.08 \mathrm{ft}$ or 0.635 m$)$
$B=$ baffle spacing $=9.5 \mathrm{in}(0.79 \mathrm{ft}$ or 0.241 m$)$
$D_{o}=$ outside tube diameter $=0.75$ in $(0.019 \mathrm{~m})$
$s=$ tube center-to-center spacing $=0.9375$ in $(0.0238 \mathrm{~m})$
The tubes are spaced on a triangular pattern.

## Calculation Procedure

1. Select the appropriate heat-transfer coefficient equation. Heat-transfer coefficients for fluids flowing across ideal-tube banks may be calculated using the equation

$$
\frac{h}{c G}=\frac{a}{(c \mu / k)^{2 / 3}\left(D_{o} G / \mu\right)^{m}\left(\mu_{w} / \mu_{b}\right)^{0.14}}
$$

The values of $a$ and $m$ are as follows:

| Reynolds number | Tube pattern | $m$ | $a$ |
| :--- | :--- | :---: | :---: |
| Greater than 200,000 | Staggered | 0.300 | 0.166 |
| Greater than 200,000 | In-line | 0.300 | 0.124 |
| 300 to 200,000 | Staggered | 0.365 | 0.273 |
| 300 to 200,000 | In-line | 0.349 | 0.211 |
| Less than 300 | Staggered | 0.640 | 1.309 |
| Less than 300 | In-line | 0.569 | 0.742 |

In these equations,
$h=$ heat-transfer coefficient
$c=$ specific heat
$G=$ mass velocity $=W / a_{c}$
$a_{c}=$ flow area
$W=$ flow rate
$k=$ thermal conductivity
$D_{o}=$ outside tube diameter
$\mu=$ viscosity
$\mu_{w}=$ viscosity at wall temperature
$\mu_{b}=$ viscosity at bulk fluid temperature
For triangular and square tube patterns,

$$
a_{c}=\frac{B D_{s}\left(s-D_{o}\right)}{s}
$$

For rotated square tube patterns,

$$
a_{c}=\frac{1.5 B D_{s}\left(s-D_{o}\right)}{s}
$$

where $B=$ baffle spacing
$D_{s}=$ shell diameter
$s=$ tube center-to-center spacing
$D_{o}=$ tube outside diameter
The values of $a$ in the preceding table are based on heat exchangers that have no bypassing of the bundle by the fluid. For heat exchangers built to the standards of the Tubular Exchangers Manufacturers Association [11] and with an adequate number of sealing devices, the heat-transfer coefficient calculated with the preceding equation must be corrected as below to reflect the bypassing of the fluid:

$$
h_{o}=h F_{1} F_{r}
$$

where $F_{1}=0.8\left(B / D_{s}\right)^{1 / 6}$ for bundles with typical fouling
$F_{1}=0.8\left(B / D_{s}\right)^{1 / 4}$ for bundles with no fouling
$F_{r}=1.0$ for $D_{o} G / \mu$ greater than 100
$F_{r}=0.2\left(D_{o} G / \mu\right)^{1 / 3}$ for $D_{o} G / \mu$ less than 100
2. Calculate $D_{o} G / \mu$

$$
\begin{aligned}
a_{c} & =\frac{B D_{s}\left(s-D_{o}\right)}{s} \\
& =\frac{(9.5 / 12)(25 / 12)(0.9375-0.75)}{0.9375} \\
& =0.3299 \mathrm{ft}^{2}\left(0.0306 \mathrm{~m}^{2}\right) \\
G & =\frac{W}{a_{c}}=\frac{50,000}{0.3299}=151,578.9 \mathrm{lb} /(\mathrm{h})\left(\mathrm{ft}^{2}\right) \\
\frac{D_{o} G}{\mu} & =\frac{(0.75 / 12) 151,578.9}{1.95}=4858.9
\end{aligned}
$$

3. Calculate h. Now,

$$
h=\frac{0.273 c G}{(c \mu / k)^{2 / 3}\left(D_{o} G / \mu\right)^{0.365}\left(\mu_{w} / \mu_{b}\right)^{0.14}}
$$

Thus,

$$
\begin{aligned}
h & =\frac{0.273(0.65)(151,578.9)}{[0.65(1.95) / 0.085]^{2 / 3}(4858.3)^{0.365}(4.0 / 1.95)^{0.14}} \\
& =181.2 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} F\right)\left[1029 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(K)\right]
\end{aligned}
$$

4. Calculate $\boldsymbol{h}_{\boldsymbol{o}}$ for the fouled condition. Now, $h_{o}=h F_{1} F_{r}$, where $F_{r}=1.0$ and $F_{1}=0.8$ $\times\left(B / D_{s}\right)^{1 / 6}=0.8(9.5 / 25)^{1 / 6}=0.6809$, so $h_{o}=181.5(0.6809)(1.0)=123.6 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)[702$ $\left.\mathrm{W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.
5. Calculate $\boldsymbol{h}_{\text {o }}$ for the clean condition. Here, $F_{1}=0.8\left(B / D_{s}\right)^{1 / 4}=0.8(9.5 / 25)^{1 / 4}=0.6281$, so $h_{o}=181.5(0.6281)(1.0)=114.0 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[647.5 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.

Related Calculations. The preceding equations for $F_{1}$ and $F_{r}$ are based on heat exchangers that have been fabricated to minimize bypassing of the bundle by the fluid.The assumption has also been
made that the baffle cut for segmental baffles is 20 percent of the shell diameter and that the layout includes tubes in the baffle window areas. For conditions removed from these assumptions, the effects of fluid bypassing should be evaluated. Several methods have been presented; a widely used one is that of Bell [15].

For gases, the preceding equations for the turbulent regime can be simplified because the Prandtl number $(c \mu / k)$ and viscosity for most gases are approximately constant. Assigning the values $c \mu / k=$ 0.78 and $\mu=0.0426 \mathrm{lb} /(\mathrm{ft})(\mathrm{h})(0.0176 \mathrm{cP})$ results in the equation

$$
h=\frac{b c G^{1-m}}{D_{o}^{m}}
$$

with the variables defined in English units and with $b$ having these values:

| Reynolds number | Tube pattern | $b$ |
| :--- | :--- | :---: |
| 300 to 200,000 | Staggered | 0.102 |
| 300 to 200,000 | In-line | 0.083 |
| Above 200,000 | Staggered | 0.076 |
| Above 200,000 | In-line | 0.057 |

### 7.21 MEAN TEMPERATURE DIFFERENCE FOR HEAT EXCHANGERS

A warm stream enters a heat exchanger at $200^{\circ} \mathrm{C}\left(392^{\circ} \mathrm{F}\right), T_{h}$, and is cooled to $100^{\circ} \mathrm{C}\left(212^{\circ} \mathrm{F}\right), T_{c}$. The cooling stream enters the exchanger at $20^{\circ} \mathrm{C}\left(68^{\circ} \mathrm{F}\right), t_{c}$, and is heated to $95^{\circ} \mathrm{C}\left(203^{\circ} \mathrm{F}\right), t_{h}$. Calculate the mean temperature difference for the following cases:

1. Countercurrent flow
2. Cocurrent flow (also called "parallel flow")
3. 1-2 Multipass (one pass on the shell side, two passes on the tube side)
4. 2-4 Multipass (two passes on the shell side, four passes on the tube side)
5. 1-1 Cross flow (one cross-flow pass on the shell side, one pass on the tube side)
6. 1-2 Cross flow (one cross-flow pass on the shell side, two passes on the tube side)

These flow arrangements are illustrated in Fig. 7.11.

## Calculation Procedure

1. Use equation for countercurrent flow. The mean temperature difference for countercurrent flow is the log mean temperature difference as calculated from the equation

$$
\Delta T_{L M}=\frac{\left(T_{h}-t_{h}\right)-\left(T_{c}-t_{c}\right)}{\ln \left[\left(T_{h}-t_{h}\right) /\left(T_{c}-t_{c}\right)\right]}
$$

Thus,

$$
\begin{aligned}
\Delta T_{L M} & =\frac{(200-95)-(100-20)}{\ln [(200-95) /(100-20)]} \\
& =91.93^{\circ} \mathrm{C}\left(165.47^{\circ} \mathrm{F}\right)
\end{aligned}
$$



FIGURE 7.11 Flow arrangements through heat exchangers. Note: $T$ refers to the stream being cooled; $t$ refers to the stream being heated.
2. Use the equation for cocurrent flow. The mean temperature difference for cocurrent flow is the log mean temperature difference as calculated from the equation

$$
\Delta T_{L M}=\frac{\left(T_{h}-t_{c}\right)-\left(T_{c}-t_{h}\right)}{\ln \left[\left(T_{h}-t_{c}\right) /\left(T_{c}-t_{h}\right)\right]}
$$

Thus,

$$
\begin{aligned}
\Delta T_{L M} & =\frac{(200-20)-(100-95)}{\ln [(200-20) /(100-95)]} \\
& =48.83^{\circ} \mathrm{C}\left(87.89^{\circ} \mathrm{F}\right)
\end{aligned}
$$

3. Use equation for 1-2 multipass. The mean temperature difference for a 1-2 multipass heat exchanger can be calculated from the equation

$$
\Delta T_{m}=\frac{M}{\ln [(P+M) /(P-M)]}
$$

where $P=\left(T_{h}-t_{h}\right)+\left(T_{c}-t_{c}\right)$ and $M=\left[\left(T_{h}-T_{c}\right)^{2}+\left(t_{h}-t_{c}\right)^{2}\right]^{1 / 2}$. Thus, $P=(200-95)+$ $(100-20)=185, M=\left[(200-100)^{2}+(95-20)^{2}\right]^{1 / 2}=125$, and

$$
\begin{aligned}
\Delta T_{m} & =\frac{125}{\ln [(185+125) /(185-125)]} \\
& =76.12^{\circ} \mathrm{C}\left(137.02^{\circ} \mathrm{F}\right)
\end{aligned}
$$

4. Use equation for 2-4 multipass. The mean temperature difference for a $2-4$ multipass heat exchanger can be calculated from the equation

$$
\Delta T_{m}=\frac{M / 2}{\ln [(Q+M) /(Q-M)]}
$$

where $M$ is defined above and

$$
Q=\left[\left(T_{h}-t_{h}\right)^{1 / 2}+\left(T_{c}-t_{c}\right)^{1 / 2}\right]^{2}
$$

Thus, $Q=\left[(200-95)^{1 / 2}+(100-20)^{1 / 2}\right]^{2}=368.30$, and

$$
\begin{aligned}
\Delta T_{m} & =\frac{125 / 2}{\ln [(368.30+125) /(368.30-125)]} \\
& =88.42^{\circ} \mathrm{C}\left(159.16^{\circ} \mathrm{F}\right)
\end{aligned}
$$

5. Use the correction factor for a 1-1 cross flow. The mean temperature difference for a 1-1 crossflow heat exchanger can be calculated by using the correction factor determined from Fig. 7.12. The mean temperature difference will be the product of this factor and the log mean temperature difference for countercurrent flow. To obtain the correction factor $F$, calculate the value of two parameters $P$ and $R$ :

$$
\begin{aligned}
P & =\frac{t_{h}-t_{c}}{T_{h}-t_{c}} \\
& =\frac{95-20}{200-20}=0.42 \\
R & =\frac{T_{h}-T_{c}}{t_{h}-t_{c}} \\
& =\frac{200-100}{95-20}=1.33
\end{aligned}
$$

From Fig. 7.12; with these values of $P$ and $R, F$ is found to be 0.91 . Then,

$$
\Delta T_{m}=F \Delta T_{L M}=0.91(91.93)=83.66^{\circ} \mathrm{C}\left(150.58^{\circ} \mathrm{F}\right)
$$

6. Use the correction factor for a 1-2 cross flow. The mean temperature difference for a 1-2 cross-flow heat exchanger can be calculated using the same procedure as used for a 1-1 cross-flow heat exchanger, except that the value of $F$ is determined from Fig. 7.13.


FIGURE 7.12 Correction factor for one-pass crossflow. (From "Engineering Data Book, 1966, "Natural Gas Processors Suppliers Association.)


FIGURE 7.13 Correction factor for two-pass crossflow. (From "Engineering Data Book, 1966," Natural Gas Processors Suppliers Association.)

For $P=0.42$ and $R=1.33, F=0.98$ (from Fig. 7.13), so

$$
\Delta T_{m}=F \Delta T_{L M}=0.98(91.93)=90.09^{\circ} \mathrm{C}\left(162.16^{\circ} \mathrm{F}\right)
$$

Related Calculations. Mean temperature differences for multipass heat exchangers may also be calculated by using appropriate correction factors for the log mean temperature difference for countercurrent flow

$$
\Delta T_{m}=F \Delta T_{L M}
$$

Curves for determining values of $F$ are presented in many of the references [1-4,6,10,11].
For shell-and-tube heat exchangers with cross-flow baffles, the preceding methods assume that an adequate number of baffles has been provided. If the shell-side fluid makes less than eight passes across the tube bundle, the mean temperature difference may need to be corrected for this cross-flow condition. Appropriate curves are presented in Caglayan and Buthod [20]. The curves in this reference may also be used to determine correction factors for cross-flow exchangers with one shell pass and more than two tube passes.

The methods presented above are applicable only for conditions in which the heat transferred is a straight-line function of temperature. For systems that do not meet this condition, the total heatrelease curve can be treated in sections, each section of which closely approximates the straight-line requirement. A log mean temperature difference can then be calculated for each section. Common examples in which this approach is encountered include (1) total condensers in which the condensate is subcooled after condensation, and (2) vaporizers in which the fluid enters as a subcooled liquid, the liquid is heated to the saturation temperature, the fluid is vaporized, and the vapor is heated and leaves in a superheated state.

Other types of heat-exchanger configurations not illustrated here are sometimes used. Curves for determining the value of $F$ for these are presented in Ref. 11. These configurations include dividedflow and split-flow exchangers.

### 7.22 OVERALL HEAT-TRANSFER COEFFICIENT FOR SHELL-AND-TUBE HEAT EXCHANGER

A shell-and-tube exchanger with the following geometry is available:

$$
\begin{aligned}
D_{s} & =\text { shell diameter }=25 \mathrm{in}(0.635 \mathrm{~m}) \\
n & =\text { number of tubes }=532 \\
D_{o} & =\text { tube outside diameter }=0.75 \mathrm{in}(0.019 \mathrm{~m}) \\
D_{i} & =\text { tube inside diameter }=0.62 \text { in }(0.016 \mathrm{~m}) \\
L & =\text { tube length }=16 \mathrm{ft}(4.88 \mathrm{~m}) \\
s & =\text { tube spacing }=0.9375 \mathrm{in}, \text { triangular }(0.024 \mathrm{~m}) \\
B & =\text { baffle spacing }=9.5 \mathrm{in}(0.241 \mathrm{~m})
\end{aligned}
$$

There is one tube-side pass and one shell-side pass, and the tube material is stainless steel with a thermal conductivity of $10 \mathrm{Btu} /(\mathrm{h})(\mathrm{ftt})\left({ }^{\circ} \mathrm{F}\right)[17 \mathrm{~W} /(\mathrm{m})(\mathrm{K})]$.

Calculate the overall heat-transfer coefficient for this heat exchanger under the following service conditions:

## Tube Side

Liquid undergoing sensible-heat transfer:

$$
\begin{aligned}
W_{t} & =\text { flow rate }=500,000 \mathrm{lb} / \mathrm{h}(226,795 \mathrm{~kg} / \mathrm{h}) \\
c & =\text { specific heat }=0.5 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)[2.1 \mathrm{~kJ} /(\mathrm{kg})(\mathrm{K})]
\end{aligned}
$$

```
\(\mu=\) viscosity \(=1.21 \mathrm{lb} /(\mathrm{ft})(\mathrm{h})(0.5 \mathrm{cP})\)
        specific gravity \(=0.8\)
    \(k=\) thermal conductivity \(=0.075 \mathrm{Btu} /(\mathrm{h})(\mathrm{ft})\left({ }^{\circ} \mathrm{F}\right)[0.13 \mathrm{~W} /(\mathrm{m})(\mathrm{K})]\)
```

Shell Side
Liquid undergoing sensible-heat transfer:

```
\(W_{s}=\) flow rate \(=200,000 \mathrm{lb} / \mathrm{h}(90,718 \mathrm{~kg} / \mathrm{h})\)
    \(c=\) specific heat \(=1.0 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)[4.19 \mathrm{~kJ} /(\mathrm{kg})(\mathrm{K})]\)
    \(\mu=\) viscosity \(=2.0 \mathrm{lb} /(\mathrm{ft})(\mathrm{h})(0.83 \mathrm{cP})\)
        specific gravity \(=1.0\)
    \(k=\) thermal conductivity \(=0.36 \mathrm{Btu} /(\mathrm{h})(\mathrm{ft})\left({ }^{\circ} \mathrm{F}\right)[0.62 \mathrm{~W} /(\mathrm{m})(\mathrm{K})]\)
```

In addition, the fouling heat-transfer coefficient is $1000 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)$ [5670 W/(m $\left.\left.{ }^{2}\right)(\mathrm{K})\right]$. Assume that the change in viscosity with temperature is negligible, that is, $\mu_{w} / \mu_{b}=1.0$.

## Calculation Procedure

1. Calculate the Reynolds number inside the tubes. The Reynolds number is $D G / \mu$, where $G$ is the mass flow rate.

$$
\begin{aligned}
G & =\frac{500,000}{532 \text { tubes }(0.62 / 12)^{2}(\pi / 4)}=448,278 \mathrm{lb} /(\mathrm{h})(\mathrm{ft})^{2} \\
D G / \mu & =\frac{(0.62 / 12) 448,278}{1.21}=19,141
\end{aligned}
$$

2. Calculate $\boldsymbol{h}_{\boldsymbol{i}}$, the heat-transfer coefficient inside the tubes. For Reynolds numbers greater than 8000,

$$
h_{i}=\frac{0.023 c G}{(c \mu / k)^{2 / 3}(D G / \mu)^{0.2}}
$$

Thus,

$$
\begin{aligned}
h_{i} & =\frac{0.023(0.5)(448,278)}{[0.5(1.21) / 0.075]^{2 / 3} 19,141^{0.2}} \\
& =178.6 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[1013 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]
\end{aligned}
$$

3. Calculate the Reynolds number for the shell side. For the shell side, $G=W_{s} / a_{c}$, where the flow area $a_{c}=B D_{s}\left(s-D_{o}\right) / s$. Then,

$$
\begin{aligned}
a_{c} & =\frac{(9.5 / 12)(25 / 12)(0.9375-0.75)}{0.9375} \\
& =0.33 \mathrm{ft}^{2}\left(0.0307 \mathrm{~m}^{2}\right)
\end{aligned}
$$

So,

$$
\begin{aligned}
D_{o} G / \mu & =\frac{(0.75 / 12)(200,000 / 0.33)}{2.0} \\
& =18,940
\end{aligned}
$$

4. Calculate $\boldsymbol{h}_{\boldsymbol{o}}$, the heat-transfer coefficient outside the tubes. Now,

$$
\begin{aligned}
h & =\frac{0.273 c G}{(c \mu / k)^{2 / 3}\left(D_{o} G / \mu\right)^{0.365}} \\
& =\frac{0.273(1.0)(200,000 / 0.33)}{[1.0(2.0) / 0.36]^{2 / 3} 18,940^{0.365}} \\
& =1450.7 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)
\end{aligned}
$$

Then, correcting for flow bypassing (see Example 7.20),

$$
h_{o}=h F_{1} F_{r}=h(0.8)\left(B / D_{s}\right)^{1 / 6}(1.0)
$$

So,

$$
\begin{aligned}
h_{o} & =1450.7(0.8)(9.5 / 25)^{1 / 6}(1.0) \\
& =987.7 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[5608 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]
\end{aligned}
$$

5. Calculate $\boldsymbol{h}_{w}$, the heat-transfer coefficient across the tube wall. The heat-transfer coefficient across the tube wall $h_{w}$ can be calculated from $h_{w}=2 k /\left(D_{o}-D_{i}\right)$. Thus,

$$
\begin{aligned}
h_{w} & =\frac{2(10)}{(0.75 / 12)-(0.62 / 12)} \\
& =1846 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[10,480 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]
\end{aligned}
$$

6. Calculate the overall heat-transfer coefficient. The formula is

$$
\frac{1}{U}=\frac{1}{h_{o}}+\frac{1}{h_{i}\left(D_{i} / D_{o}\right)}+\frac{1}{h_{w}}+\frac{1}{h_{s}}
$$

where $U=$ overall heat-transfer coefficient
$h_{o}=$ outside heat-transfer coefficient
$h_{i}=$ inside heat-transfer coefficient
$h_{w}=$ heat transfer across tube wall
$h_{s}=$ fouling heat-transfer coefficient
$D_{i}=$ inside diameter
$D_{o}=$ outside diameter
Then,

$$
\frac{1}{U}=\frac{1}{987.7}+\frac{1}{178.6(0.62 / 0.75)}+\frac{1}{1846}+\frac{1}{1000}
$$

So, $U=107.2 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[608.8 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.
Related Calculations. The method described for calculating the overall heat-transfer coefficient is also used to calculate the overall resistance to conduction of heat through a composite wall containing materials in series that have different thicknesses and thermal conductivities. For this case, each individual heat-transfer coefficient is equal to the thermal conductivity of a particular material divided by its thickness. The amount of heat transferred by conduction can then be determined from the formula

$$
Q=\left(t_{1}-t_{2}\right) \frac{1}{R} A
$$

where $Q=$ heat transferred
$t_{1}=$ temperature of the hot surface
$t_{2}=$ temperature of the cold surface
$A=$ area of wall
$R=$ overall resistance, which equals

$$
\frac{x_{1}}{k_{1}}+\frac{x_{2}}{k_{2}}+\frac{x_{3}}{k_{3}}+\cdots
$$

where $x=$ thickness
$k=$ thermal conductivity
It is seen from inspection that $U=1 / R$.

### 7.23 OUTLET TEMPERATURES FOR COUNTERCURRENT HEAT EXCHANGER

For the heat exchanger described in Example 7.22, calculate the outlet temperatures and the amount of heat transferred if the tube-side fluid enters at $68^{\circ} \mathrm{F}(293 \mathrm{~K})$ and the shell-side fluid enters at $500^{\circ} \mathrm{F}$ (533 K).

## Calculation Procedure

1. Determine the heat-transfer surface. The surface $A=\pi n D_{o} L=\pi(532)(0.75 / 12)(16)$, so $A=1670 \mathrm{ft}^{2}\left(155.2 \mathrm{~m}^{2}\right)$.
2. Determine the thermal effectiveness. The thermal effectiveness of a countercurrent heat exchanger can be determined from Fig. 7.14. Now,

$$
\begin{aligned}
\frac{U A}{w c} & =\frac{107.2(1670)}{500,000(0.5)} \\
& =0.716
\end{aligned}
$$

and,

$$
\begin{aligned}
R & =\frac{500,000(0.5)}{200,000(1.0)} \\
& =1.25
\end{aligned}
$$

So, from Fig. 7.14, the thermal effectiveness $P=0.39$.
3. Determine outlet temperatures. Because $P=\left(t_{2}-t_{1}\right) /\left(T_{1}-t_{1}\right)=0.39$,

$$
\begin{aligned}
t_{2} & =t_{1}+P\left(T_{1}-t_{1}\right)=68+(0.39)(500-68) \\
& =236.5^{\circ} \mathrm{F}
\end{aligned}
$$

Now, by definition, $w c\left(t_{2}-t_{1}\right)=W C\left(T_{1}-T_{2}\right)$, and $R=w c /(W C)$, so $T_{2}=T_{1}-R\left(t_{2}-t_{1}\right)$. Thus,

$$
\begin{aligned}
T_{2} & =500-1.25(236.5-68) \\
& =289.4^{\circ} \mathrm{F}(416 \mathrm{~K})
\end{aligned}
$$



FIGURE 7.14 Temperature efficiency for counterflow exchangers [11].

## 4. Determine the amount of heat transferred. Use the formula,

$$
Q=w c\left(t_{2}-t_{1}\right)
$$

where $Q=$ heat rate
$w=$ flow rate for fluid being heated
$c=$ specific heat for fluid being heated

Then,

$$
\begin{aligned}
Q & =500,000(0.5)(236.5-68) \\
& =42,120,000 \mathrm{Btu} / \mathrm{h}(12,343,000 \mathrm{~W})
\end{aligned}
$$

(The calculation can instead be based on the temperatures, flow rate, and specific heat for the fluid being cooled.)

Related Calculations. Figure 7.14 can also be used to determine the thermal effectiveness for exchangers in which one fluid is isothermal. For this case, $R=0$.

### 7.24 OUTLET TEMPERATURES FOR 1-2 MULTIPASS HEAT EXCHANGER

Calculate the outlet temperatures and the amount of heat transferred for the exchanger described in Example 7.23 if the tube side is converted from single-pass to two-pass.

## Calculation Procedure

1. Determine the overall heat-transfer coefficient. The heat-transfer coefficient on the tube side is proportional to $G^{0.8}$. The mass velocity $G$ will be doubled because the exchanger is to be converted to two passes on the tube side. Therefore, $h_{i}=178.6(2)^{0.8}=310.9 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[1764 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$. The new overall heat-transfer coefficient can now be calculated:

$$
\begin{aligned}
\frac{1}{U} & =\frac{1}{987.7}+\frac{1}{(310.9)(0.62 / 0.75)}+\frac{1}{1846}+\frac{1}{1000} \\
& =155.2 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[880.4 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]
\end{aligned}
$$

2. Determine the thermal effectiveness. The thermal effectiveness of a $1-2$ multipass exchanger can be determined from Fig. 7.15. Now,

$$
\begin{aligned}
\frac{U A}{w c} & =\frac{155.2(1670)}{500,000(0.5)} \\
& =1.037
\end{aligned}
$$

and $R=1.25$, so from Fig. 7.15, the thermal effectiveness $P=0.43$.
3. Determine the outlet temperatures. See Example 7.23, step 3. Now, $t_{2}-t_{1}=0.43(500-$ 68) $=185.8^{\circ} \mathrm{F}$, so $t_{2}=185.8+68=253.8^{\circ} \mathrm{F}$; and $T_{2}-T_{1}=R\left(t_{2}-t_{1}\right)=1.25(185.8)=232.2^{\circ} \mathrm{F}$, so $T_{2}=500-232.2=267.8^{\circ} \mathrm{F}(404 \mathrm{~K})$.
4. Calculate the amount of heat transferred. See Example 7.23, step 4. Now, $Q=500,000$ $\times(0.5)(185.8)=46,450,000 \mathrm{Btu} / \mathrm{h}(13,610,000 \mathrm{~W})$.

Related Calculations. The thermal effectiveness of a 2-4 multipass heat exchanger can be determined from Fig. 7.16. The value of $R$ for exchangers that have one isothermal fluid is zero, for both $1-2$ and 2-4 multipass heat exchangers.


FIGURE 7.15 Temperature efficiency for heat exchangers with one shell pass and even number of tube passes [11].

### 7.25 CONDENSATION FOR VERTICAL TUBES

Calculate the condensing coefficient for a vertical tube with an inside diameter of 0.62 in ( 0.016 m ) if steam with these properties is condensing on the inside of the tube at a rate of $50 \mathrm{lb} / \mathrm{h}$ ( $22.68 \mathrm{~kg} / \mathrm{h}$ ):


FIGURE 7.16 Temperature efficiency for heat exchangers with two shell passes and with four or a multiple of four tube passes [11].

$$
\begin{aligned}
\rho_{L} & =\text { liquid density }=60 \mathrm{lb} / \mathrm{ft}^{3}\left(961.1 \mathrm{~kg} / \mathrm{m}^{3}\right) \\
\rho_{v} & =\text { vapor density }=0.0372 \mathrm{lb} / \mathrm{ft}^{3}\left(0.60 \mathrm{~kg} / \mathrm{m}^{3}\right) \\
\mu_{L} & =\text { liquid viscosity }=0.72 \mathrm{lb} /(\mathrm{ft})(\mathrm{h})(0.298 \mathrm{cP}) \\
\mu_{v} & =\text { vapor viscosity }=0.0313 \mathrm{lb} /(\mathrm{ft})(\mathrm{h})(0.0129 \mathrm{cP}) \\
c & =\text { liquid specific heat }=1.0 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)[4.19 \mathrm{~kJ} /(\mathrm{kg})(\mathrm{K})] \\
k & =\text { liquid thermal conductivity }=0.395 \mathrm{Btu} /(\mathrm{h})(\mathrm{ftt})\left({ }^{\circ} \mathrm{F}\right)[0.683 \mathrm{~W} /(\mathrm{m})(\mathrm{K})]
\end{aligned}
$$



FIGURE 7.17 Dukler plot for condensing-film coefficients.

## Calculation Procedure

1. Select the calculation method to be used. Use the Dukler theory [18], which assumes that three fixed factors must be known to establish the value of the average heat-transfer coefficient for condensing inside vertical tubes. These are the terminal Reynolds number ( $4 \Gamma / \mu$ ), the Prandtl number $(c \mu / k)$ of the condensed phase, and a dimensionless group designated $A_{d}$ and defined as follows:

$$
A_{d}=\frac{0.250 \mu_{L}^{1.173} \mu_{v}^{0.16}}{g^{2 / 3} D_{i}^{2} \rho_{L}^{0.553} \rho_{v}^{0.78}}
$$

In these equations,

$$
\Gamma=W /\left(n \pi D_{i}\right)
$$

where $W=$ mass flow rate
$n=$ number of tubes
$D_{i}=$ inside tube diameter
$\rho_{L}=$ liquid density
$\rho_{v}=$ vapor density
$g=$ gravitational constant
$\mu_{L}=$ liquid viscosity
$\mu_{o}=$ vapor viscosity
The Reynolds and Prandtl numbers are related to the condensing coefficient in Fig. 7.17. However, that figure is based on $A_{d}=0$, which assumes no interfacial shear. The following factors can be used to evaluate the effects of any interfacial shear ( $h=$ coefficient with interfacial shear; $h_{0}=$ coefficient with no interfacial shear):

| Terminal Reynolds <br> number $4 \Gamma / \mu$ | $A_{d}=0$ | $A_{d}=10^{-5}$ | $A_{d}=10^{-4}$ | $A_{d}=2 \times 10^{-4}$ |
| :---: | :---: | :---: | :---: | :---: |
|  | 1.0 | 1.0 | 1.03 | 1.05 |
| 500 | 1.0 | 1.03 | 1.15 | 1.28 |
| 1000 | 1.0 | 1.07 | 1.40 | 1.68 |
| 3000 | 1.0 | 1.25 | 2.25 | 2.80 |
| 10,000 | 1.0 | 1.90 | 4.35 | 6.00 |
| 30,000 | 1.0 | 3.30 | 8.75 | 13.00 |

2. Calculate the terminal Reynolds number $\mathbf{4} \boldsymbol{\Gamma} / \boldsymbol{\mu}$. Since $\Gamma=W /\left(n \pi D_{i}\right)=50 /[1.0 \pi(0.62 /$ $12)]=308 \mathrm{lb} /(\mathrm{h})(\mathrm{ft}), 4 \Gamma / \mu=4(308) / 0.72=1711.3$.
3. Calculate the Prandtl number. Thus, $c \mu / k=1.0(0.72) / 0.395=1.82$.
4. Calculate $\boldsymbol{h}_{\mathbf{0}}$. Refer to Fig. 7.17. For $4 \Gamma / \mu=1711.3$ and $c \mu / k=1.82$, $\left(h \mu_{L}^{2} / \rho_{L}^{2} g k^{3}\right)^{1 / 3}=$ 0.21 . Therefore,

$$
\begin{aligned}
h & =0.21\left[\frac{60^{2}\left(4.18 \times 10^{8}\right) 0.395^{3}}{0.72^{2}}\right]^{1 / 3} \cdot \\
& =1183 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[6720 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]
\end{aligned}
$$

5. Calculate $\boldsymbol{A}_{d}$. Thus,

$$
\begin{aligned}
A_{d} & =\frac{0.250 \mu_{L}^{1.173} \mu_{v}^{0.16}}{g^{2 / 3} D_{i}^{2} \rho_{L}^{0.553} \rho_{v}^{0.78}} \\
& =\frac{(0.250)(0.72)^{1.173}(0.0313)^{0.16}}{\left(4.18 \times 10^{8}\right)^{2 / 3}(0.62 / 12)^{2}(60)^{0.553}(0.0374)^{0.78}} \\
& =8.876 \times 10^{-5}
\end{aligned}
$$

6. Calculate $\boldsymbol{h}$. For $A_{d}=8.876 \times 10^{-5}$ and $4 \Gamma / \mu=1711.3, h / h_{0}$ is approximately 1.65 from step 1. Then, $h=1.65 h_{0}=1.65(1183)=1952 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[11,088 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.

Related Calculations. For low values of Reynolds number $(4 \Gamma / \mu)$, the Nusselt equation can be used to predict condensing heat-transfer coefficients for vertical tubes:

$$
h=0.925 k\left(\frac{\rho^{2} g}{\mu \Gamma}\right)^{1 / 3}
$$

where $h=$ heat-transfer coefficient
$k=$ liquid thermal conductivity
$\rho=$ liquid density
$g=$ gravitational constant
$\mu=$ liquid viscosity
$\Gamma=$ condensate rate per unit periphery
It can be seen from Fig. 7.17 that the condensing heat-transfer coefficient for a fluid with a Prandtl number of approximately 2 (for instance, steam) is not strongly dependent on flow rate or Reynolds number. For this reason, heat-transfer coefficients for steam condensing on vertical tubes are frequently not calculated, but are assigned a value of 1500 to $2000 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)$ [8500 to $\left.11,340 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.

This approach can be used for condensing on the outside of vertical tubes. The equivalent diameter should be used in evaluating the value of $A_{d}$, and the outside tube diameter should be used in calculating the terminal Reynolds number.

Heat-transfer coefficients for falling films can also be predicted from Fig. 7.17. The coefficient obtained should be multiplied by 0.75 to obtain heat-transfer coefficients for falling-film mechanisms.

A minimum flow rate is required to produce a falling film on vertical tubes when not condensing. The minimum flow rate can be predicted with the equation

$$
\Gamma_{\min }=19.5\left(\mu s \sigma^{3}\right)^{1 / 5}
$$

where $\Gamma_{\text {min }}=$ tube loading, in $\mathrm{lb} /(\mathrm{h})(\mathrm{ft})$
$\mu=$ liquid viscosity, in centipoise
$s=$ liquid specific gravity
$\sigma=$ surface tension, in dyn $/ \mathrm{cm}$
If this minimum is not achieved, the perimeter of the tube will not be uniformly wetted. Once a falling film has been induced, however, a lower terminal flow rate can be realized without destroying the film. This minimum terminal rate can be predicted with the equation

$$
\Gamma_{T}=2.4\left(\mu s \sigma^{3}\right)^{1 / 5}
$$

where $\Gamma_{T}=$ terminal tube loading, in $\mathrm{lb} /(\mathrm{h})(\mathrm{ft})$
This criterion establishes the maximum amount of material that can be vaporized with a fallingfilm vaporizer. Approximately 85 percent of the entering material can be vaporized in a single pass without destroying the film. If tube loadings below the terminal loading are attempted, the film will break and form rivulets. Part of the tube surface will not be wetted, and the result will be reduced heat transfer with possible increased fouling of the heat-transfer surface.

For vertical condensers, condensate can be readily subcooled if required. The subcooling occurs as falling-film heat transfer, so the procedure discussed for falling-film heat exchangers can be used to calculate heat-transfer coefficients.

Condensation of mixed vapors of immiscible liquids is not well understood. The conservative approach is to assume that two condensate films are present and all the heat must be transferred through both films in series. Another approach is to use a mass fraction average thermal conductivity and calculate the heat-transfer coefficient using the viscosity of the film-forming component (the organic component for water-organic mixtures).

The recommended approach is to use a shared-surface model and calculate the effective heattransfer coefficient as

$$
h_{L}=V_{A} h_{A}+\left(1-V_{A}\right) h_{B}
$$

where $h_{L}=$ the effective heat-transfer coefficient
$h_{A}=$ the heat-transfer coefficient for liquid $A$ assuming it only is present
$h_{B}=$ the heat-transfer coefficient for liquid $B$ assuming it only is present
$V_{A}=$ the volume fraction of liquid $A$ in the condensate

### 7.26 CONDENSATION INSIDE HORIZONTAL TUBES

Calculate the effective condensing coefficient for a horizontal tube with an inside diameter of 0.62 in $(0.016 \mathrm{~m})$ and a length of $9 \mathrm{ft}(2.74 \mathrm{~m})$ for a fluid with the following properties condensing at a rate of $126 \mathrm{lb} / \mathrm{h}(57.15 \mathrm{~kg} / \mathrm{h})$ :

```
\(\rho_{L}=\) liquid density \(=50 \mathrm{lb} / \mathrm{ft}^{3}\left(800.9 \mathrm{~kg} / \mathrm{m}^{3}\right)\)
\(\rho_{v}=\) vapor density \(=1.0 \mathrm{lb} / \mathrm{ft}^{3}\left(16.02 \mathrm{~kg} / \mathrm{m}^{3}\right)\)
\(\mu=\) liquid viscosity \(=0.25 \mathrm{lb} /(\mathrm{ft})(\mathrm{h})(0.104 \mathrm{cP})\)
    \(c=\) liquid specific heat \(=0.55 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)[2.30 \mathrm{~kJ} /(\mathrm{kg})(\mathrm{K})]\)
    \(k=\) liquid thermal conductivity \(=0.08 \mathrm{Btu} /(\mathrm{h})(\mathrm{ft})\left({ }^{\circ} \mathrm{F}\right)[0.14 \mathrm{~W} /(\mathrm{m})(\mathrm{K})]\)
```


## Calculation Procedure

1. Select the calculation method to be used. Condensation inside horizontal tubes can be predicted assuming two mechanisms. The first assumes stratified flow, with laminar film condensation. The
second assumes annular flow and is approximated with single-phase heat transfer using an equivalent mass velocity to reflect the two-phase flow. For the stratified-flow assumption, the further assumption is made that the rate of condensation on the stratified layer of liquid running along the bottom of the tube is negligible. Consequently, this layer of liquid must not exceed values assumed without being appropriately accounted for.

The following equations can be used to predict heat-transfer coefficients for condensation inside horizontal tubes: For stratified flow,

$$
h_{c}=0.767 k\left(\frac{\rho_{L}^{2} g L}{n \mu W}\right)^{1 / 3}
$$

For annular flows,
a. $h_{a} D_{i} / k=0.0265(c \mu / k)^{1 / 3}\left(D G_{E} / \mu\right)^{0.8}$
when $R e_{L}$ is greater than 5000 and $R e_{v}$ greater then 20,000 , or
b. $h_{a} D_{i} / k=5.03(c \mu / k)^{1 / 3}\left(D G_{E} / \mu\right)^{1 / 3}$
when $R e_{L}$ is less than 5000 or $R e_{v}$ less than 20,000.

In these equations, $R e_{L}=D G_{L} / \mu, R e_{v}=\left(D G_{v} / \mu\right)\left(\rho_{L} / \rho_{v}\right)^{1 / 2}$, and $G_{E}=G_{L}+G_{v}\left(\rho_{L} / \rho_{v}\right)^{1 / 2}$,
where $h=$ heat-transfer coefficient
$\rho_{L}=$ liquid density
$\rho_{v}=$ vapor density
$g=$ gravitational constant
$k=$ liquid thermal conductivity
$\mu=$ liquid viscosity
$L=$ tube length
$n=$ number of tubes
$W=$ condensate flow rate
$G_{E}=$ equivalent mass velocity
$G_{L}=$ liquid mass velocity assuming only liquid is flowing
$G_{v}=$ vapor mass velocity assuming only vapor is flowing
$D_{i}=$ inside tube diameter
$c=$ liquid specific heat
$R e_{L}=$ liquid Reynolds number
$R e_{v}=$ vapor Reynolds number, defined above

Calculate the heat-transfer coefficient using both mechanisms and select the higher value calculated as the effective heat-transfer coefficient $h_{L}$. The annular-flow assumption results in heat-transfer coefficients that vary along the tube length. The condenser should be broken into increments, with the average vapor and liquid flow rates for each increment used to calculate heat-transfer coefficients. The total is the integrated value of all the increments.

For this problem, we calculate the heat-transfer coefficient for nine increments, each 1 ft $(0.305 \mathrm{~m})$ long and each condensing the same amount. The actual calculations are shown for only three increments-the first, the middle, and the last. All nine increments, however, are shown in the summary.
2. Calculate $\boldsymbol{h}_{\boldsymbol{c}}$, the condensing coefficient if stratified flow is assumed. Because an equal amount condenses in each increment, $h_{c}$ will be thesame in each increment. Thus, $W_{c, a v}=126 / 9=14 \mathrm{lb} /$

TABLE 7.3 Effect of Condensate Loading on Condensing
Coefficient

| $W /\left(n \rho D_{i}^{2.56}\right)$ | $h / h_{c}$ | $W /\left(n \rho D_{i}^{2.56}\right)$ | $h / h_{c}$ |
| :---: | :---: | :---: | :---: |
| 0 | 1.30 | 7000 | 0.85 |
| 50 | 1.25 | 9000 | 0.80 |
| 200 | 1.20 | 10,000 | 0.75 |
| 500 | 1.15 | 12,000 | 0.70 |
| 750 | 1.10 | 17,000 | 0.60 |
| 1500 | 1.05 | 20,000 | 0.50 |
| 2650 | 1.00 | 25,000 | 0.40 |
| 4000 | 0.95 | 30,000 | 0.25 |
| 6000 | 0.90 | 35,000 | 0.00 |

(h)(ft). Therefore,

$$
\begin{aligned}
h_{c} & =0.767 k\left(\frac{\rho_{L}^{2} g L}{n \mu W_{c, a v}}\right)^{1 / 3} \\
& =0.767(0.08)\left[\frac{50^{2}\left(4.18 \times 10^{8}\right)(1.0)}{1(0.25)(14)}\right]^{1 / 3} . \\
& =410.1 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[2330 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]
\end{aligned}
$$

3. Evaluate the effect of condensate loading on $\boldsymbol{h}_{\boldsymbol{c}}$. The preceding equation for $h_{c}$ assumes a certain condensate level on the bottom of the tube. This should be evaluated, which can be done by comparing the value of $W /\left(n \rho D_{i}^{2.56}\right)$ with the values shown in Table 7.3, $W$ being the condensate flow rate at the end of the tube, in pounds per hour, $\rho$ is the density, in pounds per cubic foot, and $D_{i}$ is the inside diameter, in feet.

Now, $W /\left(n \rho D_{i}^{2.56}\right)=126 /\left[1(50)(0.62 / 12)^{2.56}\right]=4961$. From Table $7.3, h / h_{c}=0.92$, so $h=$ $0.92(410.1)=377.3 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[2144 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.
4. Calculate $\boldsymbol{h}_{a}$, the condensing coefficient if annular flow is assumed. As noted earlier, this coefficient must be calculated separately for each increment of tube length. Here are the calculations for three of the nine increments:

First Increment
a. Determine average liquid and vapor flow rates. Of the total vapor input, $126 \mathrm{lb} / \mathrm{h}$, there is $14 \mathrm{lb} / \mathrm{h}$ condensed in this increment. Therefore, $W_{L 1}=(0+14) / 2=7 \mathrm{lb} / \mathrm{h}$ of liquid, and $W_{v 1}=126-$ $7=119 \mathrm{lb} / \mathrm{h}$ of vapor.
b. Calculate $G_{E}$ and $D_{i} G_{E / \mu}$. Thus,

$$
\begin{aligned}
G_{L}= & \frac{W_{L 1}}{a}=\frac{7}{(0.62 / 12)^{2}(\pi / 4)}=3338.8 \mathrm{lb} /(\mathrm{h})\left(\mathrm{ft}^{2}\right) \\
G_{v} & =\frac{W_{v 1}}{a}=\frac{119}{(0.62 / 12)^{2}(\pi / 4)}=56,759.2 \\
G_{E}= & G_{L}+G_{v}\left(\rho_{L} / \rho_{v}\right)^{1 / 2}=3338.8+(56,759.2)(50 / 1.0)^{1 / 2} \\
= & 3338.8+401,348.1=404,686.9 \mathrm{lb} /(\mathrm{h})\left(\mathrm{ft}^{2}\right) \\
& \quad \frac{D_{i} G_{E}}{\mu}=\frac{(0.62 / 12) 404,686.9}{0.25}=83,635.3
\end{aligned}
$$

c. Determine $R e_{v}$ and $R e_{L}$. Thus,

$$
\begin{aligned}
R e_{v} & =\frac{D_{i} G_{v}\left(\rho_{L} / \rho_{v}\right)^{1 / 2}}{\mu}=\frac{(0.62 / 12) 401,348.1}{0.25} \\
& =82,945.3 \\
R e_{L} & =\frac{D_{i} G_{L}}{\mu}=\frac{(0.62 / 12) 3338.8}{0.25} \\
& =690.0
\end{aligned}
$$

d. Calculate $h_{a}$. Since $R e_{v}$ is greater than 20,000 but $R e_{L}$ less than $5000, h_{a}=5.03\left(k / D_{i}\right)$ $(c \mu / k)^{1 / 3}\left(D_{i} G_{E} / \mu\right)^{1 / 3}$. Now, $(c \mu / k)^{1 / 3}=\left[0.55(0.25) / 0.08^{1 / 3}\right]=1.1979$, so

$$
\begin{aligned}
h_{a} & =5.03 \frac{0.08}{(0.62 / 12)} 1.1979(83,635.3)^{1 / 3} \\
& =408.0 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[2318 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]
\end{aligned}
$$

Middle (Fifth) Increment
a. Determine average liquid and vapor flow rates. Since the four upstream increments each condensed $14 \mathrm{lb} / \mathrm{h}, W_{L 5}=14(4+5) / 2=63 \mathrm{lb} / \mathrm{h}$ and $W_{v 5}=126-63=63 \mathrm{lb} / \mathrm{h}$.
b. Calculate $G_{E}$ and $D_{i} G_{E} / \mu$. Now, $G_{L}=G_{v}=W_{L 5} / a=63 /\left[(0.62 / 12)^{2}(\pi / 4)\right]=30,049.0 \mathrm{lb} /(\mathrm{h})$ $\left(\mathrm{ft}^{2}\right) ; G_{E}=G_{L}+G_{v}\left(\rho_{L} / \rho_{v}\right)^{1 / 2}=30,049.0+30,049.0(50 / 1.0)^{1 / 2}=30,049.0+212,478.4=$ $242,527.4 \mathrm{lb} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)$; and $D_{i} G_{E} / \mu=(0.62 / 12) 242,527.4 / 0.25=50,122.3$.
c. Determine $R e_{v}$ and $R e_{L}$. Now,

$$
\begin{aligned}
R e_{v} & =\frac{D_{i} G_{v}\left(\rho_{L} / \rho_{v}\right)^{1 / 2}}{\mu}=\frac{(0.62 / 12) 212,478.4}{0.25} \\
& =43,912.2 \\
R e_{L} & =\frac{D_{i} G_{L}}{\mu}=\frac{(0.62 / 12) 30,049.0}{0.25} \\
& =6210.1
\end{aligned}
$$

d. Calculate $h_{a}$. Since $R e_{v}$ is greater than 20,000 and $R e_{L}$ is greater than 5000,

$$
\begin{aligned}
h_{a} & =0.0265\left(k / D_{i}\right)(c \mu / k)^{1 / 3}\left(D_{i} G_{E} / \mu\right)^{0.8} \\
& =0.0265[0.08 /(0.62 / 12)] 1.1979(50,122.3)^{0.8} \\
& =282.8 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[1607 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]
\end{aligned}
$$

Last Increment
a. Determine average liquid and vapor flow rates. Now, $W_{L 9}=14(8+9) / 2=119 \mathrm{lb} / \mathrm{h}$ and $W_{v 9}=$ $126-119=7 \mathrm{lb} / \mathrm{h}$.
b. Calculate $G_{E}$ and $D_{i} G_{E} / \mu$. Now, $G_{L}=119 /\left[(0.62 / 12)^{2}(\pi / 4)\right]=56,759.2 \mathrm{lb} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)$; $G_{v}=7 /\left[(0.62 / 12)^{2}(\pi / 4)\right]=3338.8 \quad \mathrm{lb} /(\mathrm{h})\left(\mathrm{ft}^{2}\right) ; \quad G_{E}=G_{L}+G_{v}\left(\rho_{L} / \rho_{v}\right)^{1 / 2}=56,759.2+$ $3338.8(50 / 1.0)^{1 / 2}=56,759.2+23,608.7=80,367.9 \mathrm{lb} /(\mathrm{h})\left(\mathrm{ft}^{2}\right) ; \quad$ and $\quad D_{i} G_{E} / \mu=(0.62 / 12)$ 80,367.9/0.25 $=16,609.4$.
c. Determine $R e_{v}$ and $R e_{L}$. Thus, $\operatorname{Re}_{L}=D_{i} G_{L} / \mu=(0.62 / 12) 56,759.2 / 0.25=11,730.2 ; R e_{v}=$ $D_{i} G_{v}\left(\rho_{L} / \rho_{v}\right)^{1 / 2} / \mu=(0.62 / 12) 23,608.7 / 0.25=4879.1$.
d. Calculate $h_{a}$. Since $R e_{v}$ is less than 20,000 and $R e_{L}$ greater than 5000,

$$
\begin{aligned}
h_{a} & =5.03\left(k / D_{i}\right)(c \mu / k)^{1 / 3}\left(D_{i} G_{E} / \mu\right)^{1 / 3} \\
& =5.03[0.08 /(0.62 / 12)] 1.1979(16,609.4)^{1 / 3} \\
& =238.0 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[1353 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]
\end{aligned}
$$

5. Compare heat-transfer coefficients. The effective heat-transfer coefficient $h_{L}$ is the larger value of $h_{c}$ and $h_{a}$, as indicated here:

| Increment | $h_{c}$ | $h_{a}$ | $h_{L}$ |
| :---: | :---: | :---: | :---: |
| 1 | 377.3 | 408.0 | 408.0 |
| 2 | 377.3 | 392.7 | 392.7 |
| 3 | 377.3 | 378.7 | 378.7 |
| 4 | 377.3 | 362.2 | 377.3 |
| 5 | 377.3 | 282.8 | 377.3 |
| 6 | 377.3 | 244.3 | 377.3 |
| 7 | 377.3 | 204.3 | 377.3 |
| 8 | 377.3 | 272.8 | 377.3 |
| 9 | 377.3 | 238.0 | 377.3 |

The average value of $h_{L}$ is $382.6 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[2174 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.
Related Calculations. Condensation of mixed vapors of immiscible liquids can be treated in the same manner as outlined in Example 7.25.

No good methods are available for calculating heat-transfer coefficients when appreciable subcooling of the condensate is required. A conservative approach is to calculate a superficial mass velocity assuming the condensate fills the entire tube and use the equations presented above for single-phase heat transfer inside tubes. This method is less conservative for higher condensate loads.

### 7.27 CONDENSATION OUTSIDE HORIZONTAL TUBES

For the following conditions, calculate the heat-transfer coefficient when condensing at a rate of $54,000 \mathrm{lb} / \mathrm{h}(24,493.9 \mathrm{~kg} / \mathrm{h})$ on the outside of a tube bundle with a diameter of $25 \mathrm{in}(0.635 \mathrm{~m})$ with nine baffle sections each 12 in $(0.305 \mathrm{~m})$ long. The bundle contains 532 tubes with an outside diameter of $0.75 \mathrm{in}(0.019 \mathrm{~m})$. The tubes are on a triangular pitch and are spaced $0.9375 \mathrm{in}(0.02381 \mathrm{~m})$ center to center. Assume equal amounts condense in each baffle section.

## Physical Properties

```
\(\rho_{L}=\) liquid density \(=87.5 \mathrm{lb} / \mathrm{ft}^{3}\left(1401.6 \mathrm{~kg} / \mathrm{m}^{3}\right)\)
\(\rho_{v}=\) vapor density \(=1.03 \mathrm{lb} / \mathrm{ft}^{3}\left(16.5 \mathrm{~kg} / \mathrm{m}^{3}\right)\)
    \(\mu=\) liquid viscosity \(=0.7 \mathrm{lb} /(\mathrm{ft})(\mathrm{h})(0.29 \mathrm{cP})\)
    \(c=\) liquid specific heat \(=0.22 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)[0.92 \mathrm{~kJ} /(\mathrm{kg})(\mathrm{K})]\)
    \(k=\) liquid thermal conductivity \(=0.05 \mathrm{Btu} /(\mathrm{h})(\mathrm{ft})\left({ }^{\circ} \mathrm{F}\right)[0.086 \mathrm{~W} /(\mathrm{m})(\mathrm{K})]\)
```


## Calculation Procedure

1. Select the calculation method to be used. Condensation on the outside of banks of horizontal tubes can be predicted assuming two mechanisms. The first assumes laminar condensate flow; the second assumes that vapor shear dominates the heat transfer. The following equations can be used to predict heat-transfer coefficients for condensation on banks of horizontal tubes: For laminar-film condensation,

$$
h_{c}=a k\left(\frac{\rho_{L}^{2} g n L}{\mu W}\right)^{1 / 3}\left(\frac{1}{N_{r}}\right)^{1 / 6}
$$

where $a=0.951$ for triangular tube patterns, 0.904 for rotated square tube patterns, or 0.856 for square tube patterns.

For vapor-shear-dominated condensation,

$$
\frac{h_{s} D_{o}}{k}=b\left(\frac{D_{o} \rho_{L} v_{G}}{\mu}\right)^{1 / 2}\left(\frac{1}{N_{r}}\right)^{1 / 6}
$$

where $b=0.42$ for triangular tube patterns, 0.39 for square tube patterns, or 0.43 for rotated square tube patterns. In these equations, $h_{c}$ is the laminar-film heat-transfer coefficient, $h_{s}$ is the vapor-shear-dominated heat-transfer coefficient, $k$ is liquid thermal conductivity, $\rho_{L}$ is liquid density, $g$ is the gravitational constant, $\mu$ is liquid viscosity, $D_{o}$ is outside tube diameter, $L$ is tube length, $W$ is condensate flow rate, $n$ is the number of tubes, $v_{G}$ is maximum vapor velocity (defined below), and $N_{r}$ is the number of vertical tube rows (defined below). Specifically,

$$
N_{r}=\frac{m D_{s}}{s}
$$

where $D_{s}=$ shell diameter
$s=$ tube center-to-center spacing
$m=1.0$ for square tube patterns, 1.155 for triangular tube patterns, or 0.707 for rotated square tube patterns

And,

$$
v_{G}=\frac{W_{v}}{\rho_{v} a_{c}}
$$

where $W_{v}=$ vapor flow rate
$\rho_{v}=$ vapor density
$a_{c}=$ minimum flow area
In this equation, $a_{c}=B D_{s}\left(s-D_{o}\right) / s$ for square and triangular tube patterns or $a_{c}=1.5 B D_{s}(s-$ $\left.D_{o}\right) / s$ for rotated square tube patterns, $B$ being the baffle spacing.

Calculate the heat-transfer coefficient using both mechanisms, and select the higher value calculated as the effective heat-transfer coefficient $h_{L}$. The vapor-shear effects vary for each typical baffle section. The condenser should be calculated in increments, with the average vapor velocity for each increment used to calculate vapor-shear heat-transfer coefficients.

When the heat-transfer coefficients for laminar flow and for vapor shear are nearly equal, the effective heat-transfer coefficient is increased above the higher of the two values. The following table permits the increase to be approximated:

| $h_{s} / h_{c}$ | $h_{L} / h_{c}$ |
| :--- | :--- |
| 0.5 | 1.05 |
| 0.75 | 1.125 |
| 1.0 | 1.20 |
| 1.25 | 1.125 |
| 1.5 | 1.05 |

For this problem, we calculate the heat-transfer coefficient for the first increment, the middle increment, and the last increment. The summary will show the results of all increments. The increment chosen for illustration is one baffle section.
2. Calculate $h_{c}$, the condensing coefficient if laminar-film condensation is assumed. Because an equal amount condenses in each increment, $h_{c}$ will be the same in each increment. The average condensate flow rate in each increment will be $W_{i}=W_{c} / 9=54,000 / 9=6000 \mathrm{lb} / \mathrm{h}$. Now,

$$
h_{c}=0.951 k\left(\frac{\rho_{L}^{2 g n} L}{\mu W_{i}}\right)^{1 / 3}\left(\frac{1}{N_{r}}\right)^{1 / 6}
$$

where $N_{r}=1.155 D_{s} / s=1.155(25) / 0.9375=30.8$. So,

$$
\begin{aligned}
h_{c} & =0.951(0.05)\left[\frac{87.5^{2}\left(4.18 \times 10^{8}\right)(532) 1.0}{0.7(6000)}\right]^{1 / 3}\left(\frac{1}{30.8}\right)^{1 / 6} \\
& =198.7 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[1129 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]
\end{aligned}
$$

3. Calculate $\boldsymbol{h}_{s}$, the coefficient if vapor-shear domination is assumed. As noted earlier, this must be calculated separately for each increment. Here are the calculations for three of the nine increments:

First Increment
a. Calculate average vapor velocity. Now, $W_{v 1}=(54,000+54,000-6000) / 2=51,000 \mathrm{lb} / \mathrm{h}$. And,

$$
\begin{aligned}
a_{c} & =\frac{B D_{s}\left(s-D_{o}\right)}{s} \\
& =\frac{(12 / 12)(25 / 12)(0.9375-0.75)}{0.9375} \\
& =0.4167 \mathrm{ft}^{2}\left(0.0387 \mathrm{~m}^{2}\right)
\end{aligned}
$$

Therefore,

$$
\begin{aligned}
v_{G} & =\frac{W_{v 1}}{\rho a_{c}} \\
& =\frac{51,000}{1.03(0.4167)} \\
& =118,825.4 \mathrm{ft} / \mathrm{h}
\end{aligned}
$$

b. Calculate $h_{s}$. Now,

$$
\begin{aligned}
h_{s} & =0.42\left(\frac{k}{D_{o}}\right)\left(\frac{D_{o} \rho_{L} v_{G}}{\mu}\right)^{1 / 2}\left(\frac{1}{N_{r}}\right)^{1 / 6} \\
& =0.42 \frac{0.05}{(0.75 / 12)}\left[\frac{(0.75 / 12)(87.5) 118,825.4}{0.7}\right]^{1 / 2}\left(\frac{1}{30.8}\right)^{1 / 6} \\
& =182.9 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\left({ }^{\circ} \mathrm{F}\right)\left[1039 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]\right.
\end{aligned}
$$

c. Calculate $h_{L}$. Now, $h_{s} / h_{c}=182.9 / 198.7=0.921$. From the preceding table, $h_{L} / h_{c}=1.18$. So, $h_{L}=1.18(198.7)=234.5 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[1332 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.

Middle (Fifth) Increment
a. Determine average vapor flow rate. Thus, $W_{v 5}=54,000-4(6000)-0.5(6000)=27,000 \mathrm{lb} / \mathrm{h}$.
b. Calculate $h_{s}$. Refer to the calculation for the first increment. Then, $h_{s}=182.9(27,000 /$ $51,000)^{1 / 2}=133.1 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)$.
c. Calculate $h_{L}$. Thus, $h_{s} / h_{c}=133.1 / 198.7=0.67$. From the preceding table, $h_{L} / h_{c}=1.105$. So, $h_{L}=1.105(198.7)=219.6 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[1248 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.

Last Increment
a. Determine average vapor flow rate. Thus, $W_{v 9}=54,000-8(6000)-0.5(6000)=3000 \mathrm{lb} / \mathrm{h}$.
b. Calculate $h_{s}$. Refer to the calculation for the first increment. Then, $h_{s}=182.9(3000 / 51,000)^{1 / 2}=$ 44.4 Btu/(h) $\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)$.
c. Calculate $h_{L}$. Now, $h_{s} / h_{c}=44.4 / 198.7=0.223$. For this low value, assume that $h_{L}=h_{c}=$ 198.7 Btu/(h)(ft $\left.{ }^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[1129 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.
4. Summarize the results. The following table summarizes the calculations for all nine increments:

| Increment | $h_{c}$ | $h_{s}$ | $h_{L}$ |
| :---: | :---: | :---: | :---: |
| 1 | 198.7 | 182.7 | 234.5 |
| 2 | 198.7 | 171.8 | 231.5 |
| 3 | 198.7 | 159.9 | 227.5 |
| 4 | 198.7 | 147.1 | 223.5 |
| 5 | 198.7 | 133.1 | 219.6 |
| 6 | 198.7 | 117.4 | 213.6 |
| 7 | 198.7 | 99.2 | 198.7 |
| 8 | 198.7 | 76.8 | 198.7 |
| 9 | 198.7 | 44.4 | 198.7 |

The average value of $h_{L}$ is $216.3 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[1229 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.

Related Calculations. For most cases, vapor-shear condensation is not important, and the condensing heat-transfer coefficient can be calculated simply as the laminar-film coefficient.

It is important that the shell side of horizontal shell-side condensers be designed to avoid excessive condensate holdup caused by the baffle or nozzle types selected by the designer.

For bundles with slight slopes, the following correction should be applied:

$$
h_{t}=h_{c}(\cos \alpha)^{1 / 3} \quad \text { for } L / D_{o}>1.8 \tan \alpha
$$

where $h_{t}=$ heat-transfer coefficient for sloped tube
$h_{c}=$ heat-transfer coefficient for horizontal tube
$\alpha=$ angle from horizontal, in degrees
$L=$ tube length
$D_{o}=$ outside tube diameter
Condensation of mixed vapors of immiscible fluids can be treated in the same manner as outlined in Example 7.25.

Condensate subcooling when condensing on banks of horizontal tubes can be accomplished in two ways. The first method requires holding a condensate level on the shell side; heat transfer can then be calculated using the appropriate single-phase correlation. The second method requires that the vapor make a single pass across the bundle in a vertical downflow direction. Subcooling heat transfer can then be calculated using falling-film correlations.

For low-fin tubes, the laminar condensing coefficient can be calculated by applying an appropriate correction factor $F$ to the value calculated using the preceding equation for laminar-film condensation. The factor $F$ is defined thus:

$$
F=\left(\eta \frac{A_{t}}{A_{i}} \frac{D_{i}}{D_{r}}\right)^{1 / 4}
$$

where $\eta=$ weighted fin efficiency
$A_{t}=$ total outside surface
$A_{i}=$ inside surface
$D_{i}=$ inside tube diameter
$D_{r}=$ diameter at root of fins

### 7.28 CONDENSATION IN THE PRESENCE OF NONCONDENSABLES

A mixture of vapor and noncondensable gases flows through a vertical tube bundle containing 150 tubes with an inside diameter of 0.62 in $(0.016 \mathrm{~m})$ and an outside diameter of 0.75 in $(0.019 \mathrm{~m})$ at a rate of $25,000 \mathrm{lb} / \mathrm{h}(11,339.8 \mathrm{~kg} / \mathrm{h})$. The mixture enters at a temperature of $212^{\circ} \mathrm{F}(373 \mathrm{~K})$ and is cooled to a temperature of $140^{\circ} \mathrm{F}(333 \mathrm{~K})$. As cooling occurs, $15,000 \mathrm{lb} / \mathrm{h}(6803.9 \mathrm{~kg} / \mathrm{h})$ of the mixture condenses. The condensation may be assumed to be straight-line condensation. Calculate the tube length required if the outside heat-transfer coefficient is $300 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[1700 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$ and the temperature is isothermal at $104^{\circ} \mathrm{F}(313 \mathrm{~K})$. Assume the fouling heat-transfer coefficient is $1000 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[5680 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$. The tube-wall thermal conductivity is $10 \mathrm{Btu} /(\mathrm{h})(\mathrm{ft})\left({ }^{\circ} \mathrm{F}\right)$ $[17.28 \mathrm{~W} /(\mathrm{m})(\mathrm{K})]$. The physical properties of the system are as follows:

Vapor specific heat $=0.35 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)[1.47 \mathrm{~kJ} /(\mathrm{kg})(\mathrm{K})]$
Liquid specific heat $=0.7 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)[2.93 \mathrm{~kJ} /(\mathrm{kg})(\mathrm{K})$
Vapor viscosity $=0.048 \mathrm{lb} /(\mathrm{ft})(\mathrm{h})(0.020 \mathrm{cP})$
Liquid viscosity $=0.24 \mathrm{lb} /(\mathrm{ft})(\mathrm{h})(0.10 \mathrm{cP})$
Vapor thermal conductivity $=0.021 \mathrm{Btu} /(\mathrm{h})(\mathrm{ft})\left({ }^{\circ} \mathrm{F}\right)[0.036 \mathrm{~W} /(\mathrm{m})(\mathrm{K})$
Liquid thermal conductivity $=0.075 \mathrm{Btu} /(\mathrm{h})(\mathrm{ft})\left({ }^{\circ} \mathrm{F}\right)[0.13 \mathrm{~W} /(\mathrm{m})(\mathrm{K})$
Heat of vaporization $=200 \mathrm{Btu} / \mathrm{lb}(465 \mathrm{~kJ} / \mathrm{kg})$

Liquid density $=30 \mathrm{lb} / \mathrm{ft}^{3}\left(481 \mathrm{~kg} / \mathrm{m}^{3}\right)$
Vapor density $=0.9 \mathrm{lb} / \mathrm{ft}^{3}\left(14.4 \mathrm{~kg} / \mathrm{m}^{3}\right)$

## Calculation Procedure

1. Select the calculation method to be used. A heat-transfer coefficient that predicts heat transfer when both sensible heat and latent heat are being transferred can be calculated using the equation

$$
h_{c, g}=\frac{1}{\frac{Q_{g}}{Q_{T}} \frac{1}{h_{g}}+\frac{1}{h_{c}}}
$$

where $h_{c, g}=$ combined cooling-condensing heat-transfer coefficient
$h_{g}=$ heat-transfer coefficient for gas cooling only
$h_{c}=$ condensing heat-transfer coefficient
$Q_{g}=$ heat-transfer rate for cooling the gas only
$Q_{T}=$ total heat-transfer rate (includes sensible heat for gas and condensate cooling and latent heat for condensing)
2. Calculate the sensible and latent heat loads. Since straight-line condensing occurs, the mean condensing temperature may be taken as the arithmetic mean $\left(176^{\circ} \mathrm{F} ; 353 \mathrm{~K}\right)$. The heat loads are calculated assuming that all gas and vapor are cooled to the mean condensing temperature, that all condensing then occurs at this temperature, and that the uncondensed mixture plus the condensate are further cooled to the outlet temperature.

## Inlet Vapor Cooling

$$
Q_{i}=25,000(0.35)(212-176)=315,000 \mathrm{Btu} / \mathrm{h}
$$

Latent Heat of Condensation

$$
Q_{c}=15,000(200)=3,000,000 \mathrm{Btu} / \mathrm{h}
$$

## Outlet Vapor Cooling

$$
Q_{o}=10,000(0.35)(176-140)=126,000 \mathrm{Btu} / \mathrm{h}
$$

## Condensate Cooling

$$
Q_{s}=15,000(0.7)(176-140)=378,000 \mathrm{Btu} / \mathrm{h}
$$

Therefore, the total heat load $Q_{T}$ equals $Q_{i}+Q_{c}+Q_{o}+Q_{s}=3,819,000 \mathrm{Btu} / \mathrm{h}$. And $Q_{g}=Q_{i}+$ $Q_{o}=441,000 \mathrm{Btu} / \mathrm{h}$, so $Q_{T} / Q_{g}=3,819,000 / 441,000=8.66$.
3. Calculate the gas cooling heat-transfer coefficient. Use the equation $h=0.023 c G /$ $\left[(c \mu / k)^{2 / 3}(D G / \mu)^{0.2}\right]$. Base the mass velocity on the average vapor flow rate, that is, $(25,000+$ $10,000) / 2=17,500 \mathrm{lb} / \mathrm{h}$. Then $G=17,500 /\left[150(0.62 / 12)^{2}(\pi / 4)\right]=55,646.3 \mathrm{lb} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)$, and

$$
\begin{aligned}
h_{g} & =\frac{0.023(0.35)(55,646.3)}{[0.35(0.048) / 0.021]^{2 / 3}[(0.62 / 12) 55,646.3 / 0.048]^{0.2}} \\
& =57.58 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[327 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]
\end{aligned}
$$

4. Calculate the condensing coefficient. See Example 7.25. Now, $4 \Gamma / \mu=4[15,000 / 150 \pi(0.62 /$ $12)] / 0.24=10,268$, and $c \mu / k=0.7(0.24) / 0.075=2.24$. From Fig. 7.17, for the parameters calculated above, $h_{c}\left[\mu^{2} /\left(\rho^{2} g k^{3}\right)\right]^{1 / 3}=0.28$. Therefore,

$$
\begin{aligned}
h_{c} & =0.28\left[30^{2}\left(4.18 \times 10^{8}\right) 0.075^{3} / 0.24^{2}\right]^{1 / 3} \\
& =392.5 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[2229 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]
\end{aligned}
$$

5. Calculate $\boldsymbol{h}_{c, g}$. Now,

$$
\begin{aligned}
h_{c, g} & =1 /\left[\left(Q_{g} / Q_{T}\right)\left(1 / h_{g}\right)+\left(1 / h_{c}\right)\right] \\
& =1 /[(1 / 8.66)(1 / 57.58)+(1 / 392.5)] \\
& =219.6 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[1247 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]
\end{aligned}
$$

6. Calculate the overall heat-transfer coefficient. Use the equation

$$
\frac{1}{U}=\frac{1}{h_{o}}+\frac{1}{h_{s}}+\frac{1}{h_{w}}+\frac{1}{h_{c, g}\left(d_{i} / d_{o}\right)}
$$

where $U=$ overall heat-transfer coefficient
$h_{o}=$ outside heat-transfer coefficient
$h_{s}=$ fouling heat-transfer coefficient
$h_{w}=$ heat-transfer coefficient through the wall (thermal conductivity of the wall divided by its thickness)
$h_{c, g}=$ inside heat-transfer coefficient
$d_{i}=$ inside tube diameter
$d_{o}=$ outside tube diameter
Then,

$$
\begin{aligned}
\frac{1}{U} & =\frac{1}{300}+\frac{1}{1000}+\frac{1}{10 /[(0.75-0.62) / 12(2)]}+\frac{1}{219.6(0.62 / 0.75)} \\
& =96.3 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[547 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]
\end{aligned}
$$

7. Calculate the log mean temperature difference. See Example 7.21 and use the equation for countercurrent flow. Thus,

$$
\begin{aligned}
\Delta T_{L M} & =\frac{(212-104)-(140-104)}{\ln [(212-104) /(140-104)]} \\
& =65.5^{\circ} \mathrm{F}(36.4 \mathrm{~K})
\end{aligned}
$$

8. Calculate the heat-transfer surface required. The equation is

$$
\begin{aligned}
A & =\frac{Q_{T}}{U \Delta T_{L M}}=\frac{3,819,00}{96.3(65.5)} \\
& =605.4 \mathrm{ft}^{2}\left(56.24 \mathrm{~m}^{2}\right)
\end{aligned}
$$

9. Calculate the tube length required. Since $A=n \pi D_{o} L, L=605.4 /[150 \pi(0.75 / 12)]=$ $20.6 \mathrm{ft}(6.27 \mathrm{~m})$.

Related Calculations. For condensers that do not exhibit straight-line condensing, this procedure can be used by treating the problem as a series of condensing zones that approximate straight-line segments. The vapor and condensate flow rates, the heat load, the overall heat-transfer coefficient, and the log mean temperature difference will vary with each zone. The total answer is obtained by integrating all the segments. It is usually not necessary to use a large number of zones. The accuracy lost by using less than 10 zones is not significant in most cases.

For horizontal shell-side condensers, the condensate falls to the bottom of the shell, and vapor and liquid do not coexist, as assumed by the preceding method. The effect this has on the heat transfer must be considered. It is recommended that shell-side condensers with noncondensable gases present be somewhat overdesigned; perhaps 20 percent excess surface should be provided.

### 7.29 MAXIMUM VAPOR VELOCITY FOR CONDENSERS WITH UPFLOW VAPOR

Calculate the maximum velocity to avoid flooding for the vapor conditions of Example 7.28. Flooding occurs in upflow condensers when the vapor velocity is too high to permit the condensate to drain. Unstable conditions exist when flooding occurs.

## Calculation Procedure

1. Select the appropriate equation. The following equation can be used to establish the condition for flooding of vertical-upflow vapor condensers:

$$
v_{v}^{1 / 2} \rho_{v}^{1 / 4}+v_{L}^{1 / 2} \rho_{L}^{1 / 4} \leq 0.6\left[g D_{i}\left(\rho_{L}-\rho_{v}\right)\right]^{1 / 4}
$$

where $v_{L}=$ vapor velocity assuming only vapor is flowing in the tube
$v_{L}=$ liquid velocity of the condensate assuming only condensate is flowing in the tube
$\rho_{v}=$ vapor density
$\rho_{L}=$ liquid density
$D_{i}=$ inside tube diameter
$g=$ acceleration of gravity
2. Calculate the maximum allowable vapor mass-flow rate $\boldsymbol{G}_{\boldsymbol{v}}$. Now, $v_{L}=G_{L} / \rho_{L}$, and $v_{v}=$ $G_{v} / \rho_{v}$, where $G$ is mass flow rate and the subscripts $L$ and $v$ refer to liquid and vapor. For the problem at hand, $G_{L}=(15,000 / 25,000) G_{v}=0.6 G_{v}$; therefore, $v_{L}=0.6 G_{v} / \rho_{L}$. Then, substituting into the expression in step $1,\left(G_{v} / \rho_{v}\right)^{1 / 2} \rho_{v}^{1 / 4}+\left(0.6 G_{v} / \rho_{L}\right)^{1 / 2} \rho_{L}^{1 / 4}=0.6\left[g D_{i}\left(\rho_{L}-\rho_{v}\right)\right]^{1 / 4}$, or $G_{v}^{1 / 2} / \rho_{v}^{1 / 4}+0.6^{1 / 2} G_{v}^{1 / 2} / \rho_{L}^{1 / 4}=0.6\left[g D_{i}\left(\rho_{L}-\rho_{v}\right)\right]^{1 / 4}$. Then, $G_{v}^{1 / 2} / 0.9^{1 / 4}+0.6^{1 / 2} G_{v}^{1 / 2} / 30^{1 / 4}=$ $0.6[32.2(0.62 / 12)(30-0.9)]^{1 / 4}$, and $G_{v}=1.3589 \mathrm{lb} /\left(\mathrm{ft}^{2}\right)(\mathrm{s})$.
3. Calculate the maximum allowable velocity. Now, $G_{v}=\rho_{v} v_{v}$, so $v_{v}=G_{v} / \rho_{v}=1.3589 / 0.9=$ $1.51 \mathrm{ft} / \mathrm{s}(0.46 \mathrm{~m} / \mathrm{s})$.

Related Calculations. The velocity calculated above is the threshold for flooding of the condenser. Flooding causes unstable operation. A safety factor of 0.85 is commonly used when designing upflow condensers. The maximum velocity at which flooding occurs can be increased by cutting the bottom of the tube at an angle. Improvements that can be achieved are as follows:

| Angle of cut (measured <br> from horizontal) | Increase in maximum <br> flooding velocity |
| :---: | :---: |
| $30^{\circ}$ | $5 \%$ |
| $60^{\circ}$ | $25 \%$ |
| $75^{\circ}$ | $55 \%$ |

### 7.30 NUCLEATE-BOILING HEAT TRANSFER

A steel tube 1 in $(0.025 \mathrm{~m})$ in diameter and $12 \mathrm{ft}(3.66 \mathrm{~m})$ long is cooled by employing it to boil water at $1 \mathrm{~atm}(101.35 \mathrm{kPa})$. Calculate the nucleate-boiling heat-transfer coefficient if $300 \mathrm{lb} / \mathrm{h}(136.1 \mathrm{~kg} / \mathrm{h})$ of vapor is generated.

The physical properties are as follows:

```
    \(c=\) liquid specific heat \(=1.0 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)[4.2 \mathrm{~kJ} /(\mathrm{kg})(\mathrm{K})]\)
\(\rho_{L}=\) liquid density \(=60 \mathrm{lb} / \mathrm{ft}^{3}\left(961.1 \mathrm{~kg} / \mathrm{m}^{3}\right)\)
\(\rho_{v}=\) vapor density \(=0.0372 \mathrm{lb} / \mathrm{ft}^{3}\left(0.596 \mathrm{~kg} / \mathrm{m}^{3}\right)\)
\(k=\) liquid thermal conductivity \(=0.396 \mathrm{Btu} /(\mathrm{h})(\mathrm{ft})\left({ }^{\circ} \mathrm{F}\right)[0.684 \mathrm{~W} /(\mathrm{m})(\mathrm{K})]\)
\(\mu=\) liquid viscosity \(=0.72 \mathrm{lb} /(\mathrm{ft})(\mathrm{h})(0.298 \mathrm{cP})\)
\(\sigma=\) surface tension \(=0.0034 \mathrm{lb} / \mathrm{ft}(50 \mathrm{dyn} / \mathrm{cm})\)
```

$\left(\right.$ Note that $\left.1 \mathrm{~atm}=2116.8 \mathrm{lb} / \mathrm{ft}^{2}.\right)$

## Calculation Procedure

1. Select the appropriate equation. Nucleate-boiling heat-transfer coefficients can be calculated from the equation

$$
\frac{h}{c G}=\frac{\phi}{(c \mu / k)^{0.6}(D G / \mu)^{0.3}\left(\rho_{L} \sigma / P^{2}\right)^{0.425}}
$$

where $G=W \rho_{L} /\left(A \rho_{v}\right)$
$h=$ heat-transfer coefficient
$G=$ mass velocity
$P=$ absolute pressure
$A=$ heat-transfer surface (not cross-sectional flow area)
$D=$ diameter
$W=$ vapor flow rate
$\phi=$ a constant that depends on the surface condition (number of nucleation sites that can support boiling), e.g., 0.001 for steel and copper, 0.0006 for stainless steel, and 0.0004 for polished surfaces
2. Calculate G. Thus, $G=W \rho_{L} /\left(A \rho_{v}\right)=300(60) /[(1 / 12) \pi 12(0.0372)]=154,020.9$.
3. Calculate h. For a steel tube,

$$
\begin{aligned}
h & =\frac{0.001 c G}{(c \mu / k)^{0.6}(D G / \mu)^{0.3}\left(\rho_{L} \sigma / P^{2}\right)^{0.425}} \\
& =\frac{0.001(1.0)(154,020.9)}{\left[\frac{1.0(0.72)}{0.395}\right]^{0.6}\left[\frac{(1 / 12) 154,020.9}{0.72}\right]^{0.3}\left[\frac{60(0.0034)}{2116.8^{2}}\right]^{0.425}} \\
& =7517.2 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[42,698 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]
\end{aligned}
$$

Related Calculations. The mechanism of nucleate boiling has not been clearly established, but several expressions are available from which reasonable values of heat-transfer coefficients may be obtained. These do not yield exactly the same numerical results even though based on much of the same data. There is thus neither a prominent nor a unique equation for nucleate-boiling heat transfer. Either convenience or familiarity usually governs the user's selection.

Surface conditions have a profound effect on boiling heat transfer. The values of $\phi$ presented above have been obtained from plots of data. Extreme accuracy cannot be claimed for these values because of the variable condition of the surfaces in these tests.

There are upper and lower limits of applicability of the equation above. The lower limit results because natural-convection heat transfer governs at low temperature differences between the surface and the fluid. The upper limit results because a transition to film boiling occurs at high temperature differences. In film boiling, a layer of vapor blankets the heat-transfer surface and no liquid reaches the surface. Heat transfer occurs as a result of conduction across the vapor film as well as by radiation. Film-boiling heat-transfer coefficients are much less than those for nucleate boiling. For further discussion of boiling heat transfer, see Refs. 5 and 6.

### 7.31 MINIMUM TEMPERATURE DIFFERENCE TO ACHIEVE NUCLEATE BOILING

For water boiling on a 1 -in $(0.025-\mathrm{m})$ tube under the conditions of Example 7.30, determine the minimum difference between the temperature of the surface of the tube and the bulk fluid temperature required in order for nucleate boiling to occur. The coefficient of expansion for water is 0.0004 per degree Fahrenheit, and the heat of vaporization is $970 \mathrm{Btu} / \mathrm{lb}(2256 \mathrm{~kJ} / \mathrm{kg})$.

## Calculation Procedure

1. Consider the criteria required for nucleate boiling. Nucleate boiling occurs when the difference between the temperature of the hot surface and the bulk fluid temperature is above a certain value. At temperature differences less than this value, heat transfer occurs as a result of natural convection. Nucleate-boiling heat-transfer coefficients for a steel tube may be calculated using the equation

$$
\frac{h}{c G}=\frac{0.001}{(c \mu / k)^{0.6}(D G / \mu)^{0.3}\left(\rho_{L} \sigma / P^{2}\right)^{0.425}}
$$

where the nomenclature is the same as listed for Example 7.30.
Natural-convection heat-transfer coefficients may be calculated using the equations

$$
\frac{h}{c G}=\frac{0.53}{(c \mu / k)^{3 / 4}(D G / \mu)^{1 / 2}} \quad \text { and } \quad G=\left(g \beta \rho_{L}^{2} D \Delta T\right)^{1 / 2}
$$

where $g$ is the acceleration of gravity $\left(4.18 \times 10^{8} \mathrm{ft} / \mathrm{h}^{2}\right)$ and $\beta$ is the coefficient of expansion for water (for further discussion, see Example 7.17).

The equation for nucleate-boiling heat transfer can be rearranged to become a function of $\Delta T$, the temperature difference between the surface and the fluid. The minimum temperature difference required to effect nucleate boiling will occur when the heat-transfer coefficients for nucleate boiling and natural convection are equal. This will permit solution for the temperature difference $\Delta T$.
2. Obtain an equation for nucleate-boiling heat-transfer coefficient as a function of $\Delta T$. The heat load $Q=h A \Delta T=W \lambda$, where $\lambda$ is the heat of vaporization. Therefore, $W=h A \Delta T / \lambda$. Now, $G=W \rho_{L} /\left(A \rho_{v}\right)=h A \Delta T \rho_{L} /\left(A \rho_{v} \lambda\right)=h \Delta T \rho_{L} /\left(\rho_{v} \lambda\right)$.
Furthermore,

$$
\begin{aligned}
h & =\frac{0.001 c G}{(c \mu / k)^{0.6}(D G / \mu)^{0.3}\left(\rho_{L} \sigma / P^{2}\right)^{0.425}} \\
& =\frac{0.001 c G^{0.7}}{(c \mu / k)^{0.6}(D / \mu)^{0.3}\left(\rho_{L} \sigma / P^{2}\right)^{0.425}}
\end{aligned}
$$

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From above, $G^{0.7}=\left[h \Delta T \rho_{L} /\left(\rho_{\nu} \lambda\right)\right]^{0.7}$. Therefore, $h=0.001 c\left[h \Delta T \rho_{L} /\left(\rho_{\nu} \lambda\right)\right]^{0.7} /\left[(c \mu / k)^{0.6}\right.$ $\left.\times(D / \mu)^{0.3}\left(\rho_{L} \sigma / P^{2}\right)^{0.425}\right]$, or $\left.h^{0.3}=0.001 c\left[\rho_{L} /\left(\rho_{v} \lambda\right)\right]^{0.7}(\Delta T)^{0.7} /(c \mu / k)^{0.6}(D / \mu)^{0.3}\left(\rho_{L} \sigma / P^{2}\right)^{0.425}\right]$, or $h=\left\{0.001 c\left[\rho_{L} /\left(\rho_{v} \lambda\right]^{0.7} /\left[(c \mu / k)^{0.6}(D / \mu)^{0.3}\left(\rho_{L} \sigma / P^{2}\right)^{0.425}\right]\right\}^{1 / 0.3} \Delta T^{0.7 / 0.3}\right.$. Thus,

$$
\begin{aligned}
h & =\left\{\frac{0.001(1.0)\{60 /[0.0372(970)]\}^{0.7}}{\left[\frac{1.0(0.72)}{0.395}\right]^{0.6}\left[\frac{1 / 12}{0.72}\right]^{0.3}\left[\frac{60(0.0034)}{2116.8^{2}}\right]^{0.425}}\right\}^{1 / 0.3} \Delta T^{7 / 3} \\
& =21.43 \Delta T^{7 / 3}
\end{aligned}
$$

where $h$ is in Btus per hour per square foot per degree Fahrenheit, and the temperature difference is in degrees Fahrenheit.
3. Obtain an equation for natural-convection heat transfer as a function of $\Delta T$. From step $1, h=0.53 c G /\left[(c \mu / k)^{3 / 4}(D G / \mu)^{1 / 2}\right]$, and $G=\left(g \beta \rho_{L}^{2} D \Delta T\right)^{1 / 2}$. By algebra, $h=0.53 c G^{1 / 2} /$ $\left[(c \mu / k)^{3 / 4}(D / \mu)^{1 / 2}\right]$, and by substitution,

$$
\begin{aligned}
h & =0.53 c\left[\left(g \beta \rho_{L}^{2} D \Delta T\right)^{1 / 2}\right]^{1 / 2} /\left[(c \mu / k)^{3 / 4}(D / \mu)^{1 / 2}\right] \\
& =0.53 c\left(g \beta \rho_{L}^{2} D\right)^{1 / 4} \Delta T^{1 / 4} /\left[(c \mu / k)^{3 / 4}(D / \mu)^{1 / 2}\right]
\end{aligned}
$$

Thus,

$$
\begin{aligned}
h & =\frac{0.53(1.0)\left[\left(4.18 \times 10^{8}\right)(0.0004)(60)^{2}(1 / 12)\right]^{1 / 4}}{[1.0(0.72) / 0.395]^{3 / 4}[(1 / 12) / 0.72]^{1 / 2}} \Delta T^{1 / 4} \\
& =83.57 \Delta T^{1 / 4}
\end{aligned}
$$

where $h$ is in Btus per hour per square foot per degree Fahrenheit, and the temperature difference is in degrees Fahrenheit.
4. Calculate the minimum required temperature difference required for nucleate boiling. The minimum temperature difference at which nucleate boiling will occur can be calculated by equating the heat-transfer coefficients for natural convection and nucleate boiling and solving for the temperature difference. Thus, $h=21.43 \Delta T^{7 / 3}=83.57 \Delta T^{1 / 4}$. Therefore, $\Delta T\left({ }^{7 / 3-1 / 4}\right)=\Delta T^{25 / 12}=$ $83.57 / 21.43$, or $\Delta T=1.92^{\circ} \mathrm{F}(1.07 \mathrm{~K})$. Thus the minimum temperature difference between the tube surface and the water at which nucleate boiling will occur is $1.92^{\circ} \mathrm{F}$.

Related Calculations. The minimum temperature difference required for nucleate boiling to occur can also be determined by plotting the equations for nucleate-boiling and natural-convection heattransfer coefficients. The intersection of these two lines represents the required temperature difference $\Delta T$.

The procedure illustrated here can be used to obtain the minimum temperature difference required for nucleate boiling for any correlation for nucleate-boiling heat-transfer coefficients preferred by the user.

Low-fin tubes, often used for horizontal-pool boiling, reduce the minimum temperature difference required to achieve nucleate boiling. In addition, the boiling coefficients for low-fin tubes are higher than those for bare tubes at a given temperature difference.

Special boiling surfaces are available commercially that permit nucleate-boiling heat transfer at extremely low temperature differences. These surfaces also achieve much higher heat-transfer coefficients than conventional tubes; see Gottzmann, O'Neill, and Minton [32].

A kettle-type reboiler with a shell diameter of 30 in $(0.76 \mathrm{~m})$ contains a tube bundle with a diameter of $15 \mathrm{in}(0.38 \mathrm{~m})$. The bundle contains 80 tubes, each with a diameter of $1 \mathrm{in}(0.025 \mathrm{~m})$ and a length of $12 \mathrm{ft}(3.66 \mathrm{~m})$. Determine the maximum heat flux for a fluid with the following physical properties: heat of vaporization of $895 \mathrm{Btu} / \mathrm{lb}(2082 \mathrm{~kJ} / \mathrm{kg})$, surface tension of $0.00308 \mathrm{lb} / \mathrm{ft}(0.045 \mathrm{~N} / \mathrm{m})$, liquid density of $56.5 \mathrm{lb} / \mathrm{ft}^{3}\left(905 \mathrm{~kg} / \mathrm{m}^{3}\right)$, and vapor density of $0.2 \mathrm{lb} / \mathrm{ft}^{3}\left(3.204 \mathrm{~kg} / \mathrm{m}^{3}\right)$.

## Calculation Procedure

1. Determine the maximum superficial vapor velocity. The maximum superficial vapor velocity to avoid film boiling can be calculated using the equation

$$
v_{c}=\frac{3\left(\rho_{L}-\rho_{v}\right)^{1 / 4} \sigma^{1 / 4}}{\rho_{v}^{1 / 2}}
$$

where $v_{c}=$ superficial vapor velocity, in $\mathrm{ft} / \mathrm{s}$
$\rho_{L}=$ liquid density, in lb/ft ${ }^{3}$
$\rho_{v}=$ vapor density, in lb/ft ${ }^{3}$
$\sigma=$ surface tension, in lb/ft
For this problem,

$$
\begin{aligned}
v_{c} & =\frac{3(56.5-0.2)^{1 / 4} 0.00308^{1 / 4}}{0.2^{1 / 2}} \\
& =4.33 \mathrm{ft} / \mathrm{s}(1.329 \mathrm{~m} / \mathrm{s})
\end{aligned}
$$

2. Determine the maximum heat rate. The superficial vapor velocity is based on the projected area of the tube bundle

$$
a=D_{b} L
$$

where $a=$ projected area of the bundle
$D_{b}=$ bundle diameter
$L=$ bundle length
In this case, $a=(15 / 12) 12=15 \mathrm{ft}^{2}\left(1.39 \mathrm{~m}^{2}\right)$.
The maximum heat transferred is determined from the equation

$$
Q=3600 a v_{c} \rho_{v} \lambda
$$

where $Q=$ heat transferred, in Btu/h
$a=$ projected area, in $\mathrm{ft}^{2}$
$v_{c}=$ superficial vapor velocity, in $\mathrm{ft} / \mathrm{s}$
$\rho_{v}=$ vapor density, in $\mathrm{lb} / \mathrm{ft}^{3}$
$\lambda=$ heat of vaporization, in Btu/lb
In this case, $Q=3600(15)(4.33)(0.2)(895)=41,854,000 \mathrm{Btu} / \mathrm{h}(12,266 \mathrm{~kW})$.
3. Calculate the maximum heat flux. Maximum heat flux $=Q / A$, where $Q$ is maximum heat transferred and $A$ is total heat-transfer surface for all $n$ tubes. In this case, $A=n \pi D L=$ $80 \pi(1 / 12) 12=251 \mathrm{ft}^{2}\left(23.35 \mathrm{~m}^{2}\right)$, so maximum heat flux $=41,854,000 / 251=166,750 \mathrm{Btu} /(\mathrm{h})$ $\left(\mathrm{ft}^{2}\right)\left(525,600 \mathrm{~W} / \mathrm{m}^{2}\right)$.

Related Calculations. The preceding equation for maximum superficial vapor velocity is applicable only to kettle-type reboilers having a shell diameter 1.3 to 2.0 times greater than the diameter of the tube bundle. (For small-diameter bundles, the ratio required is greater than that for large bundles.) This ratio is generally sufficient to permit liquid circulation adequate to obtain the superficial vapor velocity predicted by the equation presented here. For single tubes or for tube bundles with geometries that do not permit adequate liquid circulation, the superficial vapor velocity calculated using this equation should be multiplied by 0.3.

For vertical tubes, the superficial vapor velocity (based on the total heat-transfer surface) can be obtained by multiplying the value calculated from the preceding equation by 0.22 . This assumes that there is adequate liquid circulating past the surface to satisfy the mass balance. For thermosiphon reboilers, a detailed analysis must be made to establish circulation rate, boiling pressure, sensible heat-transfer zone, boiling heat-transfer zone, and mean temperature difference. If liquid circulation rates are not adequate, all liquid will be vaporized and superheating of the vapor will occur with a resultant decrease in heat-transfer rates.

The procedure for design of thermosiphon reboilers presented by Fair [23] has been widely used. Special surfaces are available commercially that permit much higher superficial vapor velocities than calculated by the method presented here; see Gottzmann, O'Neill, and Minton [32].

### 7.33 DOUBLE-PIPE HEAT EXCHANGERS WITH BARE TUBES

Calculate the outlet temperature for air entering the annulus of a double-pipe exchanger at $68^{\circ} \mathrm{F}$ $(293 \mathrm{~K})$ at a flow rate of $500 \mathrm{lb} / \mathrm{h}(226.8 \mathrm{~kg} / \mathrm{h})$ if steam is condensing inside the tube at $320^{\circ} \mathrm{F}$ ( 433 K ). The shell of the double-pipe exchanger is 3.068 in $(0.0779 \mathrm{~m})$ in diameter. The steel tube is 1.9 in $(0.048 \mathrm{~m})$ in outside diameter and 1.61 in $(0.0409 \mathrm{~m})$ in inside diameter and has a thermal conductivity of $25 \mathrm{Btu} /(\mathrm{h})(\mathrm{ft})\left({ }^{\circ} \mathrm{F}\right)[43 \mathrm{~W} /(\mathrm{m})(\mathrm{K})]$. The tube length is $20 \mathrm{ft}(6.1 \mathrm{~m})$. Air has a viscosity of $0.0426 \mathrm{lb} /(\mathrm{ft})(\mathrm{h})$ and a specific heat of $0.24 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)[1.01 \mathrm{~kJ} /(\mathrm{kg})(\mathrm{K})]$. The fouling coefficient is $1000 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[5680 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.

The physical properties for the steam condensate are:

```
\(\mu=\) liquid viscosity \(=0.5 \mathrm{lb} /(\mathrm{ft})(\mathrm{h})(0.207 \mathrm{cP})\)
\(\rho=\) liquid density \(=55.5 \mathrm{lb} / \mathrm{ft}^{3}\left(889 \mathrm{~kg} / \mathrm{m}^{3}\right)\)
\(\lambda=\) heat of vaporization \(=895 \mathrm{Btu} / \mathrm{lb}(2,081,770 \mathrm{~J} / \mathrm{kg})\)
\(k=\) liquid thermal conductivity \(=0.395 \mathrm{Btu} /(\mathrm{h})(\mathrm{ft})\left({ }^{\circ} \mathrm{F}\right)[0.683 \mathrm{~W} /(\mathrm{m})(\mathrm{K})]\)
```


## Calculation Procedure

1. Calculate condensing coefficient $\boldsymbol{h}_{\boldsymbol{i}}$. The steam-condensing coefficient will be much larger than the air-side coefficient; this permits us to approximate the condensing coefficient by assuming the maximum steam condensate loading. The maximum heat transferred would occur if the air were heated to the steam temperature. Thus, $Q_{\text {max }}=W_{\text {air }} c\left(T_{\text {steam }}-t_{\text {air }}\right)$, where $W$ is mass flow rate and $c$ is specific heat. Or, $Q_{\max }=500(0.24)(320-68)=30,240 \mathrm{Btu} / \mathrm{h}$. Then, maximum condensate flow $W_{c, \text { max }}=Q_{\text {max }} / \lambda=30,240 / 895=33.8 \mathrm{lb} / \mathrm{h}$.

Now, with reference to Example 7.26, $W_{c} / n \rho D_{i}^{2.56}=33.8 /\left[1(55.5)(1.61 / 12)^{2.56}\right]=104$. This is a relatively low value, so stratified flow can be assumed. Then,

$$
\begin{aligned}
h_{c} & =0.767 k\left(\frac{\rho^{2} g L}{n \mu W}\right)^{1 / 3} \\
& =0.767(0.39)\left(\frac{55.5^{2}\left(4.18 \times 10^{8}\right)(20)}{1(0.5)(33.8)}\right)^{1 / 3} \\
& =3486 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)
\end{aligned}
$$

Now, for a $W_{c} /\left(n \rho D_{i}^{2.56}\right)$ of $104, h_{i}=1.2 h_{c}$, as indicated in Example 7.26. Thus, $h_{i}=1.2(3486)=$ $4183 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)$, and $h_{i}\left(D_{i} / D_{o}\right)=4183(1.61 / 1.9)=3545 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[20,136 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.
2. Calculate $\boldsymbol{h}_{\boldsymbol{w}}$, the heat-transfer coefficient through the tube wall. By definition, $h_{w}=2 k$ / $\left(D_{o}-D_{i}\right)=2(25) /(1.9-1.61)(1 / 12)=2068 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[11,750 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.
3. Calculate $h_{\boldsymbol{o}}$, the heat-transfer coefficient for the outside of the tube. Because the fluid flowing is air, we can use simplified equations for heat-transfer coefficients. Cross-sectional area of the annulus $a_{c}=(\pi / 4)\left(D_{s}^{2}-D_{o}^{2}\right)=(\pi / 4)\left(3.068^{2}-1.9^{2}\right)(1 / 12)^{2}=0.0316 \mathrm{ft}^{2}$. Then, mass flow rate through the annulus $G=W_{\text {air }} / a_{c}=500 / 0.0316=15,800 \mathrm{lb} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)$, and equivalent diameter $D_{c}=$ $4 a_{c} / P$, where $P=\pi\left(D_{s}+D_{o}\right)$. Thus, by algebraic simplification, $D_{e}=D_{s}-D_{o}=(3.068 / 12)-$ $(1.9 / 12)=0.0973 \mathrm{ft}(0.0297 \mathrm{~m})$.

Since the Reynolds number, that is, $D_{e} G / \mu=0.0973(15,800) / 0.0426=36,088$, is greater than 8000 (see Related Calculations in Example 7.18),

$$
\begin{aligned}
h_{o} & =0.0144 c G^{0.8} / D_{e}^{0.2} \\
& =0.0144(0.24)(15,800)^{0.8} / 0.0973^{0.2} \\
& =12.58 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[71.45 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]
\end{aligned}
$$

4. Calculate U, the overall heat-transfer coefficient. Now,

$$
\begin{aligned}
\frac{1}{U} & =\frac{1}{h_{o}}+\frac{1}{h_{i}\left(D_{i} / D_{o}\right)}+\frac{1}{h_{w}}+\frac{1}{h_{s}} \\
& =\frac{1}{12.58}+\frac{1}{3545}+\frac{1}{2068}+\frac{1}{1000}
\end{aligned}
$$

So, $U=12.32 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[69.97 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.
5. Calculate outlet air temperature. Use Fig. 7.14. Now, $A=\pi D_{o} L=\pi(1.9 / 12)(20)=9.95$ $\mathrm{ft}^{2}$, so $U A /(w c)=12.32(9.95) /[500(0.24)]=1.02$. In addition, $R=0$ (isothermal on steam side).

For these values of $U A /(w c)$ and $R, P=0.64$ from Fig. 7.14. Then $t_{2}=t_{1}+P\left(T_{s}-t_{1}\right)=68+$ $0.64(320-68)=229.2^{\circ} \mathrm{F}(382.8 \mathrm{~K})$.

### 7.34 DOUBLE-PIPE HEAT EXCHANGERS WITH LONGITUDINALLY FINNED TUBES

Calculate the outlet air temperature for the double-pipe heat exchanger under the conditions of Example 7.33 if the tube has 24 steel fins 0.5 in $(0.013 \mathrm{~m})$ high and 0.03125 in $(0.794 \mathrm{~mm})$ thick.

## Calculation Procedure

1. Calculate the relevant fin areas. The relevant areas are cross-sectional flow area $a_{c}$, fin surface $A_{f}$, outside bare surface $A_{o}$, and inside surface $A_{i}$. Now,

$$
a_{c}=(\pi / 4)\left(D_{s}^{2}-D_{o}^{2}\right)-n l b
$$

where $n=$ number of fins
$l=$ fin height
$b=$ fin thickness
Thus, $a_{c}=0.0316-24(0.5 / 12)(0.03125 / 12)=0.029 \mathrm{ft}^{2}\left(0.0028 \mathrm{~m}^{2}\right)$.
Further, $A_{f}$ is the heat-transfer surface on both sides and the tip of the fins, and it equals $2 n l+n b=$ $2(24)(0.5 / 12)+24(0.03125 / 12)=2.0625 \mathrm{ft}^{2}$ per foot of tube length. And, $A_{o}$ is the outside bare surface exclusive of the area beneath the fins, and it equals $\pi D_{o}-n b=\pi(1.9 / 12)-24(0.03125 / 12)=$ $0.4349 \mathrm{ft}^{2}$ per foot of tube length. Finally, $A_{i}=\pi D_{i}=\pi(1.61 / 12)=0.4215 \mathrm{ft}^{2}$ per foot of tube length.
2. Calculate $\boldsymbol{D}_{\boldsymbol{e}}$ for the fin tube. Use the formula $D_{e}=4 a_{c} / P$, where $P=\pi\left(D_{s}+D_{o}\right)+2 n l$. Now, $P=\pi(3.068+1.9)(1 / 12)+2(24)(0.5 / 12)=3.3006 \mathrm{ft}$. Then, $D_{e}=4(0.029) / 3.3006=$ $0.0351 \mathrm{ft}(0.0107 \mathrm{~m})$.
3. Calculate $\boldsymbol{h}_{\boldsymbol{o}}$. Mass flow rate through the annulus $G=W_{\text {air }} / a_{c}=500 / 0.029=17,241.4$ $\mathrm{lb} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)$. Since the Reynolds number, that is, $D_{e} G / \mu=0.0351(17,241.4) / 0.0426=14,206$, is greater than 8000 ,

$$
\begin{aligned}
h_{o} & =0.0144 c G^{0.8} / D_{e}^{0.2} \\
& =0.0144(0.24)(17,241.4)^{0.8} / 0.0351^{0.2} \\
& =16.55 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[93.99 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]
\end{aligned}
$$

4. Calculate fin efficiency. Because the heat must be transferred through the fin by conduction, the fin is not as effective as a bare tube with the same heat-transfer surface and heat-transfer coefficient. The fin efficiency is a measure of the actual heat transferred compared with the amount that could be transferred if the fin were uniformly at the temperature of the base of the fin.

For a fin with rectangular cross section,

$$
\eta=\frac{\tanh m l}{m l}
$$

where $\eta=$ fin efficiency
$l=$ fin height
$m=\left(2 h_{o} / k b\right)^{1 / 2}$, where $k$ is fin thermal conductivity, and $b$ is fin thickness
For this problem, $m=\{2(16.55) /[25(0.03125 / 12)]\}^{1 / 2}=22.55$, so $m l=22.55(0.5 / 12)=$ 0.9395 and $\eta=(\tanh 0.9395) / 0.9395$. Now, $\tanh x=\left(e^{x}-e^{-x}\right) /\left(e^{x}+e^{-x}\right)$, so

$$
\begin{aligned}
\tanh 0.9395 & =\frac{e^{0.9395}-e^{-0.9395}}{e^{0.9395}+e^{-0.9395}} \\
& =0.735
\end{aligned}
$$

Therefore, $\eta=0.735 / 0.9395=0.782$.
5. Calculate $\boldsymbol{h}_{f, i}$, pertaining to the outside of the fin tube. It is convenient to base the overall heat-transfer coefficient on the inside area of a fin tube. Then the relevant outside coefficient is

$$
\begin{aligned}
h_{f, i} & =\left(\eta A_{f}+A_{o}\right)\left(h_{o} / A_{i}\right) \\
& =[0.782(2.0625)+0.4349] \frac{16.55}{0.4215} \\
& =80.40 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[456.6 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]
\end{aligned}
$$

6. Calculate $\boldsymbol{U}_{\boldsymbol{i}}$. The formula is

$$
\frac{1}{U_{i}}=\frac{1}{h_{f, i}}+\frac{1}{h_{i}}+\frac{1}{h_{w}}+\frac{1}{h_{s}}
$$

Thus, $1 / U_{i}=1 / 80.4+1 / 4183+1 / 2068+1 / 1000$, so $U_{i}=70.6 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[401 \mathrm{~W} /\left(\mathrm{m}^{2}\right)\right.$ (K)].
7. Calculate outlet air temperature. From step 1 , total area $A_{i}=0.4215(20)=8.43 \mathrm{ft}^{2}$ $\left(0.783 \mathrm{~m}^{2}\right)$. Then, $U_{i} A_{i} /(w c)=70.6(8.43) /[500(0.24)]=4.96$. From Fig. 7.14, for $R=0, P=$ 0.99. Then $t_{2}=t_{1}+P\left(T_{s}-t_{1}\right)=68+0.99(320-68)=317.5^{\circ} \mathrm{F}(431.8 \mathrm{~K})$.

Related Calculations. This procedure can also be used for fins with cross sections other than rectangular. Fin-efficiency curves for some of these shapes are presented in Refs. 2 through 4.

### 7.35 HEAT TRANSFER FOR LOW-FIN TUBES

An existing heat exchanger with the following geometry must be retubed. Bare copper-alloy tubes $\left[k=65 \mathrm{Btu} /(\mathrm{h})(\mathrm{ft})\left({ }^{\circ} \mathrm{F}\right)\right.$ or $\left.112 \mathrm{~W} /(\mathrm{m})(\mathrm{K})\right]$ cost $\$ 1$ per foot; low-fin copper-alloy tubes cost $\$ 1.75$ per foot. Heat is to be exchanged between two process streams operating under the following conditions. The cool stream must be further heated downstream with steam that has a heat of vaporization of $895 \mathrm{Btu} / \mathrm{lb}(2082 \mathrm{~kJ} / \mathrm{kg})$. The warm stream must be further cooled downstream with cooling water that can accept a maximum temperature rise of $30^{\circ} \mathrm{F}(16.67 \mathrm{~K})$. Pressure drop for the tube side is not a penalty because the tube-side fluid must be throttled downstream. Is it economical to retube the exchanger with low-fin tubes if the evaluated cost of the steam is $\$ 50$ per pound per hour and the evaluated cost of the cooling water is $\$ 25$ per gallon per minute?

## Tube-Side Fluid

Condition $=$ liquid, sensible-heat transfer
Flow rate $=50,000 \mathrm{lb} / \mathrm{h}(22,679.5 \mathrm{~kg} / \mathrm{h})$
$c=$ specific heat, $1.0 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)[4.2 \mathrm{~kJ} /(\mathrm{kg})(\mathrm{K})]$
$\mu=$ viscosity, $1.21 \mathrm{lb} /(\mathrm{ft})(\mathrm{h})(0.5 \mathrm{cP})$
$k=$ thermal conductivity, $0.38 \mathrm{Btu} /(\mathrm{h})(\mathrm{ft})\left({ }^{\circ} \mathrm{F}\right)[0.66 \mathrm{~W} /(\mathrm{m})(\mathrm{K})]$
Inlet temperature $=320^{\circ} \mathrm{F}(433 \mathrm{~K})$
Assume that $\left(\mu_{w} / \mu_{b}\right)^{0.14}=1.0$

## Shell-Side Fluid

Condition $=$ liquid, sensible-heat transfer
Flow rate $=30,000 \mathrm{lb} / \mathrm{h}(13,607.7 \mathrm{~kg} / \mathrm{h})$
$c=$ specific heat, $0.7 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)[2.9 \mathrm{~kJ} /(\mathrm{kg})(\mathrm{K})]$
$\mu=$ viscosity, $10 \mathrm{lb} /(\mathrm{h})(\mathrm{ft})(4.13 \mathrm{cP})$
$k=$ thermal conductivity, $0.12 \mathrm{Btu} /(\mathrm{h})(\mathrm{ft})\left({ }^{\circ} \mathrm{F}\right)[0.21 \mathrm{~W} /(\mathrm{m})(\mathrm{K})]$
Inlet temperature $=41^{\circ} \mathrm{F}(278 \mathrm{~K})$
Assume that $=\left(\mu_{w} / \mu_{b}\right)^{0.14}=0.9$
Heat-Exchanger Geometry
$D_{s}=$ shell diameter, 8.071 in ( 0.205 m )
$n=$ number of tubes, 36
$D_{o}=$ tube outside diameter, 0.75 in ( 0.019 m )
$D_{i}=$ tube inside diameter, 0.62 in $(0.016 \mathrm{~m})$ for bare tube and 0.495 in $(0.0126 \mathrm{~m})$ for low-fin tube
$L=$ tube length, $16 \mathrm{ft}(4.88 \mathrm{~m})$
$B=$ baffle spacing, 4 in ( 0.102 m )
$s=$ tube spacing, 0.9375 in $(0.02381 \mathrm{~m})$ with a triangular pitch
$D_{r}=$ root diameter of fin tube, 0.625 in $(0.0159 \mathrm{~m})$
$A_{o} / A_{i}=3.84$
There is one tube pass, one shell pass. Assume an overall fouling coefficient of $1000 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)$ $\left[5680 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.

## Calculation Procedure

1. Calculate $\boldsymbol{h}_{\boldsymbol{i}}$, the inside film coefficient, for bare tubes. See Example 7.22. Here, $G=W / a_{c}=$ $50,000 /\left[36(0.62 / 12)^{2}(\pi / 4)\right]=662,455.5 \mathrm{lb} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)$. Then $D_{i} G / \mu=(0.62 / 12) 662,455.5 / 1.21=$ $28,286.7$, and

$$
\begin{aligned}
h_{i} & =\frac{0.023 c G}{(c \mu / k)^{2 / 3}\left(D_{i} G / \mu\right)^{0.2}} \\
& =\frac{0.023(1.0)(662,455.5)}{[1.0(1.21) / 0.38]^{2 / 3} 28,286.7^{0.2}} \\
& =906.9 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[5151 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]
\end{aligned}
$$

2. Calculate $\boldsymbol{h}_{\boldsymbol{i}}$ for low-fin tubes. Use the relationship $h_{i, \text { fin }}=h_{i, \text { bare }}\left(D_{i, \text { bare }} / D_{i, \text { fin }}\right)^{1.8}$. Thus, $h_{i, \text { fin }}=$ $906.9(0.62 / 0.495)^{1.8}=1360.1 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[7725 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.
3. Calculate $\boldsymbol{h}_{\boldsymbol{o}}$, the outside film coefficient, for bare tubes. See Example 7.22. Here, $a_{c}=$ $D_{s} B\left(s-D_{o}\right) / s=(8.071 / 12)(4 / 12)(0.9375-0.75) / 0.9375=0.0448 \mathrm{ft}^{2}$. Then, $G=W / a_{c}=$ $30,000 / 0.0448=669,062 \mathrm{lb} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)$, and the Reynolds number $D_{o} G / \mu=(0.75 / 12) 669,062 / 10=$ 4181.6. Therefore, $h=0.273 c G /\left[(c \mu / k)^{2 / 3}\left(D_{o} G / \mu\right)^{0.365}\left(\mu_{w} / \mu_{o}\right)^{0.14}\right]$. Now, $(c \mu / k)^{2 / 3}=[0.7(10) /$ $0.12]^{2 / 3}=15.04$, and $h=0.273(0.7)(669,062) /\left[15.04(4181.6)^{0.365} 0.9\right]=450.2 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)$. Finally, $h_{o}=h F_{1} F_{r}, F_{r}=1.0$, and $F_{1}=0.8\left(B / D_{s}\right)^{1 / 6}$. Thus, $h_{o}=450.2(0.8)(4 / 8.071)^{1 / 6}(1.0)=$ 320.4 Btu/(h)(ft $\left.{ }^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[1819 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.

TABLE 7.4 Weighted Fin Efficiency for Low-Fin Tubes

|  | Weighted fin efficiency $\eta$ |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $h_{o}$ | $k=10[17.3]$ | $k=25[43.3]$ | $k=65[112]$ | $k=125[216]$ | $k=225[389]$ |
| $10[56.7]$ | 0.97 | 0.98 | 0.99 | 1.00 | 1.00 |
| $50[284]$ | 0.94 | 0.97 | 0.98 | 0.99 | 1.00 |
| $100[567]$ | 0.89 | 0.94 | 0.97 | 0.98 | 0.99 |
| $200[1134]$ | 0.81 | 0.90 | 0.95 | 0.97 | 0.98 |
| $500[2840]$ | 0.68 | 0.80 | 0.90 | 0.93 | 0.96 |

Note: $\quad h_{o}$, the outside film coefficient, is in $\mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[\mathrm{W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right] ; k$, the thermal conductivity, is in $\mathrm{Btu} /(\mathrm{h})(\mathrm{ft})\left({ }^{\circ} \mathrm{F}\right)$ [W/(m)(K)].
4. Calculate $\boldsymbol{h}_{\boldsymbol{o}}$ for low-fin tubes. For low-fin tubes, the shell-side mass velocity is reduced because of the space between the fins. This reduction can be closely approximated with the expression $\left(s-D_{o}\right) /\left(s-D_{o}+0.09\right)$, each term being expressed in inches.

For this problem, the expression has the value $(0.9375-0.75) /(0.9375-0.75+0.09)=0.676$. The diameter that should be used for calculating the Reynolds number is the root diameter of the fin tube. By applying the diameter ratio and the velocity reduction to the Reynolds number from step 3, the result is a Reynolds number for this case of $D_{r} G / \mu=4181.6(0.625 / 0.75)(0.676)=$ 2355.6. Then,

$$
\begin{aligned}
h & =\frac{0.273 c G}{(c \mu / k)^{2 / 3}\left(D_{r} G / \mu\right)^{0.365}\left(\mu_{w} / \mu_{b}\right)^{0.14}} \\
& =\frac{0.273(0.7)(669,062)(0.676)}{15.04(2355.6)^{0.365} 0.9} \\
& =375.3 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)
\end{aligned}
$$

Then, as in step $3, h_{o}=375.3(0.8)(4 / 8.071)^{1 / 6} 1.0=267.1 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[1517 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.
5. Determine weighted fin efficiency. Weighted fin efficiencies for low-fin tubes are functions of the outside heat-transfer coefficient. Weighted fin efficiencies $\eta$ can be determined from curves provided by various manufacturers. Table 7.4 permits approximation of weighted fin efficiencies. For this problem, the weighted efficiency $\eta$ is 0.94 .
6. Calculate $\boldsymbol{h}_{f, i}$, pertaining to the outside of the fin tubes. For fin tubes, it is convenient to base the overall heat-transfer coefficient on the inside surface of the tube. Then the relevant outside coefficient is $h_{f, i}=\eta\left(A_{o} / A_{i}\right) h_{o}=0.94(3.84)(267.1)=964.1 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[5476.2 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.
7. Calculate $\boldsymbol{h}_{\boldsymbol{w}}$, the coefficient for heat transfer through the tube wall. The formulas are $h_{w}=$ $2 k /\left(D_{o}-D_{i}\right)$ for bare tubes, and $h_{w}=2 k /\left(D_{r}-D_{i}\right)$ for low-fin tubes. For this problem, $D_{o}-D_{i}=$ $D_{r}-D_{i}=0.13 / 12$, so $h_{w}=2(65) /(0.13 / 12)=12,000 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[68,160 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.
8. Calculate $\boldsymbol{U}_{\boldsymbol{o}}$ for bare tubes. The formula is

$$
\frac{1}{U_{o}}=\frac{1}{h_{i}\left(D_{i} / D_{o}\right)}+\frac{1}{h_{o}}+\frac{1}{h_{w}}+\frac{1}{h_{s}}
$$

Thus, $\quad 1 / U_{o}=1 /[906.9(0.62 / 0.75)]+1 / 320.4+1 / 12,000+1 / 1000$, so $U_{o}=180.6 \mathrm{Btu} /(\mathrm{h})$ $\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[1026 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.
9. Calculate $\boldsymbol{U}_{\boldsymbol{i}}$ for low-fin tubes. Again, $1 / U_{i}=1 / h_{i}+1 / h_{f, i}+1 / h_{w}+1 / h_{s}$. Thus, $1 / U_{i}=$ $1 / 1360.1+1 / 964.1+1 / 12,000+1 / 1000$, so $U_{i}=350.2 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[1989 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.
10. Determine outlet temperatures for bare tubes. Use Fig. 7.14. Now, $A_{o}=n \pi D_{o} L=$ $36 \pi(0.75 / 12) 16=113.1 \mathrm{ft}^{2}$, so $U A /(w c)=180.6(113.1) /[30,000(0.7)]=0.973$, and $R=$ $w c /(W C)=30,000(0.7) /[50,000(1.0)]=0.420$. For these values, $P=0.57$. Therefore, $t_{2}=t_{1}+$ $P\left(T_{1}-t_{1}\right)=41+0.57(320-41)=200.0^{\circ} \mathrm{F}(366.5 \mathrm{~K})$.
11. Determine outlet temperatures for low-fin tubes. Use Fig. 7.14 again. In this case, the calculation is based on the inside diameter. So, $A_{i}=n \pi D_{i} L=36 \pi(0.495 / 12) 16=74.6 \mathrm{ft}^{2}$. And $U A /(w c)=350.2(74.6) /[30,000(0.7)]=1.244$. For this value and $R=0.42, P=0.65$. Therefore, $t_{2}=t_{1}+P\left(T_{1}-t_{1}\right)=41+0.65(320-41)=222.4^{\circ} \mathrm{F}(378.9 \mathrm{~K})$.
12. Calculate water savings using low-fin tubes. The tube-side fluid must be further cooled; the water savings is represented by the difference in heat recovery between bare and low-fin tubes. Thus,

$$
\begin{aligned}
Q_{\text {saved }} & =w c \Delta t=30,000(0.7)(222.4-200.0) \\
& =470,400 \mathrm{Btu} / \mathrm{h}
\end{aligned}
$$

Since the cooling water can accept a temperature rise of $30^{\circ} \mathrm{C}$, the water rate $=Q_{\text {saved }} /(c \Delta T)=$ $470,400 /[1(30)]=15,680 \mathrm{lb} / \mathrm{h}$. Then, dollars saved $(\mathrm{lb}$ water $/ \mathrm{h})[(\mathrm{gal} / \mathrm{min}) /(\mathrm{lb} / \mathrm{h})][\$ /(\mathrm{gal} / \mathrm{min})]=$ $15,680(1 / 500)(25)=\$ 784$.
13. Calculate steam savings using low-fin tubes. The shell-side fluid must be further heated; the steam savings is represented by the difference in heat recovery between bare and low-fin tubes:

$$
\text { Steam rate }=Q_{\text {saved }} / \lambda=470,400 / 895=525.6 \mathrm{lb} / \mathrm{h}
$$

Then dollars saved $=(\mathrm{lb}$ steam $/ \mathrm{h})[\$ /(\mathrm{lb} / \mathrm{h})]=$ equivalent savings $=525.6(50)=\$ 26,280$.
14. Compare energy savings with additional tubing cost. Additional cost for retubing is $n L(\$ 1.75-\$ 1.00)=36(16)(1.75-1.00)=\$ 432$. The equivalent energy savings is $\$ 784+$ $\$ 26,280=\$ 27,064$.

Related Calculations. Low-fin tubes are tubes with extended surfaces that have the same outside diameter as bare tubes. They can therefore be used interchangeably with bare tubes in tubular exchangers. Various geometries and materials of construction are available from several manufacturers.

Low-fin tubes find wide application when the heat-transfer coefficient on the inside of the tube is much greater than the coefficient on the outside of the tube. A guideline suggests that low-fin tubes should be considered when the outside coefficient is less than one-third that on the inside. Low-fin tubes also find application in some fouling services because the fin tubes are more easily cleaned by hydroblasting than are bare tubes. In addition, low-fin tubes are used when boiling at low temperature differences, because the minimum temperature difference required for nucleate boiling is reduced with the use of low-fin tubes. Low-fin tubes are also used for condensing, primarily for materials with low surface tension.

The procedure outlined in this example can also be used when designing equipment using low-fin tubes. The same approach is used when condensing or boiling on the outside of low-fin tubes.

### 7.36 HEAT TRANSFER FOR BANKS OF FINNED TUBES

Calculate the outlet temperature from a duct cooler if hydrogen is flowing at a rate of $1000 \mathrm{lb} / \mathrm{h}$ $(453.6 \mathrm{~kg} / \mathrm{h})$ with a duct velocity of $500 \mathrm{ft} / \mathrm{min}(152.4 \mathrm{~m} / \mathrm{min})$. The duct cooler contains a bank of
finned tubes described below. Hydrogen enters the cooler at $200^{\circ} \mathrm{F}(366.5 \mathrm{~K})$ and has a specific heat of $3.4 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)[14.2 \mathrm{~kJ} /(\mathrm{kg})(\mathrm{K})]$, a viscosity of $0.225 \mathrm{lb} /(\mathrm{ft})(\mathrm{h}),(0.0093 \mathrm{cP})$, a thermal conductivity of $0.11 \mathrm{Btu} /(\mathrm{h})(\mathrm{ft})\left({ }^{\circ} \mathrm{F}\right)[0.19 \mathrm{~W} /(\mathrm{m})(\mathrm{K})]$, and a density of $0.0049 \mathrm{lb} / \mathrm{ft}^{3}\left(0.0785 \mathrm{~kg} / \mathrm{m}^{3}\right)$. The coolant is water entering the tubes at $86^{\circ} \mathrm{F}(303 \mathrm{~K})$ and a rate of $10,000 \mathrm{lb} / \mathrm{h}(4535.0 \mathrm{~kg} / \mathrm{h})$. The water-side heat-transfer coefficient $h_{i}$ is $1200 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[6800 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$, the heat-transfer coefficient through the tube wall $h_{w}$ is $77,140 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[437,380 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$, and the overall fouling coefficient is $1000 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[5680 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.

## Duct Cooler (Finned-Tube Bank)

$D_{r}=$ root diameter $($ bare-tube outside diameter $)=0.625$ in $(0.0159 \mathrm{~m})$
$l=$ fin height $=0.5 \mathrm{in}(0.013 \mathrm{~m})$
$b=$ fin thickness $=0.012$ in $(0.305 \mathrm{~mm})$
$n=$ number of fins per inch $=12$
$s=$ tube spacing $=1.75$ in $(0.0445 \mathrm{~m})$
$x=$ tube-wall thickness $=0.035$ in $(0.889 \mathrm{~mm})$
$A_{o}=$ bare heat-transfer surface $=50 \mathrm{ft}^{2}\left(4.64 \mathrm{~m}^{2}\right)$
The tube pattern is triangular, the fin material is aluminum, and the tube material is copper.

## Calculation Procedure

1. Select the appropriate equation for the outside heat-transfer coefficient. The heat-transfer coefficient for finned tubes can be calculated using the equation

$$
\frac{h D_{r}}{k}=a\left(\frac{c \mu}{k}\right)^{1 / 3}\left(\frac{D_{r} G}{\mu}\right)^{0.681}\left(\frac{y^{3}}{l^{2} b}\right)^{0.1}
$$

where $a=0.134$ for triangular tube patterns or $0.128(y / l)^{0.15} /\left[1+\left(s-D_{f}\right) /\left(s-D_{r}\right)\right]$ for inline tube patterns
$h=$ outside heat-transfer coefficient
$D_{r}=$ root diameter (diameter at base of fins)
$D_{f}=$ diameter of fins (equal to $D_{r}+2 l$ )
$k=$ thermal conductivity
$c=$ specific heat
$\mu=$ viscosity
$G=$ mass velocity, based on minimum flow area
$l=$ fin height
$b=$ fin thickness
$y=$ distance between fins $=(1 / n)-b$
$n=$ number of fins per unit length
$s=$ tube spacing perpendicular to flow
$p=$ tube spacing parallel to flow
The equation is valid for triangular spacings with $s / p$ ranging from 0.7 to 1.1 .
2. Calculate the relevant fin areas. These are heat-transfer surface of fins $A_{f}$, outside heattransfer surface of bare tube $A_{o}$, total outside heat-transfer surface $A_{t}$ (equal to $A_{f}+A_{o}$ ), and ratio of maximum flow area to minimum flow area $a_{r}$. For this problem

$$
\begin{aligned}
A_{f} & =\left(D_{f}^{2}-D_{r}^{2}\right)(\pi / 4) 2 n \\
& =\left(1.625^{2}-0.625^{2}\right)(1 / 12)^{2}(\pi / 4)(2)(12)(12) \\
& =3.5343 \mathrm{ft}^{2} \text { per foot of tube length }
\end{aligned}
$$

TABLE 7.5 Weighted Fin Efficiency for Transverse Fins

|  | Weighted fin efficiency $\eta$ |  |  |  |
| ---: | :---: | :---: | :---: | :---: |
| $h_{o}$ | Copper, $k=$ <br> $220[381]$ | Aluminum, $k=$ <br> $125[216]$ | Steel, $k=$ <br> $25[43.3]$ | Stainless steel, $k=$ <br> $10[17.3]$ |
| $5[28.4]$ | 0.95 | 0.90 | 0.70 | 0.50 |
| $10[56.7]$ | 0.90 | 0.85 | 0.60 | 0.35 |
| $25[142]$ | 0.85 | 0.70 | 0.40 | 0.20 |
| $50[284]$ | 0.70 | 0.55 | 0.25 | 0.15 |
| $100[567]$ | 0.55 | 0.40 | 0.15 | 0.10 |

> Note: $h_{o}$, the outside film coefficient, is in $\mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[\mathrm{W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right] ; k$, the thermal conductivity, is in $\mathrm{Btu} /(\mathrm{h})(\mathrm{ft})\left({ }^{\circ} \mathrm{F}\right)[\mathrm{W} /(\mathrm{m})(\mathrm{K})]$. This table is valid for fin heights in the vicinity of 0.5 in and fin thicknesses around 0.012 in .

And $A_{o}=\pi D_{o}=\pi(0.625 / 12)=0.1636 \mathrm{ft}^{2}$ per foot of tube length. Then, $A_{t}=A_{f}+A_{o}=$ $3.5343+0.1636=3.6979 \mathrm{ft}^{2}$ per foot of tube length, and $A_{t} / A_{o}=3.6979 / 0.1636=22.6$. Finally, $a_{r}=s /\left(s-D_{o}-2 n l b\right)=1.75 /[1.75-0.625-2(12)(0.5)(0.012)]=1.7839$.
3. Calculate $\boldsymbol{h}_{\boldsymbol{o}}$, the outside film coefficient. From step $1, h_{o}=0.134\left(k / D_{r}\right)(c \pi / k)^{1 / 3}$ $\times\left(D_{r} G / \mu\right)^{0.681}\left(y^{3} / l^{2} b\right)^{0.1}$. Now, $G=60 \rho F V a_{r}$, where $\rho$ is the density in pounds per cubic foot and $F V$ is the face velocity (duct velocity) in feet per minute. Then, $G=60(0.0049)(500)(1.7839)=$ $262.2 \mathrm{lb} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)$, and $D_{r} G / \mu=(0.625 / 12) 262.2 / 0.0225=607.0$. Now, $y=(1 / n)-b=(1 / 12)-$ $0.012=0.0713$ in $(1.812 \mathrm{~mm})$.

The Prandtl number for hydrogen $(c \mu / k)=0.7$, so

$$
\begin{aligned}
h_{o} & =0.134\left(\frac{0.11}{0.625 / 12}\right) 0.7^{1 / 3} 607.0^{0.681}\left[\frac{0.0713^{3}}{0.5^{2}(0.012)}\right]^{0.1} \\
& =15.99 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[90.82 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]
\end{aligned}
$$

4. Calculate $\boldsymbol{h}_{f, o}$, pertaining to the outside of the finned tubes. For transverse fins fabricated by finning a bare tube, it is convenient to base the overall heat-transfer coefficient on the outside surface of the bare tube. Thus

$$
h_{f, o}=h_{o}\left(A_{t} / A_{o}\right) \eta
$$

where $\eta$ is the weighted fin efficiency.
The weighted fin efficiency may be approximated from Table 7.5. For the present problem, use a value of 0.80 . Then, $h_{f, o}=15.99(22.6)(0.80)=289.1 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[1642 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.
5. Calculate $\boldsymbol{U}_{\boldsymbol{o}}$. The formula is

$$
\begin{aligned}
\frac{1}{U_{o}} & =\frac{1}{h_{f, o}}+\frac{1}{h_{i}\left(D_{i} / D_{o}\right)}+\frac{1}{h_{w}}+\frac{1}{h_{s}} \\
& =\frac{1}{289.1}+\frac{1}{1200(0.555 / 0.625)}+\frac{1}{77,140}+\frac{1}{1000} \\
& =185 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[1050 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]
\end{aligned}
$$

6. Calculate the outlet temperature. Assume that there are several tube-side passes. The outlet temperature can then be calculated using Fig. 7.14. This figure can be employed to directly calculate the outlet temperature of the hot fluid (which is of interest in this example); in such a case, the
abscissa becomes $U A /(W C), R=W C /(w c)$, and $P=\left(T_{2}-T_{1}\right) /\left(t_{1}-T_{1}\right)$. Then, for the present example, $U A /(W C)=185(50) /[1000(3.4)]=2.72$, and $R=1000(3.4) /[10,000(1.0)]=0.34$. For these parameters, Fig. 7.14 shows $P$ to be 0.88 . Therefore, $T_{2}=T_{1}+P\left(t_{1}-T_{1}\right)=200+0.88$ (86$200)=99.7^{\circ} \mathrm{F}(310.6 \mathrm{~K})$.

### 7.37 AIR-COOLED HEAT EXCHANGERS

Design an air-cooled heat exchanger to cool water under the following conditions. The design ambient air temperature is $35^{\circ} \mathrm{C}\left(95^{\circ} \mathrm{F}\right)$. The tubes to be used are steel tubes [thermal conductivity $=25 \mathrm{Btu} /$ $(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)$, or $\left.43 \mathrm{~W} /(\mathrm{m})(\mathrm{K})\right]$ with aluminum fins. The steel tube is $1 \mathrm{in}(0.0254 \mathrm{~m})$ outside diameter and 0.834 in $(0.0212 \mathrm{~m})$ inside diameter. The inside heat-transfer coefficient $h_{i}$ and the fouling coefficient $h_{s}$ are each $1000 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[5680 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$. Heat-exchanger purchase cost is $\$ 22$ per square foot for four-tube-row units, $\$ 20$ per square foot for five-tube-row units, and $\$ 18$ per square foot for six-tube-row units.

## Water Conditions

Flow rate $=500,000 \mathrm{lb} / \mathrm{h}(226,795 \mathrm{~kg} / \mathrm{h})$, multipass
Inlet temperature $=150^{\circ} \mathrm{C}\left(302^{\circ} \mathrm{F}\right)$
Outlet temperature $=50^{\circ} \mathrm{C}\left(122^{\circ} \mathrm{F}\right)$

## Calculation Procedure

1. Decide on the design approach. A four-tube-row unit, a five-tube-row unit, and a six-tube-row unit will be designed and the cost compared. Standard tube geometries for air-cooled exchangers are 1 in $(0.0254 \mathrm{~m})$ outside diameter with $5 / 8$ in $(0.0159 \mathrm{~m})$ high aluminum fins spaced 10 fins per inch. Also available are 8 fins per inch. Standard spacings for tubes are listed in Table 7.6.

Typical face velocities ( $F V \mathrm{~s}$ ) used for design are also tabulated in Table 7.6. These values result in air-cooled heat exchangers that approach an optimum cost, taking into account the purchase cost, the cost for installation, and the cost of power to drive the fans. Each designer may wish to establish his or her own values of typical design face velocities; these should not vary greatly from those tabulated.

For air-cooled equipment, the tube spacing is normally determined by the relative values of the inside heat-transfer coefficient and the air-side heat-transfer coefficient. For inside coefficients much greater than the air-side coefficient, tubes spaced on $2.5-\mathrm{in}(0.064-\mathrm{m})$ centers are normally justified. For low values of the inside coefficient, tubes spaced on $2.375-\mathrm{in}(0.060-\mathrm{m})$ centers are normally justified. In the present case, because water is being cooled, the inside coefficient is indeed likely to be much greater, so specify the use of tubes on 2.5 -in centers.

TABLE 7.6 Design Face Velocities for Air-Cooled Exchangers

| Number of tube rows | Face velocity, ft/min (m/s) |  |  |
| :---: | :---: | :---: | :---: |
|  | 8 fins/in (315 fins/m), $2.375-\mathrm{in}(0.0603-\mathrm{m})$ pitch | 10 fins/in (394 fins/m), 2.375-in ( $0.0603-\mathrm{m}$ ) pitch | 10 fins/in (394 fins/m), $2.5-\mathrm{in}(0.0635-\mathrm{m})$ pitch |
| 3 | 650 (3.30) | 625 (3.18) | 700 (3.56) |
| 4 | 615 (3.12) | 600 (3.05) | 660 (3.35) |
| 5 | 585 (2.97) | 575 (2.92) | 625 (3.18) |
| 6 | 560 (2.84) | 550 (2.79) | 600 (3.05) |

2. Determine $\boldsymbol{h}_{a}$, the air-side heat-transfer coefficient. The air-side coefficient is frequently calculated on the basis of the outside surface of a bare tube. The equations for air can be simplified as follows:

$$
\begin{array}{lr}
h_{a}=8(F V)^{1 / 2} \quad \text { for } 10 \text { fins per inch } \\
h_{a}=6.75(F V)^{1 / 2} \quad \text { for } 8 \text { fins per inch }
\end{array}
$$

where $h_{a}$ is in Btus per hour per square foot per degree Fahrenheit and $F V$ is in feet per minute.
For this problem, $F V$ for 5 rows $=625 \mathrm{ft} / \mathrm{min}$, so $h_{a}=8(625)^{1 / 2}=200 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)[1136 \mathrm{~W} /$ $\left.\left(\mathrm{m}^{2}\right)(\mathrm{K})\right] . F V$ for 4 rows $=660 \mathrm{ft} / \mathrm{min}$, so $h_{a}=8(660)^{1 / 2}=205 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[1164 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$. $F V$ for 6 rows $=600 \mathrm{ft} / \mathrm{min}$, so $h_{a}=8(600)^{1 / 2}=196 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[1113 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.
3. Calculate $\boldsymbol{h}_{\boldsymbol{w}}$, the coefficient of heat transfer through the tube wall. The formula is $h_{w}=2 k$ / $\left(D_{o}-D_{i}\right)=2(25) /[(1-0.834)(1 / 12)]=3614 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[20,520 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.
4. Calculate $\boldsymbol{U}$, the overall heat-transfer coefficient. The formula is

$$
\frac{1}{U}=\frac{1}{h_{a}}+\frac{1}{h_{i}\left(D_{i} / D_{o}\right)}+\frac{1}{h_{w}}+\frac{1}{h_{s}}
$$

For five-tube rows, $1 / U=1 / 200+1 /[1000(0.834 / 1)]+1 / 3614+1 / 1000$, so $U=134 \mathrm{Btu} /$ (h) $\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)$. For four-tube rows, $1 / U=1 / 205+1 /[1000(0.834 / 1)]+1 / 3614+1 / 1000$, so $U=$ $136 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)$. For six-tube rows, $1 / U=1 / 196+1 /[1000(0.834 / 1)]+1 / 3614+1 / 1000$, so $U=132 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)$. Since the values are so close, use the same value of $U$ for four, five, and six rows, namely, $U=135 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[767 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.
5. Design a five-row unit. Air-cooled equipment is fabricated in standard modules. The standards begin with fin-tube bundles 48 in ( 1.22 m ) wide and increase in 6 -in $(0.152-\mathrm{m})$ increments up to a $144-\mathrm{in}(3.66-\mathrm{m})$ maximum. These modules can then be placed in parallel to obtain any size exchanger needed. The maximum tube length is $48 \mathrm{ft}(14.63 \mathrm{~m})$. In general, long tubes result in economical heat exchangers. In the present case, assume that the plant layout allows a maximum tube length of 40 ft ( 12.2 m ).

The design of heat-transfer equipment is a trial-and-error procedure because various design standards are followed in order to reduce equipment cost. To design an air-cooled exchanger, an outlet air temperature and a tube length are assumed, which establishes the amount of air to be pumped by the fan. The amount of air to be pumped establishes a face area, because we have assumed a face velocity. The face area fixes the heat-transfer area for a given tube length and number of tube rows. Table 7.7 permits an estimate of the outlet air temperature, based on 90 to $95^{\circ} \mathrm{F}$ ( 305 to 308 K ) design ambient air temperature.

For this problem, $U=135$ and inlet process temperature $=150^{\circ} \mathrm{C}$, so assume an outlet air temperature of $83^{\circ} \mathrm{C}$. Then, $Q=$ heat load $=w c\left(t_{2}-t_{1}\right)=500,000(1.0)(150-50)\left(1.8^{\circ} \mathrm{F} /{ }^{\circ} \mathrm{C}\right)=$ $90,000,000 \mathrm{Btu} / \mathrm{h}$. The face area $F A$ can be estimated from the equation

$$
F A=\frac{Q}{F V\left(T_{2}-T_{1}\right)(1.95)}
$$

where $Q$ is the heat load in Btu/h, $F A$ is the face area in square feet, $F V$ is the face velocity in feet per minute, and $T_{1}$ and $T_{2}$ are inlet and outlet air temperatures in degrees Celsius. Thus, $F A=90,000,000 /[625(83-35)(1.95)]=1540 \mathrm{ft}^{2}$.

The exchanger width can now be determined:

$$
Y=\text { width }=\text { face area } / \text { tube length }=F A / L=1540 / 40=38.5 \mathrm{ft}
$$

TABLE 7.7 Estimated Outlet Air Temperatures for Air-Cooled Exchangers

| Process inlet <br> temperature, ${ }^{\circ} \mathrm{C}$ | Outlet air temperature, ${ }^{\circ} \mathrm{C}$ |  |  |
| :---: | :---: | :---: | :---: |
|  | $U=50$ | $U=100$ | $U=150$ |
| 175 | 90 | 95 | 100 |
| 150 | 75 | 80 | 85 |
| 125 | 70 | 75 | 80 |
| 100 | 60 | 65 | 70 |
| 90 | 55 | 60 | 65 |
| 80 | 50 | 55 | 60 |
| 70 | 48 | 50 | 55 |
| 60 | 45 | 48 | 50 |
| 50 | 40 | 41 | 42 |

Note: $U$ is the overall heat-transfer coefficient in $\mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)$ $\left[1 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)=5.67 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.

However, standard widths have 6-in increments. Therefore, assume four 9.5 -ft-wide bundles. Then, $F A=4(9.5)=38 \mathrm{ft}$.

For this face area, calculate the outlet air temperature. First, air temperature rise (in ${ }^{\circ} \mathrm{C}$ ) is

$$
\begin{aligned}
\Delta T_{a} & =\frac{Q}{Y(F V)(L) 1.95} \\
& =\frac{90,000}{36(625)(40) 1.95} \\
& =48.5^{\circ} \mathrm{C}
\end{aligned}
$$

Then, $T_{2}=T_{1}+\Delta T_{a}=35+48.5=83.5^{\circ} \mathrm{C}$. Next, calculate mean temperature difference. The formula is

$$
\Delta T_{m}=\frac{\left(t_{1}-T_{2}\right)-\left(t_{2}-T_{1}\right)}{\ln \left[\left(t_{1}-T_{2}\right) /\left(t_{2}-T_{1}\right)\right]}
$$

Thus, $\Delta T_{m}=[(150-83.5)-(50-35)] / \ln [(150-83.5) /(50-35)]=34.6^{\circ} \mathrm{C}\left(62.3^{\circ} \mathrm{F}\right)$.
Now, calculate the area required if this is the available temperature difference. Thus, $A=$ $Q /\left(U \Delta T_{m}\right)=90,000,000 /[135(34.6)(1.8)]=10,705 \mathrm{ft}^{2}\left(994.4 \mathrm{~m}^{2}\right)$. Next, calculate the area actually available. The number of tubes per row $N_{t}$ can be approximated by dividing the bundle width by the tube spacing, that is, $N_{t}=Y / s=38 /(2.5 / 12)=182$ per row. Then, letting $N_{r}$ equal the number of rows, $A=N_{r} N_{t} \pi D_{o} L=5(182) \pi(1 / 12)(40)=9530 \mathrm{ft}^{2}$. Therefore, the area available is less than that required. Accordingly, increase the bundle width from 9.5 to 10 ft and calculate the new $\Delta T_{a}$ :

$$
\Delta T_{a}=48.5(9.5 / 10)=46.1^{\circ} \mathrm{C}
$$

Therefore, $T_{2}=35+46.1=81.1^{\circ} \mathrm{C}$.
Next, calculate the new $\Delta T_{m}$ :

$$
\begin{aligned}
\Delta T_{m} & =[(150-81.1)-(50-35)] / \ln [(150-81.1) /(50-35)] \\
& =35.4^{\circ} \mathrm{C}\left(63.7^{\circ} \mathrm{F}\right)
\end{aligned}
$$

And calculate the new area required

$$
A=90,000,000 /[135(35.4)(1.8)]=10,460 \mathrm{ft}^{2}
$$

Finally, calculate the new area available: $N_{t}=40 /(2.5 / 12)=192$, so $A=5(192) \pi(1 / 12)(40)=$ $10,050 \mathrm{ft}^{2}$. Or more precisely, the actual tube count provided by manufacturers' standards for a bundle 10 ft wide with five tube rows is 243 . Letting $N_{b}$ equal the number of bundles, $A=N_{b} N \pi D_{o} L=$ $4(243) \pi(1 / 12)(40)=10,180 \mathrm{ft}^{2}\left(945.7 \mathrm{~m}^{2}\right)$. This area would normally be accepted because the relatively high design air temperature occurs for relatively short periods and the fouling coefficient is usually arbitrarily assigned. If the design air temperature must be met at all times, then a wider bundle or greater face velocity would be required.

With the dimensions of the cooler established, the next step is to calculate the air-side pressure drop. For air, the following relations can be used:

$$
\begin{array}{ll}
\Delta P_{a}=0.0047 N_{r}(F V / 100)^{1.8} & \text { for } 10 \text { fins per inch, 2.375-in spacing } \\
\Delta P_{a}=0.0044 N_{r}(F V / 100)^{1.8} & \text { for } 8 \text { fins per inch, 2.375-in spacing } \\
\Delta P_{a}=0.0037 N_{r}(F V / 100)^{1.8} & \text { for } 10 \text { fins per inch, 2.5-in spacing }
\end{array}
$$

In these equations, $\Delta P_{a}$ is air-side pressure drop, in inches of water, $N_{r}$ is the number of tube rows, and $F V$ is face velocity, in feet per minute. For this problem, $\Delta P_{a}=0.0037(5)(625 / 100)^{1.8}=0.501$ in water.

Now, calculate the power required to pump the air. Use the formula

$$
b h p=(F V)(F A)\left(T_{2}+273\right)\left(\Delta P_{a}+0.1\right) /\left(1.15 \times 10^{6}\right)
$$

where $b h p=$ brake horsepower
$F V=$ face velocity, in $\mathrm{ft} / \mathrm{min}$
$F A=$ face area, in $\mathrm{ft}^{2}$ (equals $N_{b} Y L$ )
$T_{2}=$ outlet air temperature, in ${ }^{\circ} \mathrm{C}$
$\Delta P_{a}=$ air-side pressure drop, in inches of water
In this case, $F A=N_{b} Y L=4(10)(40)=1600 \mathrm{ft}^{2}$, so $b h p=625(1600)(81.1+273)(0.501+0.1) /$ $\left(1.15 \times 10^{6}\right)=185 \mathrm{hp}(138 \mathrm{~kW})$.
6. Compare costs. The same procedure can be followed to design a six-row unit and a four-row unit. The following comparison can then be made:

|  | Number of tube rows |  |  |
| :--- | :---: | :---: | :---: |
|  | 4 | 5 | 6 |
| Number of bundles | 4 | 4 | 4 |
| Bundle width, ft | 12 | 10 | 9.5 |
| Heat transfer area, $\mathrm{ft}^{2}$ | 9,800 | 10,180 | 11,510 |
| Equipment cost, dollars | 215,600 | 203,600 | 207,180 |
| Power required, bhp | 195 | 185 | 189 |

From this comparison, a five-row unit would be the most economical.

### 7.38 PRESSURE DROP FOR FLOW INSIDE TUBES: SINGLE-PHASE FLUIDS

Calculate the pressure drop for the water flowing through the air-cooled heat exchanger designed in Example 7.37 if the number of tube-side passes is 10 . The density of the water is $60 \mathrm{lb} / \mathrm{ft}^{3}(961.1 \mathrm{~kg} /$ $\left.\mathrm{m}^{3}\right)$, and the viscosity is $0.74 \mathrm{lb} /(\mathrm{ft})(\mathrm{h})(0.31 \mathrm{cP})$. Assume that the velocity in the nozzles is $10 \mathrm{ft} / \mathrm{s}$ $(3.05 \mathrm{~m} / \mathrm{s})$ and that the viscosity change with temperature is negligible.

## Calculation Procedure

1. Consider the causes of the pressure drop and the equations to find each. The total pressure drop for fluids flowing through tubes results from frictional pressure drop as the fluid flows along the tube, from pressure drop as the fluid enters and leaves the tube-side heads or channels, and from pressure drop as the fluid enters and leaves the tubes from the heads or channels.

The frictional pressure drop can be calculated from the equation

$$
\Delta P_{f}=\frac{4 f G^{2} L N_{p}}{2(144) g \rho D}
$$

where $\Delta P_{f}=$ pressure drop, in lb/in ${ }^{2}$
$f=$ friction factor
$G=$ mass velocity, in $\mathrm{lb} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)$
$L=$ tube length, in ft
$N_{p}=$ number of tube-side passes
$g=$ the gravitational constant
$\rho=$ density, in lb/ft ${ }^{3}$
$D=$ tube inside diameter, in ft
For fluids with temperature-dependent viscosities, the pressure drop must be corrected by the ratio of

$$
\left(\mu_{w} / \mu_{b}\right)^{n}
$$

where $\mu_{w}=$ viscosity at the surface temperature
$\mu_{b}=$ viscosity at the bulk fluid temperature
$n=0.14$ for turbulent flow or 0.25 for laminar flow
The friction factor $f$ can be calculated from the equations

$$
\begin{aligned}
& f=16 /(D G / \mu) \quad \text { for } D G / \mu \text { less than } 2100 \\
& f=0.054 /(D G / \mu)^{0.2} \quad \text { for } D G / \mu \text { greater than } 2100
\end{aligned}
$$

where $\mu$ is viscosity, in $\mathrm{lb} /(\mathrm{ft})(\mathrm{h})$.
The pressure drop as the fluid enters and leaves a radial nozzle at the heads or channels can be calculated from

$$
\Delta P_{n}=k \rho v_{n}^{2} / 9266
$$

```
where \(\Delta P_{n}=\) pressure drop, in \(\mathrm{lb} / \mathrm{in}^{2}\)
    \(\rho=\) density, in lb/ft \({ }^{3}\)
    \(v_{n}=\) velocity in the nozzle, in ft/s
    \(k=0\) for inlet nozzles or 1.25 for outlet nozzles
```

The pressure drop associated with inlet and outlet nozzles can be reduced by selection of other channel types, but the expense is not warranted except for situations in which pressure drop is critical or costly.

The pressure drop as a result of entry and exit from the tubes can be calculated from

$$
\Delta P_{e}=k N_{p} \rho v_{t}^{2} / 9266
$$

where $\Delta P_{e}=$ pressure drop, in $1 \mathrm{~b} / \mathrm{in}^{2}$
$N_{p}=$ number of tube-side passes
$v_{t}=$ velocity in tube, in $\mathrm{ft} / \mathrm{s}$
$\rho=$ density, in $\mathrm{lb} / \mathrm{ft}^{3}$
$k=1.8$
The total pressure drop is the sum of all these components:

$$
\Delta P_{t}=\Delta P_{f}+\Delta P_{n}+\Delta P_{e}
$$

2. Calculate frictional pressure drop. The total number of tubes from the previous design is $4(243)=972$. The number of tubes per pass is $972 / 10=97.2$. Letting $a_{c}$ be flow area,

$$
\begin{aligned}
G & =\frac{W}{a_{c}}=\frac{500,000}{97.2(0.834 / 12)^{2}(\pi / 4)} \\
& =1,355,952 \mathrm{lb} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left[6,619,758 \mathrm{~kg} /(\mathrm{h})\left(\mathrm{m}^{2}\right)\right]
\end{aligned}
$$

Then, $D G / \mu=(0.834 / 12) 1,355,952 / 0.74=127,350$. Therefore, $f=0.054 /(D G / \mu)^{0.2}=0.054 /$ $127,350^{0.2}=0.0051$, and

$$
\begin{aligned}
\Delta P_{f} & =\frac{4 f G^{2} L N_{p}}{2(144) g \rho D} \\
& =\frac{4(0.0051)(1,355,952)^{2}(40) 10}{2(144)\left(4.18 \times 10^{8}\right)(60)(0.834 / 12)} \\
& =29.89 \mathrm{lb} / \mathrm{in}^{2}
\end{aligned}
$$

3. Calculate nozzle pressure drop. From step $1, \Delta P_{n}=1.25 \rho v_{n}^{2} / 9266=1.25(60)(10)^{2} / 9266=$ $0.81 \mathrm{lb} / \mathrm{in}^{2}$
4. Calculate tube entry/exit pressure drop. From step $1, \Delta P_{e}=1.8 N_{p} \rho v_{t}^{2} / 9266$. Now, by definition, $v_{t}=G / 3600 \rho=1,355,952 /[3600(60)]=6.28 \mathrm{ft} / \mathrm{s}(1.91 \mathrm{~m} / \mathrm{s})$. So, $\Delta P_{e}=1.8(10)(60)$ $(6.28)^{2} / 9266=4.59 \mathrm{lb} / \mathrm{in}^{2}$.
5. Calculate total pressure drop. Thus, $\Delta P_{t}=\Delta P_{f}+\Delta P_{n}+\Delta P_{e}=29.89+0.81+4.59=$ $35.29 \mathrm{lb} / \mathrm{in}^{2}$ ( 243.32 kPa ).

Related Calculations. Helical Coils. The same procedure can be used to calculate the pressure drop in helical coils. For turbulent flow, a friction factor for curved flow is substituted for the friction factor for straight tubes. For laminar flow, the friction loss for a curved tube is expressed as an equivalent length of straight tube and the friction factor for straight tubes is used. The Reynolds number required for turbulent flow is $2100\left[1+12\left(D_{i} / D_{c}\right)^{1 / 2}\right]$, where $D_{i}$ is the inside diameter of the tube and $D_{c}$ is the coil diameter.

The friction factor for turbulent flow is calculated from the equation $f_{c}\left(D_{c} / D_{i}\right)^{1 / 2}=0.0073+$ $0.076\left[(D G / \mu)\left(D_{i} / D_{c}\right)^{2}\right]^{-1 / 4}$, for $(D G / \mu)\left(D_{i} / D_{c}\right)^{2}$ between 0.034 and 300 , where $f_{c}$ is the friction factor for curved flow. For values of $(D G / \mu)\left(D_{i} / D_{c}\right)^{2}$ below 0.034 , the friction factor for curved flow is practically the same as that for straight pipes.

For laminar flow, the equivalent length $L_{e}$ can be predicted as follows: For $(D G / \mu)\left(D_{i} / D_{c}\right)^{1 / 2}$ between 150 and 2000,

$$
L_{e} / L=0.23\left[(D G / \mu)\left(D_{i} / D_{c}\right)^{1 / 2}\right]^{0.4}
$$

For $(D G / \mu)\left(D_{i} / D_{c}\right)^{1 / 2}$ between 10 and 150 ,

$$
L_{e} / L=0.63\left[(D G / \mu)\left(D_{i} / D_{c}\right)^{1 / 2}\right]^{0.2}
$$

For $(D G / \mu)\left(D_{i} / D_{c}\right)^{1 / 2}$ less than 10,

$$
L_{e} / L=1
$$

In these equations, $L$ is straight length, and $L_{e}$ is equivalent length of a curved tube.
Longitudinal fin tubes. The same procedure can be used for longitudinally finned tubes. The equivalent diameter $D_{e}$ is substituted for $D_{i}$. The friction factor can be determined from these equations: For Reynolds numbers below 2100,

$$
f_{l f}=\frac{16}{\left(D_{e} G / \mu\right)}
$$

For Reynolds numbers greater than 2100,

$$
f_{l f}=\frac{0.103}{\left(D_{e} G / \mu\right)^{0.25}}
$$

In these equations, $f_{l f}$ is the friction factor for longitudinally finned tubes, and $D_{e}$ is equivalent diameter ( $=4 a_{c} / P$, where $a_{c}$ is the cross-sectional flow area and $P$ is the wetted perimeter).

### 7.39 PRESSURE DROP FOR FLOW INSIDE TUBES: TWO-PHASE FLUIDS

Calculate the frictional pressure drop for a two-phase fluid flowing through a tube 0.62 in $(0.0158 \mathrm{~m})$ in inside diameter $D$ and $20 \mathrm{ft}(6.1 \mathrm{~m})$ in length $L$ at a rate of $100 \mathrm{lb} / \mathrm{h}(45.4 \mathrm{~kg} / \mathrm{h})$. The mixture is 50 percent gas by weight and 50 percent liquid by weight, having the following properties:

## Liquid Properties

$\rho=$ density $=50 \mathrm{lb} / \mathrm{ft}^{3}\left(800 \mathrm{~kg} / \mathrm{m}^{3}\right)$
$\mu=\mathrm{viscosity}=2.0 \mathrm{lb} /(\mathrm{ft})(\mathrm{h})(0.84 \mathrm{cP})$

## Gas Properties

$\rho=$ density $=0.1 \mathrm{lb} / \mathrm{ft}^{3}\left(1.6 \mathrm{~kg} / \mathrm{m}^{3}\right)$
$\mu=$ viscosity $=0.045 \mathrm{lb} /(\mathrm{ft})(\mathrm{h})(0.019 \mathrm{cP})$

## Procedure

1. Select the method to be used. For two-phase flow, the friction pressure drop inside a tube can be calculated using the equation [31]

$$
\Delta P_{t p}=\left[\Delta P_{L}^{1 / n}+\Delta P_{G}^{1 / n}\right]^{n}
$$

where $\Delta P_{t p}=$ two-phase pressure drop
$\Delta P_{L}=$ pressure drop for the liquid phase, assuming only the liquid phase is present
$\Delta P_{G}=$ pressure drop for the gas phase, assuming only the gas phase is present
$n=4.0$ when both phases are in turbulent flow or 3.5 when one or both phases are in laminar flow
2. Calculate the liquid-phase pressure drop. Let $W_{L}$ be the mass flow rate of the liquid, equal to 50 percent of $100 \mathrm{lb} / \mathrm{h}$, or $50 \mathrm{lb} / \mathrm{h}$, and let $a_{c}$ be the cross-sectional area of the tube. Then $G_{L}=$ mass velocity of liquid phase $=W_{L} / a_{c}=50 /\left[(0.62 / 12)^{2}(\pi / 4)\right]=23,848.4 \mathrm{lb} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)$. Then the Reynolds number $D G_{L} / \mu=(0.62 / 12) 23,848.4 / 2.0=616.1$. Then, as in step 1 of Example 7.38, $f=$ friction factor $=16 /\left(D G_{L} / \mu\right)=16 / 616.1=0.026$, and

$$
\begin{aligned}
\Delta P_{L} & =\frac{4 f G_{L}^{2} L N_{p}}{2(144) g \rho D} \\
& =\frac{4(0.026)(23,848.4)^{2}(20)(1)}{2(144)\left(4.18 \times 10^{8}\right)(50)(0.62 / 12)} \\
& =0.0038 \mathrm{lb} / \mathrm{in}^{2}
\end{aligned}
$$

3. Calculate the gas-phase pressure drop. The mixture is 50 percent each phase, so $G_{G}=$ mass velocity of gas phase $=G_{L}$ from step 2. Then $D G_{G} / \mu=(0.62 / 12) 23,848 \cdot 4 / 0.045=27,381.5$. Again referring to step 1 of Example 7.38, $f=$ friction factor $=0.054 /\left(D G_{G} / \mu\right)^{0.2}=0.054 / 27,381.5^{0.2}=$ 0.0070 , and

$$
\begin{aligned}
\Delta P_{G} & =\frac{4 f G_{G}^{2} L N_{p}}{2(144) g \rho D} \\
& =\frac{4(0.0070)(23,848.4)^{2}(20)(1)}{2(144)\left(4.18 \times 10^{8}\right)(0.1)(0.62 / 12)} \\
& =0.5120 \mathrm{lb} / \mathrm{in}^{2}
\end{aligned}
$$

4. Calculate the two-phase pressure drop. The liquid phase is in laminar flow; the gas phase is in turbulent flow. Therefore,

$$
\begin{aligned}
\Delta P_{t p} & =\left[\Delta P_{L}^{1 / 3.5}+\Delta P_{G}^{1 / 3.5}\right]^{3.5} \\
& =\left(0.0038^{1 / 3.5}+0.5120^{1 / 3.5}\right)^{3.5} \\
& =1.107 \mathrm{lb} / \mathrm{in}^{3}(7.633 \mathrm{kPa})
\end{aligned}
$$

Related Calculations. Homogeneous flow method. Two-phase flow pressure drop can also be calculated using a homogeneous-flow model that assumes that gas and liquid flow at the same velocity (no slip) and that the physical properties of the fluids can be suitably averaged. The correct averages are

$$
\rho_{n s}=\rho_{L} \lambda_{L}+\rho_{G}\left(1-\lambda_{L}\right) \quad \text { and } \quad \mu_{n s}=\mu_{L} \lambda_{L}+\mu_{G}\left(1-\lambda_{L}\right)
$$

where $\lambda_{L}=Q_{L} /\left(Q_{L}+Q_{G}\right)$
$\rho_{n s}=$ no-slip density
$\mu_{n s}=$ no-slip viscosity
$\rho_{L}=$ liquid density
$\rho_{G}=$ gas density
$\mu_{L}=$ liquid viscosity
$\mu_{G}=$ gas viscosity
$Q_{L}=$ liquid volumetric flow rate
$Q_{G}=$ gas volumetric flow rate

Once the average density and viscosity are calculated, an average no-slip Reynolds number can be calculated:

$$
\text { No-slip Reynolds number }=D G_{T} / \mu_{n s}
$$

where $G_{T}=$ total mass velocity $=G_{L}+G_{G}$
$D=$ tube diameter
The frictional pressure drop is then

$$
\Delta P_{f}=\frac{4 f G_{T}^{2} \mathrm{LN}_{p}}{2(144) g \rho_{n s} D}
$$

where $f$ is the friction factor calculated using the method presented for single-phase fluids but based on the no-slip Reynolds number.

In addition to the frictional pressure drop, there will be a pressure loss associated with the expansion of the gas, termed an "acceleration loss" and calculated from

$$
\Delta P_{a}=\frac{G_{T}^{2}}{2(144) g}\left(\frac{1}{\rho_{G 2}}-\frac{1}{\rho_{G 1}}\right)
$$

where $\Delta P_{a}=$ acceleration pressure drop, in $\mathrm{lb} / \mathrm{in}^{2}$
$G_{T}=$ total mass velocity $=G_{L}+G_{G}$, in $\mathrm{lb} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)$
$\rho_{G 2}=$ gas density at outlet, in lb/ft ${ }^{3}$
$\rho_{G 1}=$ gas density at inlet, in $\mathrm{lb} / \mathrm{ft}^{3}$
$g=$ gravitational constant, in $\mathrm{ft} / \mathrm{h}^{2}$
The total pressure drop $\Delta P_{t p}$ is, then,

$$
\Delta P_{t p}=\Delta P_{f}+\Delta P_{a}
$$

For flashing flow, the pressure drop is

$$
\Delta P_{t p}=\frac{G_{T}^{2}}{2(144) g}\left[2\left(\frac{x_{2}}{\rho_{G 2}}-\frac{x_{1}}{\rho_{G 1}}\right)+\frac{4 f L N_{p}}{D \rho_{n s, \text { avg }}}\right]
$$

where $x_{1}=$ mass fraction vapor at inlet
$x_{2}=$ mass fraction vapor at outlet
$\rho_{n s, \text { avg }}=$ average no-slip density
Pressure drop for condensers. For condensers, the frictional pressure drop can be estimated using the relation

$$
\Delta P_{c}=1 / 2 \frac{1+v_{2}}{v_{1}} \Delta P_{1}
$$

where $\Delta P_{c}=$ condensing pressure drop
$\Delta P_{1}=$ pressure drop based on the inlet conditions of flow rate, density, and viscosity
$v_{2}=$ vapor velocity at the outlet
$v_{1}=$ vapor velocity at the inlet
For a total condenser, this becomes

$$
\Delta P_{c}=\frac{\Delta P_{1}}{2}
$$

### 7.40 PRESSURE DROP FOR FLOW ACROSS TUBE BANKS: SINGLE-PHASE FLUIDS

Calculate the pressure drop for the conditions of Example 7.20. Assume that the nozzle velocities are $5 \mathrm{ft} / \mathrm{s}(1.52 \mathrm{~m} / \mathrm{s})$, that the fluid density is $55 \mathrm{lb} / \mathrm{ft}^{3}\left(881 \mathrm{~kg} / \mathrm{m}^{3}\right)$, and that there are 24 baffles. Assume that there is also an impingement plate at the inlet nozzle. Calculate the pressure drop for both fouled and clean conditions.

## Calculation Procedure

1. Consider the causes of the pressure drop, and select equations to calculate each. The pressure drop for fluids flowing across tube banks may be determined by calculating the following components:
2. Inlet-nozzle pressure drop
3. Outlet-nozzle pressure drop
4. Frictional pressure drop for inlet and outlet baffle sections
5. Frictional pressure drop for intermediate baffle sections
6. Pressure drop for flow through the baffle windows

Heat exchangers with well-constructed shell sides will have a certain amount of bypassing that will reduce the pressure drop experienced with an ideal-tube bundle (one with no fluid bypassing or leakage). The amount of bypassing for a clean heat exchanger is more than that for a fouled heat exchanger. The following leakage factors are based on data from operating heat exchangers and include the typical effects of fouling on pressure drop.

Pressure drop for nozzles may be calculated from

$$
\Delta P_{n}=\frac{k \rho v_{n}^{2}}{9266}
$$

where $k=0$ for inlet nozzles with no impingement plate, 1.0 for inlet nozzles with impingement
plates, or 1.25 for outlet nozzles
$\Delta P_{n}=$ pressure drop, in $\mathrm{lb} / \mathrm{in}^{2}$
$\rho=$ density, in lb/ft ${ }^{3}$
$v_{n}=$ velocity in the nozzle, in $\mathrm{ft} / \mathrm{s}$
Frictional pressure drop for tube banks may be calculated as follows: For intermediate baffle sections,

$$
\Delta P_{f}=\frac{4 f G^{2} N_{r}\left(N_{b}-1\right) R_{1} R_{b} \phi}{2(144) g \rho}
$$

and for inlet and outlet baffle sections combined,

$$
\Delta P_{f i}=\frac{4(2.66) f G^{2} N_{r} R_{b} \phi}{2(144) g \rho}
$$

where $R_{1}=0.6\left(B / D_{s}\right)^{1 / 2}$ for clean bundles or $0.75\left(B / D_{s}\right)^{1 / 3}$ for bundles with assumed fouling
$R_{b}=0.80\left(D_{s}\right)^{0.08}$ for clean bundles or $0.85\left(D_{s}\right)^{0.08}$ for bundles with assumed fouling
$\phi=\left(\mu_{w} / \mu_{b}\right)^{n}$, where $n=0.14$ for $D G / \mu$ greater than 300 or 0.25 for $D G / \mu$ less than 300
$N_{r}=b D_{s} / s$, where $b=0.7$ for triangular tube spacing, 0.6 for square tube spacing, or 0.85 for rotated square tube spacing

The friction factor $f$ can be calculated. For $D_{g} G / \mu$ greater than 100 ,

$$
f=\frac{z}{\left(D_{g} G / \mu\right)^{0.25}}
$$

where $z=1.0$ for square and triangular tube patterns or 0.75 for rotated square tube patterns. For $D_{g} G / \mu$ less than 100,

$$
f=\frac{r}{\left(D_{g} G / \mu\right)^{0.725}}
$$

where $r=10$ for triangular tube patterns or 5.7 for square and rotated square tube patterns. In these equations, $D_{g}$ is defined as the gap between the tubes, that is, $D_{g}=s-D_{o}$.

Pressure drop for baffle windows may be calculated as follows: For $D_{o} G / \mu$ greater than 100,

$$
\Delta P_{w}=\frac{G^{2}}{2(144) g \rho} \frac{a_{c}}{a_{w}}\left(2+0.6 N_{w}\right) N_{b} R_{1}
$$

in which the factor $\left(2+0.6 N_{w}\right)$ can be approximated with the term $2+0.6 N_{w}=m\left(D_{s}\right)^{5 / 8}$, where $m=3.5$ for triangular tube patterns, 3.2 for square tube patterns, or 3.9 for rotated square tube patterns. For $D_{o} G / \mu$ less than 100 ,

$$
\Delta P_{w}=\frac{26 \mu G}{g \rho}\left(\frac{a_{c}}{a_{w}}\right)^{1 / 2}\left(\frac{N_{w}}{s-D_{o}}+\frac{B}{D_{e}^{2}}\right)+\frac{2 G^{2}}{2 g \rho} \frac{a_{c}}{a_{w}}
$$

Baffles are normally cut on the centerline of a row of tubes. Baffles should be cut on the centerline of a row whose location is nearest the value of $20 \%$ of the shell diameter. For baffle cuts meeting this criterion, the following values can be used:

| Tube geometry | $N_{w} /\left(s-D_{o}\right)$ | $D_{e}, \mathrm{ft}$ |
| :--- | :---: | :---: |
| $D_{o}=5 / 8$ in $(0.016 \mathrm{~m}) ; s=13 / 16$ in $(0.020 \mathrm{~m})$; triangular pitch | $173 D_{s}$ | 0.059 |
| $D_{o}=5 / 8$ in $(0.016 \mathrm{~m}) ; s=7 / 8$ in $(0.022 \mathrm{~m})$; square pitch | $105 D_{s}$ | 0.090 |
| $D_{o}=3 / 4$ in $(0.019 \mathrm{~m}) ; s=15 / 16$ in $(0.024 \mathrm{~m})$; triangular pitch | $151 D_{s}$ | 0.063 |
| $D_{o}=3 / 4$ in $(0.019 \mathrm{~m}) ; s=1$ in $(0.025 \mathrm{~m}) ;$ square pitch | $92 D_{s}$ | 0.097 |
| $D_{o}=1$ in $(0.025 \mathrm{~m}) ; s=11 / 4$ in $(0.032 \mathrm{~m})$; triangular pitch | $85 D_{s}$ | 0.083 |
| $D_{o}=1$ in $(0.025 \mathrm{~m}) ; s=11 / 4$ in $(0.032 \mathrm{~m}) ;$ square pitch | $73.5 D_{s}$ | 0.104 |

In these equations, $a_{c}=B D_{s}\left(s-D_{o}\right) / s$ for triangular and square tube patterns or $1.5 B D_{s}\left(s-D_{o}\right) / s$ for rotated square tube patterns, and $a_{w}=0.055 D_{s}^{2}$ for triangular tube patterns or $0.066 D_{s}^{2}$ for square and rotated square tube patterns. Moreover, the units for the various terms are as follows:
$\Delta P_{f}=$ total pressure drop for intermediate baffle sections, in $\mathrm{lb} / \mathrm{in}^{2}$
$\Delta P_{f i}=$ total pressure drop for inlet and outlet baffle sections, in $\mathrm{lb} / \mathrm{in}^{2}$
$\Delta P_{w}=$ total pressure drop for baffle windows, in $\mathrm{lb} / \mathrm{in}^{2}$
$f=$ friction factor (dimensionless)
$G=$ mass velocity, in $\mathrm{lb} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left(=W / a_{c}\right.$, where $W=$ flow rate $)$
$g=$ gravitational constant, in ft/ $h^{2}$
$\rho=$ density, in $\mathrm{lb} / \mathrm{ft}^{3}$
$N_{r}=$ number of tube rows crossed
$N_{b}=$ number of baffles
$a_{c}=$ minimum flow area for cross flow, in $\mathrm{ft}^{2}$
$a_{w}=$ flow area in baffle window, in $\mathrm{ft}^{2}$
$D_{s}=$ shell diameter, in ft
$s=$ tube center-to-center spacing, in ft
$B=$ baffle spacing, in ft
$D, D_{o}=$ outside tube diameter, in ft
$D_{g}=$ gap between tubes, in $\mathrm{ft}\left(=s-D_{o}\right)$
$\mu=$ viscosity, in $\mathrm{lb} /(\mathrm{ft})(\mathrm{h})$
$\mu_{w}=$ viscosity at wall temperature, in $\mathrm{lb} /(\mathrm{ft})(\mathrm{h})$
$\mu_{b}=$ viscosity at bulk fluid temperature, in $\mathrm{lb} /(\mathrm{ft})(\mathrm{h})$
$R_{1}=$ correction factor for baffle leakage
$R_{b}=$ correction factor for bundle bypass
$D_{e}=$ equivalent diameter of baffle window, in ft
The total pressure drop is the sum of all these components:

$$
\Delta P=\Delta P_{n}+\Delta P_{f}+\Delta P_{f i}+\Delta P_{w}
$$

## 2. Calculate the total pressure drop assuming fouled conditions.

a. Calculate nozzle pressure drops. The equation is

$$
\begin{aligned}
\Delta P_{n} & =\frac{k \rho v_{n}^{2}}{9266} \\
& =\frac{2.25 \rho v_{n}^{2}}{9266}
\end{aligned}
$$

Thus, with $k$ equal to 1.0 plus 1.25 ,

$$
\begin{aligned}
\Delta P_{n} & =\frac{2.25(55)(5)^{2}}{9266} \\
& =0.334 \mathrm{lb} / \mathrm{in}^{2}(2.303 \mathrm{kPa})
\end{aligned}
$$

b. Calculate frictional pressure for intermediate baffle sections. Now, $a_{c}=B D_{s}\left(s-D_{o}\right) / s=(9.5 /$ 12) $(25 / 12)(0.9375-0.75) / 0.9375=0.3299 \mathrm{ft}^{2}\left(0.0306 \mathrm{~m}^{2}\right)$. Therefore, $G=W / a_{c}=50,000 /$ $0.3299=151,561.1 \mathrm{lb} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)$, and $D_{g} G / \mu=(0.9375-0.75)(1 / 12) 151,561.1 / 1.95=1214.4$. Accordingly, $\quad f=1 /\left(D_{g} G / \mu\right)^{0.25}=1 / 1214.4^{0.25}=0.1694$. And in the equation $\Delta P_{f}=$ $4 f G^{2} N_{r}\left(N_{b}-1\right) R_{1} R_{b} \phi /[2(144) g \rho], \quad R_{1}=0.75\left(B / D_{s}\right)^{1 / 3}=0.75(9.5 / 25)^{1 / 3}=0.5432, \quad R_{b}=$ $0.85\left(D_{s}\right)^{0.08}=0.85(25 / 12)^{0.08}=0.9014, \phi=(4.0 / 1.95)^{0.14}=1.1058$, and $N_{r}=0.7 D_{\mathrm{s}} / s=$ $0.7(25) / 0.9375=18.7$. Therefore,

$$
\begin{aligned}
\Delta P_{f} & =\frac{4(0.1694)(151,561.1)^{2}(18.7)(24-1)(0.5432)(0.9014) 1.1058}{2(144)\left(4.18 \times 10^{8}\right) 55} \\
& =0.547 \mathrm{lb} / \mathrm{in}^{2}(3.774 \mathrm{kPa})
\end{aligned}
$$

c. Calculate frictional pressure drop for inlet and outlet baffle sections. The equation is

$$
\Delta P_{f i}=\frac{4(2.66) f G^{2} N_{r} R_{b} \phi}{2(144) g \rho}
$$

Thus,

$$
\begin{aligned}
\Delta P_{f i} & =\frac{4(2.66)(0.1694)(151,561.1)^{2}(18.7)(0.9014) 1.1058}{2(144)\left(4.18 \times 10^{8}\right) 55} \\
& =0.117{\mathrm{lb} / \mathrm{in}^{2}(0.803 \mathrm{kPa})}^{\text {( }} \text {. }
\end{aligned}
$$

d. Calculate pressure drop for window sections. The equation is

$$
\Delta P_{w}=\frac{3.5 G^{2}}{2(144) g \rho} \frac{a_{c}}{a_{w}} D_{s}^{5 / 8} N_{b} R_{1}
$$

Now, $a_{w}=0.055 D_{s}^{2}=0.055(25 / 12)^{2}=0.2387 \mathrm{ft}^{2}$. Therefore,

$$
\begin{aligned}
\Delta P_{w} & =\frac{3.5(151,561.1)^{2}(0.3299 / 0.2387)(25 / 12)^{5 / 8}(24) 0.5432}{2(144)\left(4.18 \times 10^{8}\right) 55} \\
& =0.346 \mathrm{lb} / \mathrm{in}^{2}(2.38 \mathrm{kPa})
\end{aligned}
$$

e. Calculate total pressure drop. The equation is

$$
\Delta P=\Delta P_{n}+\Delta P_{f}+\Delta P_{f i}+\Delta P_{w}
$$

Thus, $\Delta P=0.334+0.547+0.117+0.346=1.344 \mathrm{lb} / \mathrm{in}^{2}(9.267 \mathrm{kPa})$.

## 3. Calculate the total pressure drop assuming clean conditions

a. Calculate $R_{1}$ and $R_{b}$ for clean conditions. Here, $R_{1}=0.6\left(B / D_{s}\right)^{1 / 2}=0.6(9.5 / 25)^{1 / 2}=0.3699$, and $R_{b}=0.80\left(D_{s}\right)^{0.08}=0.80(25 / 12)^{0.08}=0.848$.
b. Calculate total pressure drop. The clean-pressure-drop components will be the fouled-pressuredrop components multiplied by the appropriate ratios of $R_{1}$ and $R_{b}$ for the clean and fouled conditions. Thus,

$$
\begin{aligned}
\Delta P & =\Delta P_{n}+\Delta P_{f} \frac{R_{1}}{R_{1}} \frac{R_{b}}{R_{b}}+\Delta P_{f i} \frac{R_{b}}{R_{b}}+\Delta P_{w} \frac{R_{1}}{R_{1}} \\
& =0.334+0.547+\frac{0.3699}{0.5432} \frac{0.848}{0.9014}+0.117 \frac{0.848}{0.9014}+0.346 \frac{0.3699}{0.5432} \\
& =0.334+0.350+0.110+0.236 \\
& =1.03 \mathrm{lb} / \mathrm{in}^{2}(7.102 \mathrm{kPa})
\end{aligned}
$$

Related Calculations. The preceding equations for pressure drop assume a well-constructed tube bundle with baffle cuts amounting to 20 percent of the shell diameter and tubes included in the baffle windows. The corrections for fluid bypassing ( $R_{1}$ and $R_{b}$ ) are based on the standards of the Tubular Exchangers Manufacturers Association [11] and assume an adequate number of sealing devices. The values for fouling are based on plant data for typical services. Methods that evaluate the effects of the various bypass streams have been presented; the most widely used is that of Bell [15]. For poorly constructed tube bundles or for conditions greatly different from those assumed, this reference should be used for evaluating the effects on the calculated pressure drop.

Bundles with tubes omitted from baffle windows. Frequently, tubes are omitted from the bafflewindow areas. For this configuration, maldistribution of the fluid as it flows across the bank of tubes may occur as a result of the momentum of the fluid as it flows through the baffle window. For this reason, baffle cuts less than 20 percent of the shell diameter should only be used with caution. Maldistribution will normally be minimized if the fluid velocity in the baffle window is equal to or
less than the fluid velocity in cross-flow across the bundle. This frequently requires baffle cuts greater than 20 percent of the shell diameter. For such cases, the number of tubes in cross-flow will be less than that assumed in the preceding methods, so a correction is required. In addition, the pressure drop for the first and last baffle sections assumes tubes in the baffle windows; the factor 2.66 should be reduced to 2.0 for the case of 20 percent baffle cuts.

For baffles with no tubes in the baffle windows, the pressure drop for the window section can be calculated from

$$
\Delta P_{w}=\frac{1.8 \rho v_{w}^{2} N_{b}}{9266}
$$

where $\Delta P_{w}=$ pressure drop, in $\mathrm{lb} / \mathrm{in}^{2}$
$\rho=$ density, in lb/ft ${ }^{3}$
$v_{w}=$ velocity in the baffle window, in $\mathrm{ft} / \mathrm{s}$
$N_{b}=$ number of baffles
The flow area may be calculated from $a_{w}=0.11 D_{s}^{2}$ for 20 percent baffle cuts or $0.15 D_{s}^{2}$ for 25 percent baffle cuts, where $D_{s}$ is the shell diameter.

Low-fin tubes. The method presented above can be used to predict pressure drop for banks of low-fin tubes. For low-fin tubes, the pressure drop is calculated assuming that the tubes are bare. The mass velocity and tube diameter used for calculation are those for a bare tube with the same diameter as the fins of the low-fin tube.

Banks of finned tubes. For fin tubes other than low-fin tubes, the pressure drop for flowing across banks of transverse fin tubes can be calculated from

$$
\Delta P_{f}=\frac{4 f_{r} G_{m}^{2} N_{r} \phi}{2(144) g \rho}
$$

In this equation, for values of $D_{r} G_{m} / \mu$ from 2000 to 50,000 ,

$$
f_{r}=\frac{a}{\left(D_{r} G_{m} / \mu\right)^{0.316}\left(s / D_{r}\right)^{0.927}}
$$

where $a=10.5(a / p)^{1 / 2}$ for triangular tube patterns or $6.5\left(D_{f} / s\right)^{1 / 2}$ for square tube patterns. The units for the various terms are as follows:

$$
\begin{aligned}
\Delta P_{f} & =\text { frictional pressure drop, in } \mathrm{lb} / \mathrm{in}^{2} \\
f_{r} & =\text { friction factor (dimensionless) } \\
G_{m} & =\text { mass velocity based on minimum flow area }\left(=W / a_{c}\right) \text { in } \mathrm{lb} /(\mathrm{h})\left(\mathrm{ft}^{2}\right) \\
N_{r} & =\text { number of tube rows crossed by the fluid } \\
\rho & =\text { density, in } \mathrm{lb} / \mathrm{ft}^{3} \\
g & =\text { gravitational constant, in } \mathrm{ft} / \mathrm{h}^{2} \\
D_{r} & =\text { root diameter of fin, in } \mathrm{ft} \\
\mu & =\text { viscosity, in } \mathrm{lb} / \mathrm{ft}(\mathrm{~h}) \\
s & =\text { tube spacing perpendicular to flow, in } \mathrm{ft} \\
p & =\text { tube spacing parallel to flow, in } \mathrm{ft} \\
D_{f} & =\text { diameter of fins, in } \mathrm{ft} \\
a_{c} & =\text { minimum flow area, in } \mathrm{ft}^{2}
\end{aligned}
$$

And,

$$
\phi=\left(\mu_{w} / \mu_{b}\right)^{0.14}
$$

where $\mu_{w}$ is the viscosity at the wall temperature and $\mu_{b}$ is the viscosity at the bulk fluid temperature, and

$$
a_{c}=s-D_{r}-2 n l b
$$

where $n=$ number of fins per foot
$l=$ fin height, in ft
$b=$ fin thickness, in ft

### 7.41 PRESSURE DROP FOR FLOW ACROSS TUBE BUNDLES: TWO-PHASE FLOW

Calculate the pressure drop for the conditions of Example 7.40 if $10,000 \mathrm{lb} / \mathrm{h}(4535.9 \mathrm{~kg} / \mathrm{h})$ of the total fluid is a gas with a density of $0.5 \mathrm{lb} / \mathrm{ft}^{3}\left(8.01 \mathrm{~kg} / \mathrm{m}^{3}\right)$ and a viscosity of $0.05 \mathrm{lb} /(\mathrm{ft})(\mathrm{h})(0.0207 \mathrm{cP})$. Assume the nozzle velocities are $50 \mathrm{ft} / \mathrm{s}(15.24 \mathrm{~m} / \mathrm{s})$. The flow is vertical up-and-down flow.

## Calculation Procedure

1. Select the appropriate equation. Two-phase-flow pressure drop for flow across tube bundles may be calculated using the equation

$$
\frac{\Delta P_{t p}}{\Delta P_{L O}}=1+\left(K^{2}-1\right)\left[B x^{(2-n) / n}(1-x)^{(2-n) / n}+x^{2-n}\right]
$$

where $\Delta P_{t p}=$ the two-phase pressure drop
$\Delta P_{L O}=$ the pressure drop for the total mass flowing as liquid
$x=$ the mass fraction vapor
$K=\underset{\text { vapor }}{\left(\Delta P_{G O} / \Delta P_{L O}\right)^{1 / 2}, \text { where } \Delta P_{G O} \text { is the pressure drop for the total mass flowing as }}$ vapor
$B=$ for vertical up-and-down flow, 0.75 for horizontal flow other than stratified flow, or 0.25 for horizontal stratified flow

The value of $n$ can be calculated from the relation

$$
K=\left(\Delta P_{G O} / \Delta P_{L O}\right)^{1 / 2}=\left(\rho_{L} / \rho_{G}\right)^{1 / 2}\left(\mu_{G} / \mu_{L}\right)^{n / 2}
$$

where $\rho_{G}=$ gas density

$$
\begin{aligned}
\rho_{L} & =\text { liquid density } \\
\mu_{G} & =\text { gas viscosity } \\
\mu_{L} & =\text { liquid viscosity }
\end{aligned}
$$

For the baffle windows, $n=0$, and the preceding equation becomes

$$
\frac{\Delta P_{t p}}{\Delta P_{L O}}=1+\left(K^{2}-1\right)\left[B x(1-x)+x^{2}\right]
$$

where $B=\left(\rho_{n s} / \rho_{L}\right)^{1 / 4}$ for vertical up-and-down flow or $2 /(K+1)$ for horizontal flow, and where $\rho_{L}$ is liquid density and $\rho_{n s}$ is no-slip density (homogeneous density).
2. Determine $\boldsymbol{\Delta} \boldsymbol{P}_{\boldsymbol{L} \text { o for }}$ cross flow. The pressure drop for the total mass flowing as liquid was calculated in the preceding example. The total friction pressure drop across the bundle is $\Delta P_{f}+\Delta P_{f i}$. Thus, $\Delta P_{f}+\Delta P_{f i}=0.547+0.117=0.664 \mathrm{lb} / \mathrm{in}^{2}\left(4.578 \mathrm{kI}{ }^{\prime} \mathrm{a}\right)$.
3. Calculate $\rho_{n r}$. The formula is

$$
\rho_{n s}=\rho_{L} \lambda_{L}+\rho_{G}\left(1-\lambda_{L}\right)
$$

where $\lambda_{L}=Q_{L} /\left(Q_{L}+Q_{G}\right)$
$Q_{L}=$ liquid volumetric flow rate $=40,000 / 55=727.3 \mathrm{ft}^{3} / \mathrm{h}$
$Q_{G}=$ gas volumetric flow rate $=10,000 / 0.5=20,000 \mathrm{ft}^{3} / \mathrm{h}$
Thus $\lambda_{L}=727.3 /(727.3+20,000)=0.0351$, so $\rho_{n s}=55(0.0351)+0.5(1-0.0351)=2.412 \mathrm{lb} /$ $\mathrm{ft}^{3}\left(38.64 \mathrm{~kg} / \mathrm{m}^{3}\right)$.
4. Calculate $\Delta \boldsymbol{P}_{G O}$ for cross flow. Analogously to step $2, \Delta P_{G O}=\Delta P_{f}+\Delta P_{f i}$. From the preceding example, $G=151,561.1 \mathrm{lb} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)$. Then, $D_{g} G / \mu=(0.9375-0.75)(1 / 12) 151,561.1 /$ $0.05=47,362.8$, and $f=1 /\left(D_{g} G / \mu\right)^{0.25}=1 / 47,362.8^{0.25}=0.0678$. Now,

$$
\Delta P_{f}=\frac{4 f G^{2} N_{r}\left(N_{b}-1\right) R_{1} R_{b} \phi}{2(144) g \rho}
$$

From the preceding example,
$N_{r}=18.7$
$N_{b}-1=23$
$R_{1}=0.5432$
$R_{b}=0.9014$
For the gas, $\phi=1.0$. Then,

$$
\begin{aligned}
\Delta P_{f} & =\frac{4(0.0678)(151,561.1)^{2}(18.7)(23)(0.5432)(0.9014) 1.0}{2(144)\left(4.18 \times 10^{8}\right) 0.5} \\
& =21.796 \mathrm{lb}_{\mathrm{b}} \mathrm{in}^{2}(150.28 \mathrm{kPa})
\end{aligned}
$$

Also,

$$
\begin{aligned}
\Delta P_{f i} & =\frac{4(2.66) f G^{2} N_{r} R_{b} \phi}{2(144) g \rho} \\
& =\frac{4(2.66)(0.0678)(151,561.1)^{2}(18.7)(0.9014) 1.0}{2(144)\left(4.18 \times 10^{8}\right) 0.5} \\
& =4.641 \mathrm{lb} / \mathrm{in}^{2}(32.00 \mathrm{kPa})
\end{aligned}
$$

Thus, $\Delta P_{G O}=21.796+4.641=26.437 \mathrm{lb} / \mathrm{in}^{2}(182.28 \mathrm{kPa})$.
5. Calculate $K$ for cross flow. As noted above, $K=\left(\Delta P_{G O} / \Delta P_{L O}\right)^{1 / 2}=(26.437 / 0.664)^{1 / 2}=$ 6.3099 .
6. Calculate $\boldsymbol{n}$ for cross flow. As noted above, $K=\left(\rho_{L} / \rho_{G}\right)^{1 / 2}\left(\mu_{G} / \mu_{L}\right)^{n / 2}$. Then, $K=6.3099=$ $(55 / 0.5)^{1 / 2}(0.05 / 1.95)^{n / 2}$, so $n=0.2774$.
7. Calculate $\boldsymbol{x}$, the mass friction of vapor. $\quad$ Straightforwardly, $x=10,000 / 50,000=0.2$.
8. Calculate $\boldsymbol{P}_{t \boldsymbol{t}}$ for cross flow. As noted above, $\Delta P_{t p} / \Delta P_{L O}=1+\left(K^{2}-1\right)\left[B x^{(2-n) / 2}\right.$ $\left.(1-x)^{(2-n) / 2}+x^{2-n}\right]$. Thus,

$$
\begin{aligned}
\frac{\Delta P_{t p}}{\Delta P_{L O}} & =1+\left(6.3099^{2}-1\right)\left[1.0(0.2)^{(2-0.2774) / 2}(1-0.2)^{(2-0.2774) / 2}+(0.2)^{(2-0.2774)}\right] \\
& =11.434
\end{aligned}
$$

Therefore, $\Delta P_{t p}=11.434 \Delta P_{L O}=11.434(0.664)=7.592 \mathrm{lb} / \mathrm{in}^{2}(52.35 \mathrm{kPa})$.
9. Calculate $\Delta P_{w}$, the pressure drop for the baffle windows, for the total mass flowing as gas. From the preceding example, $\Delta P_{w}$ for the total mass flowing as a liquid is $0.346 \mathrm{lb} / \mathrm{in}^{2}$. Now, $\Delta P_{w}$ for the gas $=\Delta P_{w}$ for the liquid $\left(\rho_{L} / \rho_{G}\right)$. So, $\Delta P_{w}=0.346(55 / 0.5)=38.06 \mathrm{lb} / \mathrm{in}^{2}(262.42 \mathrm{kPa})$.
10. Calculate $K$ for the flow through the baffle windows. Here, $K=\left(\Delta P_{G O} / \Delta P_{L O}\right)^{1 / 2}=$ $(38.06 / 0.346)^{1 / 2}=10.4881$.
11. Calculate $\boldsymbol{\Delta} \boldsymbol{P}_{\boldsymbol{t} \boldsymbol{p}}$ for the baffle windows. As noted in step $1, \Delta P_{t p} / \Delta P_{L O}=1+\left(K^{2}-1\right)$ $\left[B x(1-x)+x^{2}\right]$. Now, $B=\left(\rho_{n s} / \rho_{L}\right)^{1 / 4}=(2.412 / 55)^{1 / 4}=0.4576 . \quad$ So, $\Delta P_{t p} / \Delta P_{L O}=1+$ $\left(10.4881^{2}-1\right)\left[0.4576(0.2)(1-0.2)+0.2^{2}\right]=13.34$. Therefore, $\quad \Delta P_{t p}=13.34 \Delta P_{L O}=13.34$ $\times(0.346)=4.616 \mathrm{lb} / \mathrm{in}^{2}(31.82 \mathrm{kPa})$.
12. Calculate $\Delta P_{n}$, the pressure drop through the nozzles. Use the same approach as in step 2 a of the previous example, employing the no-slip density. Thus, $\Delta P_{n}=2.25 \rho_{n s} U_{n}^{2} / 9266=$ $2.25(2.412)(50)^{2} / 9266=1.464 \mathrm{lb} / \mathrm{in}^{2}(10.09 \mathrm{kPa})$.
13. Calculate total two-phase pressure drop. The total is the sum of the pressure drops for cross flow, window flow, and nozzle flow. Therefore $\Delta P_{t p}=7.592+4.616+1.464=13.672 \mathrm{lb} / \mathrm{in}^{2}$ ( 94.27 kPa ).

Related Calculations. For situations where $\Delta P_{t p} / \Delta P_{G O}$ is much less than $1 / K^{2}$ and $1 / K^{2}$ is much less than 1, the equation for two-phase pressure drop can be written as

$$
\frac{\Delta P_{t p}}{\Delta P_{G O}}=B x^{(2-n) / 2}(1-x)^{(2-n) / 2}+x^{(2-n)}
$$

This form may be more convenient for condensers.
The method presented here is taken from Grant and Chisholm [16]. This reference should be consulted to determine the flow regime for a given two-phase system.

Acceleration pressure drop. When the gas density or the vapor mass fraction changes, there is an acceleration pressure drop calculated from

$$
\Delta P_{a}=\frac{G_{T}^{2}}{144 g}\left(\frac{x_{2}}{\rho_{G 2}}-\frac{x_{1}}{\rho_{G 1}}\right)
$$

where $\Delta P_{a}=$ acceleration pressure drop, in $\mathrm{lb} / \mathrm{in}^{2}$
$G_{T}=$ total mass velocity, in $\mathrm{lb} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)$
$x_{2}=$ mass fraction gas at outlet
$x_{1}=$ mass fraction gas at inlet
$\rho_{G 2}=$ gas density at outlet, in $\mathrm{lb} / \mathrm{ft}^{3}$

$$
\begin{aligned}
\rho_{G 1} & =\text { gas density at inlet, in } \mathrm{lb} / \mathrm{ft}^{3} \\
g & =\text { gravitational constant, in } \mathrm{ft} /(\mathrm{h})^{2}
\end{aligned}
$$

Shell-side condensation. The frictional pressure drop for shell-side condensation can be calculated from the equation

$$
\Delta P_{c}=1 / 2\left(1+\frac{v_{2}}{v_{1}}\right) \Delta P_{1}
$$

where $\Delta P_{c}=$ condensing pressure drop
$\Delta P_{1}=$ pressure drop based on the inlet conditions of flow rate, density, and viscosity
$v_{1}=$ vapor velocity at the inlet
$v_{2}=$ vapor velocity at the outlet
For a total condenser, this becomes

$$
\Delta P_{c}=\frac{\Delta P_{1}}{2}
$$

### 7.42 CONDENSER-SUBCOOLER TEST DATA

Test data were obtained on a vertical condenser-subcooler for a pure component. Compare the observed heat-transfer coefficient to that expected, and calculate the apparent fouling coefficient. Data were obtained in late autumn and the water flow was cocurrent with the process flow in order to minimize the amount of subcooling. Design inlet water temperature was $30^{\circ} \mathrm{C}\left(86^{\circ} \mathrm{F}\right)$.

The condenser data are as follows:

```
\(D_{s}=\) shell diameter \(=36\) in \((0.914 \mathrm{~m})\)
\(D_{o}=\) tube outside diameter \(=0.625\) in \((0.0159 \mathrm{~m})\)
\(D_{i}=\) tube inside diameter \(=0.495\) in \((0.0126 \mathrm{~m})\)
    \(L=\) effective tube length \(=21 \mathrm{ft}(6.4 \mathrm{~m})\)
    \(B=\) baffle spacing \(=36\) in \((0.914 \mathrm{~m})\)
    \(n=\) number of tubes \(=1477\)
    \(s=\) tube spacing (center-to-center) \(=0.8125\) in \((0.02064 \mathrm{~m})\)
\(k_{w}=\) tube-wall thermal conductivity \(=220 \mathrm{Btu} /(\mathrm{h})(\mathrm{ft})\left({ }^{\circ} \mathrm{F}\right)[380 \mathrm{~W} /(\mathrm{m})(\mathrm{K})]\).
```

Tubes have been omitted from the baffle window areas. The performance data are as follows:

```
\(W_{v}=\) vapor flow rate \(=170,860 \mathrm{lb} / \mathrm{h}(77,500.4 \mathrm{~kg} / \mathrm{h})\)
\(\rho_{L}=\) liquid density \(=54.3 \mathrm{lb} / \mathrm{ft}^{3}\left(869.6 \mathrm{~kg} / \mathrm{m}^{3}\right)\)
\(\rho_{v}=\) vapor density \(=0.49 \mathrm{lb} / \mathrm{ft}^{3}\left(7.85 \mathrm{~kg} / \mathrm{m}^{3}\right)\)
\(\mu_{L}=\) liquid viscosity \(=0.484 \mathrm{lb} /(\mathrm{ft})(\mathrm{h})(0.2 \mathrm{cP})\)
\(\mu_{v}=\) vapor viscosity \(=0.036 \mathrm{lb} /(\mathrm{ft})(\mathrm{h})(0.015 \mathrm{cP})\)
    \(c=\) liquid specific heat \(=0.44 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)[1.84 \mathrm{~kJ} /(\mathrm{kg})(\mathrm{K})]\)
    \(k=\) liquid thermal conductivity \(=0.089 \mathrm{Btu} /(\mathrm{h})(\mathrm{ft})\left({ }^{\circ} \mathrm{F}\right)[0.15 \mathrm{~W} /(\mathrm{m})(\mathrm{K})]\)
    \(\lambda=\) heat of vaporization \(=250 \mathrm{Btu} / \mathrm{lb}(582 \mathrm{~kJ} / \mathrm{kg})\)
    \(t_{1}=\) inlet vapor temperature \(=54^{\circ} \mathrm{C}\left(129.2^{\circ} \mathrm{F}\right)\)
    \(t_{2}=\) outlet condensate temperature \(=40.5^{\circ} \mathrm{C}\left(104.9^{\circ} \mathrm{F}\right)\)
    \(T_{1}=\) inlet water temperature \(=16.1^{\circ} \mathrm{C}\left(61^{\circ} \mathrm{F}\right)\)
    \(T_{2}=\) outlet water temperature \(=40^{\circ} \mathrm{C}\left(104^{\circ} \mathrm{F}\right)\)
```

The water properties are as follows:
$c=$ specific heat $=1.0 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)$
$\mu=$ viscosity $=2.1 \mathrm{lb} /(\mathrm{ft})(\mathrm{h})$
$k=$ thermal conductivity $=0.35 \mathrm{Btu} /(\mathrm{h})(\mathrm{ft})\left({ }^{\circ} \mathrm{F}\right)[0.60 \mathrm{~W} /(\mathrm{m})(\mathrm{K})]$

## Calculation Procedure

1. Set out the overall approach. This exchanger must be evaluated in two sections, the condensing section and the sub-cooling section. The observed and calculated heat-transfer coefficients will be compared. An apparent fouling coefficient can then be calculated by trial and error.
2. Calculate water flow rate. Total heat load $Q_{T}$ is the sum of condensing heat load $Q_{c}$ and subcooling heat load $Q_{s}$. Now,

$$
Q_{c}=W_{v} \lambda \quad \text { and } \quad Q_{s}=W_{v} c\left(t_{2}-t_{1}\right)
$$

Thus, $\quad Q_{c}=170,860(250)=42,715,000 \quad \mathrm{Btu} / \mathrm{h}, \quad$ and $\quad Q_{s}=170,860(0.44)(54-40.5)(1.8)=$ $1,827,000 \quad \mathrm{Btu} / \mathrm{h}$. Then $\quad Q_{T}=Q_{c}+Q_{s}=42,715,000+1,827,000=44,542,000 \quad \mathrm{Btu} / \mathrm{h}$ $(13,051,000 \mathrm{~W})$. Then, letting $W_{w}$ be the mass flow rate for the water

$$
W_{w}=\frac{Q_{T}}{c\left(T_{2}-T_{1}\right)}=\frac{44,542,000}{1.0(40-16.1)(1.8)}=1,035,380 \mathrm{lb} / \mathrm{h}(469,638 \mathrm{~kg} / \mathrm{h})
$$

3. Calculate intermediate water temperature. The water-temperature rise for the condensing zone can be calculated as follows, letting $T_{m}$ be the intermediate water temperature:

$$
T_{m}-T_{1}=\frac{Q_{c}}{Q_{T}}\left(T_{2}-T_{1}\right)
$$

Then $T_{m}=16.1+(42,715,000 / 44,542,000)(40-16.1)=39.0^{\circ} \mathrm{C}\left(102.2^{\circ} \mathrm{F}\right)$.
4. Calculate mean temperature differences. See Example 7.21. In the present case, on the process side, $t_{1}=54^{\circ} \mathrm{C}, t_{m}=54^{\circ} \mathrm{C}$, and $t_{2}=40.5^{\circ} \mathrm{C}$. On the water side, $T_{1}=16.1^{\circ} \mathrm{C}, T_{m}=39^{\circ} \mathrm{C}$, and $T_{2}=$ $40^{\circ} \mathrm{C}$. For the condensing zone, then

$$
\begin{aligned}
\Delta T_{m c} & =\frac{\left(t_{1}-T_{1}\right)-\left(t_{m}-T_{m}\right)}{\ln \left[\left(t_{1}-T_{1}\right) /\left(t_{m}-T_{m}\right)\right]} \\
& =\frac{(54-16.1)-(54-39)}{\ln [(54-16.1) /(54-39)]} \\
& =24.71^{\circ} \mathrm{C}\left(44.47^{\circ} \mathrm{F}\right)
\end{aligned}
$$

And for the subcooling zone

$$
\begin{aligned}
\Delta T_{m s} & =\frac{\left(t_{m}-T_{m}\right)-\left(t_{2}-T_{2}\right)}{\ln \left[\left(t_{m}-T_{m}\right) /\left(t_{2}-T_{2}\right)\right]} \\
& =\frac{(54-39)-(40.5-40)}{\ln [(54-39) /(40.5-40)]} \\
& =4.26^{\circ} \mathrm{C}\left(7.67^{\circ} \mathrm{F}\right)
\end{aligned}
$$

5. Calculate $\boldsymbol{h}_{\boldsymbol{o}}$. Use the procedure outlined in Example 7.20. In the present case,

$$
\begin{aligned}
a_{c} & =B D_{s}\left(s-D_{o}\right) / s \\
& =(36 / 12)(36 / 12)(0.8125-0.625) / 0.8125 \\
& =2.0769 \mathrm{ft}^{2}\left(0.1929 \mathrm{~m}^{2}\right)
\end{aligned}
$$

Therefore, $\quad G=W_{w} / a_{c}=1,035,380 / 2.0769=498,520 \mathrm{lb} /(\mathrm{h})\left(\mathrm{ft}^{2}\right), \quad$ and $\quad D_{o} G / \mu=(0.625 / 12)$ $498,520 / 2.1=12,364$. Therefore,

$$
\begin{aligned}
h & =\frac{0.273 c G}{(c \mu / k)^{2 / 3}\left(D_{o} G / \mu\right)^{0.365}} \\
& =\frac{0.273(1.0) 498,520}{[1.0(2.1) / 0.35]^{2 / 3} 12,364^{0.365}} \\
& =1322.6 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)
\end{aligned}
$$

Correcting for fluid bypassing, $h_{o}=h F_{1} F_{r} ; F_{1}=0.8\left(B / D_{s}\right)^{1 / 6} ; F_{r}=1.0$. Thus, $h_{o}=1322.6(0.8)$ $\times(36 / 36)^{1 / 6} 1.0=1058.1 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[6009.9 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.
6. Calculate condensing coefficient. Use the procedure outlined in Example 7.25. In this case, $c \mu / k=0.44(0.484) / 0.089=2.393$, and $4 \Gamma / \mu=4\{170,860 /[1477 \pi(0.495 / 12)]\} / 0.484=$ 7377. From Fig. 7.17, for $c \mu / k=2.393$ and $4 \Gamma / \mu=7377, h_{o}\left(\mu^{2} / \rho^{2} g k^{3}\right)^{1 / 3}=0.26$, so $\quad h_{o}=0.26\left(\rho^{2} g k^{3} / \mu^{2}\right)^{1 / 3}=0.26\left[54.3^{2}\left(4.18 \times 10^{8}\right) 0.089^{3} / 0.484^{2}\right]^{1 / 3}=402.5 \quad \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)$ $\left[2285 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.
7. Calculate the dimensionless group $A_{d}$ and the condensing coefficient corrected for shear. From Example 7.25,

$$
\begin{aligned}
A_{d} & =\frac{0.250 \mu_{L}^{1.173} \mu_{v}^{0.16}}{g^{2 / 3} D_{i}^{2} \rho_{L}^{0.553} \rho_{v}^{0.78}} \\
& =\frac{0.250(0.484)^{1.173} 0.036^{0.16}}{\left(4.18 \times 10^{8}\right)^{2 / 3}(0.495 / 12)^{2} 54.3^{0.553} 0.49^{0.78}} \\
& =1.25 \times 10^{-5}
\end{aligned}
$$

For $A_{d}=1.25 \times 10^{-5}, h / h_{o}=1.7$, from Example 7.25. Therefore, $h=1.7 h_{o}=1.7(402.5)=$ 684.3 Btu/(h)(ft $\left.{ }^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[3887 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.
8. Calculate subcooling coefficient. No interfacial shear will occur in the subcooling zone. Therefore, taking into account the falling-film behavior (see Example 7.25, under Related Calculations), $h_{s c}=0.75 h_{o}=0.75(402.5)=301.9 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[1714 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.
9. Calculate $h_{w}$, the coefficient of heat transfer through the tube wall. The formula is

$$
\begin{aligned}
h_{w} & =\frac{2 k}{D_{o}-D_{i}}=\frac{2(220)}{(0.625-0.495)(1 / 12)} \\
& =40,615 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[230,700 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]
\end{aligned}
$$

10. Calculate overall coefficients (clean condition). For the condensing zone,

$$
\begin{aligned}
\frac{1}{U_{c}} & =\frac{1}{h_{c}\left(D_{i} / D_{o}\right)}+\frac{1}{h_{o}}+\frac{1}{h_{w}} \\
& =\frac{1}{684.3(0.495 / 0.625)}+\frac{1}{1058.1}+\frac{1}{40,615}
\end{aligned}
$$

Therefore, $U_{c}=355.3 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[2018 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$. For the subcooling zone,

$$
\begin{aligned}
\frac{1}{U_{s c}} & =\frac{1}{h_{s c}\left(D_{i} / D_{o}\right)}+\frac{1}{h_{o}}+\frac{1}{h_{w}} \\
& =\frac{1}{301.9(0.495 / 0.625)}+\frac{1}{1058.1}+\frac{1}{40,615}
\end{aligned}
$$

Therefore, $U_{s c}=194.1 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[1102 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.
11. Calculate required areas. For the condensing zone,

$$
\begin{aligned}
A_{c} & =\frac{Q_{c}}{U_{c} \Delta T_{m c}}=\frac{42,715,000}{355.3(24.71)(1.8)} \\
& =2702 \mathrm{ft}^{2}\left(251.1 \mathrm{~m}^{2}\right)
\end{aligned}
$$

For the subcooling zone,

$$
\begin{aligned}
A_{s} & =\frac{Q_{s}}{U_{s c} \Delta T_{m s}}=\frac{1,827,000}{194.1(4.26)(1.8)} \\
& =1228 \mathrm{ft}^{2}\left(114.0 \mathrm{~m}^{2}\right)
\end{aligned}
$$

Then, $A_{t}=$ total area $=A_{c}+A_{s}=2702+1228=3930 \mathrm{ft}^{2}\left(365.1 \mathrm{~m}^{2}\right)$.
12. Calculate available area. The formula is $A=n \pi D_{o} L=1477 \pi(0.625 / 12)(21)=5075 \mathrm{ft}^{2}$ ( $471.5 \mathrm{~m}^{2}$ ).
13. Calculate apparent fouling coefficient $\boldsymbol{h}_{s}$. Assume that fouling is uniform along the tube length. The calculation for fouling coefficient is then a trial-and-error solution. As a first approximation, assume the observed coefficient $U_{o}$ will be the clean coefficient multiplied by the ratio of calculated to available areas. Thus, $U_{o c}=U_{c}\left(A_{t} / A\right)=355.3(3930 / 5075)=275.1 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)$ and $U_{o s}=U_{s}\left(A_{t} / A\right)=194.1(3930 / 5075)=150.3 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)$. Now, $1 / U_{o c}=1 / U_{c}+1 / h_{s}=$ $1 / 355.3+1 / h_{s}=1 / 275.1$. Therefore, $h_{s}=1219 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)$, and $1 / U_{o s}=1 / U_{s}+1 / h_{s}=$ $1 / 194.1+1 / h_{s}=1 / 150.3$, so $h_{s}=666 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)$.

However, the value of $h_{s}$ should be constant. Assume a new value of $h_{s}$, calculate $U_{o c}$ and $U_{o s}$, and compare $A$ to $A_{t}$. For the first trial, assume $h_{s}=1000 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)$. Then $1 / U_{o c}=$ $1 / 355.3+1 / 1000$ and $U_{o c}=262.2$, and $1 / U_{o c}=1 / 194.1+1 / 1000$ and $U_{o s}=162.5$. Therefore, $A_{c}=42,715,000 / 262.2(24.71) 1.8=3663 \mathrm{ft}^{2}, A_{s}=1,827,000 / 162.5(4.26) 1.8=1466 \mathrm{ft}^{2}$, and therefore, $A_{t}=3663+1466=5129 \mathrm{ft}^{2}$.

The value of $A_{t}$ is now greater than $A$. Therefore, $h_{s}$ must be greater than 1000 . Repeating the procedure above leads to a value of $h_{s}$ that satisfies the parameters: $h_{s}=1050 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)$. The observed apparent fouling coefficient is thus $1050 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[5960 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.


FIGURE 7.18 A low-temperature distillation process.

### 7.43 <br> HEAT EXCHANGER NETWORKING

For the low-temperature distillation process shown in the flow diagram in Fig. 7.18, calculate the minimum hot-utility requirement and the location of the heat recovery pinch. Assume that the minimum acceptable temperature difference, $\Delta T_{\min }$, equals $5^{\circ} \mathrm{C}$. The specifics of the process streams passing through the seven heat exchangers appear in the first five columns of Table 7.8, the mass flowrates of the streams being represented within the enthalpy $(\Delta H)$ values.

## Calculation Procedure

1. For each stream, calculate its heat capacity flowrate. For a given stream, the heat capacity flowrate, $C P$, is defined as $\Delta H$ divided by the absolute value of the difference between the supply temperature and the target temperature. For instance, for Stream 1, the feed to Column $1, C P=$ $0.8 /(20-0)=0.04$. The heat capacity flowrates for the seven streams appears as the last column of Table 7.8.

TABLE 7.8 Stream Data for Low-Temperature Distillation Process

| Stream | Type | Supply temp. <br> $T_{\mathrm{S}}\left({ }^{\circ} \mathrm{C}\right)$ | Target temp. <br> $T_{\mathrm{T}}\left({ }^{\circ} \mathrm{C}\right)$ | $\Delta H$ <br> $(\mathrm{MW})$ | Heat capacity <br> flow rate $C P$ <br> $\left(\mathrm{MW}{ }^{\circ} \mathrm{C}^{-1}\right)$ |
| :--- | :--- | :---: | :---: | :---: | :---: |
| 1. Feed to column 1 | Hot | -20 | 0 | 0.8 | 0.04 |
| 2. Column 1 condenser | Hot | -19 | -20 | 1.2 | 1.2 |
| 3. Column 2 condenser | Hot | -39 | -40 | 0.8 | 0.8 |
| 4. Column 1 reboiler | Cold | 19 | 20 | 1.2 | 1.2 |
| 5. Column 2 reboiler | Cold | -1 | 0 | 0.8 | 0.8 |
| 6. Column 2 bottoms | Cold | 0 | 20 | 0.2 | 0.01 |
| 7. Column 2 overheads | Cold | -40 | 20 | 0.6 | 0.01 |

TABLE 7.9 Shifted Temperatures for the Data in Table 7.8

| Stream | Type | $T_{\mathrm{S}}$ | $T_{\mathrm{T}}$ | $T_{\mathrm{S}}^{*}$ | $T_{\mathrm{T}}^{*}$ |
| :---: | :--- | ---: | ---: | ---: | ---: |
| 1 | Hot | 20 | 0 | 17.5 | -2.5 |
| 2 | Hot | -19 | -20 | -21.5 | -22.5 |
| 3 | Hot | -39 | -40 | -41.5 | -42.5 |
| 4 | Cold | 19 | 20 | 21.5 | 22.5 |
| 5 | Cold | -1 | 0 | 1.5 | 2.5 |
| 6 | Cold | 0 | 20 | 2.5 | 22.5 |
| 7 | Cold | -40 | 20 | -37.5 | 22.5 |

2. For each stream, modify the supply and target temperatures to assure that the minimum-temperature-difference requirement is met. This step consists of lowering the supply and target temperatures of each hot stream by $\Delta T_{\min } / 2$ and raising the supply and target temperatures of each cold stream by $\Delta T_{\min } / 2$. For Stream 1 (a hot stream), for instance, the supply temperature drops from 20 to $17.5^{\circ} \mathrm{C}$, and the target temperature drops from 0 to $-2.5^{\circ} \mathrm{C}$. The shifted temperatures for the seven streams appear in Table 7.9.
3. Carry out a heat balance within each interval between the shifted temperatures. To display the temperature intervals, take all the 14 shifted supply and target temperatures (two for each of the seven streams) and list them in descending order (noting that a few temperatures, such as $22.5^{\circ} \mathrm{C}$, appear more than once). The resulting list is the first column in Fig. 7.19. Draw horizontal lines extending leftward through each temperature value on the list. The regions between the lines are the temperature intervals, whose numerical values appear in the third column of Fig. 7.19. For example, the region between 21.5 and $17.5^{\circ} \mathrm{C}$ represents a temperature interval of $(21.5-17.5)$, or $4^{\circ} \mathrm{C}$.

| Interval Temperature | Stream <br> Population | $\Delta T_{\text {interval }} \mid$ | ${ }^{\Sigma C P_{C}}$ | $\triangle H_{\text {INTERVAL }}$ | Surpius/ Deficit |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $22.5{ }^{\circ} \mathrm{C}$ |  |  |  |  |  |
|  |  | 1 | 1.22 | 1.22 | Deficit |
| $17.5^{\circ} \mathrm{C}$ | - | 4 | 0.02 | 0.08 | Deficit |
|  |  | 15 | -0.02 | - 0.30 | Surplus |
|  |  | 1 | 0.77 | 0.77 | Deficit |
| .50 |  | 4 | - 0.03 | - 0.12 | Surplus |
| $-2.5{ }^{\circ} \mathrm{C}$ |  | 19 | 0.01 | 0.19 | Deficit |
| $-21.5^{\circ} \mathrm{C}$ |  | 1 | - 1.19 | - 1.19 | Surplus |
| - 22.5 |  | 15 | 0.01 | 0.15 | Deficit |
| $-37.5^{\circ} \mathrm{C}$ |  | 4 | 0 | 0 | - |
| $-42.5^{\circ} \mathrm{C}$ | - | 1 | - 0.8 | - 0.8 | Surplus |

FIGURE 7.19 Temperature-interval heat balances for Example 7.43.

Then, represent each of the seven streams by drawing vertical lines, starting at the shifted supply temperature and extending downward (for hot streams being cooled) or upward (for cold streams being heated) until reaching the shifted target temperature. For Stream 1, for instance, the line begins at the line for $17.5^{\circ} \mathrm{C}$ and extends downward to $-2.5^{\circ} \mathrm{C}$. Label each line with its $C P$ value (for instance, $C P=0.04$ for Stream 1). The resulting seven vertical stream lines appear in the second column of Fig. 7.19, labeled "Stream population."

For each of the 10 temperature intervals, sum the heat capacity flowrates for the cold streams being heated that fall within that interval, then subtract the heat capacity flowrate of each hot stream being cooled that falls within the interval. The resulting algebraic sums are in the fourth column of Fig. 7.19. For example, there are three streams within the interval between 17.5 and $2.5^{\circ} \mathrm{C}$, namely, Stream 1,

## (a) HOT UTILITY


(b) HOT UTILITY


FIGURE 7.20 The problem table cascade for Example 7.43.
being cooled, with $C P=0.04$; Stream 6 , being heated, with $C P=0.01$, and Stream 7, being heated, with $C P=0.01$. The resulting algebraic sum is $(0.01+0.01-0.04)$, or -0.02 .

Finally, multiply each temperature difference in Column 3 by the corresponding algebraic sum of heat capacity flowrates in Column 4 . The result is the heat balance, or enthalpy change, $\Delta H$, in megawatts for that interval. The intervals having a negative $\Delta H$, such as the interval between 17.5 and $2.5^{\circ} \mathrm{C}$, are designated as being in surplus; regions with a positive $\Delta H$ are designated as being in deficit. The results are in the fifth and sixth columns of Fig. 7.19.
4. Cascade the surplus and deficit heat down the temperature scale from interval to interval, and note the largest net deficit that results. That number is the minimum hot-utility requirement. Arrange the $\Delta H$ values as shown in Fig. 7.20a, with the temperatures taken from the first column of Fig. 7.19. Working downward, calculate at each temperature the cumulative sum of the $\Delta H$ values above it. Assign a positive number if the cumulative value is surplus or a negative number if it is instead in deficit.

For example: working downward to $17.5^{\circ} \mathrm{C}$, we add up two successive deficits of 1.22 and 0.08 MW, so the cumulative sum on the $17.5^{\circ} \mathrm{C}$ line is -1.30 MW ; but, in the next downward step to $2.5^{\circ} \mathrm{C}$, we pick up a surplus of 0.30 MW , so the cumulative sum on the $2.5^{\circ} \mathrm{C}$ line is -1.00 MW .

Upon completing the task, we note that the largest net deficit is 1.84 MW , on the line for $-21.5^{\circ} \mathrm{C}$. Thus, the minimum hot-utility requirement is 1.84 MW .

To confirm this, repeat the downward cascading but begin with an assumed input of 1.84 MW at the top of the cascade, as shown in Fig. 7.20b. Note that, as a result, no deficit results.
5. Find the heat-recovery pinch point. The pinch arises at the point where, after adding the minimum heat utility, the cumulative sum of $\Delta H$ values is zero. In this case, it occurs at $-21.5^{\circ} \mathrm{C}$. Assuming that the heat exchangers become networked appropriately, and keeping in mind that the pinch result of $-21.5^{\circ} \mathrm{C}$ emerges after the temperatures were shifted, in step 2 , we note that, at the pinch, the hot stream being cooled is at a temperature of $\left(-21.5+\Delta T_{\min } / 2\right)$, or $(-21.5+2.5)$, or $-19^{\circ} \mathrm{C}$, and the cold stream being heated is at $\left(-21.5-\Delta T_{\min } / 2\right)$, or $-24^{\circ} \mathrm{C}$.

Related Calculations. Heat-exchanger networking problems can instead be solved by the morefamiliar composite diagrams, consisting of graphs in which enthalpy is the horizontal axis, temperature is the vertical axis, individual cold streams are combined into a composite cold stream, and individual hot streams are combined into a composite hot stream. However, the table algorithm used in the example here is more convenient for calculations.

With respect to economizing on thermal energy, the networking and pinch technology principle can be extended beyond heat exchangers and condensers to also embrace other operations within the plant that involve heat generation or transfer, such as reactors and heat pumps. Beyond that, networking and pinch technology principles also have relevance for optimal use of other plant resources, such as water or hydrogen.

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## SECTION 8

DISTILLATION*

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### 8.1 CALCULATION OF EOUILIBRIUM STAGES 8.1 <br> 8.2 DISTILLATION-TRAY SELECTION AND DESIGN 8.10 <br> 8.3 COLUMN EFFICIENCY 8.18

### 8.4 PACKED-COLUMN DESIGN <br> 8.21

8.5 BATCH DISTILLATION 8.24
8.6 BATCH-COLUMN DESIGN 8.25
8.7 OVERALL COLUMN SELECTION AND DESIGN 8.31

### 8.1 CALCULATION OF EQUILIBRIUM STAGES

Design a distillation column to separate benzene, toluene, and xylene, using (1) the McCabe-Thiele $x y$ diagram and (2) the Fenske-Underwood-Gilliland (FUG) method. Compare the results with each other. Assume that the system is ideal.

Feed consists of $60 \mathrm{~mol} / \mathrm{h}$ benzene, $30 \mathrm{~mol} / \mathrm{h}$ toluene, and $10 \mathrm{~mol} / \mathrm{h}$ xylene. There must be no xylene in the overhead, and the concentration of toluene must be no greater than 0.2 percent. Benzene concentration in the bottoms should be minimized; however, recognizing that only one end of a column can be closely controlled (in this case, the overhead is being so controlled), a $2 \%$ concentration is specified. Feed temperature is $40^{\circ} \mathrm{C}\left(104^{\circ} \mathrm{F}\right)$; the reflux is not subcooled. The column will be operated at atmospheric conditions, with an average internal back pressure of $850 \mathrm{mmHg}(113.343 \mathrm{kPa}$ or $1.13 \mathrm{bar})$.

## Calculation Procedure

1. Assess the problem to make sure that a hand-calculation approach is adequate. The separation of multicomponent and nonideal mixtures is difficult to calculate by hand and is evaluated largely by the application of proper computer programs. However, under certain conditions, hand calculation can be justified, and it will be necessary for the designer to have access to suitable shortcut procedures. This may be the case when (1) making preliminary cost estimates, (2) performing parametric evaluations of operating variables, (3) dealing with situations that call for separations having only coarse purity requirements, or (4) dealing with a system that is thermodynamically ideal or nearly so. For guidelines as to ideality, see Table 8.1.
[^12]TABLE 8.1 Rules of Thumb on Equilibrium Properties of Vapor-Liquid Mixtures

|  | Mixtures of isomers usually form ideal solutions. <br> Mixtures of close-boiling aliphatic hydrocarbons are nearly ideal below a pressure of 10 atm. <br> Mixtures of compounds close in molecular weight and structure frequently do not deviate greatly from <br> ideality (e.g., ring compounds, unsaturated compounds, naphthenes, etc.). |
| :--- | :--- |
| Mixtures of simple aliphatics with aromatic compounds deviate modestly from ideality. |  |
| "Inerts," such as $\mathrm{CO}_{2}, \mathrm{H}_{2} \mathrm{~S}, \mathrm{H}_{2}, \mathrm{~N}_{2}$, etc., that are present in mixtures of heavier components tend to |  |
| behave nonideally with respect to the other compounds. |  |
| Mixtures of polar and nonpolar compounds are always strongly nonideal. (Look for polarity in molecules |  |
| containing oxygen, chlorine, fluorine, or nitrogen, in which electrons in bonds between these atoms |  |
| and hydrogen are not equally shared). |  |
| Azeotropes and phase separation represent the ultimate in nonideality, and their occurrence should |  |
| always be confirmed before detailed distillation studies are undertaken. |  |

Source: Otto Frank, "Shortcuts for Distillation Design," Chemical Engineering, March 14, 1977.

In the present case, hand calculation and shortcut procedures are adequate because the benzene-toluene-xylene system is close to ideal.
2. Establish the equilibrium relationship among the constituents. The equilibrium data are based on vapor pressures. Therefore, this step consists of plotting the vapor pressure-temperature curves for benzene, toluene, and xylene. The vapor pressures can be determined by methods such as those discussed in Section 1 or can be found in the literature. In any case, the results are shown in Fig. 8.1.
3. Convert the given ternary system to a pseudobinary system. This step greatly reduces the complexity of calculation, although at some expense in accuracy. (Based on limited data, a rough estimate as to the loss in accuracy is 10 percent, i.e., a 10 percent error). Benzene is the lightest-boiling component in the bottoms stream, so it is designated the "light key" and taken as one component of the binary system. Toluene is the higher-boiling of the two constituents in the overhead stream, so it is designated the "heavy key" and taken as the other component of the binary system.

Since there are $60 \mathrm{~mol} / \mathrm{h}$ benzene and $30 \mathrm{~mol} / \mathrm{h}$ toluene in the feed stream, the percentage composition of the pseudobinary feed is $100[60 /(30+60)]$, i.e., $66.7 \%$ benzene and $100[30 /(30+60)]=$ $33.3 \%$ toluene.

The overhead composition is stipulated to be $99.8 \%$ benzene and $0.2 \%$ toluene. By materialbalance calculation, the bottoms is found to be $2.6 \%$ benzene and $97.4 \%$ toluene.

## 4. Apply the McCabe-Thiele method of column design, based on an xy diagram

a. Develop the equilibrium line or $x y$ curve. This can be done using the procedure described in Example 3.12. The result appears as the upper curve in Fig. 8.2 (including both the full figure and the portion that depicts in expanded form the enriching section). This curve shows the composition of vapor $y$ that is in equilibrium with any given liquid of composition $x$ in the benzene-toluene binary system.

Another way of plotting the curve is to employ the equation

$$
y=\frac{\alpha x}{1+(\alpha-1) x}
$$

where $\alpha$ is the relative volatility of benzene with respect to toluene (see Section 3). Relative volatility may vary with temperature from point to point along the column; if the values at the top and bottom of the column are within 15 percent of each other, an average can be used to establish the equilibrium line. The present example meets this criterion, and its average volatility is 2.58 .


FIGURE 8.1 Vapor pressures of benzene, toluene, and xylene (Example 8.1). Note: $1 \mathrm{mmHg}=0.133 \mathrm{kPa}$.
b. Calculate the bubble point of the feed. This is done via procedures outlined in Section 3. In the present case, where both the vapor and liquid phases can be considered ideal, the vapor-liquid equilibrium ratio $K_{i}$ equals vapor pressure of $i$ th component divided by system pressure. The bubble point is found to be $94^{\circ} \mathrm{C}$. At $40^{\circ} \mathrm{C}$, then, the feed is subcooled $54^{\circ} \mathrm{C}$.
c. Calculate the $q$-line slope, to compensate for the feed not entering at its bubble point $\left(40^{\circ} \mathrm{C}\right.$ versus $94^{\circ} C$ ). The thermal condition of the feed is taken into account by the slope of a $q$ line, where

$$
q=\frac{\text { heat needed to convert } 1 \mathrm{~mol} \text { feed to saturated vapor }}{\text { molar heat of vaporization }}
$$

The enthalpy to raise the temperature of the benzene to the bubble point and vaporize it is Sensible heat required + latent heat of vaporization, or $\left(94-40^{\circ} \mathrm{C}\right)\left[32.8 \mathrm{cal} /(\mathrm{mol})\left({ }^{\circ} \mathrm{C}\right)\right]+7566 \mathrm{cal} / \mathrm{mol}=$ $9337 \mathrm{cal} / \mathrm{mol}$. The enthalpy to raise the temperature of the toluene to the bubble point and vaporize it is $\left(94-40^{\circ} \mathrm{C}\right)\left[40.5 \mathrm{cal} /(\mathrm{mol})\left({ }^{\circ} \mathrm{C}\right)\right]+7912 \mathrm{cal} / \mathrm{mol}=10,100 \mathrm{cal} / \mathrm{mol}$.

Then

$$
\begin{aligned}
q & =\frac{(0.667 \mathrm{~mol} \text { benzene }) 9337+(0.333 \mathrm{~mol} \text { toluene }) 10,100}{(0.667 \mathrm{~mol} \text { benzene }) 7566+(0.333 \mathrm{~mol} \text { toluene }) 7912} \\
& =1.25
\end{aligned}
$$

And by definition of the $q$ line, its slope is $q /(q-1)$, or $1.25 / 0.25=5$.
d. Plot the $q$ line on the xy diagram. This line, also known as the "feed line," has the slope calculated in the previous step, and it passes through the point on the $x y$ diagram diagonal that has its abscissa (and ordinate) corresponding to the feed composition $x_{F}$. In Fig. 8.2, the diagonal is $A B$ and the $q$ line is $C D$. The operating lines, calculated in the next step, intersect with each other along the $q$ line.


FIGURE 8.2 Application of McCabe-Thiele method of column design (Example 8.1).
$\boldsymbol{e}$. Construct the operating lines. There are two operating lines, one for the enriching (upper) section of the column and the other for the stripping (lower) section, the feed plate marking the point of separation between the two. The upper line intersects the diagonal at the abscissa corresponding to the overhead-product composition (in Fig. 8.2, at point $E$ ); the lower line intersects it at the abscissa corresponding to the bottoms composition. The slope of each is the ratio of (descending)
liquid flow to (ascending) vapor flow, or $L / V$, in that particular section of the column. The two lines intersect along the $q$ line, as noted earlier.

The ratio $L / V$ depends on the amount of reflux in the column. At minimum reflux, the operating lines intersect each other and the $q$ line at the point where the $q$ line intersects the $x y$ curve (in Fig. 8.2, at point $D$ ).

In this example, the approach used for constructing the operating lines is based on the relationship that typically holds, in practice, between the minimum reflux and the amount of reflux actually employed. First, draw the operating line that would pertain for minimum reflux in the enriching section. As noted earlier, this line is defined by points $D$ and $E$. Next, measure its slope $(L / V)_{\text {min }}$ on the diagram. This is found to be 0.5 .

For water- or air-cooled columns, the actual reflux ratio $R_{\text {actual }}$ is normally 1.1 to 1.3 times the minimum reflux ratio $R_{\min }$. The optimal relationship between $R_{\text {actual }}$ and $R_{\min }$ can be established by an economic analysis that compares the cost of energy (which rises with rising reflux) with number of column trays (which declines with rising reflux). For the present example, assume that $R_{\text {actual }} / R_{\min }=1.2$.

In the enriching section of the column, the descending liquid consists of the reflux. So, $R=L /(V-L)$. By algebra, $1 / R=(V-L) / L=V / L-1$. Since $(L / V)_{\min }$ in the present example is $0.5,1 / R_{\min }=1 / 0.5-1=1$. Therefore, $R_{\min }=1$, and $R_{\text {actual }}=1.2 R_{\min }=1.2(1)=1.2$. Therefore, $1 / 1.2=V / L-1$, so $V / L=1.83$, and $L / V$, the slope of the actual operating line for the enriching section, is 0.55 . This line, then, is constructed by passing a line through point $E$ having a slope of 0.55 . This intersects the $q$ line at $F$ in Fig. 8.2. Finally, the operating line for the stripping section is constructed by drawing a line connecting point $F$ with the point on the diagonal that corresponds to the bottoms composition, namely, point $G$. The two operating lines for the actual column, then, are $E F$ and $F G$.
f. Step off the actual number of theoretical stages. Draw a horizontal line through point $E$, intersecting the $x y$ curve. Through that intersection, draw a vertical line intersecting the operating line $E F$. Through the latter intersection, draw a horizontal line intersecting the $x y$ curve. Continue the process until a horizontal line extends to the left of point $G$ (as for the steps after the one in which a horizontal line crosses the $q$ line, the vertical lines, of course, intersect operating line $F G$ rather than $E F$ ). Count the number of horizontal lines; this number is found to be 22.2 (taking into account the shortness of the last line). That is the number of theoretical stages required for the column. The number of lines through or above the $q$ line, in this case 14 , is the number of stages in the enriching section, i.e., above the feed plate.
g. Consider the advantages and disadvantages of the McCabe-Thiele method. This example illustrates both the advantages and the disadvantages. On the positive side, it is easy to alter the slope of the operating line and thus the reflux ratio, changes introduced by varying the feed quality and feed location can be judged visually, and the effect of the top and bottom concentrations on number of equilibrium stages can be readily established by moving the operating lines to new points of origin. On the negative side, the example indicates the limit to which the $x y$ diagram can be reasonably applied: when the number of stages exceeds 25 , the accuracy of stage construction drops off drastically. This is usually the case with a small relative volatility or high purity requirements or when a very low reflux ratio is called for.

## 5. As an alternative to the McCabe-Thiele method, design the column by using the Fenske-Underwood-Gilliland correlations

a. Calculate the minimum number of stages needed (implying total reflux). Apply the Fenske correlation:

$$
N_{\min }=\frac{\log \left[\left(x_{L K} / x_{H K}\right)_{D}\left(x_{H K} / x_{L K}\right)_{B}\right]}{\log \alpha}
$$

where $N_{\text {min }}$ is the minimum number of stages, $x$ is mole fraction, mole percent, or actual number of moles, $\alpha$ is relative volatility of the light key (benzene) with respect to the heavy key (toluene), and the subscripts $L K, H K, D$, and $B$ refer to light key, heavy key, overhead (or distillate) product,
and bottoms product, respectively. In this example, $\alpha$ is 2.58 , so

$$
N_{\min }=\frac{\log (99.8 / 0.2)(97.4 / 2.6)}{\log 2.58}=10.4 \text { stages }
$$

b. Estimate the feed tray. Again, apply the Fenske correlation, but this time replace the bottomsrelated ratio in the numerator with one that relates to the feed conditions, namely, $\left(x_{H K} / x_{L K}\right)_{F}$. Thus,

$$
N_{\min }=\frac{\log (99.8 / 0.2)(33.3 / 66.7)}{\log 2.58}=5.8 \text { stages }
$$

Therefore, the ratio of feed stages to total stages is $5.8 / 10.4=0.56$, so $56 \%$ of all trays should be located above the feed point.
c. Calculate the minimum reflux required for this specific separation. Apply the Underwood correlation: $(L / D)_{\min }+1=\Sigma\left(\alpha x_{D} /(\alpha-\theta)\right]$ and $1-q=\Sigma\left[\alpha x_{F} /(\alpha-\theta)\right]$. The two summations are over each component in the distillate and feed, respectively (thus, the system is not treated as pseudobinary). Each relative volatility $\alpha$ is with respect to the heavy key (toluene), and $(L / D)_{\min }$ is minimum reflux, $x$ is mole fraction, $q$ is the heat needed to convert one mole of feed to saturated vapor divided by the molar heat of vaporization, and $\theta$ is called the "Underwood constant." The value of $q$ is 1.25 , as found in step $4 c$. The relative volatilities, handled as discussed in step $4 a$, are $\alpha_{\text {benzene-toluene }}=2.58, \alpha_{\text {toluene-toluene }}=1.00$, and $\alpha_{\text {xylene-toluene }}=0.36$.

The calculation procedure is as follows: Estimate the value of $\theta$ by trial and error using the second of the two preceding equations; then employ this value in the first equation to calculate $(L / D)_{\min }$.

Thus, it is first necessary to assume values of $\theta$ in the equation

$$
1-q=\frac{\alpha_{B-T} x_{B}}{\alpha_{B-T}-\theta}+\frac{\alpha_{T-T} x_{T}}{\alpha_{T-T}-\theta}+\frac{\alpha_{X-T} x_{X}}{\alpha_{X-T}-\theta}
$$

where the mole fractions pertain to the feed and where $B, T$, and $X$ refer to benzene, toluene, and xylene, respectively. Trial and error shows the value of $\theta$ to be 1.22 ; in other words, 2.58(0.60)/ $(2.58-1.22)+1(0.30) /(1-1.22)+0.36(0.1) /(0.36-1.22)=-0.26$, which is close enough to $(1-1.25)$.

Now, substitute $\theta=1.22$ into

$$
(L / D)_{\min }+1=\frac{\alpha_{B-T} x_{B}}{\alpha_{B-T}-\theta}+\frac{\alpha_{T-T} x_{T}}{\alpha_{T-T}-\theta}
$$

where the mole fractions pertain to the overhead product (there is no xylene-related term because there is no xylene in the overhead). Thus,

$$
\begin{aligned}
(L / D)_{\min }+1 & =\frac{2.58(0.998)}{2.58-1.22}+\frac{1(0.002)}{1-1.22} \\
& =0.88
\end{aligned}
$$

(Note that because $(L / D)_{\min }=R_{\min }$ and $1 / R=V / L-1$, this $(L / D)_{\min }$ of 0.88 corresponds to an $(L / V)_{\min }$ of 0.47 , versus the value of 0.5 that was found in the McCabe-Thiele method, step $4 e$ above.)

A direct solution for $\theta$ can be obtained by using a graph developed by Van Winkle and Todd (Fig. 8.3) in which the abscissa is based on the system being treated as pseudobinary. Strictly
speaking, this graph applies only to a liquid at its bubble point, but in the present case, with $\left(x_{L K} / x_{H K}\right)_{F}=\left(x_{B} / x_{T}\right)_{F}=66.7 / 33.3=2$, the graph shows for an $\alpha$ of 2.58 that $\theta=1.26$. Then, from the Underwood equation, $(L / D)_{\min }=0.94$ and $(L / V)_{\min }=0.48$, so for typical feed conditions (only a limited amount of subcooling or flashing), the simplification introduced by the graph is acceptable.
d. Estimate the actual number of theoretical stages using the Gilliland correlation. This step employs Fig. 8.4. From step $5 c,(L / D)_{\min }$ or $R_{\min }$ is 0.88 . Assume (as was done in the McCabe-Thiele procedure, step $4 e$ ) that the actual reflux ratio $R$ is 1.2 times $R_{\min }$. Then $R=1.2(0.88)=1.06$, and the abscissa of Fig. $8.4\left(R-R_{\min }\right) /(R+1)=$ $(1.06-0.88) /(1.06+1)=0.087$. From the graph, $\left(N-N_{\min }\right) /(N+1)=0.57$, where $N$ is the actual number of stages and $N_{\min }$ is the minimum number. From step $5 a, N_{\min }=10.4$. Then $(N-10.4) /(N+$ 1) $=0.57$, so $N=25.5$ theoretical stages. (Note that if the $R_{\min }$ of 0.94 , based on the graphically derived Underwood constant, is employed, the resulting number of theoretical stages is nearly the same, at 24.9.)
$\boldsymbol{e}$. Comment on the usage of the Fenske-UnderwoodGilliland method. A reasonably good estimate of $N$ can be obtained by simply doubling the $N_{\text {min }}$ that emerges from the Fenske correlation. The Underwood correlation can handle multicomponent systems, whereas the McCabe-Thiele $x y$ diagram is confined to binary (or pseudobinary) systems. However, if there is a component that has a vapor pressure between that of the light and heavy keys, then the Underwood-calculation procedure becomes more complicated than the one outlined


FIGURE 8.3 Underwood constant as a function of feed composition and relative volatility. above.
6. Compare the results of the McCabe-Thiele and the Fenske-Underwood-Gilliland methods. Summarizing the results found in this example, the comparison is as follows:

|  | Results |  |  |
| :--- | :---: | :---: | :---: |
|  | Reflux <br> ratio | Number of <br> theoretical <br> stages | Optimal <br> feed <br> stage |
| Method | 1.2 | 22.2 | 14 |
| McCabe-Thiele | 1.06 | 25.5 | 14 |
| Fenske-Underwood-Gilliland: <br> $\quad$ Using calculated $\theta$ | 1.13 | 24.9 | 14 |
| Using $\theta$ from graph | - | 22 | - |
| $\quad$ Using nomograph | - | 20.8 | 12 |

Related Calculations. Special McCabe-Thiele graph paper that expands the top and bottom of the $x y$ diagram is available. This makes stepping off stages easier and more precise. However, it does not materially improve the accuracy of the procedure.


FIGURE 8.4 Gilliland correlation relating number of stages to reflux ratio. (From Chemical Engineering, McGraw-Hill, 1977.)

Variations of the basic McCabe-Thiele method, such as incorporating tray efficiencies, nonconstant molal overflow, side streams, or a partial condenser, are often outlined in standard texts. These modifications usually are not justified; modern computer programs can calculate complex column arrangements and nonideal systems considerably faster and more accurately than use of any handdrawn diagram can.

A nomograph for the overall Fenske-Underwood-Gilliland method has been derived that considerably reduces the required calculation effort without undue loss of accuracy. It is based on Fig. 8.5, where the subscripts $D$ and $B$ in the abscissa refer to overhead and bottoms product streams,


FIGURE 8.5 Graphical representation of Fenske-Underwood-Gilliland procedure. (From Chemical Engineering, McGraw-Hill, 1977.)
respectively, and the other symbols are as used in step 5. Find the relevant abscissa; in this case, $(99.8 / 0.2)(97.4 / 2.6)=18,700$. Erect a vertical line and let it intersect the positively sloped line that represents the assumed ratio of actual to minimum reflux ratios, in this case, 1.2. Through this intersection, draw a horizontal line that intersects the right-hand vertical border of the diagram. Finally, draw a line through the latter intersection and the relevant $\alpha_{L K-H K}$ point (in this case, 2.58) on the negatively sloped line that represents relative volatilities, and extend this last-constructed line until it intersects the left-hand border of the diagram. The point of intersection (in this case, it turns out to be 22) represents the number of theoretical stages.

More recently, a different approach for using the McCabe-Thiele diagram has been presented in the literature: Instead of the vapor mole fraction, $y$, being plotted on the vertical axis, the difference between vapor and liquid mole fraction $(y-x)$ is plotted. The horizontal axis remains the liquid mole fraction, $x$. An example appears in the figure.* This transformation is claimed to be especially useful for situations involving relative volatilities less than 1.25 ; when such cases are plotted on the conventional McCabe-Thiele diagram, the stage-equilibria data and the operating-line data alike lie very close to the diagonal line, which complicates the usage of the diagram. Plotting $(y-x)$ instead of $y$ spreads out the conventionally close-to-the-diagonal region over the entire height of the plot, because the diagonal coincides with the abscissa.


* Source: Ryan, J., Replotting the McCabe-Thiele Diagram, Chemical Engineering, May 2001, pp. 109-113. With permission.


### 8.2 DISTILLATION-TRAY SELECTION AND DESIGN

Design the trays for a distillation column separating dichlorobenzene (DCB) from a high-boiling reaction product. Include designs for sieve trays and valve trays, and discuss the applications of each. The product is temperature-sensitive, so sump pressure should be held at about $100 \mathrm{mmHg}(3.9 \mathrm{inHg}$ or 0.13 bar . The separation requires 20 actual trays.

Column conditions in the top section are as follows:
Vapor flow rate $=69,000 \mathrm{lb} / \mathrm{h}(31,300 \mathrm{~kg} / \mathrm{h})$
Liquid flow rate $=20,100 \mathrm{lb} / \mathrm{h}(9120 \mathrm{~kg} / \mathrm{h})$
Liquid viscosity $=0.35 \mathrm{cP}\left(3.5 \times 10^{-4} \mathrm{~Pa} \cdot \mathrm{~s}\right)$
Liquid density $=76.7 \mathrm{lb} / \mathrm{ft}^{3}\left(1230 \mathrm{~kg} / \mathrm{m}^{3}\right)$
Surface tension of DCB liquid $=16.5 \mathrm{dyn} / \mathrm{cm}\left(1.65 \times 10^{-4} \mathrm{~N} / \mathrm{cm}\right)$
Temperature (average for top section) $=200^{\circ} \mathrm{F}(366 \mathrm{~K})$
Pressure (average for top section) $=50 \mathrm{mmHg}(6.67 \mathrm{kPa})$
Molecular weight of $\mathrm{DCB}=147$
Note: Pressure drop for the vapor stream is assumed to be $3 \mathrm{mmHg}(0.4 \mathrm{kPa})$ per tray; therefore, the pressure at the top of the column is set at $40 \mathrm{mmHg}(5.3 \mathrm{kPa})$, given that the sump pressure is to be no greater than $100 \mathrm{mmHg}(13.3 \mathrm{kPa})$.

## Calculation Procedure

1. Set tray spacing. Tray spacing is selected to minimize entrainment. A large distance between trays is needed in vacuum columns, where vapor velocities are high and excessive liquid carryover can drastically reduce tray efficiencies. A tradeoff between column diameter (affecting vapor velocity) and tray spacing (affecting the disengaging height) is often possible.

Trays are normally 12 to 30 in ( 0.305 to 0.762 m ) apart. A close spacing of 12 to 15 in $(0.305$ to 0.381 m ) is usually quite suitable for moderate- or high-pressure columns. Frequently, 18 in ( 0.457 m ) is selected for atmospheric columns. High-vacuum systems may require a tray spacing of 24 to 30 in ( 0.61 to 0.762 m ). A spacing as low as $9 \mathrm{in}(0.229 \mathrm{~m})$ is sometimes found in high-pressure systems. Spacings greater than 30 in are seldom if ever justified. As a starting point for the column in question, select a $24-$ in $(0.61-\mathrm{m})$ tray spacing.
2. Estimate column diameter. In high-pressure columns, liquid flow is the dominant design consideration for calculating column diameter. However, at moderate and low pressures (generally below 150 psig or 10.34 bar ), as is the case for the column in this example, vapor flow governs the diameter.

In vacuum columns, the calculations furthermore are based on conditions at the column top, where vapor density is lowest and vapor velocity highest. The $F$-factor method used here is quite satisfactory for single- and two-pass trays; it has an accuracy well within $\pm 15$ percent. The $F$ factor $F_{c}$ is defined as follows:

$$
F_{c}=v \rho_{v}^{1 / 2}
$$

where $v$ is the superficial vapor velocity in the tower (in $\mathrm{ft} / \mathrm{s}$ ), and $\rho_{v}$ is the vapor density ( $\mathrm{in} \mathrm{lb} / \mathrm{ft}^{3}$ ). In the calculation procedure, first the appropriate value of $F_{c}$ is determined from Fig. 8.6, which gives $F_{c}$ as a function of column pressure (in this case, 0.97 psia ) and tray spacing (in this case, 24 in , from step 1). The figure shows $F_{c}$ to be 1.6. (Note that if the straight-line portion of the curve for 24-in tray spacing were continued at pressures below about 15 psia , the value of $F_{c}$ would instead be about 1.87. The lower value, 1.6, takes into account the efficiency loss at low pressures that is due to entrainment.)


FIGURE 8.6 $F$ factor as a function of column pressure and tray spacing.

Next, the $F_{c}$ value is used in calculating required free area for vapor flow, via the relation

$$
A_{F}=\frac{W}{F_{c} \rho_{v}^{1 / 2}}
$$

where $A_{F}$ is free area (in $\mathrm{ft}^{2}$ ), and $W$ is vapor mass flow rate (in $\mathrm{lb} / \mathrm{s}$ ). (Note that this is merely a rearrangement of the preceding definition for $F_{c}$.) In this case, $W=(69,000 \mathrm{lb} / \mathrm{h}) /(3600 \mathrm{~s} / \mathrm{h})=19.17$ $\mathrm{lb} / \mathrm{s}$, and (from the ideal-gas law, which is acceptable at up to moderate pressures) $\rho=(0.97 \mathrm{psia})(147$ $\left.\mathrm{lb} / \mathrm{lb} \cdot \mathrm{mol}) /\left(10.73 \mathrm{psia} \cdot \mathrm{ft}^{3} / R\right)[200+460) R\right]=0.02 \mathrm{lb} / \mathrm{ft}^{3}$. Therefore, $A_{F}=19.17 / 1.6(0.02)^{1 / 2}=$ $84.72 \mathrm{ft}^{2}$.

Actual column cross-sectional area $A_{T}$ is the sum of the free area $A_{F}$ plus the downcomer area $A_{D}$. Downcomer cross-sectional area must be adequate to permit proper separation of vapor and liquid. Although downcomer size is a direct function of liquid flow, total downcomer area usually ranges between 3 and 20 percent of total column area, and for vacuum columns it is usually 3 to 5 percent. In this example, assume for now that it is 5 percent; then $A_{T}=A_{F} / 0.95=84.72 / 0.95=89.18$ $\mathrm{ft}^{2}$. Then, by geometry, column diameter $=\left[A_{T} /(\pi / 4)\right]^{1 / 2}=(89.18 / 0.785)^{1 / 2}=10.66 \mathrm{ft}$; say, 11 ft ( 3.4 m ).
3. Calculate the flooding velocity. Use the Fair calculation. Flooding velocity $U_{f}=$ $C(\sigma / 20)^{0.2}\left[\left(\rho_{L}-\rho_{V}\right) / \rho_{V}\right]^{0.5}$, where $\sigma$ is surface tension (in dyn/cm), $\rho$ is density, the subscripts $L$ and $V$ refer to liquid and vapor, respectively, and $C$ is a parameter that is related to tray spacing, liquid flow rate $L$, vapor flow rate $G$, and liquid and vapor densities by the graph in Fig. 8.7. In this case, the abscissa is $(20,100 / 69,000)[0.02 /(76.7-0.02)]^{0.5}=0.005$, and tray spacing is 24 in from step 1 , so $C$ is found from the graph to be 0.3 . Then,

$$
\begin{aligned}
U_{f} & =0.3\left(\frac{16.5}{20}\right)^{0.2}\left(\frac{76.7-.02}{0.02}\right)^{0.5} \\
& =17.9 \mathrm{ft} / \mathrm{s}
\end{aligned}
$$



FIGURE 8.7 Determination of parameter $C$ for Fair calculation of flooding velocity.

The following adjustments, however, must be incorporated into the calculated flooding velocity to assure a reasonable design safety factor:

| Open area (cap slots or holes) | Multiplying factor |
| :--- | :---: |
| 10 percent of active tray area | 1.0 |
| 8 percent of active tray area | 0.95 |
| 6 percent of active tray area | 0.90 |


| System properties | Multiplying factor |
| :--- | :---: |
| Known nonfoaming system at atmospheric or moderate pressures | 0.9 |
| Nonfoaming systems; no prior experience | 0.85 |
| Systems thought to foam | 0.75 |
| Severely foaming systems | 0.70 |
| Vacuum systems (based on entrainment curves; see Fig. 8.17) | 0.60 to 0.80 |
| For downcomerless trays if the open area is less than 20 percent of | 0.85 |
| $\quad$ active tray area (Note: it should never be less than 15 percent) |  |

In this example, no adjustment is necessary for percent holes per active tray area, because in lowpressure systems, the hole area is usually greater than 10 percent. However, because we are dealing with a vacuum system, the flooding velocity must be downgraded. Referring to Fig. 8.17, take as the maximum acceptable fractional entrainment a $\psi$ of 0.15 . Then for an abscissa of $(L / G)\left(\rho_{V} / \rho_{L}\right)^{0.5}=$ $(20,100 / 69,000)(0.02 / 76.7)^{0.5}=0.005$, establish at what percent of flooding the column can be operated. The graph shows this to be 60 percent. Therefore, the column should be designed for a vapor velocity of $0.6(17.9)=10.74 \mathrm{ft} / \mathrm{s}(3.27 \mathrm{~m} / \mathrm{s})$.


FIGURE 8.8 Downcomer area as a function of densities and tray spacing. Note: Multiply clear liquid rate (ordinate) by 0.7 for foaming systems.
4. Reestimate the required free cross-sectional area, this time to accommodate the maximum allowable vapor velocity. Since mass flow rate equals density times cross-sectional area times velocity, free column area $A_{F}=(69,000 \mathrm{lb} / \mathrm{h}) /\left[\left(0.02 \mathrm{lb} / \mathrm{ft}^{3}\right)(3600 \mathrm{~s} / \mathrm{h})(10.74 \mathrm{ft} / \mathrm{s})\right]=89.23 \mathrm{ft}^{2}$. Note that this turns out to be slightly larger than the area calculated in step 2.
5. Set the downcomer configuration. A downcomer area can be selected from Fig. 8.8. In this case, the abscissa is $(76.7-0.02)$ and the tray spacing is 24 in , so Design $\mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{2}\right)$ is read to be 175 (by extrapolating the horizontal lines on the graph to the right). Since $76.7 \mathrm{lb} / \mathrm{ft}^{3}=10.25 \mathrm{lb} / \mathrm{gal}$, the $\mathrm{gal} / \mathrm{min}$ rate is $(20,100 \mathrm{lb} / \mathrm{h}) /[(60 \mathrm{~min} / \mathrm{h})(10.25 \mathrm{lb} / \mathrm{gal})]=32.68 \mathrm{gal} / \mathrm{min}$. Therefore, the minimum required downcomer area is $32.68 / 175=0.187 \mathrm{ft}^{2}$.

However, flow distribution across the tray must also be taken into account. To optimize this distribution, it is usually recommended that weir length be no less than 50 percent of the column diameter. Thus, from Fig. 8.9, the downcomer area subtended by a weir having half the length of the column diameter should be at least 3 percent of the column area ( 5 percent was assumed in step 2 during the initial estimate of column diameter).

Allowing 3\% for downcomer area, then, total cross-sectional area for the column must be $89.23 / 0.97=91.99 \mathrm{ft}^{2}\left(8.55 \mathrm{~m}^{2}\right)$, and the downcomer area required for good flow distribution is $(91.99-89.23)=2.76 \mathrm{ft}^{2}\left(0.26 \mathrm{~m}^{2}\right)$. (Note that this is considerably larger than the minimum $0.187 \mathrm{ft}^{2}$ required for flow in the downcomer itself). Finally, the required column diameter is $(91.99 / 0.785)^{1 / 2}=10.83 \mathrm{ft}$; say, $11 \mathrm{ft}(3.4 \mathrm{~m})$. (This turns out the same as the diameter estimated in step 2.)

Because of the low liquid rates in vacuum systems, downcomers will usually be oversized, and specific flow rates across the weir will be low. However, liquid rates in high-pressure columns may exceed values recommended for optimum tray performance across a single weir. The maximum specific flow is $70 \mathrm{gal} /(\min \cdot \mathrm{ft})\left[53 \mathrm{~m}^{3} /(\mathrm{h} \cdot \mathrm{m})\right]$ for a straight segmental weir and $80 \mathrm{gal} /(\mathrm{min} \cdot \mathrm{ft})[60$ $\left.\mathrm{m}^{3} /(\mathrm{h} \cdot \mathrm{m})\right]$ for a weir with relief wings. Above $80 \mathrm{gal} /(\mathrm{min} \cdot \mathrm{ft})$, a multiple downcomer arrangement should be considered.

When dealing with foaming or high-pressure systems, a frequent recommendation is the installation of sloped downcomers. This provides for adequate liquid-vapor disengaging volume at the top, while leaving a maximum active area on the tray below.


FIGURE 8.9 Design chart for segmental downcomers. (Glitsch, Inc.)


FIGURE 8.10 Approximate operating range of sieve trays. Note: 1 psia $=6.895 \mathrm{kPa}$.

## 6. Design suitable sieve trays

a. Determine the required hole area. A workable hole-area calculation can be based on the empirically developed relationship shown in Fig. 8.10. In this $F$ factor (the ordinate), $v_{h}$ is the velocity of vapor passing through the holes. The graph shows that columns operating at low pressures have less flexibility (lower turndown ratios) than those operating at higher pressures.

Assume that $F_{H}$ is 12 . Then $v_{h}=F_{H} / \rho_{v}^{0.5}=12 . / 0.02^{0.5}=85 \mathrm{ft} / \mathrm{s}(26 \mathrm{~m} / \mathrm{s})$. Therefore, total hole area required is $(69,000 \mathrm{lb} / \mathrm{h}) /\left[\left(0.02 \mathrm{lb} / \mathrm{ft}^{3}\right)(3600 \mathrm{~s} / \mathrm{h})(85 \mathrm{ft} / \mathrm{s})\right]=11.27 \mathrm{ft}^{2}$. Note that since each tray is fed by one downcomer and drained by another and each downcomer occupies 3 percent of the total tray area according to step 5, the hole area as a percent of active area is

$$
\frac{\left(11.27 \mathrm{ft}^{2}\right)(100)}{[1.00-(2)(0.03)](11 \mathrm{ft})^{2}(\pi / 4)}=12.62 \text { percent }
$$

b. Specify hole size, weir height, and downcomer. Guidelines for this step are as follows:

Hole pitch-to-diameter ratio
Hole size
Open area/active area Weir height

Downcomer seal

2 to 4.5
Use $1 / 2$ in $(0.0127 \mathrm{~m})$ for normal service, $3 / 8$ or $1 / 4$ in ( 0.0095 or 0.0064 m ) for clean vacuum systems, or $3 / 4$ in $(0.0191 \mathrm{~m})$ for fouling service.
Use 4 to 16 percent, depending on system pressure and vapor velocity.
Use 1 to 4 in ( 0.025 to 0.102 m ) (but no higher than 15 percent of tray spacing) as follows: 1 to 2 in ( 0.025 to 0.051 m ) for vacuum and atmospheric columns or $1 \frac{1}{2}$ to 3 in ( 0.038 to 0.076 m ) for moderate to high pressures.
Use one-half of weir height or $3 / 4$ in $(0.0191 \mathrm{~m})$, whichever is greater. Clearance between downcomer and tray deck should never be less than $1 / 2$ in $(0.0127 \mathrm{~m})$, and the velocity through the clearance should be under $1 \mathrm{ft} / \mathrm{s}(0.30 \mathrm{~m} / \mathrm{s})$.

Select $1 / 4$-in $(6.4-\mathrm{mm})$ holes and a 1 -in $(2.54-\mathrm{mm})$ high weir, with a $3 / 4$-in downcomer clearance.
c. Calculate pressure drop to confirm suitability of design. The total pressure drop $h_{t}$ is the sum of the pressure drop across the holes $h_{\text {dry }}$ and the drop through the aerated material above the holes $h_{\text {liq }}$. Now,

$$
h_{\mathrm{dry}}=0.186 \frac{\rho_{V}}{\rho_{L}}\left(\frac{v_{h}}{C}\right)^{2}
$$

where $C$ is a discharge coefficient obtainable from Fig. 8.11. From step $6 b$, hole area divided by active area is 0.1262 , and for a 14 -gauge tray $(0.078$ in or 2 mm , a reasonable thickness for this service), the tray thickness divided by hole diameter ratio is $0.078 / 0.25=0.31$. Therefore, $C$ is read as 0.74 . Then, $h_{\text {dry }}=0.186(0.02 / 76.7)(85 / 0.74)^{2}=$ 0.64 in of liquid. However, this must be adjusted for entrainment:

$$
h_{\mathrm{dry}}(\text { corrected })=h_{\mathrm{dry}}\left(1+\frac{\psi}{1-\psi}\right)
$$



FIGURE 8.11 Discharge coefficient for sieve-tray performance. Note: Most perforated trays are fabricated from 14-gauge stainless steel or 12-gauge carbon-steel plates.


FIGURE 8.12 Estimate of excessive weeping. Note: Operating points above the respective lines represent "salf" designs. A point below the line may indicate uncertainty, but not necessarily a dumping station. (From Chemical Engineering, McGraw-Hill, 1977.)
where $\psi$ is the entrainment function. Since this is 0.15 (see step 3 ),

$$
h_{\mathrm{dry}}(\text { corrected })=0.64\left(1+\frac{0.15}{0.85}\right)=0.75 \text { in liquid }
$$

Dry pressure drop for sieve trays should fall between 0.75 and 3 in of liquid ( 19 and 76 mm ) to prevent excessive weeping on the one hand or jetting on the other. Since, in this case, the dry pressure drop is barely within the recommended range, it is desirable that the tray be checked for weeping using Fig. 8.12.

Now, $A_{h} / A_{A}=0.1262$, from step $6 a$. And

$$
h_{\sigma}=\frac{0.04 \sigma}{\rho_{L}(\text { hole diameter })}=\frac{0.04(16.5)}{76.7(0.25)}=0.034 \text { in liquid }
$$

Therefore, the ordinate in Fig. 8.12, $\left(h_{\text {dry }}+h_{\sigma}\right)$, is $0.75+0.03=0.78$. As for the abscissa, $h_{w}$ (weir height) was chosen to be 1 in , and $h_{o w}=0.5[$ (liquid flow, gal $/ \mathrm{min}$ ) $/($ weir length, in) $]^{0.67}=0.5\{32.68 /[1 / 2(11 \mathrm{ft})(12 \mathrm{in} / \mathrm{ft})]\}^{0.67}=0.31$ in liquid, so $h_{w}+h_{o w}=1.00+0.31=1.31$. In Fig. 8.12, the point $(1.31,0.78)$ falls above the line $A_{H} / A_{A}=0.12$; therefore, weeping will not be excessive.

As for the pressure drop through the aerated material,

$$
h_{\text {liq }}=\beta\left(h_{w}+h_{o w}\right)
$$

where $\beta$ is an aeration factor obtainable from Fig. 8.13. In the abscissa, the vapor-velocity term refers to velocity through the column ( $10.74 \mathrm{ft} / \mathrm{s}$ from step 3 ) rather than to velocity through the holes, so $F_{c}=10.74(0.02)^{1 / 2}=1.52$. Thus $\beta$ is read to be 0.6 . So, $h_{\text {liq }}=0.6(1.31)=0.79$ in liquid. Finally, the total pressure drop $h_{t}=0.75+0.79=1.54$ in liquid. Liquid density is 76.7 $\mathrm{lb} / \mathrm{ft}^{3}$, so the equivalent pressure drop is $1.54(76.7 / 62.4)=1.89$ in water or $3.5 \mathrm{mmHg}(0.47 \mathrm{kPa})$ per tray.
A calculated pressure drop of 3.5 mmHg , although somewhat higher than the assumed 3.0 mmHg , falls within the range of accuracy for the outlined procedure. However, if there is an overriding concern to avoid exceeding the specified 100 mmHg pressure in the column sump, the
following options could be considered: (1) redesign the trays using an $F_{H}$ factor (in step $6 a$ ) of 11.0 or 11.5, or (2) lower the design top pressure to 20 to 30 mmHg and redesign the trays for a pressure drop of 4 or 3.5 mmHg , respectively.

Note that the 3 mmHg pressure drop for this column can in fact be attained if turndown requirements are not excessive. A turndown to 80 percent of the design vapor load is probably the lower limit at which this column can be operated without loss of efficiency. At higher pressures, when pressure drop is not critical, the base design should be for a pressure drop greater than 4.5 mmHg ; this will usually permit operation at turndown rates as high as 50 percent.
d. Discuss the applicability of sieve trays. The sieve tray is probably the most versatile contacting device. It should be considered first for the design of a tray column. It has the lowest installed cost of any equilibrium-stage-type device, its fouling tendencies are low, and it offers good efficiency when properly designed.

However, sieve trays are not recommended for the following conditions: (1) when very low pres-


FIGURE 8.13 Aeration factor for pressure-drop calculations. sure drop (less than 2.5 mmHg , or 0.39 kPa ) is required; (2) when high turndown ratios are required at low pressure drop; or (3) when very low liquid rates are required: below either $0.25 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{2}\right)\left[0.6 \mathrm{~m}^{3} /(\mathrm{h})\left(\mathrm{m}^{2}\right)\right]$ of active tray area, or $1 \mathrm{gal} /(\mathrm{min})(\mathrm{ft})\left[0.75 \mathrm{~m}^{3} /(\mathrm{h})(\mathrm{m})\right]$ of average flow-path width.

## 7. Design suitable valve trays (as an alternative to sieve trays)

a. Select the valve layout. Although valve trays come in several configurations, all have the same basic operational principle: Vapor passing through orifices in the tray lifts small metal disks or strips, thereby producing a variable opening that is proportional to the flow rate.

Because of their proprietary nature, valve trays are usually designed by their respective vendors based on process specifications supplied by the customer. However, most fabricators publish technical manuals that make it possible to estimate some of the design parameters. The procedure for calculating valve-tray pressure drop outlined here has been adapted from the Koch Design Manual. As for the other column specifications required, they can be obtained via the same calculation procedures outlined above for the sieve-tray design.

The number of valve caps that can be fitted on a tray is at best an estimate unless a detailed tray layout is prepared. However, a standard has evolved for low- and moderate-pressure operations: a $3 \times 2 \frac{1}{2}$ in pattern that is the tightest arrangement available, accommodating about 14 caps $/ \mathrm{ft}^{2}(150$ $\mathrm{caps} / \mathrm{m}^{2}$ ). The active area does not take into account liquid-distribution areas at the inlet and outlet, nor edge losses due to support rings, nor unavailable space over tray-support beams. In smaller columns, it is possible that as much as 25 percent of the active tray area may not be available for functioning valves. For this column, which operates at low pressure, select the standard $3 \times 2 \frac{1}{2}$ in pitch.
b. Calculate the pressure drop per tray. The vapor velocity at the top of the column is $(69,000$ $\mathrm{lb} / \mathrm{h}) /\left[(60 \mathrm{~min} / \mathrm{h})\left(0.02 \mathrm{lb} / \mathrm{ft}^{3}\right)\right]=57,500 \mathrm{ft}^{3} / \mathrm{min}$. Assume that 15 percent of the tray is not available for functioning valves. Then, since the active tray area (subtracting both the descending and ascending downcomers; see step $6 a$ ) is $0.94(11)^{2}(\pi / 4)=89.3 \mathrm{ft}^{2}$, the number of valves per tray is $0.85\left(89.3 \mathrm{ft}^{2}\right)\left(14 \mathrm{caps} / \mathrm{ft}^{2}\right)=1063$ valves. Then, in entering Fig. 8.14 so as to find the pressure drop $h_{\text {dry }}$ through the valves, the abscissa $\left(\mathrm{ft}^{3} / \mathrm{min}\right)$ air/cap is $\left[\left(57,500 \mathrm{ft}^{3} / \mathrm{min}\right) / 1063\right.$ valves] $(0.02 / 0.0735)^{0.5}=28.2$. From Fig. 8.14, using the curve for the Venturi orifice valve, $\Delta P=0.8$ in water, or 0.65 in liquid, or 1.5 mmHg , which when corrected for entrainment (same as for sieve trays; see step $6 c$ ) becomes $0.65(1+0.15 / 0.85)=0.76$ in liquid.


FIGURE 8.14 Dry pressure drop $h_{\text {dry }}$ across valve trays. (From Chemical Engineering, McGraw-Hill, 1977.)

The pressure drop $h_{\text {liq }}$ through the aerated liquid can be obtained directly from Fig. 8.15. For a liquid rate of $32.68 \mathrm{gal} / \mathrm{min}$ (see step 5) flowing over a $5.5-\mathrm{ft}$-long, 1 -in weir (see steps 5 and 6 b ), or $6 \mathrm{gal} /(\mathrm{min})(\mathrm{ft}), h_{\text {liq }}$ is found to be 0.5 in liquid. Therefore, the total pressure drop across a valve tray is $0.76+0.5=1.26$ in liquid, or 1.55 in water, or $2.9 \mathrm{mmHg}(0.39 \mathrm{kPa})$.
c. Discuss the applicability of valve trays. The relatively low pressure drop that can be maintained without undue loss of turndown in vacuum columns is probably the valve tray's greatest attribute. Although the accuracy of either the sieve or valve-tray calculation procedure is probably no better than $\pm 20$ percent, a lower pressure drop is likely to be achieved with Venturi orifice valves than with sieve trays if a reasonable turndown ratio (say 60 percent) is required. This is of little concern at column pressures above $400 \mathrm{mmHg}(53 \mathrm{kPa})$, when pressure drop becomes a minor consideration. A word of caution: When the valves are exposed to a corrosive environment, it is likely that their constant movement will induce fatigue stresses, which frequently lead to the rapid deterioration of the retaining lugs and valve caps. It is not unusual to find valves missing in that part of the column where corrosive constituents are concentrated.

## COLUMN EFFICIENCY

Determine the efficiency in the upper portion of the DCB distillation column designed in the preceding example. Relative volatility for the system is 3.6.

## Procedure

1. Determine the effects of the physical properties of the system on column efficiency. Tray efficiency is a function of (1) physical properties of the system, such as viscosity, surface tension, relative volatility, and diffusivity; (2) tray hydraulics, such as liquid height, hole size, fraction of tray area open, length of liquid flow path, and weir configuration; and (3) degree of separation of the liquid and vapor streams leaving the tray. Overall column efficiency is based on the same factors, but will ordinarily be less than individual-tray efficiency.

The effect of physical properties on column efficiency can be roughly estimated from Fig. 8.16. For this system, viscosity is 0.35 cP (see statement of previous example) and relative volatility is 3.6, so the abscissa is 1.26 . The ordinate, or column efficiency, is read to be 68 percent.


FIGURE 8.15 Effective liquid depth (pressure drop through aerated liquid, $h_{\text {liq }}$ ) on valve trays. (From Chemical Engineering, McGraw-Hill, 1977.)
2. Determine the effects of tray hydraulics on the efficiency. Tray hydraulics will affect efficiency adversely only if submergence, hole size, open tray area, and weir configuration are outside the recommended limits outlined in the previous example. Since that is not the case, no adverse effects need be expected.
3. Determine the effects of inadequate separation of liquid and vapor (e.g., entrainment) on the efficiency. The effects of entrainment on efficiency can be quite drastic, especially in vacuum columns, as the vapor rate in the column approaches flooding velocities. The corrected-for-entrainment efficiency can be calculated as follows:

$$
E_{c}=\frac{E_{i}}{1+E_{i}[\psi /(1-\psi)]}
$$

where $E_{c}$ is the corrected efficiency, $E_{i}$ is the efficiency that would prevail if entrainment were no problem (i.e., 68 percent, from step 1), and $\psi$ is the fractional entrainment, whose relationship to other column parameters is defined in Fig. 8.17. In step 3 of the previous example, $\psi$ was assumed to be 0.15 . Therefore, $E_{c}=0.68 /\{1+0.68[0.15 /(1-0.15)]\}=0.607$; say, 60 percent.


FIGURE 8.16 Column efficiency as a function of average column viscosity and relative volatility.

Accordingly, an actual column efficiency of 60 percent for the top section of the column would be reasonable.

Related Calculations. Since efficiencies are likely to vary from column top to bottom, it is usually well to estimate them at various points (at least two) along the column.
"Normal" column efficiencies run between 60 and 85 percent. They will tend toward the lower part of this range in vacuum columns, where entrainment can be a major factor, and in systems where


FIGURE 8.17 Fractional entrainment.
high purities are demanded ( $<100 \mathrm{ppm}$ of a contaminant). Moderate-pressure systems frequently show higher efficiencies. For instance, the benzene-toluene-xylene system outlined in Example 8.1 has a viscosity of 0.3 cP and a 2.58 relative volatility. From Fig 8.16, this calls for an efficiency of 71 percent. Little if any correction for entrainment will be necessary, and a final assumed efficiency of 70 percent would not be unreasonable.

Apparent efficiencies for high-pressure systems have frequently been reported in the 90 to 100 percent range.

Weeping is considered excessive and will adversely affect efficiency when the major fraction of the liquid drops through the holes rather than flows over the weir. Figure 8.12 provides a good guide for selecting safe operating conditions of trays; no derating of the basic efficiency is necessary if the operating point falls above the appropriate area-ratio curve.

A correction for dynamic column instability must be made in order to adjust for the continuous shifting of the concentration profile that results from the interaction of controllers with changes in feed flow, cooling water rates, and the ambient temperature. To ensure that product quality will always stay within specifications, it is recommended that 10 percent, but not less than three trays, be added to the calculated number of trays. For instance, recall that the benzene-toluene-xylene system in Example 8.1 requires 25 theoretical stages. With a 70 percent column efficiency, this is now raised to 36 actual trays. Another 4 trays should be added to account for dynamic instability, making a total of 40 installed trays. (Although texts frequently suggest that reboilers and condensers be counted as a theoretical stage, this is, strictly speaking, true only of kettle-type reboilers and partial condensers. Generally, the safest approach in a column design is to ignore both the reboiler and condenser when counting equilibrium stages.)

There may be a drop in efficiency for very large diameter columns ( $>12 \mathrm{ft}$ ) due to their size, unless special jets or baffles are provided to ensure an even flow pattern.

As pointed out by Humphrey and Keller in Separation Process Technology (McGraw-Hill, 1997), a rate-based design method for distillation (and other staged processes) has been developed. Component material and energy balances for each phase, together with mass and energy transfer-rate equations, as well as equilibrium equations for the phase interface, are solved to determine the actual separation directly. Calculations take place on an incremental basis as the designer proceeds through the column. The uncertainties of computations that use average tray efficiencies, based on individual components, are entirely avoided.

### 8.4 PACKED-COLUMN DESIGN

Specify a packing and the column dimensions for a distillation column separating ethyl benzene and styrene at 1200 mmHg ( 23.21 psia ). The separation requires 30 theoretical stages. Vapor flow is $12,000 \mathrm{lb} / \mathrm{h}(5455 \mathrm{~kg} / \mathrm{h})$, average vapor density is $0.3 \mathrm{lb} / \mathrm{ft}^{3}\left(4.8 \mathrm{~kg} / \mathrm{m}^{3}\right)$, liquid flow is $10,000 \mathrm{lb} / \mathrm{h}$ $(4545 \mathrm{~kg} / \mathrm{h})$, and average liquid density is $52 \mathrm{lb} / \mathrm{ft}^{3}\left(833 \mathrm{~kg} / \mathrm{m}^{3}\right)$. Liquid kinematic viscosity is 0.48 cSt ( $4.8 \times 10^{-7} \mathrm{~m}^{2} / \mathrm{s}$ ).

## Calculation Procedure

1. Select a type, arrangement, and size of packing. For this particular system, if one is dealing with a new column, the use of random (dumped) packing is probably a better economic choice than a systematically packed column. Although there is no clear line of demarcation between the two, the latter type is generally favored for very low pressure operations and for expanding the capacity of an existing column.

Somewhat arbitrarily, let us choose a metal slotted ring, say Hy-Pak, as the packing type to be used for this service. Hy-Pak is the Norton Company (Akron, Ohio) version of a slotted ring. There are other packing devices, such as metal saddles and half or pyramidal Pall rings, that would be equally suitable for this service.


FIGURE 8.18 Generalized pressure-drop correlation for packed towers. Note: Parameter of curves is pressure drop in inches of water per foot. Numbers in parentheses are millimeters of water per meter of packed height.

A packing size should be selected so that the column-diameter-to-packing-size ratio is greater than 30 for Raschig rings, 15 for ceramic saddles, and 10 for slotted rings or plastic saddles. When dealing with distillation columns larger than 24 in ( 0.6 m ) in diameter, a 2 -in, or no. 2 , packing should probably be given the first consideration. Assume (essentially based on trial and error) that this column will be larger than 24 in . Therefore, select a 2 -in size for the packing.
2. Determine the column diameter. The generally accepted design procedures for sizing randomly packed columns are modifications of the Sherwood correlation. A widely applied version is that developed by the Norton Company. It has been adapted slightly for this text to permit its application to low-pressure systems.

Tower diameter is primarily a function of throughput rate and packing configuration. A specific design gas rate $G$ can be determined from Fig. 8.18 if liquid and vapor flows are known and a suitable packing and the proper pressure drop have been selected. Recommended design pressure drops are as follows: 0.4 to 0.75 in water per foot of packing ( 32 to 63 mm water per meter) for moderate- and high-pressure distillation; 0.1 to 0.2 in water per foot of packing ( 8 to 16 mm water per meter) for vacuum distillation; and 0.2 to 0.6 in water per foot of packing ( 16 to 48 mm per meter) for absorbers and strippers.

TABLE 8.2 Packing Factors for Column Packings ( 1 in $=0.0254 \mathrm{~m}$ )

| Packing type | Material | Nominal packing size, in |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | 1/4 | $3 / 8$ | 1/2 | 5/8 | $3 / 4$ | 1 or no. 1 | $11 / 4$ | $11 / 2$ | 2 or no. 2 | 3 | $31 / 2$ or no. 3 |
| Hy-Pak | Metal |  |  |  |  |  | 43 |  |  | 18 |  | 15 |
| Super Intalox saddles | Ceramic |  |  |  |  |  | 60 |  |  | 30 |  |  |
| Super Intalox saddles | Plastic |  |  |  |  |  | 33 |  |  | 21 |  | 16 |
| Pall rings | Plastic |  |  |  | 97 |  | 52 |  | 40 | 24 |  | 16 |
| Pall rings | Metal |  |  |  | 70 |  | 48 |  | 33 | 20 |  | 16 |
| Intalox saddles | Ceramic | 725 | 330 | 200 |  | 145 | 92 |  | 52 | 40 | 22 |  |
| Raschig rings | Ceramic | 1600 | 1000 | 580 | 380 | 255 | 155 | 125 | 95 | 65 | 37 |  |
| Raschig rings | Metal, $1 / 32$ in | 700 | 390 | 300 | 170 | 155 | 115 |  |  |  |  |  |
| Raschig rings | Metal, $1 / 16$ in |  |  | 410 | 290 | 220 | 137 | 110 | 83 | 57 | 32 |  |
| Berl saddles | Ceramic | 900 |  | 240 |  | 170 | 110 |  | 65 | 45 |  |  |
| Tellerettes | Plastic |  |  |  |  |  | 38 |  |  | 19 |  |  |
| Mas Pac | Plastic |  |  |  |  |  |  |  |  | 32 |  | 20 |
| Quartz rock |  |  |  |  |  |  |  |  |  | 160 |  |  |
| Cross partition | Ceramic |  |  |  |  |  |  |  |  |  | 80 |  |
| Flexipac | Metal |  |  |  |  |  | 33 |  |  | 22 |  | 16 |
| Interlox | Metal |  |  |  |  |  | 41 |  |  | 27 |  | 18 |
| Chempak | Metal |  |  |  |  |  | 29 |  |  |  |  |  |

Note: Many of values are those listed in vendors' literature and are frequently based solely on pilot tests. It may be prudent on occasion to assume slightly larger packing factors in order to represent more precisely the pressure drop of newly marketed packing in commercial columns. Consult with vendors for data on newer, proprietary packings.

First, evaluate the abscissa for Fig. 8.18. Thus, $(L / V)\left(\rho_{V} / \rho_{L}\right)^{0.5}=(10,000 / 12,000)(0.3 /$ $52)^{0.5}=0.063$. (Note: $\rho_{V}$, especially for vacuum columns, should be determined for the top of the bed, because this is where the density is lowest and the vapor velocity highest.)

Next, select a pressure drop of $0.15 \mathrm{in} / \mathrm{ft}$ of packing, and on the figure read 0.55 as the ordinate. Thus, $0.55=C G^{2} F v^{0.1} /\left[\rho_{V}\left(\rho_{L}-\rho_{V}\right)\right]$. From Table 8.2, $F$ is 18. Solving for $G, G=[0.55(0.3)(52-$ $\left.0.3) / 1(18)(0.48)^{0.1}\right]^{0.5}=0.71 \mathrm{lb} /\left(\mathrm{ft}^{2}\right)(\mathrm{s})$.

Accordingly, the required column cross-sectional area is $(12,000 \mathrm{lb} / \mathrm{h}) /\left[(3600 \mathrm{~s} / \mathrm{h}) 0.71 \mathrm{lb} /\left(\mathrm{ft}^{2}\right)(\mathrm{s})\right]$ $=4.7 \mathrm{ft}^{2}$. Finally, column diameter is $\left[\left(4.7 \mathrm{ft}^{2}\right) /(\pi / 4)\right]^{0.5}=2.45 \mathrm{ft}$; say, $2.5 \mathrm{ft}(0.75 \mathrm{~m})$. (Thus the initial assumption in step 1 that column diameter would be greater than 24 in is valid.)
3. Determine the column height. To translate the 30 required theoretical stages into an actual column height, use the height equivalent to a theoretical plate (HETP) concept. HETP values are remarkably constant for a large number of organic and inorganic systems.

As long as dumped packing in commercial columns is properly wetted [more than $1000 \mathrm{lb} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)$ or $5000 \mathrm{~kg} /(\mathrm{h})\left(\mathrm{m}^{2}\right)$, the following HETP values will result in a workable column:

| Nominal packing size, for slotted <br> rings or Intalox saddles | HETP |
| :---: | :---: |
| 1 in (or no. 1) | $1.5 \mathrm{ft}(0.46 \mathrm{~m})$ |
| $11 / 2$ in | $2.2 \mathrm{ft}(0.67 \mathrm{~m})$ |
| 2 in (or no. 2) | $3.0 \mathrm{ft}(0.91 \mathrm{~m})$ |

Because the irrigation rate in vacuum columns often falls below $1000 \mathrm{lb} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)$, it may be wise to add another 6 in to the listed HETP values as a safety factor. For the ethylbenzene/styrene system
in this example, the specific irrigation rate is $(10,000 \mathrm{lb} / \mathrm{h}) / 4.7 \mathrm{ft}^{2}=2128 \mathrm{lb} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)$, which is well above the minimum required for good wetting. Total packing height is $30(3.0)=90 \mathrm{ft}$.

Since liquid maldistribution may become a problem unless the flow is periodically redistributed in a tall column, the total packing height must be broken up into a number of individual beds:

| Packing | Maximum bed height |
| :--- | :--- |
| Raschig rings | 2.5 to 3.0 bed diameters |
| Ceramic saddles | 5 to 8 bed diameters |
| Slotted rings and plastic saddles | 5 to 10 bed diameters |

With 2-in slotted ring packing in a $2.5-\mathrm{ft}(0.75-\mathrm{m})$ column, each bed should be no higher than $25 \mathrm{ft}(7.6 \mathrm{~m})$. Therefore, for the given system, four $23-\mathrm{ft}(7-\mathrm{m})$ beds would be appropriate.

Related Calculations. With ceramic packing, the height of a single bed is, for structural reasons, frequently restricted to no more than $20 \mathrm{ft}(\simeq 6 \mathrm{~m})$.

In step 1, the column-diameter-to-packing-size ratio for Raschig rings can be less than 30 for scrubbing applications in which the liquid-irrigation rate is high and the column is operated at above 70 percent of flooding.

If it is desirable to have systematically packed column internals, then the choice is from among various types of mesh pads, open-grid configurations, springs, spirals, and corrugated elements. Since no generalized design correlations can be applied to all configurations, it will be necessary to have the respective manufacturers develop the final packing design.

The question arises whether trays or packing should be selected for a given distillation task. Humphrey and Keller (see reference at end of Example 8.3) cite the following factors as favoring trays: high liquid rate (occurs when high column pressures are involved); large column diameter (because packing is prone to maldistribution); complex columns with multiple feeds and takeoffs; and variation in feed composition. Furthermore, scaleup is less risky with trays, and trayed columns weigh less than packed columns. Conversely, the following factors favor packings: vacuum conditions; a need for low pressure drop; corrosive systems; foaming systems; and systems with low liquid holdup.

Establish the separation capability of a single-stage (differential) batch still processing a mixture of two compounds having a relative volatility of 4.0. At the start of the batch separation, there are 600 mol of the more-volatile compound $A$ and 400 mol of compound $B$ in the kettle. When the remaining charge in the kettle is 80 percent $B$, how much total material has been boiled off, and what is the composition of the accumulated distillate?

## Calculation Procedure

1. Calculate the amount of material boiled off. Use the integrated form of the Rayleigh equation

$$
\ln \frac{L_{1}}{L_{2}}=\frac{1}{\alpha-1}\left(\ln \frac{x_{1}}{x_{2}}+\alpha \ln \frac{1-x_{2}}{1-x_{1}}\right)
$$

where $L_{1}$ is the amount of initial liquid in the kettle (in moles), $L_{2}$ is the amount of final residual liquid (in moles), $\alpha$ is the relative volatility (4.0), $x_{1}$ is the initial mole fraction of more-volatile compound in the kettle (0.6), and $x_{2}$ is the final mole fraction of more-volatile component in the kettle (0.2). Then,

$$
\ln \frac{L_{1}}{L_{2}}=\frac{1}{4-1}\left(\ln \frac{0.6}{0.2}+4 \ln \frac{1-0.2}{1-0.6}\right)=1.29
$$

So, $L_{1} / L_{2}=3.63$, or $L_{2}=1000 / 3.63=275 \mathrm{~mol}$. Therefore, the amount of material distilled over is $1000-275=725 \mathrm{~mol}$.
2. Calculate the distillate composition. Compound $A$ in the initial charge consisted of 600 mol . Compound $A$ in the residue amounts to $275(0.2)=55 \mathrm{~mol}$. Therefore, compound $A$ in the distillate amounts to $600-55=545 \mathrm{~mol}$. Therefore, mole fraction $A$ in the distillate is $54 / 725=0.75$, and mole fraction $B$ is $1-0.75=0.25$.

Related Calculations. Since a simple batch kettle provides only a single theoretical stage, it is impossible to achieve any reasonable separation unless the magnitude of the relative volatility approaches infinity. This is the case with the removal of very light components of a mixture, particularly of heavy residues. In this example, even with a comfortable relative volatility of 4 , it was only possible to increase the concentration of $A$ from 60 to $75 \%$ and to strip the residue to $20 \%$.

Obviously, the more distillate that is boiled over, the lower will be the separation efficiency. Conversely, higher overhead concentrations can be obtained at the expense of a larger loss of compound $A$ in the residue. For instance, if distillation in this example is stopped after 50 percent of the charge has been boiled off, the final concentration of $A$ in the kettle $x_{2}$ can be obtained as follows:

$$
\ln \frac{1000}{500}=\frac{1}{4-1}\left(\ln \frac{0.6}{x_{2}}+4 \ln \frac{1-x_{2}}{1-0.6}\right)
$$

from which $x_{2}=0.395$ (by trial-and-error calculation). The amount of $A$ remaining in the residue is 198 mol , making a $40 \%$ concentration, and the amount of $A$ in the distillate is 402 mol , making an $80 \%$ concentration.

### 8.6 BATCH-COLUMN DESIGN

Estimate the required size of a batch still, with vapor rectification, to recover a dye intermediate from its coproduct and some low- and high-boiling impurities. It has been specified that $13,000 \mathrm{lb}$ ( 5900 kg ), consisting of fresh reactor product and recycled "slop" cuts, must be processed per batch.

The initial composition in the kettle is as follows:
Low-boiling impurities: 500 lb ( 227 kg )
Dye intermediate: $5500 \mathrm{lb}(2500 \mathrm{~kg})$
Coproduct: 5000 lb ( 2273 kg )
High-boiling impurities: 2000 lb ( 909 kg )
Tests in laboratory columns have indicated that to ensure adequate removal of the low-boiling impurities, $500 \mathrm{lb}(227 \mathrm{~kg})$ of the dye intermediate is lost in the low boiler's cut. Similarly, high boilers remaining in the kettle at the end of the distillation will retain $500 \mathrm{lb}(227 \mathrm{~kg})$ of the coproduct. This leaves $9500 \mathrm{lb}(4320 \mathrm{~kg})$ of the two recoverable products. The specification for the dye intermediate
requires a concentration of less than $0.5 \mathrm{~mol} \%$ of the coproduct. Of the two, the coproduct has the higher boiling point.

The conditions for the separation of the dye intermediate from the coproduct are as follows:
Relative volatility $\alpha=2$
Molecular weight of dye intermediate $=80$
Molecular weight of coproduct $=100$
Average liquid density $=62.0 \mathrm{lb} / \mathrm{ft}^{3}\left(993 \mathrm{~kg} / \mathrm{m}^{3}\right)$
Column pressure $(\mathrm{top})=350 \mathrm{mmHg}(46.6 \mathrm{kPa})$
Column temperature $($ top $)=185^{\circ} \mathrm{F}(358 \mathrm{~K})$

## Calculation Procedure

1. Assess the applicability of a design not based on computer analyses. The precise design of a batch still is extremely complex because of the transient behavior of the column. Not only do compositions change continuously during the rectification of a charge, but successive batches may start with varying compositions as "slop" cuts and heels are recycled. Only sophisticated software programs can optimize the size, collection time, and reflux ratios for each cut. In addition to the recycle streams, these programs must also take into account nonideal equilibrium (where applicable) and the effect of holdup on trays. The following is not a detailed design for batch rectification, but instead an outline of how to estimate a "workable" facility with reasonable assurance that it will do the desired job.

Before continuing with a step-by-step procedure, consider these rules of thumb for batch stills:

1. Too low a reflux ratio cannot produce the required product specification no matter how many trays are installed. Conversely, even infinite reflux will not be sufficient if an inadequate number of equilibrium stages has been provided.
2. For optimum separation efficiency, reflux holdup should be minimized by eliminating surge drums and using flow splitters that retain little or no liquid.
3. Too little or too much holdup in the column is detrimental to separation efficiency. A reasonable amount provides a flywheel effect that dampens the effects of equilibrium-condition fluctuations; too much, especially at higher reflux ratios, makes it difficult to achieve good purity levels. A holdup equivalent to 10 or 15 percent of the initial batch charge is recommended.
4. Since the column consists solely of a rectifying section, there is a limit to how many trays can be profitably installed. The system will "pinch" regardless of stages once the low-boiler concentration in the reboiler approaches the intersection of the operating line with the equilibrium curve.
5. Once a workable column has been installed, capacity to produce at a given rate and product specification is only minimally affected by changes in reflux ratio or length of a cut.
6. As the more-volatile component is being removed from the reboiler, separation becomes progressively more difficult.
7. It is impossible to recover in a single operation, at high purity, a low-boiling component that represents only a small fraction of the initial charge.
8. Set up an estimated batch-processing time schedule. A reasonable time schedule is as follows:

Charge new batch into kettle; heat up charge: 3 h
Run column at total reflux to stabilize concentration; distill off the low-boilers cut: 6 h

Recover (i.e., distill off) the dye intermediate while increasing the reflux ratio one or two times: 6 h Distill off center (slop) cut while further increasing reflux ratio one or two times: 6 h
Distill off coproduct from its mixture with the high boilers while again increasing reflux ratio once (if necessary): 4 h
Drain the high-boiling residue and get ready for next batch; recycle the center cut and prepare to charge fresh feed: 3 h
Total elapsed time: 28 h
3. Estimate the number of theoretical trays needed to recover the dye intermediate. Enter Fig. 8.19 along its ordinate at a relative volatility of 2 . For product purity of 99.5 percent, the graph shows that 11 stages are needed.
4. Draw the relevant xy diagram (equilibrium curve). The relevant diagram is one that pertains to a relative volatility $\alpha$ of 2 . As indicated in Example 8.1, it can be plotted from the equation


FIGURE 8.19 Estimate of theoretical stages, or of reflux ratio, for batch distillation.


FIGURE 8.20 McCabe-Thiele diagram for Example 8.6.
$y=\alpha x /[1+(\alpha-1) x]$. This is the uppermost curve in Fig. 8.20 (including both the full portion at the top of the diagram and the expanded upper-column section at the bottom).
5. Applying the McCabe-Thiele principles, position an operating line on the xy diagram that will accommodate 11 stages between the initial kettle composition and the distillate composition that pertain to the time-schedule step in which the dye intermediate is recovered. The McCabe-Thiele principles applied here are outlined in more detail in Example 8.1. Using the dye intermediate and the
coproduct as the two key components, the initial kettle composition after removal of the low boilers cut (based on the key components only) is $(5000 / 80) /[(5000 / 80)+(5000 / 100)]=0.556$ mole fraction, or $55.6 \mathrm{~mol} \%$, dye intermediate and $(100-55.6)=44.4 \mathrm{~mol} \%$ coproduct. The abscissa corresponding to this composition $x_{B 1}$ marks one end (the "feed" end) of the 11 -stage separation; the other end (the overhead-product end) is marked by the abscissa $x_{D 1}$ that corresponds to the required dye-intermediate purity, $99.5 \%$.

By trial-and-error positioning, it is found that an operating line having a slope of 0.833 will accommodate 11 stages (the overhead product corresponding to this line is very slightly purer than $99.5 \%$, namely, $99.7 \%$ ). In Fig. 8.20, the operating line is line $A B$. By definition (see Example 8.1), its 0.833 slope establishes (and is equal to) the ratio $L / V$ of descending liquid to rising vapor. This in turn establishes the reflux ratio $L / D$, or $L /(V-L)$, where $D$ is the amount of overhead product taken. Since $L / V=0.833$, then $L / D=0.833 \mathrm{~V} /(V-0.833 \mathrm{~V})=5$. Thus, during this period, the column must be operated at a reflux ratio of 5 .
6. Determine the effect of elapsed time on overhead-product concentration. It is reasonable to assume that about 35 to 50 percent of the dye intermediate can be removed efficiently at the initial, relatively low reflux ratio of 5 . In this case, assume that 2100 lb of the 5000 lb is thus removed. It is also reasonable to assume that this takes place during half of the 6 h allotted in step 2 for recovering this intermediate. (Note that the shorter the allotted time, the bigger the required column diameter.)

Therefore, $D=2100 / 3=700 \mathrm{lb} / \mathrm{h}$. Because $L / D=5, L=3500 \mathrm{lb} / \mathrm{h}$. And since $D=V-$ $L, V=4200 \mathrm{lb} / \mathrm{h}$. After 3 h (assuming negligible column holdup), the kettle will contain (5000 $-2100) / 80=36.25 \mathrm{~mol}$ dye intermediate. Since the overhead stream contains (initially, at least) only $0.3 \%$ coproduct, the amount of coproduct in the kettle after 3 h is about $[5000-0.005(2100)] / 100=$ 49.9 mol. The mole percentages thus are $42 \%$ intermediate and $58 \%$ coproduct. If the abscissa corresponding to this new kettle composition $x_{B 2}$ is extended upward to the operating line and equilibrium curve, it can be seen that this "feed" composition has shifted downward by 1.3 stages. This will likewise lower the overhead (distillate) composition by 1.3 stages, which means that the concentration of dye intermediate drops to $99.4 \%$ after 2100 lb of distillate has boiled over and been collected. Average concentration during this period of operating at a reflux ratio of 5 is thus $(99.7+99.4) / 2=99.55$ percent, just slightly above the specified purity.
7. Adjust the reflux ratio so as to maintain the required overhead-product composition. It is necessary to raise the reflux ratio in order to keep the concentration of dye intermediate in the overhead product high enough. In this case, assume that an additional 1400 lb intermediate can be recovered in the remaining 3 h while maintaining the original vapor rate of $4200 \mathrm{lb} / \mathrm{h}$. Then $D$ for this latter 3 h is $1400 / 3=467 \mathrm{lb} / \mathrm{h}$; $L$ is $(4200-467)=3733 \mathrm{lb} / \mathrm{h}$; and the reflux ratio $L / D$ for this portion of operation must be $3733 / 467=8$.

The slope $L / V$ of the new operating line is $3733 / 4200=0.89$. Drawing this line on the replotted $x y$ diagram in Fig. 8.21 and stepping off 11 stages, we find that the initial overhead concentration $x_{D 3}$ while operating at the new reflux ratio is $99.7 \%$ dye intermediate. (Note that $x_{B 3}$ in Fig. 8.21 is a deliberate repetition of $x_{B 2}$ in Fig. 8.20, whereas $x_{D 3}$ is not a deliberate repetition but instead a coincidental result that emerges from the stepping off of the stages.)

## 8. Again determine the effect of elapsed time on overhead-product composition and readjust the

 reflux ratio of step 7 if necessary. It follows from the preceding two steps that after the second 3 h , the kettle will contain $(2900-1400) / 80=18.75 \mathrm{~mol}$ dye intermediate and about [5000 $0.005(3500)] / 100=49.8 \mathrm{~mol}$ coproduct. Thus the mole percentages will be $27 \%$ intermediate and $73 \%$ coproduct. The abscissa $x_{B 4}$ corresponding to this in Fig. 8.21 indicates that the composition will have shifted downward about 1.6 stages. This in turn means that the distillate composition will have dropped 1.6 stages during the 3 h , to a composition $x_{D 4}$ of $99.2 \%$ dye intermediate. Average concentration while operating at a reflux ratio of 8 is therefore $(99.7+99.2) / 2=99.45$ percent.Since this average concentration is slightly below the required purity of $99.5 \%$, it would be wise to recalculate step 7 at a higher reflux ratio with a correspondingly longer time for removing the same 1400 lb . A 4 -h removal time, corresponding to a reflux ratio of 11 , should be more than adequate.


FIGURE 8.21 Second McCabe-Thiele diagram for Example 8.6.
9. Determine the column diameter. The column diameter can be determined by taking the boil-up rate established for the separation of components having the smallest relative volatility (which, in this case, is given to be the dye-intermediate/coproduct separation) and using the design procedures outlined in Examples 8.2 and 8.4.

For a $4200 \mathrm{lb} / \mathrm{h}$ boil-up rate (from step 6) of dye intermediate having a density $\rho_{V}$ of $(80 \mathrm{lb} / \mathrm{mol})(6.77$ $\left.\mathrm{lb} / \mathrm{in}^{2}\right) /[10.73(460+185 R)]=0.078 \mathrm{lb} / \mathrm{ft}^{3}$ (where 10.73 is the gas constant), the total vapor flow rate is $4200 /[0.078(3600)]=14.9 \mathrm{ft}^{3} / \mathrm{s}$. A tray spacing of 18 in seems appropriate. The column diameter required for an 18 -in tray spacing can be obtained with the aid of Fig. 8.6, where $F_{c}$ is found to be
about $1.4\left[\mathrm{lb} /\left(\mathrm{ft} \cdot \mathrm{s}^{2}\right)\right]^{0.5}$. Then free tray area $A_{F}=W /\left(F_{c} \rho_{V}^{0.5}\right)=(4200 \mathrm{lb} / \mathrm{h}) /[3600 \mathrm{~s} / \mathrm{h})(1.4)(0.078$ $\left.\left.\mathrm{lb} / \mathrm{ft}^{3}\right)^{0.5}\right]=2.98 \mathrm{ft}^{2}$. Allowing 5 percent of the tray area for segmental downcomers, total tray area is $2.98 / 0.95=3.14 \mathrm{ft}^{2}$. Finally, column diameter is $[3.14 /(\pi / 4)]^{0.5}=2 \mathrm{ft}(0.41 \mathrm{~m})$.
10. Determine the column height. Efficiencies of batch columns vary greatly, since the concentration profile in the column shifts over a wide range. For appreciable intervals, separation may of necessity take place under pinched conditions, conducive to low efficiencies. So an overall column efficiency of 50 percent is not unreasonable. Thus the total number of trays provided is ( 11 stages)/ $0.5=22$ trays. At a spacing of 18 in , the required column height is $33 \mathrm{ft}(10 \mathrm{~m})$. The trays should be cartridge-type trays, because normal trays cannot be readily installed in a 2 - ft column.

Related Calculations. Alternatively, a packed column can be considered for this separation. Its design should follow the procedure outlined in Example 8.4.

If the coproduct must also be recovered at a reasonably high purity, then steps 5 through 8 should also be repeated for distilling off the slop cut (essentially a mixture of dye intermediate and coproduct) and for the coproduct cut (a mixture of coproduct and high-boiling residue).

In the final analysis, processing time is the main criterion of batch-still design. To achieve optimal cost-effective performance requires a large number of trial calculations, such that the best combination of equilibrium stages, reflux ratio, batch size, and batch-processing time can be established. It is extremely difficult to successfully carry out such a procedure by hand calculation.

### 8.7 OVERALL COLUMN SELECTION AND DESIGN

Select and specify an efficient distillation column to separate ethylbenzene (EB) and ethyl cyclohexane (ECH), and develop the appropriate heat and material balances. Feed rate is $10 \mathrm{lb} \cdot \mathrm{mol} / \mathrm{h}(4.54$ $\mathrm{kg} \cdot \mathrm{mol} / \mathrm{h}): 75 \mathrm{~mol} \% \mathrm{ECH}$ and $25 \mathrm{~mol} \% \mathrm{~EB}$. Concentration of EB in the overhead product must be less than $0.1 \%$; concentration of ECH in the bottoms stream must be less than $5 \%$. Feed is at ambient temperature $\left(25^{\circ} \mathrm{C}\right)$. Specific heat of the distillate and bottoms streams can be taken as 0.39 and $0.45 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)[1.63$ and $1.89 \mathrm{~kJ} /(\mathrm{kg})(\mathrm{K})]$, respectively. The normal boiling points for EB and ECH are $136.19^{\circ} \mathrm{C}$ and $131.78^{\circ} \mathrm{C}$, respectively; their latent heats of vaporization can be taken as 153 and $147 \mathrm{Btu} / \mathrm{lb}$ ( 356 and $342 \mathrm{~kJ} / \mathrm{kg}$ ), respectively. It can be assumed that EB and ECH form an ideal mixture.

## Calculation Procedure

1. Make a rough estimate of the number of theoretical stages required. This step employs the procedures developed in Example 8.1. Use the Fenske-Underwood-Gilliland approach rather than the McCabe-Thiele, because the small boiling-point difference indicates that a large number of stages will be needed.

The appropriate vapor pressures can be obtained from the Antoine equation:

$$
\log P=A-\frac{B}{t+C}
$$

where $P$ is vapor pressure (in mmHg ), $t$ is temperature (in ${ }^{\circ} \mathrm{C}$ ), and the other letters are the Antoine constants, which in this case are

|  | $A$ | $B$ | $C$ |
| :--- | :---: | :---: | :---: |
| Ethylbenzene (EB) | 6.96 | 1424 | 213 |
| Ethyl cyclohexane (ECH) | 6.87 | 1384 | 215 |



FIGURE 8.22 Vapor pressures of ethylbenzene and ethyl cyclohexane (Example 8.7). Note: $1 \mathrm{mmHg}=$ 0.133 kPa .

The resulting vapor-pressure plots are shown in Fig. 8.22.
Since the system is ideal, relative volatility $\alpha$ can be determined from the vapor-pressure ratio $P_{\mathrm{ECH}} / P_{\mathrm{EB}}$. If this is determined at, say, 50,100 , and $135^{\circ} \mathrm{C}$, the effect of temperature (and thus, of system pressure) on relative volatility can be gaged as follows:

| Temperature, ${ }^{\circ} \mathrm{C}\left({ }^{\circ} \mathrm{F}\right)$ | $P_{\mathrm{EB}}, \mathrm{mmHg}$ | $P_{\mathrm{ECH}}, \mathrm{mmHg}$ | $\alpha$ |
| :---: | :---: | :---: | :---: |
| $50(122)$ | 35.1 | 44.4 | 1.265 |
| $100(212)$ | 257 | 300 | 1.167 |
| $135(275)$ | 738 | 824 | 1.117 |

There is a noticeable increase in the relative volatility as the system temperature and pressure are lowered. In the case of two closely boiling liquids, as is the present case, this can mean a substantial lessening of required equilibrium stages. This can be seen by employing the Fenske-Underwood-Gilliland correlations as expressed graphically in Fig. 8.5. The abscissa is $(0.999 / 0.001) /(0.95 / 0.05)=19,000$, and assuming an $R / R_{\min }$ of 1.3 , an $\alpha$ of 1.265 calls for 86 theoretical stages (as read along the ordinate), whereas an $\alpha$ of 1.117 calls for 176 stages (by extrapolating the ordinate downward). However, this comparison assumes an isobaric column. In actual practice, the bottoms pressures will be considerably higher, so the difference in stages, although substantial, will not be quite so dramatic. Depending on column pressures, it seems reasonable to assume that roughly 100 stages will be needed.
2. Evaluate the effects of choosing trays, random packing, or systematic packing. It is recommended that the top column pressure be set for the lowest reasonable overhead pressure consistent with the use of a water- or air-cooled condenser. In this case, pressure would be 50 mmHg , corresponding to a temperature of $53^{\circ} \mathrm{C}\left(127^{\circ} \mathrm{F}\right)$.

The bottoms pressure is usually selected to permit use of a readily available heating medium (steam or hot oil), as well as to stay below a temperature that could cause product degradation. In the ECH-EB system, degradation is not considered a problem, and column bottoms pressure is solely a function of the pressure drop across the tower internals. Because, as seen in step 1, relative volatility can vary appreciably with pressure, it is advantageous in this case to install low-pressure-drop, high-efficiency tower internals.
a. Evaluation of cross-flow trays. Assume as a first try that 110 equilibrium stages are needed. Assume further that a tray column in this service will operate at 70 percent efficiency. Then the actual number of trays needed is $110 / 0.7=157$.

It is reasonable to allow a pressure drop of 3 mmHg per tray. Then the reboiler pressure will be $50+3(157)=521 \mathrm{mmHg}$. At this pressure, the relative volatility (from Fig. 8.22) is 1.14, and the average relative volatility in the column is then (see step 1) $(1.265+1.14) / 2=1.2$. From Fig. 8.5, the estimated number of equilibrium stages is 107 , which confirms that the initially selected 110 trays was a reasonable assumption.

If the upper 25 percent of the trays (where the vapor velocity and therefore entrainment are highest) are spaced 24 in apart and the distance between the remaining trays is 18 in , then the total equipment height can be estimated as follows:

|  | $\mathrm{ft}(\mathrm{m})$ |
| :--- | :---: |
| Total height of trays: $40(2 \mathrm{ft})+117(1.5 \mathrm{ft})=$ | 256 |
| Overhead disengaging area | 4 |
| Manways: $8(1.5 \mathrm{ft})=$ | 12 |
| Reboiler | $\underline{6}$ |
| Total column height | 278 |
| Skirt (minimum to ensure adequate pump suction head) | $\underline{12}$ |
| Total equipment height | $290(90)$ |

b. Evaluation of random packing. This step draws on information brought out in Example 8.4. Again, recognizing that relative volatility decreases with pressure, estimate the actual number of equilibrium stages and check the assumption from Fig. 8.5. If no. 2 slotted rings are selected, the pressure drop should be set at 0.15 in water per foot ( 12 mm water per meter), and the height equivalent to a theoretical-plate (or stage) HETP may be as large as $3.5 \mathrm{ft}(c a .1 \mathrm{~m}$ ). For dumped packing, assume that the specified separation requires 100 stages. Then the total height of packing needed is $100(3.5 \mathrm{ft})=350 \mathrm{ft}$, requiring at least 10 separate beds.

The pressure in the column reboiler can now be developed:

|  | mmHg |
| :--- | :---: |
| Pressure drop through packing (no. 2 slotted rings): |  |
| $\quad(350 \mathrm{ft})(0.15$ in water per foot $)=52.5$ in water $=$ | 98 |
| Pressure drop through 10 support plates | 10 |
| Pressure drop through 10 distributors | 10 |
| Column top pressure | 50 |
| Total reboiler pressure | 168 |

Again using Fig. 8.22, the relative volatility at the bottom is found to be 1.16 , resulting in an average of 1.21 . Again from Fig. 8.5 we find that the assumption of 100 stages is reasonable.

Now calculate the column height:

|  | $\mathrm{ft}(\mathrm{m})$ |
| :--- | ---: |
| Total height of packing | 350 |
| Spacing between beds: $(9)(4 \mathrm{ft})=$ | 36 |
| Disengaging and distribution | 6 |
| Reboiler | 6 |
| $\quad$Total column height | 398 |
| Skirt | 12 |
| Total equipment height | $410(125)$ |

c. Evaluation of a systematically packed column. One example of a high-efficiency packing (large number of stages per unit of pressure drop) is corrugated-wire-gauze elements, sections of which are assembled inside the tower. This type of packing has an HETP of 10 to 12 in ( 25 to 30 cm ) and a pressure drop of 0.3 to 0.5 mmHg ( 53 Pa or 0.22 in water) per equilibrium stage. Assume that 95 stages are needed, each entailing 12 in of packing. Then the pressure at the bottom of 95 ft of packing can be determined as follows:

|  | mmHg |
| :--- | ---: |
| Pressure drop through wire-gauze packing: $(95)(0.4 \mathrm{mmHg} /$ stage $)$ | 38 |
| Pressure drop through four distributors and four packing supports | 8 |
| Column top pressure | 50 |
| Total reboiler pressure | 96 |

The average relative volatility for the column is 1.22 , and the assumption of 95 plates is reasonable.

The next step is to calculate the column height:

|  | $\mathrm{ft}(\mathrm{m})$ |
| :--- | ---: |
| Total height of packing | 95 |
| Spacing between beds: $(3)(4 \mathrm{ft})=$ | 12 |
| Disengaging and distribution | 6 |
| Reboiler | 6 |
| $\quad$ Total column height | 119 |
| Skirt | 12 |
| Total equipment height | $131(40)$ |

3. Choose between the tray column, the randomly packed column, and the systematically packed column. It is unlikely that a single $300-\mathrm{ft}$ tray column or a $400-\mathrm{ft}$ randomly packed column would be installed for this system. In addition, multiple-column operation, by its nature, is expensive. So it is reasonable to opt for the $131-\mathrm{ft}$ column containing systematically packed corrugated-wire-gauze
packing. However, this type of packing is quite expensive. So a detailed economic analysis should be performed before a final decision is made.
4. Estimate the column diameter. This step draws on information brought out in Example 8.2. If corrugated-wire-gauze packing is the final choice, the column size can be estimated by applying an appropriate $F_{c}$ factor. The usual range for this packing is 1.6 to $1.9\left[\mathrm{lb} /(\mathrm{ft})\left(\mathrm{s}^{2}\right)\right]^{0.5}$, with 1.7 being a good design point.

In order to establish the column vapor rate, it is necessary first to determine the required reflux ratio and then to set up a column material balance.

Using the Underwood equation (see Example 8.1) and noting from Fig. 8.3 that $\theta=1.08$,

$$
\begin{aligned}
(L / D)_{\min } & =1.22(0.999) /(1.22-1.08)+1(0.001) /(1-1.08)-1 \\
& =7.69
\end{aligned}
$$

With an arbitrarily selected $R / R_{\min }$ ratio of 1.3 , then, the reflux ratio $L / D=7.69(1.3)=10$.
Material-balance calculations (see Section 2) indicate that the withdrawal rate for overhead product from the system is $7.38 \mathrm{~mol} / \mathrm{h}$; therefore, $73.8 \mathrm{~mol} / \mathrm{h}$ must be refluxed, and the vapor flow from the top of the column must be $73.8+7.38=81.18 \mathrm{~mol} / \mathrm{h}$. The vapor consists of almost pure ECH, whose molecular weight is 112 , so mass flow from the top is $81.18(112)=9092 \mathrm{lb} / \mathrm{h}(4133 \mathrm{~kg} / \mathrm{h})$. The bottoms stream is $2.62 \mathrm{~mol} / \mathrm{h}$.

Take the average pressure in the upper part of the column to be 55 mmHg ( 1.06 psia ). Assuming that this consists essentially of ECH and referring to Fig. 8.22, the corresponding temperature is $55^{\circ} \mathrm{C}\left(131^{\circ} \mathrm{F}\right)$. Then, by the ideal-gas law, vapor density $\rho_{V}=P M / R T=1.06(112) /[10.73(460+$ $131)]=0.0187 \mathrm{lb} / \mathrm{ft}^{3}$, where $P$ is pressure, $M$ is molecular weight, $R$ is the gas-law constant, and $T$ is absolute temperature. (Note: For high-pressure systems of greater than 5 atm, correlations for vapor-phase nonideality should be used instead; see Section 3.) Then, as discussed in Example 8.2 , design vapor velocity $V=F_{c} / \rho^{0.5}=1.7 / 0.0187^{0.5}=12.43 \mathrm{ft} / \mathrm{s}$. The volumetric flow rate is $(9092 \mathrm{lb} / \mathrm{h}) /\left[(3600 \mathrm{~s} / \mathrm{h})\left(0.0187 \mathrm{lb} / \mathrm{ft}^{3}\right)\right]=135 \mathrm{ft}^{3} / \mathrm{s}$. Column cross-sectional area $A$, then, must be $135 / 12.43=10.9 \mathrm{ft}^{2}$, and column diameter must be $[A /(\pi / 4)]^{0.5}=(10.9 / 0.785)^{0.5}=3.73 \mathrm{ft}(1.1 \mathrm{~m})$.
5. Calculate the heat duty of the reboiler and of the condenser. Assembly of a heat balance can be simplified by assuming constant molal overflow (not unreasonable in this case) and no subcooling in the condenser (usually, less than $5^{\circ} \mathrm{C}$ of cooling takes place in a well-designed heat exchanger). For constant molal overflow, the latent heats may be averaged, yielding 150 Btu/lb.

The reboiler duty is the sum of three parts:

1. Enthalpy to heat distillate (consisting essentially of ECH ) from 25 to $53^{\circ} \mathrm{C}$ :

$$
(7.38 \mathrm{lb} \cdot \mathrm{~mol} / \mathrm{h})(112 \mathrm{lb} / \mathrm{mol}) \times\left(53-25^{\circ} \mathrm{C}\right)\left(1.8^{\circ} \mathrm{F} /{ }^{\circ} \mathrm{C}\right)\left[0.39 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)\right]=16,240 \mathrm{Btu} / \mathrm{h}
$$

2. Enthalpy to heat bottoms (essentially EB) from 25 to $72^{\circ} \mathrm{C}$ :

$$
(2.62 \mathrm{lb} \cdot \mathrm{~mol} / \mathrm{h})(106 \mathrm{lb} / \mathrm{mol}) \times\left(72-25^{\circ} \mathrm{C}\right)\left(1.8^{\circ} \mathrm{F} /{ }^{\circ} \mathrm{C}\right)\left[0.45 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)\right]=10,570 \mathrm{Btu} / \mathrm{h}
$$

3. Enthalpy to boil up the vapor:

$$
(81.18 \mathrm{lb} \cdot \mathrm{~mol} / \mathrm{h})(106 \mathrm{lb} / \mathrm{mol})(153 \mathrm{Btu} / \mathrm{lb})=1,316,580 \mathrm{Btu} / \mathrm{h}
$$

Therefore, total reboiler duty is $16,240+10,570+1,316,580=1,343,390 \mathrm{Btu} / \mathrm{h}(393,310 \mathrm{~W})$. As for the condenser duty, it is $(81.18 \mathrm{lb} \cdot \mathrm{mol} / \mathrm{h})(112 \mathrm{lb} / \mathrm{mol})(147 \mathrm{Btu} / \mathrm{lb})=1,336,550 \mathrm{Btu} / \mathrm{h}(391,350 \mathrm{~W})$.

Related Calculations. Sequences of distillation columns are often used for separating multicomponent mixtures. The question arises: In what order should the individual components be separated? For example, should a given component be separated in the first column, the second column, the
$n$th column, or the last column? Should it be removed as the overhead or as the bottoms? Each case should be examined on its own merits, but a variety of heuristics have evolved. For example (based on Douglas, Conceptual Design of Chemical Processes, McGraw-Hill): Remove corrosive components as soon as possible; remove reactive components as soon as possible; remove desired products as distillates, not bottoms; remove the lightest components first; make the high-recovery separations last; make the difficult separations last; favor splits that are equimolar. Obviously, however, reliance on multiple heuristics can lead to contradictory results.

## SECTION 9

# EXTRACTION AND LEACHING 

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### 9.1 MULTISTAGE COUNTERCURRENT LIQUID-LIQUID EXTRACTION 9.1

### 9.2 MULTISTAGE COUNTERCURRENT LEACHING 9.5

### 9.1 MULTISTAGE COUNTERCURRENT LIQUID-LIQUID EXTRACTION

Alcohol is to be extracted from an aqueous solution by pure ether in an extraction column. The alcohol solution, containing $30 \%$ alcohol by weight, enters the top of the column at a rate of $370 \mathrm{~kg} / \mathrm{h}$. The ether is to be fed to the column bottom at $350 \mathrm{~kg} / \mathrm{h}$. About 90 percent of the alcohol is to be extracted; that is, alcohol concentration in the exiting aqueous stream should be about $3 \%$. Experimental data on the compositions of pairs of water-rich and ether-rich phases in equilibrium are given in Table 9.1. Calculate the flow rates and compositions of the exiting raffinate (i.e., alcohol-depleted, aqueous) phase and the extract (i.e., alcohol-enriched, ether) phase. Also calculate the number of extraction stages needed.

## Calculation Procedure

1. Plot the equilibrium-composition data on a right-triangular diagram. The plot, shown in Fig. 9.1, is prepared as follows: Let the vertex labeled $E$ represent $100 \%$ ether, let the one labeled $A$ represent $100 \%$ alcohol, and let the one labeled $W$ represent $100 \%$ water. Then the scale along the abscissa represents the weight fraction alcohol, and the scale along the ordinate represents the weight fraction ether. Take each pair of points in Table 9.1 and plot them, joining any given pair by a straight line, called a "tie line." (Note that for the first pair, the tie line coincides with part of the ordinate, since the alcohol concentration is 0.0 in each of the two phases.) Draw a curve through points at the lower ends of the tie lines and another curve through the points at the upper ends.

These two curves divide the diagram into three regions. Any composition falling within the uppermost region will consist solely of an ether-rich phase; any composition within the lowermost region will consist solely of an aqueous phase; any composition within the middle region will constitute a combination of those two liquid phases.
2. Calculate the mean concentrations of ether, alcohol, and water within the system. This step is easier to visualize if a stage diagram is first drawn (see Fig. 9.2). Each box represents an extraction

TABLE 9.1 Equilibrium Data for Alcohol-Water-Ether System (Example 9.1)

| Weight fraction in phase |  |  |  |  |  |
| :--- | :---: | :--- | :---: | :---: | :---: |
|  | Water phase |  |  | Ether phase |  |
| Alcohol | Ether | Water | Alcohol | Water | Ether |
| 0.0 | 0.075 | 0.925 | 0.0 | 0.225 | 0.775 |
| 0.1 | 0.077 | 0.823 | 0.090 | 0.170 | 0.740 |
| 0.2 | 0.090 | 0.710 | 0.175 | 0.120 | 0.705 |
| 0.31 | 0.095 | 0.595 | 0.250 | 0.080 | 0.670 |
| 0.44 | 0.118 | 0.442 | 0.290 | 0.05 | 0.660 |
| 0.530 | 0.150 | 0.320 | 0.31 | 0.035 | 0.655 |
| 0.645 | 0.195 | 0.160 | 0.33 | 0.019 | 0.651 |
| 0.75 | 0.25 | 0.0 | 0.35 | 0.0 | 0.65 |



FIGURE 9.1 Equilibrium phase diagram for alcohol, water, ether system (Example 9.1).
stage, with stage 1 being the stage at the top of the column. Stage $N$ is at the bottom of the column. The streams labeled $L$ are the aqueous-phase streams; those labeled $S$ are the ether-phase (i.e., solventphase) streams. Let the given letter stand for the actual flow rates.

Thus the alcohol-water feed mixture $L_{0}$ enters the top of the column, where the ether-solvent-phase stream $S_{1}$ leaves. At the bottom of the column, ether-solvent stream $S_{N+1}$ enters, while the stripped water stream $L_{N}$ leaves.

Now, the mean concentration of ether $W_{E M}$ and alcohol $W_{A M}$ in the system can be calculated from the equations

$$
\begin{aligned}
& W_{E M}=\frac{L_{0} W_{E, 0}+S_{N+1} e_{E, N+1}}{L_{0}+S_{N+1}} \\
& W_{A M}=\frac{L_{0} W_{A, 0}+S_{N+1} e_{A, N+1}}{L_{0}+S_{N+1}}
\end{aligned}
$$



FIGURE 9.2 Stage diagram for countercurrent multistage liquid-liquid extraction (Example 9.1).
where $L_{0}$ is the feed rate of the water phase, $S_{N+1}$ is the feed rate of the solvent, $W_{E, 0}$ and $W_{A, 0}$ are the concentrations of ether and alcohol, respectively, in the entering water phase, and $e_{E, N+1}$ and $e_{A, N+1}$ are the concentrations of ether and alcohol, respectively, in the entering ether (solvent) phase. Then

$$
\begin{aligned}
& W_{E M}=\frac{370(0)+350(1.0)}{370+350}=0.49 \\
& W_{A M}=\frac{370(0.3)+350(0)}{370+350}=0.154
\end{aligned}
$$

And by difference, the mean concentration of water is $(1.0-0.49-0.154)=0.356$.
3. Calculate the compositions of the exiting raffinate and extract streams. Replot (or trace) Fig. 9.1 without the tie lines (Fig. 9.3). On Fig. 9.3, plot the mean-concentration point M. Now from mass-balance considerations, the exit concentrations must lie on the two phase-boundary lines and on a straight line passing through the mean concentration point. We know we want the water phase to have an exit concentration of $3 \mathrm{wt} \%$ alcohol. Such a concentration corresponds to point $L_{N}$ on the graph. At point $L_{N}$, the ether concentration is seen to be $7.6 \mathrm{wt} \%$ (this can be found more accurately in the present case by numerical extrapolation of the water-phase data in Table 9.1). Therefore, the composition of the raffinate stream is $3 \%$ alcohol, $7.6 \%$ ether, and (by difference) $89.4 \%$ water.


FIGURE 9.3 Overall mass balance on extraction column (Example 9.1).


FIGURE 9.4 Determination of number of stages (Example 9.1).

To determine the composition of the exiting extract stream, extend line $L_{N} M$ until it intersects the ether-phase boundary, at point $S_{1}$, and read the composition graphically. It is found to be $69 \%$ ether, $22 \%$ alcohol, and (by difference) $9 \%$ water.
4. Calculate the flow rates of the exiting raffinate and extract streams. Set up an overall mass balance:

$$
S_{1}+L_{N}=L_{0}+S_{N+1}=370+350=720
$$

where (see Fig. 9.2) $L_{0}$ and $S_{N+1}$ are the entering streams (see step 2), and $S_{1}$ and $L_{N}$ are the exiting extract and raffinate streams, respectively.

Now set up a mass balance for the ether, using the compositions found in step 3:

$$
S_{1}(0.69)+L_{N}(0.076)=370(0)+350(1.0)=350
$$

Solving the overall and the ether balances simultaneously shows the exiting raffinate stream $L_{N}$ to be $239 \mathrm{~kg} / \mathrm{h}$ and the exiting extract stream $S_{1}$ to be $481 \mathrm{~kg} / \mathrm{h}$.
5. Calculate the number of stages needed. The number of stages can be found graphically on Fig. 9.1 (repeated for convenience as Fig. 9.4), including the tie lines. Plot on the graph the points corresponding to $L_{0}$ ( $30 \%$ alcohol, $0 \%$ ether) and $S_{1}$ ( $69 \%$ ether, $22 \%$ alcohol), draw a straight line through them, and extend the line upward. Similarly, plot $L_{N}$ ( $3 \%$ alcohol, $7.6 \%$ ether) and $S_{N+1}$ ( $100 \%$ ether), and draw a line through them, extending it upward. Designate the intersection of the two lines as $\Delta$.

Now, begin to step off the stages by drawing an interpolated tie line from point $S_{1}$ down to the water-phase boundary. Designate their intersection as point $L_{1}$. Draw a line joining $L_{1}$ with $\Delta$, and label the intersection of this line with the ether-phase boundary as $S_{2}$. Then repeat the procedure, drawing a tie line through $S_{2}$ and intersecting the water-phase boundary at $L_{2}$. This sequence is repeated until a point is reached on the water-phase boundary that has an alcohol content less than that of $L_{N}$. Count the number of steps involved. In this case, 6 steps are required. Thus the extraction operation requires 6 stages.

Related Calculations. This basic calculation procedure can be extended to the case of countercurrent multistage extraction with reflux. A schematic of the basic extractor is shown in Fig. 9.5. For this extractor there are $N$ stages in the extracting section, $1 E$ to $N E$, and there are $M$ stages in the stripping section, $1 S$ to $M S$.

The overall mass balance on the entire extractor as well as the mass balances on the solvent separator, feed stage, and solvent mixer are performed separately. The calculations on the extraction section and the stripping sections are then performed as described above.

### 9.2 MULTISTAGE COUNTERCURRENT LEACHING

Hot water is to be used to leach a protein out of seaweed in an isothermal multistage countercurrent system, as shown in Fig. 9.6. The seaweed slurry, consisting of $48.1 \%$ solids, $2.9 \%$ protein, and $49 \%$ water, enters at a rate of $400 \mathrm{~kg} / \mathrm{h}$. The hot water is fed at a rate of $500 \mathrm{~kg} / \mathrm{h}$. It is desired to have the outlet underflow (the spent seaweed) have a maximum residual concentration of $0.2 \%$ protein on a solids-free basis. Table 9.2 shows experimental data for the operation, taken by (1) contacting the seaweed with hot water for a period of time with mixing, (2) stopping the mixing and letting the seaweed settle, and (3) sampling the bottom slurry (underflow) phase and the upper extract (overflow) phase. Calculate the number of equilibrium leaching stages needed.

## Calculation Procedure

1. Calculate the weight ratio of solids to total liquid and the weight concentration of protein on a solids-free basis for each of the two phases in each run of the experimental data. Let $N_{o}$ and $N_{u}$ designate the weight ratio of solids to total liquid in the
 overflow and underflow phases, respectively. Similarly, let $x_{o}$ and $x_{u}$ represent the weight concentration of protein on a solids-free basis in the overflow and underflow phases, respectively. For run 1, for instance,

$$
\begin{aligned}
& N_{o}=\frac{0.002}{0.952+0.046}=0.002 \\
& N_{u}=\frac{0.432}{0.542+0.026}=0.760 \\
& x_{o}=\frac{0.046}{0.952+0.046}=0.046 \\
& x_{u}=\frac{0.026}{0.542+0.026}=0.046
\end{aligned}
$$

The calculated results for all runs are as follows (the sequence being rearranged for convenience in step 2):

| Run <br> number | $x_{u}$ | $N_{u}$ | $x_{o}$ | $N_{o}$ |
| :---: | :---: | :---: | :---: | :--- |
| 1 | 0.046 | 0.760 | 0.046 | 0.002 |
| 2 | 0.032 | 0.715 | 0.032 | 0.001 |
| 3 | 0.022 | 0.669 | 0.021 | 0 |
| 4 | 0.011 | 0.661 | 0.011 | 0 |
| 5 | 0.006 | 0.658 | 0.006 | 0 |
| 6 | 0.002 | 0.656 | 0.002 | 0 |

2. Plot the equilibrium data. See step 2 in Example 9.1. In the present case, however, a rectangular rather than a triangular diagram is employed. The abscissa is $x$, from above; similarly, the ordinate is $N$. For each run, plot the points $x_{o}, N_{o}$ and $x_{u}, N_{u}$ and join the pair by a tie line. Then connect the $x_{o}, N_{o}$ points, thereby generating the overflow equilibrium line, and similarly, connect the $x_{u}, N_{u}$ points to generate the underflow equilibrium line. The result is shown as Fig. 9.7.


FIGURE 9.6 Stage diagram for multistage countercurrent leaching (Example 9.2).

TABLE 9.2 Equilibrium Data for Seaweed-Water System (Example 9.2)

| Runnumber | Weight fraction in phase |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Extract (overflow) phase |  |  | Slurry (underflow) phase |  |  |
|  | Water | Solution protein | Solids | Water | Solution protein | Solids |
| 1 | 0.952 | 0.046 | 0.002 | 0.542 | 0.026 | 0.432 |
| 2 | 0.967 | 0.032 | 0.001 | 0.564 | 0.019 | 0.417 |
| 3 | 0.979 | 0.021 | 0.00 | 0.586 | 0.013 | 0.401 |
| 4 | 0.989 | 0.011 | 0.0 | 0.5954 | 0.0066 | 0.398 |
| 5 | 0.994 | 0.006 | 0.0 | 0.5994 | 0.0036 | 0.397 |
| 6 | 0.998 | 0.002 | 0.0 | 0.6028 | 0.0012 | 0.396 |

3. Calculate the mean values for $\boldsymbol{x}$ and $N$. Refer to step 2 in Example 9.1. In the present case, the mean values can be found from the equations

$$
x_{M}=\frac{L_{0} W_{P, 0}+S_{N+1} e_{P, N+1}}{L_{0}\left(W_{P, 0}+W_{W, 0}\right)+S_{N+1}\left(e_{P, N+1}+e_{W, N+1}\right)}
$$

and

$$
N_{M}=\frac{L_{0} W_{S, 0}+S_{N+1} e_{S, N+1}}{L_{0}\left(W_{P, 0}+W_{W, 0}\right)+S_{N+1}\left(e_{P, N+1}+e_{W, N+1}\right)}
$$

where $x_{M}$ is the mean weight concentration of protein on a solids-free basis, $N_{M}$ is the mean weight ratio of solids to total liquid, $L_{0}$ is the feed rate of the seawater slurry, $W_{P, 0}, W_{W, 0}$, and $W_{S, 0}$ are the weight fractions of protein, water, and solids, respectively, in the seawater slurry, $S_{N+1}$ is the feed rate of the hot water, and $e_{P, N+1}, e_{W, N+1}$, and $e_{S, N+1}$ are the weight fractions of protein, water, and solids,


FIGURE 9.7 Equilibrium data for seaweed, hot water system (Example 9.2).


FIGURE 9.8 Overall mass balance on leaching system (Example 9.2).
respectively, in the entering hot water. Then,

$$
\begin{aligned}
x_{M} & =\frac{400(0.029)+500(0)}{400(0.029+0.49)+500(0+1)} \\
& =0.0164
\end{aligned}
$$

and

$$
\begin{aligned}
N_{M} & =\frac{400(0.481)+500(0)}{400(0.029+0.49)+500(0+1)} \\
& =0.272
\end{aligned}
$$

4. Calculate the concentration of protein in the product extract (overflow) stream. Replot (or trace) Fig. 9.7 without the tie lines (Fig. 9.8). On it, plot the point $x_{M}, N_{M}$. Locate along the underflow equilibrium line the point $L_{N}$ that corresponds to the desired maximum residual concentration of protein, $0.2 \%$ or 0.002 weight fraction. Now, from mass-balance considerations, the exit concentrations must lie on the two equilibrium lines and on a straight line passing through $x_{M}, N_{M}$. So draw a line through $L_{N}$ and $x_{M}, N_{M}$, and extend it to the overflow equilibrium line, labeling the intersection as $S_{1}$. The concentration of protein in the exiting overflow stream is read, then, as 0.027 weight fraction, or $2.7 \%$. (Note also that there are virtually no solids in this stream; that is, the value for $N$ at $S_{1}$ is virtually zero.)
5. Calculate the number of stages. With reference to step 1 , calculate the values of $x$ and $N$ for each of the two entering streams. Thus, for the seawater slurry,
and

$$
\begin{aligned}
N_{L, 0} & =\frac{0.481}{0.49+0.029}=0.927 \\
x_{L, 0} & =\frac{0.029}{0.49+0.029}=0.0559
\end{aligned}
$$

For the entering hot water, $N_{S, N+1}$ and $x_{S, N+1}$ both equal 0 , because this stream contains neither solids nor protein.


FIGURE 9.9 Determination of number of stages (Example 9.2).

Now, the number of stages can be found graphically on Fig. 9.7 (redrawn as Fig. 9.9), including the tie lines, in a manner analogous to that of step 5 in Example 9.1. Plot on Fig. 9.9 the points $L_{0}$ (that is, $x=0.0559, N=0.927$ ) and $S_{1}$ (from Fig. 9.8), draw a line through them, and extend it downward. Similarly, plot the points $S_{N+1}$ (that is, $x=0, N=0$ ) and $L_{N}$, draw a line through them, and extend it downward. Designate the intersection of the two lines as $\Delta$.

Now begin to step off the stages by drawing an interpolated tie line through point $S_{1}$ up to the underflow equilibrium line. Designate their intersection as point $L_{1}$. Draw a line joining $L_{1}$ with $\Delta$, and label the intersection of this line with the overflow equilibrium line as $S_{2}$. Then repeat the procedure, drawing a tie line through $S_{2}$ and intersecting the underflow equilibrium line at $L_{2}$. This sequence is repeated until a point is reached on the underflow equilibrium line that has a protein content less than that of $L_{N}$. Count the number of steps involved. In this case, 5 steps are required. Thus the leaching operation requires 5 equilibrium stages.

Related Calculations. This example is a case of variable-underflow conditions. However, the same procedure can be applied to constant underflow.

## SECTION 10

## CRYSTALLIZATION

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10.1 SOLID-PHASE GENERATION OF AN ANHYDROUS SALT BY COOLING 10.1
10.2 SOLID-PHASE GENERATION OF AN ANHYDROUS SALT BY BOILING 10.2
10.3 SOLID-PHASE GENERATION OF A HYDRATED SALT BY COOLING 10.3
10.4 SOLID-PHASE GENERATION OF A HYDRATED SALT BY BOILING 10.4
10.5 SEPARATION OF BENZENE AND NAPHTHALENE BY CRYSTALLIZATION 10.6
```

| 10.6 | ANALYSIS OF A KNOWN CRYSTAL |
| :--- | :--- |
|  | SIZE DISTRIBUTION (CSD) 10.8 |
| 10.7 | CRYSTAL SIZE DISTRIBUTION OF A |
|  | SLURRY SAMPLE 10.10 |
| 10.8 | PRODUCT CRYSTAL SIZE |
|  | DISTRIBUTION FROM A SEEDED |
|  | CRYSTALLIZER 10.11 |
| 10.9 | ANALYSIS OF DATA FROM A |
|  | MIXED SUSPENSION-MIXED |
|  | PRODUCT REMOVAL |
|  | CRYSTALLIZER (MSMPR) 10.13 |
| 10.10 | PRODUCT SCREENING |
|  | EFFECTIVENESS 10.15 |
| REFERENCES 10.17 |  |10.7 CRYSTAL SIZE DISTRIBUTION OF ASLURRY SAMPLE 10.10DISTRIBUTION FROM A SEEDEDCRYSTALLIZER 10.11MIXED SUSPENSION -MIXEDPRODUCT REMOVALCRYSTALLIZER (MSMPR) 10.13

### 10.1 SOLID-PHASE GENERATION OF AN ANHYDROUS SALT

A $65.2 \mathrm{wt} \%$ aqueous solution of potassium nitrate originally at $100^{\circ} \mathrm{C}\left(212^{\circ} \mathrm{F}\right)$ is gradually cooled to $10^{\circ} \mathrm{C}\left(50^{\circ} \mathrm{F}\right)$. What is the yield of $\mathrm{KNO}_{3}$ solids as a function of temperature? How many pounds of $\mathrm{KNO}_{3}$ solids are produced at $10^{\circ} \mathrm{C}$ if the original solution weighed $50,000 \mathrm{lb}(22,680 \mathrm{~kg})$ ?

## Calculation Procedure

1. Convert weight percent to mole percent. In order to use Fig. 10.1 in the next step, the mole fraction of $\mathrm{KNO}_{3}$ in the original solution must be determined. The calculations are as follows:
$\left.\begin{array}{cccccc}\hline & \begin{array}{c}\text { Pounds in } \\ \text { original } \\ \text { solution }\end{array} & \div & \begin{array}{c}\text { Molecular } \\ \text { weight }\end{array} & = & \text { Moles }\end{array} \begin{array}{c}\text { Mole } \\ \text { percent }\end{array}\right]$


FIGURE 10.1 Solubility of $\mathrm{KNO}_{3}$ in water versus temperature.


FIGURE 10.2 Yield of $\mathrm{KNO}_{3}$ versus temperature (Example 10.1).
2. Calculate yield of solids versus temperature. Figure 10.1 shows the composition of saturated $\mathrm{KNO}_{3}$ solution as a function of temperature. The solids formed during cooling will be 100 percent $\mathrm{KNO}_{3}$, because $\mathrm{KNO}_{3}$ is anhydrous. The yield of solids is the ratio of $\mathrm{KNO}_{3}$ solidified to the $\mathrm{KNO}_{3}$ originally dissolved. As can be seen from Fig. 10.1, no solids are formed from a $25 \mathrm{~mol} \%$ solution until the solution is cooled to $85^{\circ} \mathrm{C}$. As cooling proceeds, solid $\mathrm{KNO}_{3}$ continues to form while the (saturated) solution concentration continues to decline. At $70^{\circ} \mathrm{C}$, for instance, the solution will contain $20 \mathrm{~mol} \% \mathrm{KNO}_{3}$ ( $80 \mathrm{~mol} \% \mathrm{H}_{2} \mathrm{O}$ ). If 100 mol of the original solution is assumed, then originally there were $25 \mathrm{~mol}_{\mathrm{KNO}}^{3}$ and $75 \mathrm{~mol}_{2} \mathrm{O}$. This amount of water present does not change during cooling and solids formation. At $70^{\circ} \mathrm{C}$ there are therefore $\left[\left(0.20 \mathrm{KNO}_{3}\right) /\left(0.80 \mathrm{H}_{2} \mathrm{O}\right)\right]\left(75 \mathrm{~mol} \mathrm{H} \mathrm{H}_{2} \mathrm{O}\right)$ $=18.8 \mathrm{~mol} \mathrm{KNO}_{3}$ dissolved, or $25-18.8=$ $6.2 \mathrm{~mol} \mathrm{KNO}_{3}$ solids formed. Therefore, the crystal yield at $70^{\circ} \mathrm{C}$ is $(6.2 / 25)(100$ percent $)=24.8$ percent.

Similarly, at about $40^{\circ} \mathrm{C}$, the solubility of $\mathrm{KNO}_{3}$ is 10 percent, which leaves $[(0.10$ $\left.\left.\mathrm{KNO}_{3}\right) /\left(0.90 \quad \mathrm{H}_{2} \mathrm{O}\right)\right]\left(75 \mathrm{~mol} \mathrm{H}_{2} \mathrm{O}\right)=8.3$ mol $\mathrm{KNO}_{3}$ in solution. Therefore, $25-8.3=$ $16.7 \mathrm{~mol}^{\mathrm{KNO}_{3}}$ will have precipitated by the time the solution has cooled to that temperature. Consequently, the yield of solids at $40^{\circ} \mathrm{C}$ is $16.7 / 25=66.8$ percent. Finally, at $10^{\circ} \mathrm{C}$, the $\mathrm{KNO}_{3}$ solubility drops to $3 \mathrm{~mol} \%$, giving a yield of 91 percent. Figure 10.2 summarizes the yield of $\mathrm{KNO}_{3}$ solids as a function of temperature.
3. Calculate the weight of solids at $10^{\circ}$ C. The weight of solids formed at $10^{\circ} \mathrm{C}$ is the solids yield ( 91 percent) multiplied by the weight of $\mathrm{KNO}_{3}$ initially present in the $100^{\circ} \mathrm{C}$ mother liquor. The weight of $\mathrm{KNO}_{3}$ initially in the mother liquor of a $50,000-\mathrm{lb}$ solution is $50,000 \mathrm{lb} \times 0.652=32,600$ lb. The weight of $\mathrm{KNO}_{3}$ solids formed at $10^{\circ} \mathrm{C}$ is $32,600 \mathrm{lb} \times 0.91=29,670 \mathrm{lb}(13,460 \mathrm{~kg})$.

Related Calculations. This method can be used to calculate the yield of any anhydrous salt from batch or steady-state cooling crystallizers. For hydrated salts, see Example 10.3.

### 10.2 SOLID-PHASE GENERATION OF AN ANHYDROUS SALT BY BOILING

A $70^{\circ} \mathrm{C}\left(158^{\circ} \mathrm{F}\right)$ aqueous solution initially containing $15 \mathrm{~mol} \% \mathrm{KNO}_{3}$ is to be boiled so as to give a final yield of solid $\mathrm{KNO}_{3}$ of 60 percent. How much of the initial water must be boiled off? What is the final liquid composition?

## Calculation Procedure

1. Find the final liquid composition. Use Fig. 10.1 to determine the solubility of $\mathrm{KNO}_{3}$ in saturated water solution at $70^{\circ} \mathrm{C}$. From the figure, the $\mathrm{KNO}_{3}$ solubility is $20 \mathrm{~mol} \%$.
2. Calculate the amount of water boiled off. Take a basis of 100 mol of initial solution. Then $15 \mathrm{~mol}_{\mathrm{KNO}}^{3}$ and $85 \mathrm{~mol} \mathrm{H}_{2} \mathrm{O}$ were initially present. To give a solids yield of 60 percent, then, $0.60 \times 15 \mathrm{~mol}=9 \mathrm{~mol} \mathrm{KNO}_{3}$ must be precipitated from the solution, leaving $15-9=6 \mathrm{~mol} \mathrm{KNO} 3$ in the solution. The solubility of $\mathrm{KNO}_{3}$ at $70^{\circ} \mathrm{C}$ is $20 \mathrm{~mol} \%$, from step 1. Therefore, the amount of water still in solution is $6 \mathrm{~mol} \times(0.80 / 0.20)=24 \mathrm{~mol} \mathrm{H}_{2} \mathrm{O}$, requiring that $85-24=61 \mathrm{~mol}$ had to be boiled off. The percent water boiled off is $61 / 85=72$ percent.

Related Calculations. This method can be used to determine the amounts of water to be boiled from boiling crystallizers that yield anhydrous salts. For hydrated salts, see Example 10.4.

### 10.3 SOLID-PHASE GENERATION OF A HYDRATED SALT BY COOLING

A $35 \mathrm{wt} \%$ aqueous $\mathrm{MgSO}_{4}$ solution is originally present at $200^{\circ} \mathrm{F}$ ( 366 K ). If the solution is cooled (with no evaporation) to $70^{\circ} \mathrm{F}(294 \mathrm{~K})$, what solid-phase hydrate will form? If the crystallizer is operated at $10,000 \mathrm{lb} / \mathrm{h}(4540 \mathrm{~kg} / \mathrm{h})$ of feed, how many pounds of crystals will be produced per hour? What will be the solid-phase yield?

## Calculation Procedure

1. Determine the hydrate formation. As the phase diagram (Fig. 10.3) shows, a solution originally containing $35 \mathrm{wt} \% \mathrm{MgSO}_{4}$ will, when cooled to $70^{\circ} \mathrm{C}$, form a saturated aqueous solution containing $27 \mathrm{wt} \% \mathrm{MgSO}_{4}$ (corresponding to point $A$ ) in equilibrium with $\mathrm{MgSO}_{4} \cdot 7 \mathrm{H}_{2} \mathrm{O}$ hydrated solids (point $B)$. No other hydrate can exist at equilibrium under these conditions. Now since the molecular weights of $\mathrm{MgSO}_{4}$ and $\mathrm{MgSO}_{4} \cdot 7 \mathrm{H}_{2} \mathrm{O}$ are 120 and 246, respectively, the solid-phase hydrate is $(120 / 246)(100)$ $=48.8 \mathrm{wt} \% \mathrm{MgSO}_{4}$; the rest of the solid phase is $\mathrm{H}_{2} \mathrm{O}$ in the crystal lattice structure.
2. Calculate the crystal production rate and the solid-phase yield. Let $L$ be the weight of liquid phase formed and $S$ the weight of solid phase formed. Then, for $10,000 \mathrm{lb} / \mathrm{h}$ of feed solution, $L+$ $S=10,000$, and (by making a material balance for the $\mathrm{MgSO}_{4}$ ) $0.35(10,000)=0.27 L+0.488 S$. Solving these two equations gives $L=6330 \mathrm{lb} / \mathrm{h}$ of liquid phase and $S=3670 \mathrm{lb} / \mathrm{h}(1665 \mathrm{~kg} / \mathrm{h})$ of $\mathrm{MgSO}_{4} \cdot 7 \mathrm{H}_{2} \mathrm{O}$.

Now the solid-phase yield is based on $\mathrm{MgSO}_{4}$, not on $\mathrm{MgSO}_{4} \cdot 7 \mathrm{H}_{2} \mathrm{O}$. The $3670 \mathrm{lb} / \mathrm{h}$ of solid phase is $48.8 \mathrm{wt} \% \mathrm{MgSO}_{4}$, from step 1, so it contains $3670(0.488)=1791 \mathrm{lb} / \mathrm{h} \mathrm{MgSO}_{4}$. Total $\mathrm{MgSO}_{4}$ introduced into the system is $0.35(10,000)=3500 \mathrm{lb} / \mathrm{h}$. Therefore, solid-phase yield is $1791 / 3500=$ 51.2 percent.

As a matter of interest, the amount of $\mathrm{H}_{2} \mathrm{O}$ removed from the system by solid (hydrate) formation is $3670(1.0-0.488)=1879 \mathrm{lb} / \mathrm{h}$.

Related Calculations. This method can be used to calculate the yield of any hydrated salt from a batch or a steady-state cooling crystallizer.

In step $2, L$ and $S$ can instead be found by applying the inverse lever-arm rule to line segments $\overline{A B}$ and $\overline{A C}$ in Fig. 10.3. Thus, $S /(S+L)=S / 10,000=\overline{A B} / \overline{A C}=(0.35-0.27) /(0.488-0.27)$; therefore, $S=3670 \mathrm{lb} / \mathrm{h}$.


FIGURE 10.3 Phase diagram for $\mathrm{MgSO}_{4} \cdot \mathrm{H}_{2} \mathrm{O}$. (From Perry-Chemical Engineer's Handbook, McGrawHill, 1963.)

### 10.4 SOLID-PHASE GENERATION OF A HYDRATED SALT BY BOILING

Consider $40,000 \mathrm{lb} / \mathrm{h}(18,150 \mathrm{~kg} / \mathrm{h})$ of a $25 \mathrm{wt} \% \mathrm{MgSO}_{4}$ solution being fed at $200^{\circ} \mathrm{F}$ ( 366 K ) to an evaporative crystallizer that boils off water at a rate of $15,000 \mathrm{lb} / \mathrm{h}(6800 \mathrm{~kg} / \mathrm{h})$. The crystallizer is operated at $130^{\circ} \mathrm{F}(327 \mathrm{~K})$ under vacuum conditions. Determine the solid-phase composition, solidphase production rate, and solid-phase yield. Also calculate the required energy addition rate for the process.


FIGURE 10.4 Flow diagram for evaporative crystallizer (Example 10.4).

## Calculation Procedure

1. Determine the hydrate formation (solids composition). Since $15,000 \mathrm{lb} / \mathrm{h}$ of water is removed, the product slurry will have an overall $\mathrm{MgSO}_{4}$ composition of $0.25 \times 40,000 \mathrm{lb} /(40,000-15,000 \mathrm{lb})$ $=40.0 \mathrm{wt} \% \mathrm{MgSO}_{4}$. From Fig. 10.3, a system at $130^{\circ} \mathrm{F}$ and overall $\mathrm{MgSO}_{4}$ composition of $40 \mathrm{wt} \%$ will yield $\mathrm{MgSO}_{4} \cdot 6 \mathrm{H}_{2} \mathrm{O}$ solids in equilibrium with a $34.5 \mathrm{wt} \% \mathrm{MgSO}_{4}$ liquor. Since the molecular weights of $\mathrm{MgSO}_{4}$ and $\mathrm{MgSO}_{4} \cdot 6 \mathrm{H}_{2} \mathrm{O}$ are 120 and 228 , respectively, the solid-phase hydrate is $(120 / 228)(100)=52.7 \mathrm{wt} \% \mathrm{MgSO}_{4}$, with $47.3 \mathrm{wt} \%$ water.
2. Calculate the solids production rate. Let $L$ be the weight of liquid phase formed and $S$ the weight of solid phase formed. Then, for $40,000 \mathrm{lb} / \mathrm{h}$ of feed solution with $15,000 \mathrm{lb} / \mathrm{h}$ of water boil-off, $S+L=40,000-15,000$, and (by making a material balance for the $\mathrm{MgSO}_{4}$ ) $0.25(40,000)$ $=0.527 S+0.345 L$. Solving these two equations gives $L=17,450 \mathrm{lb} / \mathrm{h}$ of liquid phase and $S=7550 \mathrm{lb} / \mathrm{h}(3425 \mathrm{~kg} / \mathrm{h})$ of $\mathrm{MgSO}_{4} \cdot 6 \mathrm{H}_{2} \mathrm{O}$ solids.
3. Calculate the solid-phase yield. The solid-phase yield is based on $\mathrm{MgSO}_{4}$, not on $\mathrm{MgSO}_{4} \cdot 6 \mathrm{H}_{2} \mathrm{O}$. From step 1, the $7550 \mathrm{lb} / \mathrm{h}$ of solid phase is $52.7 \mathrm{wt} \% \mathrm{MgSO}_{4}$, so it contains 7550 $(0.527)=3979 \mathrm{lb} / \mathrm{h} \mathrm{MgSO}_{4}$. Total $\mathrm{MgSO}_{4}$ introduced into the system is $0.25(40,000)=10,000 \mathrm{lb} / \mathrm{h}$. Therefore, solid-phase yield is $3979 / 10,000=39.8$ percent.
4. Calculate the energy addition rate. Figure 10.4 shows the mass flow rates around the evaporative crystallizer, as well as an arrow symbolizing the energy addition. An energy balance around the crystallizer gives $Q=V H_{V}+L H_{L}+S H_{S}-F H_{F}$, where the $H$ 's are the stream enthalpies. From Fig. 10.5, $H_{L}=-32 \mathrm{Btu} / \mathrm{lb}, H_{S}=-110 \mathrm{Btu} / \mathrm{lb}$ (extrapolated to 52.7 percent), and $H_{F}=52 \mathrm{Btu} / \mathrm{lb}$. The value for the water vapor, $H_{V}$, takes a little more work to get. The enthalpy basis of water used in Fig. 10.5 is $32^{\circ} \mathrm{F}$ liquid; this can be deduced from the fact that the figure shows an enthalpy value of 0 for pure water (i.e., $0 \mathrm{wt} \% \mathrm{MgSO}_{4}$ solution) at $32^{\circ} \mathrm{F}$. The basis of most steam tables is $32^{\circ} \mathrm{F}$ liquid water. From such a steam table an $H_{V}$ value of about $1118 \mathrm{Btu} / \mathrm{lb}$ can be obtained for $130^{\circ} \mathrm{F}$ vapor water (the pressure correction is minor and can be neglected). Therefore, $Q=15,000 \times 1118+$ $17,450 \times(-32)+7550 \times(-110)-40,000 \times 52=13.3 \times 10^{6} \mathrm{Btu} / \mathrm{h}(3900 \mathrm{~kW})$ energy addition to the crystallizer. Energy addition per pound of solids produced is $13.3 \times 10^{6} / 7550=1760 \mathrm{Btu}$ (1860 kJ).

Related Calculations. This method can be used to calculate the yield, boiling (if any), and energy addition to an evaporative or cooling crystallizer that produces any hydrated or anhydrous crystal solid.


FIGURE 10.5 Enthalpy-concentration diagram for $\mathrm{MgSO}_{4} \cdot \mathrm{H}_{2} \mathrm{O}$ system. (Note: $1 \mathrm{Btu} / \mathrm{lb}=2.326 \mathrm{~kJ} / \mathrm{kg}$.) (From Perry-Chemical Engineers' Handbook, McGraw-Hill, 1963.)

## SEPARATION OF BENZENE AND NAPHTHALENE BY CRYSTALLIZATION

A $100,000 \mathrm{lb} / \mathrm{h}(4536 \mathrm{~kg} / \mathrm{h}) 70^{\circ} \mathrm{C}\left(158^{\circ} \mathrm{F}\right)$ feed containing $80 \mathrm{wt} \%$ naphthalene is fed to a cooling crystallizer. At what temperature should the crystallizer operate for maximum naphthalene-only solids production? At this temperature, what is the solids yield of naphthalene? What is the total energy removed from the crystallizer? Naphthalene solids are removed from the mother liquor by centrifugation, leaving some of the solids liquor ( $10 \mathrm{wt} \%$ of the solids) adhering to the solids. After the solids are melted, what is the final purity of the naphthalene?

## Calculation Procedure

1. Determine the appropriate operating temperature for the crystallizer. Figure 10.6 shows the mutual solubility of benzene and naphthalene. Most of the naphthalene can be crystallized by cooling to (i.e., operating the crystallizer at) the eutectic temperature of $-3.5^{\circ} \mathrm{C}\left(25.7^{\circ} \mathrm{F}\right)$, where the solubility of naphthalene in the liquor is minimized to 18.9


FIGURE 10.6 Phase diagram for the simple eutectic system naphthalene-benzene. $\mathrm{wt} \%$. (If one attempted to operate below this temperature, the whole system would become solid.)
2. Calculate the solids yield. The solids yield is the ratio of the naphthalene solids produced (corresponding to point $C$ in Fig. 10.6) to the naphthalene in the feed liquid (point $B$ ). Point $A$ corresponds to the naphthalene remaining in the mother liquor. Then, using the inverse lever-arm rule, we find the naphthalene solids rate $S$ as follows: $\quad S=100,000(\overline{A B} / \overline{A C})=100,000 \times$ $(0.8-0.189) /(1.0-0.189)=75,300 \mathrm{lb} / \mathrm{h}$. (This leaves $100,000-75,300=24,700 \mathrm{lb} / \mathrm{h}$ in the mother liquor.) The solids yield is $75,300 /$ $(100,000 \times 0.8)=94.1$ percent. The flows are shown in Fig. 10.7.
3. Calculate the energy removal. An energy balance around the crystallizer (see Fig. 10.5) gives $Q=L H_{L}+S H_{S}-F H_{F}$, where $Q$ is the heat added (or the heat removed, if the solved value proves to be negative); $L, S$, and $F$ are the flow rates for mother liquor, solid product, and feed, respectively; and $H_{L}, H_{S}$, and $H_{F}$ are the enthalpies of those streams relative to some base temperature. Select a base temperature $T_{R}$ of $70^{\circ} \mathrm{C}$, so that $H_{F}=0$.

For specifics of setting up an energy balance, see Example 2.7. From handbooks, the heat of fusion of naphthalene is found to be $64.1 \mathrm{Btu} / \mathrm{lb}$, and over the temperature range considered here, the heat capacities of liquid benzene and naphthalene can be taken as 0.43 and $0.48 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)$, respectively.

Then, for the mother liquor (which consists of $18.9 \mathrm{wt} \%$ naphthalene and $81.1 \mathrm{wt} \%$ benzene $), H_{L}=\left(-3.5^{\circ} \mathrm{C}-70^{\circ} \mathrm{C}\right)\left(1.8^{\circ} \mathrm{F} /{ }^{\circ} \mathrm{C}\right)[0.48(0.189)+0.43(0.811)]=-58.1 \mathrm{Btu} / \mathrm{lb}$. For the product naphthalene, which must cool from $70^{\circ} \mathrm{C}$ to $-3.5^{\circ} \mathrm{C}$ and then solidify, $H_{S}=\left(-3.5^{\circ} \mathrm{C}-70^{\circ} \mathrm{C}\right)$ $\left(1.8^{\circ} \mathrm{F} /{ }^{\circ} \mathrm{C}\right)(0.48)-64.1=-127.6 \mathrm{Btu} / \mathrm{lb}$.

Therefore, the heat added to the crystallizer is $Q=24,700(-58.1)+75,300(-127.6)-$ $100,000(0)=-11.0 \times 10^{6} \mathrm{Btu} / \mathrm{h}(3225 \mathrm{~kW})$. Since the value for $Q$ emerges negative, this is the energy removed from the crystallizer.


FIGURE 10.7 Flow diagram for cooling crystallizer (Example 10.5).
4. Calculate the purity of the naphthalene obtained by melting the product crystals. The weight of mother liquor adhering to the solids is 10 percent of 75,300 , or 7530 lb . The total amount of naphthalene present after melting is therefore $75,300+0.189(7530)=76,720 \mathrm{lb}$. The weight of benzene present (owing to the benzene content of the mother liquor) is $7530(1.0-0.189)=6100 \mathrm{lb}$. The product purity is therefore $76,720 /(76,720+6100)=92.6$ percent naphthalene.

Related Calculations. This method can be used to separate organic mixtures having components of different freezing points, such as the xylenes. Organic separations by crystallization have found industrial importance in situations in which close boilers have widely separated freezing temperatures. Less energy is related to freezing as opposed to boiling processes because of the low ratio of heat of fusion to heat of vaporization.

### 10.6 ANALYSIS OF A KNOWN CRYSTAL SIZE DISTRIBUTION (CSD)

A slurry contains crystals whose size-distribution function is known to be $n=2 \times 10^{5} L \exp (-L / 10)$, where $n$ is the number of particles of any size $L$ (in $\mu \mathrm{m}$ ) per cubic centimeter of slurry. The crystals are spherical, with a density of $2.5 \mathrm{~g} / \mathrm{cc}$. Determine the total number of crystals. Determine the total area, volume, and mass of the solids per volume of slurry. Determine the number-weighted average, the length-weighted average, and the area-weighted average particle size of the solids. What is the coefficient of variation of the particles? Generate a plot of the cumulative weight fraction of particles that are undersize in terms of particle size $L$.

## Calculation Procedure

1. Calculate the total number of particles per volume of slurry. This step and the subsequent calculation steps require finding $\int_{0}^{\infty} n L^{j} d L$, that is (from the equation for $n$ above), $2 \times 10^{5} \int_{0}^{\infty} L^{j+1}$ $\exp (-L / 10) d L$, where $L$ is as defined above and $j$ varies according to the particular calculation step. From a table of integrals, the general integral is found to be $2 \times 10^{5}\left[(j+1)!/(1 / 10)^{j+2}\right]$.

For calculating the number of particles, $j=0$, and the answer is the zeroth moment (designated $M_{0}$ ) of the distribution. Thus the total number $N_{T}$ of particles is $2 \times 10^{5}\left[(0+1)!/(1 / 10)^{0+2}\right]=2 \times 10^{7}$ particles per cubic centimeter of slurry.
2. Calculate the first moment of the distribution. This quantity, $M_{1}$, which corresponds to the "total length" of the particles per cubic centimeter of slurry, is not of physical significance in itself, but it is used in calculating the averages in subsequent steps. It corresponds to the integral in step 1 when $j=1$. Thus, $M_{1}=2 \times 10^{5}\left[(1+1)!/(1 / 10)^{1+2}\right]=4 \times 10^{8} \mu \mathrm{~m}$ per cubic centimeter of slurry.
3. Calculate the total area of the particles per volume of slurry. The total area $A_{T}=k_{A} M_{2}$, where $k_{A}$ is a shape factor (see below) and $M_{2}$ is the second moment of the distribution, i.e., the value of the integral in step 1 when $j=2$. Some shape factors are as follows:

| Crystal shape | Value of $k_{A}$ |
| :--- | :---: |
| Cube | 6 |
| Sphere | $\pi$ |
| Octahedron | $2 \sqrt{3}$ |

In the present case, then, $A_{T}=\pi\left(2 \times 10^{5}\right)\left[(2+1)!/(1 / 10)^{2+2}\right]=3.77 \times 10^{10} \mu \mathrm{~m}^{2}\left(377 \mathrm{~cm}^{2}\right)$ per cubic centimeter of slurry.
4. Calculate the total volume of crystals per volume of slurry. The volume of solids per volume of slurry $V_{T}=k_{V} \int_{0}^{\infty} n L^{3} d L=k_{V} M_{3}$, where $k_{V}$ is a so-called volume shape factor (see below) and
$M_{3}$ is the third moment of the distribution, i.e., the value of the integral in step 1 when $j=3$. Some volume shape factors are as follows:

| Crystal shape | Value of $k_{V}$ |
| :--- | :---: |
| Cube | 1 |
| Sphere | $\pi / 6$ |
| Octahedron | $\sqrt{2} / 3$ |

In the present case, then, $V_{T}=(\pi / 6)\left(2 \times 10^{5}\right)\left[(3+1)!/(1 / 10)^{3+2}\right]=2.51 \times 10^{11} \mu \mathrm{~m}^{3}\left(0.251 \mathrm{~cm}^{3}\right)$ per cubic centimeter of slurry.
5. Calculate the total mass of solids per volume of slurry. Total mass of solids $M_{T}=\rho_{S} V_{T}$, where $\rho_{S}$ is the crystal density. Thus, $M_{T}=\left(2.5 \mathrm{~g} / \mathrm{cm}^{3}\right)\left(0.251 \mathrm{~cm}^{3}\right.$ per cubic centimeter of slurry $)=0.628 \mathrm{~g}$ per cubic centimeter of slurry.
6. Calculate the average crystal size. The number-weighted average crystal size $\bar{L}_{1,0}=M_{1} / M_{0}$. Thus, $\bar{L}_{1,0}=\left(4 \times 10^{8}\right) /\left(2 \times 10^{7}\right)=20 \mu \mathrm{~m}$. The length weighted average $\bar{L}_{2,1}=M_{2} / M_{1}$. Thus, $\bar{L}_{2,1}=2 \times 10^{5}\left[(2+1)!/(1 / 10)^{2+2}\right] /\left(4 \times 10^{8}\right)=\left(12 \times 10^{9}\right) /\left(4 \times 10^{8}\right)=30 \mu \mathrm{~m}$. And the areaweighted average $\bar{L}_{3,2}=M_{3} / M_{2}$. Thus, $\bar{L}_{3,2}=\left(2 \times 10^{5}\right)\left[(3+1)!/(1 / 10)^{3+2}\right] /\left(12 \times 10^{9}\right)=40 \mu \mathrm{~m}$.
7. Calculate the variance of the particle size distribution. The variance $\sigma^{2}$ of the particle size distribution equals $\int_{o}^{\infty}\left(\bar{L}_{1,0}-L\right)^{2} n d L / M_{0}=M_{2} / M_{0}-\left(\bar{L}_{1,0}\right)^{2}$. Thus, $\sigma^{2}=\left(12 \times 10^{9}\right) /\left(2 \times 10^{7}\right)-$ $20^{2}=200 \mu \mathrm{~m}^{2}$.
8. Calculate the coefficient of variation for the particle size distribution. The coefficient of variation c.v. equals $\sigma / \bar{L}_{1,0}$, where $\sigma$ (the standard deviation) is the square root of the variance from step 7 . Thus, c.v. $=200^{1 / 2} / 20=0.71$.
9. Calculate and plot the cumulative weight fraction that is undersize. The weight fraction $W$ undersize of a crystal size distribution is $W=\rho_{s} k_{V} \int_{0}^{L} n L^{3} d L / M_{T}=\int_{0}^{L} n L^{3} d L / M_{3}=1-$ $\left[(L / 10)^{4} / 24+(L / 10)^{3} / 6+(L / 10)^{2} / 2+L / 10+1\right] \exp (-L / 10)$. A plot of this function (Fig. 10.8) has the characteristic $S$-shaped curvature.


FIGURE 10.8 Cumulative weight fraction undersize versus particle size (Example 10.6).

Related Calculations. This procedure can be used to calculate average sizes, moments, surface area, and mass of solids per volume of slurry for any known particle size distribution. The method can also be used for dry-solids distributions, say, from grinding operations. See Example 10.7 for an example of a situation in which the size distribution is based on an experimental sample rather than on a known size-distribution function.

### 10.7 CRYSTAL SIZE DISTRIBUTION OF A SLURRY SAMPLE

The first three columns of Table 10.1 show a sieve-screen analysis of a $100-\mathrm{cc}\left(0.0001-\mathrm{m}^{3}\right.$ or $0.0035-$ $\mathrm{ft}^{3}$ ) slurry sample. The crystals are cubic and have a solids density $\rho_{s}$ of $1.77 \mathrm{~g} / \mathrm{cc}\left(110.5 \mathrm{lb} / \mathrm{ft}^{3}\right)$. Calculate the crystal size distribution $n$ of the solids, the average crystal size, and the coefficient of variation of the crystal size distribution.

## Calculation Procedure

1. Calculate the weight fraction retained on each screen. The weight fraction $\Delta W_{i}$ retained on screen $i$ equals the weight retained on that screen divided by the total solids weight, that is, 29.87 g . For instance, the weight fraction retained on screen 28 is $0.005 / 29.87=0.000167$. The weight fractions retained on all the screens are shown in the fourth column of Table 10.1.
2. Calculate the screen average sizes. The screen average size $L_{i}$ for a given screen reflects the average size of a crystal retained on that screen. Use the average of the size of the screen and the screen above it. For instance, the average crystal size of the solids on screen 28 is $(701+589) / 2=645 \mu \mathrm{~m}$. The averages for all the screens appear in the fifth column of Table 10.1.
3. Calculate the size difference between screens. The size difference between screens $\Delta L_{i}$ is the difference between the size of the screen in question and the size of the screen directly above it. For instance, the size difference $\Delta L_{i}$ for screen 60 is $(295 \mu \mathrm{~m})-(248 \mu \mathrm{~m})=47 \mu \mathrm{~m}$. Size differences for all the screens appear in the sixth column of Table 10.1.

TABLE 10.1 Crystal Size Distribution of a Slurry Sample (Example 10.7)

| Sieve screen analysis |  |  | Summary of crystal size distribution analysis |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Tyler mesh | Opening, $\mu \mathrm{m}$ | Weight retained, g | Weight fraction retained $\Delta W_{i}$ | Average screen size $L_{i}, \mu \mathrm{~m}$ | $\Delta L_{i}, \mu \mathrm{~m}$ | $\begin{gathered} n_{i}, \text { no. } / \\ \left(\mathrm{cm}^{3}\right)(\mu \mathrm{m}) \end{gathered}$ |
| ficticious screen | (701) | - | - | - | - | - |
|  | 589 | 0.005 | 0.000167 | 645 | 112 | $9.39 \times 10^{-4}$ |
|  | 495 | 0.016 | 0.00536 | 542 | 94 | 0.0605 |
|  | 417 | 0.096 | 0.00321 | 456 | 78 | 0.0733 |
|  | 351 | 0.315 | 0.0106 | 384 | 66 | 0.479 |
|  | 295 | 1.61 | 0.0539 | 323 | 56 | 4.827 |
|  | 248 | 3.42 | 0.1145 | 272 | 47 | 20.46 |
| 65 | 208 | 7.56 | 0.253 | 228 | 40 | 90.19 |
| 80 | 175 | 8.21 | 0.275 | 192 | 33 | 199.0 |
| 100 | 147 | 5.82 | 0.195 | 161 | 28 | 282.0 |
| 115 | 124 | 2.47 | 0.0827 | 136 | 23 | 241.5 |
| 150 | 104 | 0.32 | 0.0107 | 114 | 20 | 61.0 |
| 170 | 88 | 0.025 | 0.000837 | 96 | 16 | 9.99 |
| 200 | 74 | 0.0076 | 0.000254 | 81 | 14 | 5.77 |
|  |  | al 29.87 |  |  |  |  |

4. Calculate the third moment of the crystal size distribution. The third moment $M_{3}$ of the crystal size distribution equals $M_{T} / \rho_{s} k_{V}$, where $M_{T}$ is the total weight of the crystals and $k_{V}$ is the volume shape factor; see step 4 of Example 10.6. In this case, $M_{3}=29.87 /[1.77(1)(100 \mathrm{cc})]=0.169 \mathrm{~cm}^{3}$ solids per cubic centimeter of slurry.
5. Calculate the crystal size distribution. The crystal size distribution for the $i$ th screen $n_{i}$ equals $10^{12} M_{3} \Delta W_{i} /\left(L_{i}^{3} \Delta L_{i}\right)$, in number of crystals per cubic centimeter per micron. For instance, for screen $60, n_{i}=10^{12}(0.169)(0.1145) /\left[272^{3}(47)\right]=20.46$ crystals per cubic centimeter per micron. The size distributions for all other screens appear in the seventh column of Table 10.1.
6. Calculate the zeroth, first, and second moments of the crystal size distribution. The zeroth moment $M_{0}$ is calculated as follows: $M_{0}=\Sigma_{i} n_{i} \Delta L_{i}=2.64 \times 10^{4}$ crystals per cubic centimeter. The first moment $M_{1}$ is calculated by $M_{1}=\Sigma_{i} n_{i} L_{i} \Delta L_{i}=4.64 \times 10^{6} \mu \mathrm{~m} / \mathrm{cm}^{3}$. The second moment $M_{2}$ is calculated by $M_{2}=\Sigma_{i} n_{i} L_{i}^{2} \Delta L_{i}=8.62 \times 10^{8} \mu \mathrm{~m}^{2} / \mathrm{cm}^{3}$. [The third moment $M_{3}$ can be calculated by $M_{3}=\Sigma_{i} n_{i} L_{i}^{3} \Delta L_{i}=0.169 \times 10^{12} \mathrm{~mm}^{3} / \mathrm{cm}^{3}\left(0.169 \mathrm{~cm}^{3} / \mathrm{cm}^{3}\right)$, which agrees with the calculation of the third moment from step 4.]
7. Calculate the average crystal size. The number-weighted average crystal size is $\bar{L}_{1,0}=M_{1} / M_{0}$ $=\left(4.64 \times 10^{6}\right) /\left(2.64 \times 10^{4}\right)=176 \mu \mathrm{~m}$. The length-weighted average crystal size is $\bar{L}_{2,1}=M_{2} / M_{1}$ $=\left(8.62 \times 10^{8}\right) /\left(4.64 \times 10^{6}\right)=186 \mu \mathrm{~m}$. The area-weighted average crystal size is $\bar{L}_{3,2}=M_{3} / M_{2}=$ $\left(0.169 \times 10^{12}\right) /\left(8.63 \times 18^{8}\right)=196 \mu \mathrm{~m}$.
8. Calculate the variance. The variance of the crystal size distribution is $\sigma^{2}=M_{2} / M_{0}-\left(\bar{L}_{1,0}\right)^{2}=$ $\left(8.62 \times 10^{8}\right) /\left(2.64 \times 10^{4}\right)-176^{2}=1676 \mu \mathrm{~m}^{2}$.
9. Calculate the coefficient of variation. The coefficient of variation c.v. $=\sigma / \bar{L}_{1,0}=1676^{1 / 2} /$ $176=0.23$.

Related Calculations. This procedure can be used to analyze either wet or dry solids particle size distributions. Particle size distributions from grinding or combustion and particles from crystallizers are described by the same mathematics. See Example 10.6 for an example of a situation in which the size distribution is based on a known size-distribution function rather than on an experimental sample.

### 10.8 PRODUCT CRYSTAL SIZE DISTRIBUTION FROM A SEEDED CRYSTALLIZER

A continuous crystallizer producing $25,000 \mathrm{lb} / \mathrm{h}(11,340 \mathrm{~kg} / \mathrm{h})$ of cubic solids is continuously seeded with $5000 \mathrm{lb} / \mathrm{h}(2270 \mathrm{~kg} / \mathrm{h})$ of crystals having a crystal size distribution as listed in Table 10.2. Predict the product crystal size distribution if nucleation is ignored. If the residence time of solids in the crystallizer is 2 h , calculate the average particle-diameter growth rate $G$.

## Calculation Procedure

1. Calculate the crystal-mass-increase ratio. The crystal-mass-increase ratio is the ratio of crystallizer output to seed input; in this case, $25,000 / 5000=5.0$.
2. Calculate the increase $\Delta L$ in particle size. The increase in weight of a crystal is related to the increase in particle diameter. For any given screen size, that increase $\Delta L$ is related to the initial weight $\Delta M_{s}$ and initial size $L_{s}$ of seed particles corresponding to that screen and to the product weight $\Delta M_{p}$

TABLE 10.2 Size Distribution of Seed Crystals (Example 10.8)

| Tyler <br> mesh | Weight fraction <br> retained $\Delta W_{i}$ | Average size $L_{i}$, <br> $\mu \mathrm{m}$ (from Table 10.1) |
| :---: | :---: | :---: |
| $(65)$ | - | - |
| 80 | 0.117 | 192 |
| 100 | 0.262 | 161 |
| 115 | 0.314 | 136 |
| 150 | 0.274 | 114 |
| 170 | 0.032 | 96 |
| 200 | $\underline{0.001}$ | 81 |
|  | Total | 1.000 |

of particles corresponding to that screen, by McCabe's $\Delta L$ law:

$$
\Delta M_{p}=\left(1+\frac{\Delta L}{L_{s}}\right)^{3} \Delta M_{s}
$$

This equation can be solved for $\Delta L$ by trial and error. From step 1 , and summing over all the screens, $\Sigma \Delta M_{p} / \Sigma \Delta M_{s}=5.0$. The trial-and-error procedure consists of assuming a value for $\Delta L$, calculating $\Delta M_{p}$ for each screen, summing the values of $\Delta M_{p}$ and $\Delta M_{s}$, and repeating the procedure until the ratio of these sums is close to 5.0.

For a first guess, assume that $\Delta L=100 \mu \mathrm{~m}$. Assuming that the total seed weight is 1.0 (in any units), this leads to the results shown in Table 10.3. Since $\Sigma \Delta M_{p}$ is found to be 5.26 , the ratio $\Sigma \Delta M_{p} / \Sigma \Delta M_{s}$ emerges as $5.26 / 1.0=5.26$, which is too high. A lower assumed value of $\Delta L$ is called for. At final convergence of the trial-and-error procedure, $\Delta L$ is found to be $96 \mu \mathrm{~m}$, based on the results shown in the first five columns of Table 10.4.

This leads to the crystal size distribution shown in the last two columns of the table. The sixth column, weight fraction retained $\Delta W_{i}$, is found (for each screen size) by dividing $\Delta M_{p}$ by $\Sigma \Delta M_{p}$. The screen size (seventh column) corresponding to each weight fraction consists of the original seed-crystal size $L_{s}$ plus the increase $\Delta L$.
3. Calculate the growth rate. The average particle-diameter growth rate $G$ can be found thus:

$$
G=\frac{\Delta L}{(\text { elapsed time })}=\frac{96 \mu \mathrm{~m}}{(2 \mathrm{~h})(60 \mathrm{~min} / \mathrm{h})}=0.8 \mu \mathrm{~m} / \mathrm{min}
$$

TABLE 10.3 Results from (Incorrect) Guess that $\Delta L=100 \mu \mathrm{~m}$ (Example 10.8). Basis: Total seed mass $=1.0$

| Tyler mesh | Seed mass $\Delta M_{s}$ (from Table 10.2) | Seed size $L_{s}$ (from Table 10.2) | $\left(1+\Delta L / L_{s}\right)^{3}$ | Calculated product mass $\Delta m_{p}$ |
| :---: | :---: | :---: | :---: | :---: |
| 80 | 0.117 | 192 | 3.52 | 0.412 |
| 100 | 0.262 | 161 | 4.26 | 1.12 |
| 115 | 0.314 | 136 | 5.23 | 1.64 |
| 150 | 0.274 | 114 | 6.61 | 1.81 |
| 170 | 0.032 | 96 | 8.51 | 0.272 |
| 200 | $\underline{0.001}$ | 81 | 11.16 | 0.011 |
|  | $\Sigma \Delta M_{s}=1.000$ | $\frac{\Sigma \Delta M_{p}}{\Sigma \Delta M_{s}}=\frac{5.26}{1.00}=5.26 \quad$ which is too high |  | $\Sigma \Delta M_{p}=5.26$ |
|  |  |  |  |  |

TABLE 10.4 Results from (Correct) Guess that $\Delta L=96 \mu \mathrm{~m}$ and Resulting Crystal Size Distribution (Example 10.8). Basis: Total seed mass $=1.0$


Related Calculations. This method uses McCabe's $\Delta L$ law, which assumes total growth and no nucleation. For many industrial situations, these two assumptions seem reasonable. If significant nucleation is present, however, this method will overpredict product crystal size.

The presence of nucleation can be determined by product screening: If particles of size less than the seeds can be found, then nucleation is present. In such a case, prediction of product crystal size distribution requires a knowledge of nucleation kinetics; see Randolph and Larson [3] for the basic mathematics.

### 10.9 ANALYSIS OF DATA FROM A MIXED SUSPENSION—MIXED PRODUCT REMOVAL CRYSTALLIZER (MSMPR)

The first three columns of Table 10.5 show sieve data for a 100 -cc slurry sample containing 21.0 g of solids taken from a $20,000-\mathrm{gal}\left(75-\mathrm{m}^{3}\right)$ mixed suspension-mixed product removal crystallizer (MSMPR) producing cubic ammonium sulfate crystals. Solids density is $1.77 \mathrm{~g} / \mathrm{cm}^{3}$, and the density of the clear liquor leaving the crystallizer is $1.18 \mathrm{~g} / \mathrm{cm}^{3}$. The hot feed flows to the crystallizer at $374,000 \mathrm{lb} / \mathrm{h}(47 \mathrm{~kg} / \mathrm{s})$. Calculate the residence time $\tau$, the crystal size distribution function $n$, the growth rate $G$, the nucleation density $n^{0}$, the nucleation birth rate $B^{0}$, and the area-weighted average crystal size $\bar{L}_{3,2}$ for the product crystals.

## Calculation Procedure

1. Calculate the density of the crystallizer magma. The slurry density in the crystallizer is the same as the density of the product stream. Select as a basis $100 \mathrm{~cm}^{3}$ slurry. The solids mass is 21.0 g ; therefore, the solids volume is $(21.0 \mathrm{~g}) /\left(1.77 \mathrm{~g} / \mathrm{cm}^{3}\right)=11.9 \mathrm{~cm}^{3}$. The clear-liquor volume is $100-$ $11.9=88.1 \mathrm{~cm}^{3}$, and its mass is $\left(88.1 \mathrm{~cm}^{3}\right)\left(1.18 \mathrm{~g} / \mathrm{cm}^{3}\right)=104 \mathrm{~g}$. Therefore, the density of the slurry is $(104 \mathrm{~g}+21 \mathrm{~g}) / 100 \mathrm{~cm}^{3}=1.25 \mathrm{~g} / \mathrm{cm}^{3}\left(78.0 \mathrm{lb} / \mathrm{ft}^{3}\right)$.
2. Calculate the residence time in the crystallizer. The residence time $\tau$ in the crystallizer is based on the outlet conditions (which are the same as in the crystallizer). Thus, $\tau=$ (volume of crystallizer $) /($ outlet volumetric flow rate $)=(20,000 \mathrm{gal}) /\left[(374,000 \mathrm{lb} / \mathrm{h}) /\left(78.0 \mathrm{lb} / \mathrm{ft}^{3}\right)\left(0.1337 \mathrm{ft}^{3} / \mathrm{gal}\right)\right]$ $=0.557 \mathrm{~h}=33.4 \mathrm{~min}$.

TABLE 10.5 Crystal Size Distribution from an MSMPR Crystallizer (Example 10.9)

|  |  |  | Summary of crystal size distribution analysis |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Screen <br> number | Tyler <br> mesh | Weight fraction <br> retained $\Delta W_{i}$ | Screen <br> size, $\mu \mathrm{m}$ | Average <br> screen size <br> $L_{i}, \mu \mathrm{~m}$ | $\Delta L_{i}, \mu \mathrm{~m}$ | $n_{i}$ | $\ln n_{i}$ |
| 1 | 24 | 0.081 | 701 | - | - | - | - |
| 2 | 28 | 0.075 | 589 | 645 | 112 | 0.297 | -1.21 |
| 3 | 32 | 0.120 | 495 | 542 | 94 | 0.954 | -0.047 |
| 4 | 35 | 0.100 | 417 | 456 | 78 | 1.61 | 0.476 |
| 5 | 42 | 0.160 | 351 | 384 | 60 | 5.60 | 1.72 |
| 6 | 48 | 0.110 | 295 | 323 | 56 | 6.94 | 1.94 |
| 7 | 60 | 0.102 | 248 | 272 | 47 | 12.8 | 2.55 |
| 8 | 65 | 0.090 | 208 | 228 | 40 | 22.6 | 3.12 |
| 9 | 80 | 0.060 | 175 | 192 | 33 | 30.6 | 3.42 |
| 10 | 100 | 0.040 | 147 | 161 | 28 | 40.7 | 3.71 |
| 11 | 115 | 0.024 | 124 | 136 | 23 | 49.4 | 3.90 |
| 12 | 150 | 0.017 | 104 | 114 | 20 | 68.3 | 4.22 |
| 13 | 170 | 0.010 | 88 | 96 | 16 | 84.1 | 4.43 |
| 14 | 200 | 0.005 | 74 | 81 | 14 | 80.0 | 4.38 |
| - | fines | $\underline{0.006}$ | - | - | - | - | - |
|  |  | Total | 1.000 |  |  |  |  |

3. Calculate the third moment of the solids crystal size distribution. The third moment $M_{3}$ of the crystal size distribution equals $M_{T} / \rho_{s} k_{V}$, where $M_{T}$ is the weight of crystals, $\rho_{s}$ is the solids density, and $k_{V}$ is the volume shape factor; see step 4 of Example 10.6. Thus, $M_{3}=21.0 \mathrm{~g} /\left[\left(1.77 \mathrm{~g} / \mathrm{cm}^{3}\right)\right.$ (1) $\left.\left(100 \mathrm{~cm}^{3}\right)\right]=0.119 \mathrm{~cm}^{3}$ solids per cubic centimeter of slurry.
4. Calculate the crystal size distribution function $\boldsymbol{n}$. The crystal size distribution for the $i$ th sieve tray is $n_{i}=10^{12} M_{3} \Delta W_{i} /\left(L_{i}^{3} \Delta L_{i}\right)$, where $\Delta W_{i}$ is the weight fraction retained on the $i$ th screen, $L_{i}$ is the average screen size of material retained on the $i$ th screen (see Example 10.7, step 2), and $\Delta L_{i}$ is the difference in particle sizes on the $i$ th screen (see Example 10.7, step 3). For instance, for the Tyler mesh 100 screen, $n_{10}=10^{12}(0.119)(0.040) /\left(161^{3} \times 28\right)=40.7$ crystals per cubic centimeter per micron. Table 10.5 shows the results for each sieve screen.
5. Calculate the growth rate $\boldsymbol{G}$. The growth rate for an MSMPR can be calculated from the slope of an $\ln n$ versus $L$ diagram (Fig. 10.9). Here the slope equals $-[1 /(G \tau)]=\left(\ln n_{2}-\ln n_{1}\right) /\left(L_{2}-L_{1}\right)=$ $(-0.6-5.4) /(600-0)=-0.010 \mu \mathrm{~m}^{-1}$ or $G \tau=100 \mu \mathrm{~m}$. Then the growth rate $G=100 \mu \mathrm{~m} /$ $33.4 \mathrm{~min}=3.0 \mu \mathrm{~m} / \mathrm{min}$.
6. Calculate the nucleation density $\boldsymbol{n}^{0}$. The nucleation density $n^{0}$ is the value of $n$ at size $L=0$. From Fig. 10.9, $\ln n^{0}$ at size equal to zero is 5.4. So $n^{0}=\exp \left(\ln n^{0}\right)=\exp 5.4=221$ particles per cubic centimeter per micron.
7. Calculate the nucleation birth rate $\boldsymbol{B}^{\boldsymbol{0}}$. The nucleation birth rate is $B^{0}=n^{0} G=221(3.0)=$ 663 particles per cubic centimeter per minute.
8. Calculate area-weighted average size $\bar{L}_{3,2}$. As shown in Examples 10.6 and 10.7, the areaweighted average size equals $M_{3} / M_{2}$. However, for an MSMPR, the area-weighted average particle size also happens to equal $3 G \tau$. Thus, $\bar{L}_{3,2}=3(3 \mu \mathrm{~m} / \mathrm{min})(33.4 \mathrm{~min})=300 \mu \mathrm{~m}$.


FIGURE 10.9 Ln $n$ versus $L$ for an MSMPR crystallizer (Example 10.9).

Related Calculations. Use this procedure to calculate the crystal size distribution from both class I and class II MSMPR crystallizers. This procedure cannot be used to calculate growth rates and nucleation with crystallizers having either fines destruction or product classification.

### 10.10 PRODUCT SCREENING EFFECTIVENESS

Figure 10.10 shows the sieve-screen analysis of a feed slurry, overflow slurry, and underflow slurry being separated by a $600-\mu \mathrm{m}$ classifying screen. Calculate the overall effectiveness of the classifying screen.

## Calculation Procedure

1. Calculate solids mass fractions in each stream. On Fig. 10.10, draw a vertical line through the abscissa that corresponds to the screen size, that is, $600 \mu \mathrm{~m}$. This line will intersect each of the three cumulative-weight-fraction curves. The ordinate corresponding to each intersection gives the mass fraction of total solids actually in that stream which would be in the overflow stream if the screen were instead perfectly effective. Thus the mass fraction in the feed $x_{F}$ is found to be 0.28 , the fraction in the overflow $x_{o}$ is found to be 0.77 , and the fraction in the underflow $x_{u}$ is found to be 0.055 .


FIGURE 10.10 Cumulative weight fraction oversize versus particle size (Example 10.10).
2. Calculate solids-overflow to total-solids-feed ratio. The ratio of total overflow-solids mass to total feed-solids mass $q$ equals $\left(x_{F}-x_{u}\right) /\left(x_{o}-x_{u}\right)$; that is, $q=(0.28-0.055) /(0.77-0.055)=$ 0.315 .
3. Calculate the screen effectiveness based on oversize. The screen effectiveness based on oversize material $E_{o}$ equals $q\left(x_{o} / x_{F}\right)$. Thus, $E_{o}=0.315(0.77 / 0.28)=0.87$.
4. Calculate the screen effectiveness based on undersize. The screen effectiveness based on undersize material $E_{u}$ equals $(1-q)\left(1-x_{u}\right) /\left(1-x_{F}\right)$. Thus, $E_{u}=(1-0.315)(1-0.055) /(1-0.28)$ $=0.90$.
5. Calculate the overall screen effectiveness. Overall screen effectiveness $E$ is the product of $E_{o}$ and $E_{u}$. Thus, $E=0.90(0.87)=0.78$.

Related Calculations. This method can be used for determining separation effectiveness for classifying screens, elutriators, cyclones, or hydroclones in which a known feed of a known crystal size distribution is segregated into a fine and a coarse fraction. If a cut size cannot be predetermined, assume one at a time and complete the described effectiveness analysis. The assumed cut size that gives the largest effectiveness is the cut size that best describes the separation device.

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# ABSORPTION AND STRIPPING 

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### 11.1 HYDRAULIC DESIGN OF A PACKED TOWER 11.1 <br> 11.2 HYDRAULIC RATING OF A PACKED TOWER 11.6 <br> 11.3 REQUIRED PACKING HEIGHT FOR ABSORPTION WITH STRAIGHT EQUILIBRIUM AND OPERATING LINES 11.7 <br> 11.4 PACKING HEIGHT FOR STRIPPING WITH STRAIGHT EQUILIBRIUM AND OPERATING LINES 11.13

11.5 PACKED HEIGHT FOR ABSORPTION
WITH CURVED EQUILIBRIUM AND
OPERATING LINES 11.16
11.6 DETERMINING HTUS FOR AIR
STRIPPING FROM DATA ON MODEL
SYSTEMS 11.21
11.7 PACKED HEIGHT FOR ABSORPTION
WITH EFFECTIVELY INSTANTANEOUS
IRREVERSIBLE CHEMICAL
REACTION 11.23
11.5 PACKED HEIGHT FOR ABSORPTION WITH CURVED EQUILIBRIUM AND OPERATING LINES 11.16
11.6 DETERMINING HTUS FOR AIR STRIPPING FROM DATA ON MODEL SYSTEMS 11.21
11.7 PACKED HEIGHT FOR ABSORPTION WITH EFFECTIVELY INSTANTANEOUS REACTION 11.23

### 11.1 HYDRAULIC DESIGN OF A PACKED TOWER

Gas and liquid are to be contacted countercurrently in a packed tower. The approach to flooding is not to exceed 80 percent as defined at constant liquid loading. What column diameter should be used for 2-in Koch Flexiring (FR) packing (i.e., 2-in slotted-ring random packing), and what diameter should be used for Koch Flexipac (FP) Type 2 Y packing (i.e., structured packing having $1 / 2$-in crimp height, with flow channels inclined at $45^{\circ}$ to the axis of flow)? The packings are to be of stainless steel. Calculate and compare the pressure drops per foot of packing for these two packings. The operating conditions are

Maximum liquid rate: $150,000 \mathrm{lb} / \mathrm{h}$
Maximum gas rate: $75,000 \mathrm{lb} / \mathrm{h}$
Liquid density: $62.4 \mathrm{lb} / \mathrm{ft}^{3}$
Gas density: $0.25 \mathrm{lb} / \mathrm{ft}^{3}$

## Calculation Procedure

1. Calculate the tower diameter. Various methods are available for the design and rating of packed towers. The method shown here is an extension of the CVCL model, which is more fundamentally sound than the generalized pressure drop correlation (GPDC). The basic flooding
equation is

$$
\begin{equation*}
C_{V F}^{1 / 2}+s C_{L F}^{1 / 2}=c \tag{11.1}
\end{equation*}
$$

where $C_{V F}$ is the vapor or gas capacity factor at flooding, $C_{L F}$ is the liquid capacity factor at flooding, and $s$ and $c$ are constants for a particular packing. The capacity factors for the vapor and liquid are defined as

$$
\begin{gather*}
C_{V}=U_{g}\left[\rho_{g} /\left(\rho_{l}-\rho_{g}\right)\right]^{1 / 2}  \tag{11.2}\\
C_{L}=U_{L}\left[\rho_{l} /\left(\rho_{l}-\rho_{g}\right)\right] \tag{11.3}
\end{gather*}
$$

where $U_{g}$ is the superficial velocity of the gas based on the empty-tower cross-sectional area, $U_{L}$ is the superficial liquid velocity, $\rho_{g}$ is the gas density, and $\rho_{l}$ is the liquid density. In U.S. engineering units, $C_{V}$ and $U_{g}$ are in feet per second, and $C_{L}$ and $U_{L}$ are in gallons per minute per square foot. The superficial velocities are related to the mass flow rates as follows:

$$
\begin{equation*}
U_{g}=w_{g} / \rho_{g} A \quad \text { and } \quad U_{l}=w_{i} / \rho_{l} A \tag{11.4}
\end{equation*}
$$

where $w_{g}$ and $w_{l}$ are, respectively, the mass flow rates of gas and liquid, and $A$ is the tower crosssectional area. Here, $U_{l}$ has units of feet per second; this can be converted to the more commonly used $U_{L}$ (with an uppercase subscript) having units of gallons per minute per square foot, by multiplying by $7.48 \mathrm{gal} / \mathrm{ft}^{3}$ and $60 \mathrm{~s} / \mathrm{min}$.

For flooding that is defined at constant liquid loading $L$, the flooding capacity factor $C_{L F}$ is the same as the design capacity factor $C_{L}$. The gas capacity factor at flood, $C_{V F}$, is equal to the design capacity factor divided by the fractional approach to flooding, $f: C_{V F}=C_{V} / f$. For this problem, $f$ equals 0.80 . Substituting the definitions and given values for this problem into Eq. (11.1), bearing in mind that for a circular cross section $A=\pi D^{2} / 4$ and solving for tower diameter $D$ gives
$D=\frac{1}{c} \sqrt{\frac{4}{\pi}}\left\{\left[\frac{75000}{(3600)(0.8)(0.25)} \sqrt{\frac{0.25}{(62.4-0.25)}}\right]^{1 / 2}+s\left[\frac{(150000)(7.48)}{(62.4)(60)} \sqrt{\frac{62.4}{(62.4-0.25)}}\right]^{1 / 2}\right\}$
where the quantity 3600 converts from hours to seconds, 60 converts from hours to minutes, and 7.48 converts from cubic feet to gallons.

In remains to determine values of $s$ and $c$ for the packings of interest. These values can be calculated from air-water pressure-drop data published by packing vendors. Table 11.1 provides values of $s$ and $c$ for several random and structured packings of stainless steel construction. With the appropriate constants from the table for 2-in FR and FP2Y substituted into Eq. (11.5), the diameter emerges as 4.96 ft for 2-in FR and 5.00 ft for FP2Y. Thus, for the conditions stated in this example, the capacities of these two packings are essentially identical. In subsequent calculations, a tower diameter of 5.0 ft will be used for both packings.
2. Calculate the loadings, the capacity factors, and the superficial F factor at the design conditions.

For the design conditions given and a tower of 5 ft diameter, the loadings and capacity factors are calculated as follows from Eqs. (11.2), (11.3), and (11.4):

$$
\begin{aligned}
& U_{L}=\frac{w_{l}}{\rho_{l} A}=\frac{(150,000)(4)}{\pi(62.4)(5)^{2}} \frac{(7.48)}{(60)}=15.26 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{2}\right) \\
& C_{L}=15.26 \sqrt{\frac{62.4}{62.4-0.25}}=15.29 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{2}\right)
\end{aligned}
$$

TABLE 11.1 Tower-packing Constants for Hydraulic Design and Rating of Packed Towers

| Generic shape | Typical brand | Nominal size | Void fraction, $\epsilon$ | $K_{1}$, (in $\left.w c \cdot s^{2}\right) / \mathrm{lb}$ | $s,\left[\mathrm{ft}^{3} /(\mathrm{gal} / \mathrm{min})(\mathrm{s})\right]^{1 / 2}$ | $c,(\mathrm{ft} / \mathrm{s})^{1 / 2}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Random: slotted ring | Flexiring Packing | 1 in | 0.95 | 0.14 | 0.016 | 0.67 |
|  |  | 1.5 in | 0.96 | 0.11 | 0.015 | 0.71 |
|  |  | 2 in | 0.98 | 0.069 | 0.040 | 0.74 |
|  |  | 3.5 in | 0.98 | 0.044 | 0.034 | 0.78 |
| Structured: corrugated sheet | Flexipac Packing | $\begin{aligned} & \text { Type 1Y } \\ & 1 / 4 \text { in, } 45^{\circ} \end{aligned}$ | 0.97 | 0.088 | 0.054 | 0.69 |
|  |  | $\begin{aligned} & \text { Type 2Y } \\ & 1 / 2 \text { in, } 45^{\circ} \end{aligned}$ | 0.99 | 0.041 | 0.044 | 0.75 |
|  |  | Type 3Y <br> 1 in, $45^{\circ}$ | 0.99 | 0.019 | 0.044 | 0.87 |
|  |  | Type 4Y <br> 2 in, $45^{\circ}$ | 0.99 | 0.012 | 0.035 | 0.88 |

[^13]\[

$$
\begin{aligned}
U_{g} & =\frac{w_{g}}{\rho_{g} A}=\frac{(75,000)(4)}{\pi(0.25)(5)^{2}} \frac{1}{3,600}=4.24 \mathrm{ft} / \mathrm{s} \\
C_{V} & =U_{g} \sqrt{\frac{\rho_{g}}{\rho_{l}-\rho_{g}}}=4.24 \sqrt{\frac{0.25}{62.4-0.25}}=0.269 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{2}\right)
\end{aligned}
$$
\]

The superficial $F$ factor $F_{s}$ is calculated as follows:

$$
F_{S}=U_{g} \sqrt{\rho_{g}}=4.24(0.25)^{1 / 2}=2.12(\mathrm{ft} / \mathrm{s})\left(\mathrm{lbm} / \mathrm{ft}^{3}\right)^{1 / 2}
$$

3. Construct the dry-pressure-drop line on log-log coordinates (optional). For turbulent flow, the gas-phase pressure drop for frictional loss, contraction and expansion loss, and directional change loss are all proportional to the square of the superficial $F$ factor. For the dry packing the pressure drop can be calculated from the equation

$$
\begin{equation*}
\Delta P / \Delta Z=K_{1} F_{S}^{2} \tag{11.6}
\end{equation*}
$$

where $\Delta Z$ represents a unit height of packing (e.g., 1 ft ) and $K_{1}$ is a constant whose value depends on the packing size and geometry. Values of $K_{1}$ can be determined from pressure-drop data published by packing vendors and are included in Table 11.1. For the two packings of this problem, the values of $K_{1}$ are 0.069 for 2-in FR and 0.041 for FP2Y. Using Eq. (11.6) with the design $F$ factor calculated in step 2 gives the following. For 2-in FR,

$$
\Delta P / \Delta Z=(0.069)(2.12)^{2}=0.310 \text { in } w c / \mathrm{ft}
$$

For FP2Y,

$$
\Delta P / \Delta Z=(0.041)(2.12)^{2}=0.184 \text { in } w c / \mathrm{ft}
$$

This calculation indicates that for the same nominal capacity, the random packing has a 68 percent higher pressure drop per foot than the structured packing.

To construct the dry-pressure-drop line, plot $\Delta \mathrm{P} / \Delta \mathrm{Z}$ vs. $F_{s}$ on log-log coordinates. Select appropriate values of $F_{s}$ (e.g., 1 and 3 for this example) and use Eq. (11.6) to calculate the corresponding pressure drop per foot (e.g., for 2-in FR, 0.069 in $w c / \mathrm{ft}$ at $F_{s}=1$ and $0.621 \mathrm{in} / \mathrm{ft}$ at $F_{s}=3$; and for FP2Y, $0.041 \mathrm{in} / \mathrm{ft}$ at $F_{s}=1$ and $0.369 \mathrm{in} / \mathrm{ft}$ at $F_{s}=3$ ). Plot the points on $\log$ - $\log$ coordinates and connect them with a straight line.
4. Construct the wet-pressure-drop line, on log-log coordinates, for pressure drops below column loading. For most packings of commercial interest, the relationship between the wet and dry pressure drops can be given by

$$
\begin{equation*}
\frac{(\Delta P / \Delta Z)_{W}}{(\Delta P / \Delta Z)_{D}}=\frac{1}{\left(1-\frac{0.02 U_{L}^{0.8}}{\epsilon}\right)^{2.5}} \tag{11.7}
\end{equation*}
$$

where the subscripts $W$ and $D$ refer to wet and dry, respectively, and $\epsilon$ is the void fraction of the dry packed bed. Values of $\epsilon$ for the various packings are given in Table 11.1. The liquid loading, $U_{L}$ in Eq. (11.7), is in units of gallons per minute per square foot. For the random packing,

$$
\frac{(\Delta P / \Delta Z)_{W}}{(\Delta P / \Delta Z)_{D}}=\frac{1}{\left(1-\frac{0.02(15.26)^{0.8}}{0.98}\right)^{2.5}}=1.64
$$

For the structured packing, the numerical result is the same.
To construct the wet-pressure-drop line, select values of $F_{s}$ that span the design value. For example, at $F_{s}=1$, the pressure drop for random packing is $(1.64)(0.069)(1)=0.113$ in $w c / \mathrm{ft}$, and that for structured packing is $(1.64)(0.041)(1)=0.0672$ in $w c / f \mathrm{ft}$. At $F_{s}=3$, the pressure drop for random


FIGURE 11.1 Pressure-drop curves for Example 11.1.
packing is $(1.64)(0.069)(9)=1.018$ in $w c / \mathrm{ft}$, and that for structured packing is $(1.64)(0.041)(9)=$ 0.605 in $w c / \mathrm{ft}$. Plot these points on $\log$-log coordinates and connect the points for each packing with a straight line. The solid lines of Fig. 11.1 are the wet-pressure-drop lines for the two packings.
5. Determine the pressure drop and superficial F factor at flooding. For the air-water system at ambient conditions, flooding occurs at a pressure drop of about 2 in $w c / f t$. The pressure drop at flooding for other systems can be calculated by

$$
\begin{equation*}
\Delta P_{F}=(2 \text { in } w c / \mathrm{ft})\left[\left(\rho_{l}-\rho_{g}\right) /(62.4-0.075)\right] \tag{11.8}
\end{equation*}
$$

Employing Eq. (11.8) with the density values in this problem gives a pressure drop at flooding of 1.99 in $w c / f t$.

The superficial $F$ factor at flooding $F_{S F}$ is determined with the aid of the flooding equation, Eq. (11.1). Since the pressure drop curve is being constructed for a constant liquid loading, the value of $C_{L F}$ in Eq. (11.1) is $15.29 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{2}\right)$ as determined in step 2. With appropriate values for $s$ and $c$, solve Eq. (11.1) for $C_{V F}$ and determine $F_{S F}$ from

$$
F_{S F}=C_{V F}\left(\rho_{l}-\rho_{g}\right)^{1 / 2}
$$

Thus, for 2-in FR,

$$
C_{V F}=\left[0.74-(0.040)(15.29)^{1 / 2}\right]^{2}=0.340 \mathrm{ft} / \mathrm{s}
$$

and accordingly $F_{S F}=0.340(62.4-0.25)^{1 / 2}=2.68(\mathrm{ft} / \mathrm{s})\left(\mathrm{lbm} / \mathrm{ft}^{3}\right)^{1 / 2}$.
For FP2Y,
and

$$
C_{V F}=\left[0.75-(0.044)(15.29)^{1 / 2}\right]^{2}=0.334 \mathrm{ft} / \mathrm{s}
$$

$$
F_{S F}=0.334(62.4-0.25)^{1 / 2}=2.63(\mathrm{ft} / \mathrm{s})\left(\mathrm{lbm} / \mathrm{ft}^{3}\right)^{1 / 2}
$$

Locate the flood points for the two packings on the pressure drop plot at the coordinates $\Delta P_{F}$ and $F_{S F}$. See Fig. 11.1.
6. Draw the wet-pressure-drop curve for the loading region. The "loading region" covers a range of $F$ factors from flooding downward to roughly half of the flooding $F$ factor. This is the region in which the gas flow causes additional liquid holdup in the packing and produces a pressure drop higher than the one indicated by the straight lines of Fig. 11.1.

For each packing, sketch an empirical curve such that: (a) its upper end passes through the point $F_{S F}, \Delta P_{F}$ with a slope approaching infinity, and (b) its lower end becomes tangent to the straight, wet-pressure-drop line at an abscissa value of $F_{S F} / 2$. These two pressure-drop curves for the loading regions are shown by the dashed lines of Fig. 11.1.
7. Determine the pressure drops from the curves. The overall pressure-drop curve for each packing consists of the solid curve at low gas loadings and the dashed curve at loadings between the load point and the flood point. At the design $F$ factor of $2.12(\mathrm{ft} / \mathrm{s})\left(\mathrm{lbm} / \mathrm{ft}^{3}\right)^{1 / 2}$, the pressure drops determined from the curves are

For 2-in FR, 0.65 in $w c / \mathrm{ft}$

For FP2Y, $\quad 0.44$ in $w c / f t$
Thus, the pressure drop of the random packing is 48 percent higher than that of the structured packing at the design conditions.

Related Calculations. It is usual practice in distillation operations to keep the liquid-to-vapor ratio constant as the throughput is varied. When this is the case, the percent of flood is usually defined at constant $L / V$ rather than at constant $L$. The procedures for solving for the tower diameter are similar to those in step 1, except that the liquid-capacity factor at flooding is instead given by $C_{L F}=C_{L} / f$. For the present case, this would introduce a factor of 0.8 in the denominator of the second term in the brackets of Eq. (11.5).

### 11.2 HYDRAULIC RATING OF A PACKED TOWER

A $5.5-\mathrm{ft}$-diameter tower is to be used to countercurrently contact a vapor stream and a liquid stream. The mass flow rates are $150,000 \mathrm{lb} / \mathrm{h}$ for both. The liquid density is $50 \mathrm{lb} / \mathrm{ft}^{3}$, and the gas density $1 \mathrm{lb} / \mathrm{ft}^{3}$. Determine the approach to flooding at constant liquid loading $L$ and at constant liquid-to-vapor ratio ( $L / V$ ) for Flexipac type 2Y (FP2Y) structured packing.

## Calculation Procedure

1. Calculate the liquid and vapor capacity factors, $\boldsymbol{C}_{\boldsymbol{L}}$ and $\boldsymbol{C}_{V}$. For information about these factors, see Problem 11.1. Use Eqs. (11.2), (11.3), and (11.4) from that problem to make the required calculation, bearing in mind that for a circular cross section, $A=\pi D^{2} / 4$ :

$$
\begin{aligned}
& C_{L}=\frac{(150000)(4)}{(50)(\pi)(5.5)^{2}} \frac{7.48}{60} \sqrt{\frac{50}{50-1}}=15.90 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{2}\right) \\
& C_{V}=\frac{(150000)(4)}{(1)(\pi)(5.5)^{2}} \frac{1}{3600} \sqrt{\frac{1}{50-1}}=0.250 \mathrm{ft} / \mathrm{s}
\end{aligned}
$$

2. Determine the flooding constants sand c. From Table 11.1, the values of the flooding constants for FP2Y are

$$
\begin{aligned}
& s=0.044 \\
& c=0.75
\end{aligned}
$$

3. Determine the approach to flooding at constant L. Use Eq. (11.1) with $C_{V F}=C_{V} / f$ and $C_{L F}=C_{L}$, where $f$ is the fractional approach to flooding. Solve for $f$ to give

$$
f=\left\{(0.250)^{1 / 2} /\left[0.75-(0.044)(15.90)^{1 / 2}\right]\right\}^{2}=0.757, \text { or } 75.7 \text { percent }
$$

4. Determine the approach to flooding at constant $\boldsymbol{L} / \boldsymbol{V}$. Use Eq. (11.1) with $C_{V F}=C_{V} / f$ and $C_{L F}=C_{L} / f$ where $f$ is the fractional approach to flooding. Solve for $f$ to give

$$
f=\left\{\left[(0.250)^{1 / 2}+(0.044)(15.90)^{1 / 2}\right] / 0.75\right\}^{2}=0.811, \text { or } 81.1 \text { percent }
$$

Related Calculation. To complete the hydraulic rating, the pressure drop at the design conditions is determined in the same way as for Problem 11.1.

### 11.3 REQUIRED PACKING HEIGHT FOR ABSORPTION WITH STRAIGHT EQUILIBRIUM AND OPERATING LINES

An air stream containing $2 \%$ ammonia by volume (molecular weight $=28.96$ ) is to be treated with water to remove the ammonia to a level of 53 ppm (the odor threshold concentration). The tower is to operate at 80 percent of flood defined at constant liquid to gas ratio $(L / G)$. The liquid to vapor ratio is to be 25 percent greater than the minimum value. The absorption is to occur at $80^{\circ} \mathrm{F}$ and atmospheric pressure. What is the height of packing required for 2-in Flexiring random packing (2-in FR), and what height is required for Flexipac Type 2Y structured packing (FP2Y)? Determine the height using three methods: individual transfer units, overall transfer units, and theoretical stages.

## Calculation Procedure

1. Construct the equilibrium line. The equilibrium line relates the mole fraction of ammonia in the gas phase to that in the liquid phase when the two phases are at equilibrium. Equilibrium is assumed to exist between the two phases only at the gas-liquid interface. For dilute systems, Henry's law will apply. It applies for liquid mole fractions less than 0.01 in systems in general, and, as can be seen in Example 11.5, for the ammonia-water system it applies to liquid mole fractions as high as
about 0.03. (Equilibrium data for this system are given in Perry's Chemical Engineers' Handbook, 4th ed., McGraw-Hill, New York, 1963, p. 14.4.)

From the data at low concentration, determine the Henry's law constant as a function of temperature for the temperature range of interest. To interpolate over a limited temperature range, fit the data to an equation of the form $\log _{10} \mathrm{He}=a+(b / T)$. For the data cited.

$$
\begin{equation*}
\log _{10} \mathrm{He}=5.955-(1778 \mathrm{~K}) / T \tag{11.9}
\end{equation*}
$$

where $T$ is absolute temperature in Kelvins and He is the Henry's law constant in atmospheres. Applying this equation at $80^{\circ} \mathrm{F}$ gives an He value of 1.06 atm .

Henry's law constant is defined as

$$
\begin{equation*}
\mathrm{He}=P y_{i} / x_{i} \tag{11.10}
\end{equation*}
$$

where $P$ is the total pressure in atmospheres and $y_{i}$ and $x_{i}$ are, respectively, the gas-phase and liquidphase mole fractions of ammonia in equilibrium with each other at the interface. The slope of the equilibrium line on the $x-y$ operating diagram is

$$
\begin{equation*}
m=y_{i} / x_{i}=\mathrm{He} / P \tag{11.11}
\end{equation*}
$$

For operation at 1 atm , the equilibrium line is a straight line of slope 1.06 passing through the origin of the plot as shown in Fig. 11.2.
2. Locate the operating line of minimum slope. The operating line gives the relationship between the bulk gas and liquid concentrations throughout the tower. A material balance around the tower is as follow:
or

$$
\begin{align*}
L_{M}\left(x_{1}-x_{2}\right) & =G_{M}\left(y_{1}-y_{2}\right) \\
L_{M} / G_{M} & =\left(y_{1}-y_{2}\right) /\left(x_{1}-x_{2}\right) \tag{11.12}
\end{align*}
$$

where $L_{M}$ and $G_{M}$ are the liquid and gas molar fluxes (for example, in pound-moles per square foot second), respectively, and the subscripts 1 and 2 refer to the bottom and top of the tower, respectively. For dilute systems, $L_{M}$ and $G_{M}$ can be taken as constants over the tower. From Eq. (11.12), the slope of the operating line is $L_{M} / G_{M}$, which for this example may be considered constant. This gives a straight operating line that can be constructed on the $x-y$ diagram from a knowledge of the mole fractions at the top and bottom of the tower.

The operating line of minimum slope is the operating line that just touches the equilibrium line at one end (in this case, the bottom) of the tower. At the top of the tower, $y_{2}=53 / 10^{6}=5.3 \times 10^{-5}$ and $x_{2}=0$. At the bottom of the tower, $y_{1}=0.020$ and, by Eq. (11.11), $x_{1}=0.020 / 1.06=0.01887$. The slope of the operating line of minimum slope is $\left(L_{M} / G_{M}\right)_{\min }=\left(0.020-5.3 \times 10^{-5}\right) /(0.01887-$ $0)=1.057$. Because the conditions at the top of the tower put the end of the operating line so close to the origin of the $x-y$ diagram, the operating line of minimum slope is essentially coincident with the equilibrium line. In Fig. 11.2, the operating line of minimum slope would lie just above the equilibrium line but would be indistinguishable from it unless the plot in the region of the origin were greatly expanded.
3. Construct the actual operating line. The design specifies operating at an $L / G$ value of 1.25 times the minimum value determined in step 2. Accordingly, $L_{M} / G_{M}=(1.25)(1.057)=1.32$. The values of $y_{1}, y_{2}$, and $x_{2}$ are given and remain the same as for step 2 . The value of $x_{1}$ is determined from Eq. (11.12): $x_{1}=\left(0.020-5.3 \times 10^{-5}\right) / 1.32=1.51 \times 10^{-5}$. Construct a straight line through the end points $x_{1}, y_{1}$ and $x_{2}, y_{2}$ to give the operating line as shown in Fig. 11.2.
4. Determine the liquid and gas loadings. The liquid and gas loadings are defined by the liquid-to-gas ratio determined in step 3 and by the stipulation that the tower is to operate at an approach to flooding of 80 percent at constant $L / G$. For flooding defined at constant $L / G$, Eq. (11.1) becomes

$$
\left(C_{V} / f\right)^{1 / 2}+s\left(C_{L} / f\right)^{1 / 2}=c
$$



FIGURE 11.2 $x-y$ operating diagram for Example 11.3.

From the definitions of $C_{V}$ and $C_{L}$, their ratio can be related to the ratio of molar fluxes by

$$
\begin{equation*}
C_{L} / C_{V}=\left(L_{M} / G_{M}\right)\left(M_{w l} / M_{w g}\right)\left(\rho_{g} / \rho_{l}\right)^{1 / 2}(7.48)(60)(\mathrm{gal} \cdot \mathrm{~s}) /(\mathrm{min})\left(\mathrm{ft}^{3}\right) \tag{11.14}
\end{equation*}
$$

In this equation, $\rho_{g}$ is the gas density, $\rho_{t}$ is the liquid density $\left(62.3 \mathrm{lb} / \mathrm{ft}^{3}\right), M_{w l}$ is the molecular weight of the liquid (18.02), $M_{w g}$ is the molecular weight of the gas, and the numerical values 7.48 and 60 are the number of gallons per cubic foot and the number of seconds per minute, respectively. Use of the ideal-gas law yields a gas density of $0.0735 \mathrm{lb} / \mathrm{ft}^{3}$. Accordingly, Eq. (11.14) becomes $C_{L} / C_{V}=(1.32)(18.02 / 28.96)(0.0735 / 62.3)^{1 / 2}(448.8)=12.7(\mathrm{gal} \cdot \mathrm{s}) /(\mathrm{min})\left(\mathrm{ft}^{3}\right)$. Therefore, $C_{L}$ in Eq. (11.13) can be replaced by $12.7 C_{V}$. Upon rearrangement of Eq. (11.13) and substitution of the appropriate values of $c$ and $s$ from Table 11.1, we have

For 2 in FR,

$$
C_{V}=\left(\frac{(0.74)(0.80)^{1 / 2}}{1+0.040 \sqrt{12.7}}\right)^{2}=0.336 \mathrm{ft} / \mathrm{s}
$$

For FP2Y,

$$
\begin{aligned}
C_{V} & =\left(\frac{(0.75)(0.80)^{1 / 2}}{1+0.044 \sqrt{12.7}}\right)^{2}=0.336 \mathrm{ft} / \mathrm{s} \\
C_{L} & =12.7 C_{V}=4.27 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{2}\right)
\end{aligned}
$$

Thus, for this case, the two packings give the same loadings and would require the same tower diameter to operate at 80 percent of flood.

From the definition of the capacity factors and the $F$ factor (see Example 11.1), alternative expressions for the gas and liquid loadings are
and

$$
\begin{aligned}
F_{S} & =(0.336)(62.3-0.0735)^{1 / 2}=2.65(\mathrm{ft} / \mathrm{s})\left(\mathrm{lb} / \mathrm{ft}^{3}\right)^{1 / 2} \\
U_{g} & =2.65 /(0.0735)^{1 / 2}=9.77 \mathrm{ft} / \mathrm{s} \\
U_{L} & =(4.27)((62.3-0.0735) / 62.3)^{1 / 2}=4.27 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{2}\right)
\end{aligned}
$$

5. Determine the HTUs for the packings at the design conditions. For these packings, data available from the vendor give the values of $H_{g}$, the height of a transfer unit for the gas film, and $H_{l}$, the height of a transfer unit for the liquid film. At the design conditions, these values are

| Packing | $H_{g}, \mathrm{ft}$ | $H_{l}, \mathrm{ft}$ |
| :---: | :---: | :---: |
| 2-in FR | 1.73 | 0.87 |
| FP2Y | 1.14 | 0.55 |

6. Determine the major resistance to mass transfer. The major resistance to mass transfer can be in either the gas film or the liquid film. The film with the greater resistance will exhibit the greater driving force in consistent units of concentration. For dilute systems, the rate of transport from bulk gas to bulk liquid per unit tower volume $N_{A} \alpha$ is given, at a particular elevation in the tower, by

$$
\begin{equation*}
N_{A} \alpha=k_{g} \alpha(P / R T)\left(y-y_{i}\right)=k_{l} \alpha \rho_{M l}\left(x_{i}-x\right) \tag{11.15}
\end{equation*}
$$

where $k_{g} \alpha$ and $k_{l} \alpha$ are the gas-side and liquid-side mass transfer coefficients, respectively, both in units of $\mathrm{s}^{-1}, P / R T$ and $\rho_{M l}$ are the gas and liquid molar densities, respectively, ( $\mathrm{lb} \cdot \mathrm{mol} / \mathrm{ft}{ }^{3}$ ), and $y-y_{i}$ and $x_{i}-x$ are the gas and liquid driving forces, respectively. The ratio of driving force $R_{D F}$ in the gas to that in the liquid is

$$
\begin{equation*}
R_{D F}=\left(y-y_{i}\right) /\left(x_{i}-x\right) m=k_{l} \alpha \rho_{M l} / k_{g} \alpha(P / R T) m \tag{11.16}
\end{equation*}
$$

where $m$ is the slope of the equilibrium line.
This equation can be put into a more useful form. The stripping factor $\lambda$ is defined as the ratio of the slope of the equilibrium line to that of the operating line:

$$
\begin{equation*}
\lambda=m /\left(L_{M} / G_{M}\right) \tag{11.17}
\end{equation*}
$$

For dilute systems, the height of a transfer unit for the gas resistance $H_{g}$ and that for the liquid resistance $H_{l}$ are related to their respective mass transfer coefficients by

$$
\begin{equation*}
H_{g}=U_{g} / k_{g} \alpha \quad \text { and } \quad H_{l}=U_{l} / k_{i} \alpha \tag{11.18}
\end{equation*}
$$

Noting that $L_{M}=U_{l} \rho_{M l}$ and $G_{M}=U_{g}(P / R T)$, we can use Eqs. (11.17) and (11.18) to convert Eq. (11.16) to

$$
\begin{equation*}
R_{D F}=H_{g} / \lambda H_{l} \tag{11.19}
\end{equation*}
$$

If $R_{D F}$ is greater than unity, the gas phase provides the major resistance to mass transfer; if $R_{D F}$ is less than unity, the liquid phase provides the major resistance to mass transfer. From

Eq. (11.17), $\lambda=1.06 / 1.32=0.80$. For 2-in FR, $R_{D F}=1.73 /(0.80)(0.87)=2.48$. For FP2Y, $R_{D F}=$ $1.14 /(0.80)(0.55)=2.59$. For both packings, the gas phase provides the major resistance to mass transfer. Therefore, greater precision will be obtained in the calculation of the packed height by using gas phase transfer units.
7. Construct tie lines on the $\boldsymbol{x} \boldsymbol{- y}$ operating diagram. Tie lines are straight lines that connect corresponding points on the operating and equilibrium lines. The intersection of the tie line with the operating line gives the bulk concentration at a particular point in the tower; the intersection of the tie line with the equilibrium line gives the interfacial concentration at the same point in the tower. The slope of the tie line $T L S$ is obtained from Eq. (11.15):

$$
\begin{equation*}
T L S=\left(y-y_{i}\right) /\left(x-x_{i}\right)=-k_{l} a \rho_{M l} / k_{g} a(P / R T)=\left(H_{g} / H_{l}\right)\left(L_{M} / G_{M}\right) \tag{11.20}
\end{equation*}
$$

Various tie lines can be drawn between the operating and equilibrium line as shown in Fig. 11.2. (The diagram ignores the slight difference between the slopes for 2-in FR and for FP2Y.) These lines are useful in understanding the relationships between the various concentrations in the operating diagram. In the general case, the tie lines are essential in relating the bulk and interfacial concentrations so that the mass-transfer equations can be integrated. For complete gas-phase control, the tie line will be vertical; for complete liquid-phase control, the tie line will be horizontal.
8. Determine the equations for the height of packing. Since the gas phase provides the major resistance to mass transfer, use the rate equation for transport across the gas film in the material balance on the gas phase in a differential height of the packed bed. Upon integration, this leads to the general equation for the height of packing:

$$
\begin{equation*}
Z=\int_{y_{2}}^{y_{1}} \frac{U_{g}}{k_{g} \alpha y_{B M}} \frac{y_{B M} d y}{(1-y)\left(y-y_{i}\right)} \tag{11.21}
\end{equation*}
$$

where $Z$ is the height of packing and $y_{B M}$ is the log-mean average concentration of the nondiffusing gas (air in this case) between the bulk and the interface at a particular elevation in the tower. This quantity is considered in more detail in Example 11.5. For dilute systems such as the current example, $y_{B M}$ and $(1-y)$ are both approximately unity throughout the tower. With this simplification, Eq. (11.21) becomes

$$
\begin{equation*}
Z=\int_{y_{2}}^{y_{1}} \frac{U_{g}}{k_{g} a} \frac{d y}{\left(y-y_{i}\right)}=H_{g} \int_{y_{2}}^{y_{1}} \frac{d y}{\left(y-y_{i}\right)}=H_{g} N_{g} \tag{11.22}
\end{equation*}
$$

In this equation, it is assumed that $H_{g}$ is constant over the height of the packed bed and can therefore be removed from the integral. The remaining integral function of $y$ is the number of transfer units based on the gas film resistance $N_{g}$.

For dilute systems in which the equilibrium line and operating lines are straight, various analytical solutions of Eq. (11.22) are available. These may be listed as follows.

## Individual Gas-Side Transfer Units

$$
\begin{align*}
Z & =H_{g} N_{g} \\
N_{g} & =\frac{1+\left(1 / R_{D F}\right)}{1-\lambda} \ln \left[(1-\lambda)\left(\frac{y_{1}-m x_{2}}{y_{2}-m x_{2}}\right)+\lambda\right] \\
R_{D F} & =\frac{H_{g}}{\lambda H_{l}}  \tag{11.23}\\
\lambda & =\frac{m}{L_{M} / G_{M}}=\frac{\mathrm{He} / P}{L_{M} / G_{M}}
\end{align*}
$$

When the absorption is completely gas-phase limited, $R_{D F}$ approaches infinity and the $1 / R_{D F}$ term of the above equation for $N_{g}$ drops out.

## Overall Gas-Side Transfer Units

The overall gas-side transfer units are calculated by assuming that all of the resistance to mass transfer is in the gas phase. The effect of liquid-phase resistance is taken into account by adjusting the height of the transfer unit from $H_{g}$ to $H_{o g}$. The equations are

$$
\begin{align*}
Z & =H_{o g} N_{o g} \\
H_{o g} & =H_{g}+\lambda H_{l} \\
N_{o g} & =\frac{1}{1-\lambda} \ln \left[(1-\lambda) \frac{y_{1}-m x_{2}}{y_{2}-m x_{2}}+\lambda\right]  \tag{11.24}\\
\lambda & =\frac{m}{L_{M} / G_{M}}=\frac{\mathrm{He} / P}{L_{M} / G_{M}}
\end{align*}
$$

## Overall Gas-Side Transfer Units Using the Log-Mean Driving Force

An alternative expression can be used to calculate $N_{o g}$ based on the log-mean concentration driving force across the tower. The equations are

$$
\begin{align*}
N_{o g} & =\frac{y_{1}-y_{2}}{\left(y-y^{*}\right)_{L M}}  \tag{11.25}\\
\left(y-y^{*}\right)_{L M} & =\frac{\left(y_{1}-m x_{1}\right)-\left(y_{2}-m x_{2}\right)}{\ln \left[\left(y_{1}-m x_{1}\right) /\left(y_{2}-m x_{2}\right)\right]}
\end{align*}
$$

where $y$ is the bulk concentration and $y^{*}$ is the interfacial concentration, assuming that all the resistance to mass transfer is in the gas phase; that is, assuming that the tie lines of Fig. 11.2 are vertical. The liquid mole fraction at the bottom of the tower $x_{1}$ is determined by material balance around the tower.

## Theoretical Stages

An analytical solution is also available for theoretical stages as opposed to transfer units, and the height equivalent to a theoretical plate (HETP). The number of theoretical stages or plates $N_{p}$ can be determined by counting the steps between the operating line and the equilibrium line as is done with distillation problems (see Example 8.1 in Section 8, Distillation), but a more convenient analytical solution is as follows:

$$
\begin{align*}
Z & =(\mathrm{HETP}) N_{p} \\
\mathrm{HETP} & =H_{o g} \frac{\ln \lambda}{\lambda-1} \\
H_{o g} & =H_{g}+\lambda H_{l}  \tag{11.26}\\
N_{p} & =\frac{\ln \left[(1-\lambda) \frac{\left(y_{1}-m x_{2}\right)}{\left(y_{2}-m x_{2}\right)}+\lambda\right]}{\ln \left(\frac{1}{\lambda}\right)}
\end{align*}
$$

TABLE 11.2 Values of Variables and Calculated Results for Packing Height

| Parameter | Value for 2-in FR | Value for FP2Y |
| :---: | :---: | :---: |
| $H_{g}$ | 1.73 ft | 1.14 ft |
| $H_{l}$ | 0.87 ft | 0.55 ft |
| $m$ | 1.06 | 1.06 |
| $\lambda$ | 0.80 | 0.80 |
| $R_{D F}$ | 2.48 | 2.59 |
| $y_{1}$ | 0.020 | 0.020 |
| $y_{2}$ | $5.3 \times 10^{-5}$ | $5.3 \times 10^{-5}$ |
| $x_{1}$ | 0.0151 | 0.0151 |
| $x_{2}$ | 0 | 0 |
| $N_{g}$ | 30.4 | 30.0 |
| $N_{o g}$ | 21.67 | 21.67 |
| $N_{o g}(\log$ mean $)$ | 21.67 | 21.67 |
| $N_{p}$ | 19.42 | 19.42 |
| $H_{o g}$ | 2.43 ft | 1.58 ft |
| HETP | 2.71 ft | 1.76 ft |
| $Z$ | 52.6 ft | 34.2 ft |

All of these forms are mathematically equivalent and give identical results for the height of the packing.
9. Calculate the height of packing. Table 11.2 gives the values of the variables and the calculated results for Eqs. (11.23) through (11.26). The various sets of equations all yield the same height of packing. The height for the random packing is 54 percent greater than that of the structured packing. An appropriate safety factor should be added to the height of both packings for this and for subsequent examples.

### 11.4 PACKING HEIGHT FOR STRIPPING WITH STRAIGHT EQUILIBRIUM AND OPERATING LINES

A stream of groundwater flowing at a rate of $700 \mathrm{gal} / \mathrm{min}$ and containing 100 ppm of trichloroethylene (TCE) is to be stripped with air to reduce the TCE concentration to 5 ppb (drinking water quality). The tower is to be packed with 2-in polypropylene slotted rings and is to operate at 30 percent of flooding defined at constant liquid rate $L$, at a gas flow rate four times the minimum. Determine the tower diameter and height. Assume isothermal operation at $50^{\circ} \mathrm{F}$ and 1 atm . The density of the liquid stream is $62.4 \mathrm{lb} / \mathrm{ft}^{3}$; that of the gas stream is $0.0778 \mathrm{lb} / \mathrm{ft}^{3}$.

## Calculation Procedure

1. Construct the equilibrium line. For dilute solutions, Henry's law will apply. In general, it will be applicable for pressures under 2 atm and liquid mole fractions less than 0.01 . For this example, the liquid mole fraction $x$ is $\left(100 \mathrm{lb}\right.$ TCE $/ 10^{6} \mathrm{lb}$ soln $)(18 / 132)=1.37 \times 10^{-5}$, where 18 and 132 are the molecular weights of water and trichloroethylene, respectively. Therefore, Henry's law will apply.

The Henry's law constant can be obtained from the literature (e.g., C. Munz and P. V. Roberts, Journal of the American Water Works Association, 79(5), pp. 62-69, 1987). For a temperature of $50^{\circ} \mathrm{F}$, a value of 248 atm is calculated.


FIGURE 11.3 $x-y$ operating diagram for Example 11.4.

For operation at 1 atm , accordingly, the equilibrium line is a straight line of slope 248 as shown in Fig. 11.3.
2. Locate the operating line for minimum gas-phase molar flow rate, $\boldsymbol{G}_{\boldsymbol{M}}$. Because this system is dilute, the operating line will be straight. At the bottom of the tower, the concentration of TCE in the air coming into the tower may be assumed to be zero. The liquid mole fraction at $5 \mathrm{ppb}, x_{1}$ is $\left(5 \mathrm{lb} / 10^{9} \mathrm{lb}\right)(18 / 132)$, or $6.85 \times 10^{-10}$. This places the coordinates for the bottom of the operating line very close to the origin of the $x-y$ operating diagram. (For stripping, the operating line lies below the equilibrium line. For absorption, as seen in the preceding example, it lies above the equilibrium line.) The liquid mole fraction at the top of the tower $x_{2}$ is $1.37 \times 10^{-5}$ as calculated in step 1.

The maximum slope of the operating line occurs when one end of it (in this case the top) intersects the equilibrium line. From Eq. (11.10), $y_{2}=(248)\left(1.37 \times 10^{-5}\right)$, or 0.00340 . If we use these coordinates in Eq. (11.12), the maximum slope of the operating line is essentially the same as the slope of the equilibrium line, 248 . Since the liquid-phase molar flow rate $L_{M}$ is constant for this example, the maximum operating-line slope defines the minimum value of $G_{M}$.
3. Locate the operating line. The actual gas loading is to be four times the minimum value. Thus, the slope of the operating line is one-fourth that of the operating line of maximum slope, or essentially one-fourth that of the equilibrium line. Thus, $L_{M} / G_{M}=248 / 4=62$. By Eq. (11.12) with $y_{1}=0$, we calculate $y_{2}$ as $(62)\left(1.37 \times 10^{-5}-6.85 \times 10^{-10}\right)$, or $8.49 \times 10^{-4}$. Connect the coordinates at the bottom and the top of the tower ( $x_{1}, y_{1}$ and $x_{2}, y_{2}$, respectively) with a straight line to give the operating line as shown in Fig. 11.3.
4. Calculate the gas and liquid loadings and the tower diameter. Use Eq. (11.1) with $C_{V F}=C_{V} / f$ and $C_{L F}=C_{L}$ where $f$ is the fractional approach to flooding, defined at constant liquid loading for this example. Express $C_{L}$ in terms of $C_{V}$ using Eq. (11.14). With $L_{M} / G_{M}=62, \rho_{l}=62.4 \mathrm{lb} / \mathrm{ft}^{3}$, and $\rho_{g}=0.0778 \mathrm{lb} / \mathrm{ft}^{3}$, Eq. (11.14) gives $C_{L} / C_{V}=611(\mathrm{gal} \cdot \mathrm{s}) /(\mathrm{min})\left(\mathrm{ft}^{3}\right)$.

Values of $s$ and $c$ for 2-in slotted rings in polypropylene may be obtained from the packing vendor or may be determined from air-water pressure-drop curves for the packing. The values are 0.042 and 0.72 , respectively, in the units of Table 11.1. (Note that these values for polypropylene packing are close to the corresponding values for the same size of stainless steel packing in Table 11.1.) Substituting these values into Eq. (11.1) (as in step 4 of the previous example) gives

$$
\left(C_{V} / 0.3\right)^{1 / 2}+0.042\left(611 C_{V}\right)^{1 / 2}=0.72
$$

from which $C_{V}=0.0632 \mathrm{ft} / \mathrm{s}$. And $C_{L}=611 C_{V}=38.6 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{2}\right)$. From the definition of the capacity factors and $F$ factor, other measures of the gas and liquid throughput may be given as $F_{S}=0.499(\mathrm{ft} / \mathrm{s})\left(\mathrm{lb} / \mathrm{ft}^{3}\right)^{1 / 2}, U_{g}=1.79 \mathrm{ft} / \mathrm{s}$, and $U_{L}=38.6 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{2}\right)$.

Determine the tower diameter from the given flow rate and the liquid loading calculated above. The tower area is $(700 \mathrm{gal} / \mathrm{min}) /\left[38.6 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{2}\right)\right]=18.1 \mathrm{ft}^{2}$. The tower diameter $D$ is $[(18.1)(4) / \pi]^{1 / 2}=4.8 \mathrm{ft}$.
5. Determine the HTU values for the liquid and gas resistances. Determining the values of $H_{l}$ and $H_{g}$ to use is usually the most uncertain part of absorption and stripping calculations. Values can often be obtained from the packing vendors. Generalized correlations are available in the literature, but these may not always give reliable results for aqueous systems. Published data on absorption or stripping of highly or sparingly soluble gases such as ammonia and carbon dioxide can be used, with appropriate adjustments. This method is illustrated in Example 11.6, where the following values are calculated for the conditions of this present example: $H_{l}=3.48 \mathrm{ft}$, and $H_{g}=$ 0.54 ft .
6. Determine the controlling resistance to mass transfer. The controlling resistance is determined from the ratio of the gas to the liquid driving force given by Eq. (11.19). From Eq. (11.17), $\lambda=248 / 62=4.0$. With the HTUs from step 5, Eq. (11.19) gives $R_{D F}=0.54 /(4.0)(3.48)=0.039$. Because $R_{D F}$ is less than 1, the major resistance to mass transfer is on the liquid side of the interface. In this case, 96 percent of the resistance is in the liquid. Therefore, the best precision in the calculation of packing height will be obtained by using liquid film transfer units $N_{l}$ or $N_{o l}$.
7. Calculate the number of transfer units. For dilute systems in which the equilibrium and operating lines are both straight, the equations for the number of individual liquid-phase transfer units $N_{l}$
and the number of overall liquid-phase transfer units $N_{o l}$ are

$$
\begin{align*}
& N_{l}=\frac{1+R_{D F}}{1-(1 / \lambda)} \ln \left\{\left(1-\frac{1}{\lambda}\right)\left[\frac{x_{2}-\left(y_{1} / m\right)}{x_{1}-\left(y_{1} / m\right)}\right]+\frac{1}{\lambda}\right\} \\
& N_{o l}=\frac{1}{1-(1 / \lambda)} \ln \left\{\left(1-\frac{1}{\lambda}\right)\left[\frac{x_{2}-\left(y_{1} / m\right)}{x_{1}-\left(y_{1} / m\right)}\right]+\frac{1}{\lambda}\right\} \tag{11.27}
\end{align*}
$$

Substituting the appropriate values into these equations gives

$$
\begin{aligned}
& N_{l}=\frac{1+0.039}{1-(1 / 4.0)} \ln \left[\left(1-\frac{1}{4.0}\right)\left(\frac{1.37 \times 10^{-5}-0}{6.85 \times 10^{-10}-0}\right)+\frac{1}{4.0}\right]=13.32 \\
& N_{o l}=\frac{1}{1-(1 / 4.0)} \ln \left[\left(1-\frac{1}{4.0}\right)\left(\frac{1.37 \times 10^{-5}-0}{6.85 \times 10^{-10}-0}\right)+\frac{1}{4.0}\right]=12.82
\end{aligned}
$$

8. Calculate the height of packing required. Based on individual liquid-transfer units, $Z=$ $H_{l} N_{l}=(3.48 \mathrm{ftt})(13.32)=46.3 \mathrm{ft}$. Based on overall liquid transfer units, $Z=H_{o l} N_{o l}$. The height of an overall transfer unit based on the liquid resistance is calculated as follows:

$$
\begin{equation*}
H_{o l}=H_{l}+H_{g} / \lambda \tag{11.28}
\end{equation*}
$$

From this equation, $H_{o l}=3.48+(0.54 / 4.0)=3.615 \mathrm{ft}$, and $Z=(3.615 \mathrm{ft})(12.82)=46.3 \mathrm{ft}$.
Related Calculation. When the equilibrium and/or operating lines are curved, Eqs. (11.27) and (11.28) do not apply exactly. In this case, it is necessary to base the design on the individual number of transfer units for the liquid resistance and integrate graphically to determine $N_{l}$. This is illustrated in the following example.

### 11.5 PACKED HEIGHT FOR ABSORPTION WITH CURVED EQUILIBRIUM AND OPERATING LINES

An air stream containing $30 \%$ ammonia is to be contacted with a water stream containing $0.1 \%$ ammonia by weight (thus its mole fraction $x_{2}$ is 0.00106 ) in a tower packed with 2-in stainless steel Flexing (FR) random packing. The air leaving the tower is to contain $1 \%$ ammonia. The tower is to be designed to operate at $80 \%$ of flood defined at constant liquid-to-gas ratio $L / G$, and this ratio is to be twice the minimum value. Although significant heat effects would normally occur for this absorption, assume isothermal operation at $80^{\circ} \mathrm{F}$ and 1 atm total pressure.

## Procedure

1. Construct the equilibrium line. Equilibrium data for this system are given in Perry's Chemical Engineers' Handbook, 4th ed., p. 14.4, McGraw-Hill, New York (1963). From the data given, calculate values of $y$ at temperatures of $10,20,30$, and $40^{\circ} \mathrm{C}$ for a particular range of $x$ values. For a particular $x$, fit the values of $y$ to a regression equation of the form of Eq. (11.9) [i.e., $\log y=A+(B / T)$ ], and calculate the $y$ value at $80^{\circ} \mathrm{F}\left(26.7^{\circ} \mathrm{C}\right)$. The equilibrium data interpolated in this way to $80^{\circ} \mathrm{F}$ are plotted to give the equilibrium line in Fig. 11.4. Henry's law is shown by the short dashed line in this figure. There is good agreement between the equilibrium curve and Henry's law below a liquid mole fraction of about 0.03 but increasing divergence as concentration increases above this value.


FIGURE $11.4 \quad x-y$ operating diagram for Example 11.5.
2. Construct the limiting operating line. For concentrated solutions, significant changes will occur in the molar fluxes of gas and liquid. Therefore, base the material balance around the tower on the molar fluxes of the ammonia-free water and the ammonia-free air, $L_{M}^{\prime}$ and $G_{M}^{\prime}$, respectively. Typical units are pound-moles of water (or air) per square foot second. The material balance then becomes

$$
\begin{equation*}
L_{M}^{\prime}\left(\frac{x_{1}}{1-x_{1}}-\frac{x_{2}}{1-x_{2}}\right)=G_{M}^{\prime}\left(\frac{y_{1}}{1-y_{1}}-\frac{y_{2}}{1-y_{2}}\right) \tag{11.29}
\end{equation*}
$$

The unknowns in this equation are $L_{M}^{\prime}, G_{M}^{\prime}$, and $x_{1}$. The limiting operating line is that which just touches the equilibrium line at the conditions corresponding to the bottom of the tower. From Fig. 11.4, $x_{1}$ is determined to be 0.177 from the equilibrium curve at $y_{1}=0.30$. Equation (11.29) is then solved for $L_{M}^{\prime} / G_{M}^{\prime}$, and the values for the liquid and gas mole fractions are entered to give $\left(L_{M}^{\prime} / G_{M}^{\prime}\right)_{\min }=1.955$.

It is not essential to actually construct the limiting operating line on the operating diagram. If desired, it can be constructed as shown below for the actual operating line, except that $\left(L_{M}^{\prime} / G_{M}^{\prime}\right)_{\min }$ is used rather than $L_{M}^{\prime} / G_{M}^{\prime}$.
3. Construct the actual operating line. The actual $L / G$ is specified to be two times the minimum $L / G$. Therefore, $L_{M}^{\prime} / G_{M}^{\prime}=2\left(L_{M}^{\prime} / G_{M}^{\prime}\right)_{\min }=(2)(1.955)=3.91$. Since the operating line is curved, corresponding values of $x$ and $y$ are needed at various heights between the top and bottom of the packing. These are determined by making a material balance around the top (or bottom) of the packing, where $x$ and $y$ are the mole fractions leaving the material balance control volume at some point in the bed. Equation (11.29) then becomes

$$
\begin{equation*}
\frac{y}{1-y}=\frac{L_{M}^{\prime}}{G_{M}^{\prime}}\left(\frac{x}{1-x}-\frac{x_{2}}{1-x_{2}}\right)+\frac{y_{2}}{1-y_{2}}=3.91\left(\frac{x}{1-x}-0.00106\right)+0.0101 \tag{11.30}
\end{equation*}
$$

Select various values of $x$ between $x_{1}$ and $x_{2}$, substitute into Eq. (11.30), and solve for the corresponding values of $y$. Plot these values on the $x-y$ operating diagram and draw a smooth curve through the points to give the operating line shown in Fig. 11.4. Application of Eq. (11.30) for $y=y_{1}$ gives $x_{1}=0.0975$ for the mole fraction of ammonia in the liquid leaving the tower. This defines the end of the operating line.
4. Determine the gas and liquid loadings at the bottom and top of the tower. The maximum loadings will occur at the bottom of the tower, where the approach to flooding is specified to be 80 percent defined at constant $L / G$. In order to apply Eq. (11.1), the gas and liquid densities must be determined, and the ratio of $C_{L} / C_{V}$ must be related to $L_{M}^{\prime} / G_{M}^{\prime}$. From the average molecular weight of the gas entering the tower (25.38) and the ideal-gas law, the gas density is $0.0644 \mathrm{lb} / \mathrm{ft}^{3}$. From the concentration of ammonia in the liquid leaving the tower and from published data for specific gravity of aqueous ammonia solutions, the liquid density is $59.9 \mathrm{lb} / \mathrm{ft}^{3}$.

The value of $L_{M} / G_{M}$ at the bottom of the tower is given by

$$
L_{M} / G_{M}=\left(L_{M}^{\prime} / G_{M}^{\prime}\right)\left(1-y_{1}\right) /\left(1-x_{1}\right)=(3.91)(1-0.30) /(1-0.0975)=3.03
$$

The ratio of $C_{L}$ to $C_{V}$ is given by Eq. (11.14), with the average molecular weight of the liquid equal to 17.92 and the average molecular weight of the gas equal to 25.38 . Substituting the appropriate values into Eq. (11.14) gives $C_{L} / C_{V}=31.5(\mathrm{gal} \cdot \mathrm{s}) /(\mathrm{min})\left(\mathrm{ft}^{3}\right)$.

In Eq. (11.1), $C_{V F}=C_{V} / f$ and $C_{L F}=C_{L} / f$. The values of $c$ and $s$ for 2-in Flexiring packing are 0.74 and 0.040 , respectively (see Table 11.1). Substituting these values into Eq. (11.1) gives $\left(C_{V} / 0.80\right)^{1 / 2}+0.040\left(31.5 C_{V} / 0.80\right)^{1 / 2}=0.74$. This gives $C_{V}=0.292 \mathrm{ft} / \mathrm{s}$ and $C_{L}=31.5 C_{V}=$ $9.20 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{2}\right)$. The loadings at the bottom of the tower in other units are calculated from the defining equations as $F_{S}=2.26(\mathrm{ft} / \mathrm{s})\left(\mathrm{lb} / \mathrm{ft}^{3}\right)^{1 / 2}, U_{g}=8.90 \mathrm{ft} / \mathrm{s}, U_{L}=9.20 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{2}\right)$, and $U_{l}=$ $0.0205 \mathrm{ft} / \mathrm{s}$.

Calculate the loadings at the top of the tower from the loadings at the bottom of the tower:

$$
\begin{gathered}
U_{g t}=U_{g b} \frac{1-y_{1}}{1-y_{2}}=8.90 \frac{(1-0.3)}{(1-0.01)}=6.29 \mathrm{ft} / \mathrm{s} \\
U_{l t}=U_{l b} \frac{\rho_{l b}}{M_{w l b}} \frac{\left(1-x_{1}\right)}{\left(1-x_{2}\right)} \frac{M_{w l t}}{\rho_{l t}}=0.0205\left(\frac{59.9}{17.9}\right)\left(\frac{1-0.0975}{1-0.00106}\right)\left(\frac{18.02}{62.2}\right)=0.01796 \mathrm{ft} / \mathrm{s}
\end{gathered}
$$

where the subscripts $t$ and $b$ refer to the top and bottom of the tower, respectively, and the 18.02 and 62.2 are the molecular weight and density of the liquid at the top of the tower. In terms of other units for loading, the $F$ factor at the top is $(6.29)(0.0732)^{1 / 2}=1.70(\mathrm{ft} / \mathrm{s})\left(\mathrm{lb} / \mathrm{ft}^{3}\right)^{1 / 2}$ and $U_{L}=$ $(0.01796)(7.48)(60)=8.06 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{2}\right)$. (Note that the superficial velocity in feet per second is equivalent to the volumetric flux in cubic feet per square foot-second.)
5. Determine the individual HTUs for the liquid and gas resistances at the bottom and top of the tower. Vendor data for carbon dioxide desorption from water for 2-in FR packing, when corrected to the temperature and system physical properties for this example, give $H_{l b}=0.83 \mathrm{ft}$ and $H_{l t}=0.80 \mathrm{ft}$.

Vendor data for ammonia absorption into water for 2-in FR packing, when corrected for temperature, give $H_{g b}=1.42 \mathrm{ft}$ and $H_{g t}=1.25 \mathrm{ft}$.

The values of $H_{l}$ at bottom and top and $H_{g}$ at bottom and top are close enough to permit the use of average values. The average values are $H_{l}=0.82 \mathrm{ft}$ and $H_{g}=1.34 \mathrm{ft}$.
6. Construct the tie lines. The tie line slope (TLS) is established using procedures similar to those in Example 3. Equations (11.15) and (11.16) also apply to concentrated systems. For such systems, however, $k_{g} \alpha$ and $k_{l} \alpha$ are inversely proportional to $y_{B M}$ and $x_{B M}$, respectively, which are the log mean mole fractions, between bulk and interface, of the nondiffusing component (air or water, respectively).

For concentrated systems, $y_{B M}$ and $x_{B M}$ can vary considerably across the tower. Therefore, in Eq. (11.21) the numerator and denominator are multiplied by $y_{B M}$. The first term under the integral is $H_{g}$ for concentrated systems. This term is theoretically independent of concentration and pressure and is equal to the $H_{g}$ for dilute systems, for which $y_{B M}$ equals 1 as pointed out in Example 3. The variation of $y_{B M}$ is included in the second term of Eq. (11.21), which integrates to $N_{g}$ for concentrated systems.

When the loadings at the top and bottom of the tower are such that the value of $H_{g}$ for dilute systems does not vary appreciably over the tower, as in this example, the first term under the integral of Eq. (11.21) can be considered to be constant at its average value and can be removed from the integral. The equations for a concentrated system are

$$
\begin{gather*}
Z=H_{g} N_{g} \\
H_{g}=\frac{U_{g}}{k_{g} a y_{B M}} \quad H_{l}=\frac{U_{l}}{k_{i} a x_{B M}} \\
N_{g}=\int_{y_{2}}^{y_{1}} \frac{y_{B M} d y}{(1-y)\left(y-y_{i}\right)}  \tag{11.31}\\
\mathrm{TLS}=-\frac{k_{l} a \rho_{M l}}{k_{g} a(P / R T)}=-\frac{H_{g}}{H_{l}} \frac{L_{M}}{G_{M}} \frac{y_{B M}}{x_{B M}}=-\frac{H_{g}}{H_{l}} \frac{L_{M}^{\prime}}{G_{M}^{\prime}} \frac{(1-y)}{(1-x)} \frac{y_{B M}}{x_{B M}} \\
y_{B M}=\frac{(1-y)-\left(1-y_{i}\right)}{\ln \left(\frac{1-y}{1-y_{i}}\right)} \quad x_{B M}=\frac{(1-x)-\left(1-x_{i}\right)}{\ln \left(\frac{1-x}{1-x_{i}}\right)}
\end{gather*}
$$

In applying these equations, it is helpful to remember that the $H_{g}$ for concentrated systems is the same as that for dilute systems at the same gas and liquid loadings. It is the $k_{g} a$ that varies with concentration and requires the introduction of $y_{B M}$ to keep $H_{g}$ constant.

Tie lines tie together corresponding concentrations on the operating line (bulk concentrations) and the equilibrium line (interfacial concentrations). The tie line slope is determined from the final equality for TLS in Eq. (11.31). The values of $H_{g}$ and $H_{l}$ are the average values determined in step 5 $\left(1.34 \mathrm{ft}\right.$ and 0.82 ft , respectively). The value of $L_{M}^{\prime} / G_{M}^{\prime}$ was determined in step 3 (3.91). Various tie lines are to be constructed over the entire concentration range covered by the operating line. A particular tie line will cross the operating line at $x$ and $y$, the values of which are used in Eq. (11.31) to calculate $y_{B M}$ and $x_{B M}$, and in the equation for TLS.

Unfortunately, the equations cannot be solved explicitly, because the equations for $y_{B M}$ and $x_{B M}$ contain the interfacial concentrations, which are unknown until the tie line slope is established. A
trial-and-error procedure is required to construct the tie lines. The procedure is illustrated here for the tie line that intersects the operating line at $y=0.20$ :

1. Locate $y$ on the operating line: $y=0.20$.
2. Determine $x$ from the operating line or from the material balance, Eq. (11.29): $x=0.059$.
3. Estimate the tie line slope assuming $y_{B M} / x_{B M}=1$. Thus, $\operatorname{TLS}_{1}=-(1.34 / 0.82)(3.91)(1-$ $0.20) /(1-0.059)=-5.43$.
4. Draw the estimated tie line on the operating diagram.
5. At the intersection of the estimated tie line and the equilibrium line, determine the estimated interfacial concentrations: $y_{i 1}=0.096$ and $x_{i 1}=0.078$.
6. Calculate the estimated values of $y_{B M}$ and $x_{B M}$. Thus, $y_{B M 1}=[(1-0.20)-(1-0.096)] / \ln [(1-$ $0.20) /(1-0.096)]=0.851$. Similarly, $x_{B M 1}=0.931$.
7. Calculate the second-iteration tie line slope. Thus, $\mathrm{TLS}_{2}=-(1.34 / 0.82)(3.91)[(1-0.20) /(1-$ $0.059)][(0.851) /(0.931)]=-4.96$.
8. Repeat steps 4 through 7 until there is no further change in the tie line slope. For this case, the third iteration gives no further change and accordingly the slope is -4.96 .
9. Draw the final tie line on the operating diagram. Slope $=-4.96$ passing through $y=0.20, x=$ 0.059. See Fig. 11.4.

This procedure is repeated at various intervals along the operating line. The more tie lines that are constructed, the more accurate the integration to determine $N_{g}$. Figure 11.4 shows 4 of the 20 tie lines constructed for the solution of this example.
7. Determine the controlling resistance for mass transfer. For concentrated solutions, the ratio of the gas-phase driving force to that in the liquid phase in equivalent concentration units is

$$
\begin{equation*}
R_{D F}=\left(H_{g} / \lambda H_{l}\right)\left(y_{B M} / x_{B M}\right) \tag{11.32}
\end{equation*}
$$

This differs from Eq. (11.19) for dilute solutions only by the ratio of $y_{B M}$ to $x_{B M}$. Based on the average values, $H_{g} / H_{l}=1.34 / 0.82=1.634$. Values of the other quantities in Eq. (11.32) vary over the tower. $\lambda$ is the ratio of the slope of the equilibrium line to that of the operating line. Values of $\lambda$ can be obtained directly from the operating diagram by determining the slope of the operating line at one end of a particular tie line and the slope of the equilibrium line at the other end of the same tie line. Values of $x_{B M}$ and $y_{B M}$ can be determined with the values of $x$ and $x_{i}$ and $y$ and $y_{i}$ at either end of the same tie line.

At the bottom of the tower, the slope of the operating line is 2.48 and the slope of the equilibrium line (determined at the point where it intersects a tie line of slope -4.24 ) is $1.98, y_{B M}$ is 0.76 , and $x_{B M}$ is 0.89 . Accordingly, $R_{D F b}=(1.634)(2.48 / 1.98)(0.76 / 0.89)=1.75$. Using the corresponding values at the top of the tower gives $R_{D F t}=5.90$. As these values are both greater than 1 , the gas phase provides the major resistance to mass transfer throughout the tower. Therefore, using $N_{g}$ to calculate the number of transfer units in the tower will give the greater precision.
8. Calculate the number of transfer units by graphic integration. From Eq. (11.31), $N_{g}$ is equal to the area under a plot of $f(y)$ vs. $y$ between the limits of $y_{2}$ and $y_{1}$ where $f(y)$ is $y_{B M} /\left[(1-y)\left(y-y_{i}\right)\right]$. For each point of intersection between the operating line and a tie line, $f(y)$ is calculated and plotted against $y$. The plot is shown in Fig. 11.5. The area under the curve from $y_{2}=0.01$ to $y_{1}=0.30$ is 5.74.
9. Calculate the height of packing. The height of packing is $Z=H_{g} N_{g}=(1.34 \mathrm{ft})(5.74)=7.7 \mathrm{ft}$.


FIGURE 11.5 Graphic integration to determine number of transfer units for Example 11.5.

### 11.6 DETERMINING HTUs FOR AIR STRIPPING FROM DATA ON MODEL SYSTEMS

Determine the $H_{l}$ and $H_{g}$ to be used in Example 11.4 from data published for 2-in Pall rings on carbon dioxide stripping from $23^{\circ} \mathrm{C}$ water and on ammonia absorption into $20^{\circ} \mathrm{C}$ water. (See R. Billet and J. Mackowiak, Chem. Eng. Technol. 11:213-227, 1988.)

## Calculation Procedure

1. Determine $H_{l}$ for the model system at an equivalent liquid loading. Below the load point, $H_{l}$ is insensitive to the gas loading. Therefore, $H_{l}$ can be correlated as a function of liquid loading only. For the packing of interest, the published data show a linear log-log relationship between $k_{l} \alpha$ and the volumetric liquid loading. This relationship can be described by the equation $k_{l} \alpha=0.360$ $U_{l}^{0.81}$, where $k_{l} \alpha$ is the mass transfer coefficient in $s^{-1}$ and $U_{l}$ is the superficial liquid velocity in feet per second (or equivalently, the superficial liquid flux in cubic feet per square foot-second). Since $H_{l}=U_{l} / k_{l} \alpha$, the equation for $H_{l}$ becomes $H_{l}=2.78 U_{l}^{0.19}$, where $H_{l}$ is in feet and $U_{l}$ is in feet per second. For the liquid loading of Example 11.4, $U_{l}=0.086 \mathrm{ft} / \mathrm{s}\left(U_{L}=38.6 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{2}\right)\right.$ and $H_{l}=2.78(0.086)^{0.19}=1.74 \mathrm{ft}$. This is the value of $H_{l}$ for air stripping carbon dioxide from $23^{\circ} \mathrm{C}$ water at the given liquid loading.
2. Correct the $H_{l}$ to the actual system physical properties. The value of $H_{l}$ is corrected from the model system to the actual system via the relationship that $H_{l}$ is proportional to the square root of the Schmidt number ( $\mathrm{Sc}=\mu / \rho \mathcal{D}$, where $\mu$ is viscosity, $\rho$ is density, and $\mathcal{D}$ is diffusion coefficient).

The quantities required for the Schmidt number are as follows. For the carbon dioxide-water system $\left(\mathrm{CO}_{2}-\mathrm{H}_{2} \mathrm{O}\right)$ at $23^{\circ} \mathrm{C}$,

$$
\mu=0.936 \mathrm{cP} \quad \rho=62.4 \mathrm{lb} / \mathrm{ft}^{3} \quad \mathcal{D}=1.83 \times 10^{-5} \mathrm{~cm}^{2} / \mathrm{s}
$$

For the trichloroethylene-water system $\left(\mathrm{TCE}-\mathrm{H}_{2} \mathrm{O}\right)$ at $50^{\circ} \mathrm{F}$,

$$
\begin{gathered}
\mu=1.31 \mathrm{cP} \quad \rho=62.4 \mathrm{lb} / \mathrm{ft}^{3} \quad \mathcal{D}=6.4 \times 10^{-6} \mathrm{~cm}^{2} / \mathrm{s} \\
\frac{\left(H_{l}\right)_{\mathrm{TCE}-\mathrm{H}_{2} \mathrm{O}}}{\left(H_{l}\right)_{\mathrm{CO}_{2}-\mathrm{H}_{2} \mathrm{O}}}=\left[\frac{\left(\frac{\mu}{\rho \mathcal{D}}\right)_{\mathrm{TCE}-\mathrm{H}_{2} \mathrm{O}}}{\left(\frac{\mu}{\rho \mathcal{D}}\right)_{\mathrm{CO}_{2}-\mathrm{H}_{2} \mathrm{O}}}\right]=\left[\frac{(1.31)}{(0.936)} \frac{\left(1.83 \times 10^{-5}\right)}{\left(6.4 \times 10^{-6}\right)}\right]^{1 / 2}=2.0
\end{gathered}
$$

Therefore, the value of $H_{l}$ for trichloroethylene-water is $(1.74 \mathrm{ft})(2.0)=3.48 \mathrm{ft}$.
3. Determine the value of $H_{g}$ for the model system at equivalent loadings. Determination of $H_{g}$ is somewhat more complicated, because the cited reference gives $H_{o g}$ rather than $H_{g}$ and these both depend on both the gas and liquid loadings. The data indicate that $H_{o g}$ is proportional to $U_{l}^{-0.48}$ and to $F_{s}^{0.38}$. For Example 11.4, the $F$ factor is essentially $0.50(\mathrm{ft} / \mathrm{s})\left(\mathrm{lb} / \mathrm{ft}^{3}\right)^{1 / 2}$. For this $F$ factor, the cited reference gives $H_{o g}$ as 0.80 ft . This value is for the ammonia-air-water system at $20^{\circ} \mathrm{C}$ and a liquid loading of $6.14 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{2}\right)$. Correcting this value to the proper liquid loading gives $H_{\text {og }}=(0.80 \mathrm{ft})(38.6 / 6.14)^{-0.48}=0.33 \mathrm{ft}$.
$H_{g}$ and $H_{o g}$ are related by the equation $H_{o g}=H_{g}+\lambda H_{l}$, where $\lambda$ is the ratio of the slope of the equilibrium line to that of the operating line, as discussed in Example 11.3, step 6. For the ammonia-air-water system at 293 K , Eq. (11.9) in Example 11.3 gives $\mathrm{He}=0.77 \mathrm{~atm}$. From Eq. (11.11) of Example 11.3, the slope of the equilibrium line $m$ is $\mathrm{He} / \mathrm{P}$, i.e., 0.77 . From Example $11.4, L_{M} / G_{M}=$ 62. Accordingly, $\lambda=(0.77 / 62)=0.0124$. The value of $H_{l}$ determined in step 1 is 1.74 ft for the carbon dioxide-water system at $23^{\circ} \mathrm{C}$. This value is corrected to the ammonia-water system at $20^{\circ} \mathrm{C}$ by using the square root of the Schmidt-number ratio. The values for the Schmidt number for the carbon dioxide-water system are given in step 2 . For the ammonia-water system at $20^{\circ} \mathrm{C}, \mu=$ $1.005 \mathrm{cP}, \rho=62.4 \mathrm{lb} / \mathrm{ft}^{3}$, and $\mathcal{D}=2.06 \times 10^{-5} \mathrm{~cm}^{2} / \mathrm{s}$. The value of $H_{l}$ for the ammonia-water system is $[1.74 \mathrm{ft}]\left[(1.005 / 0.936)\left(1.83 \times 10^{-5} / 2.06 \times 10^{-5}\right)\right]^{1 / 2}=1.70 \mathrm{ft}$. Then, $H_{g}=H_{o g}-\lambda H_{l}=$ $0.33-(0.0124)(1.70)=0.31 \mathrm{ft}$.
4. Correct $\boldsymbol{H}_{g}$ to the actual system properties. The $H_{g}$ for the model system is corrected to that for the actual system using the relationship that $H_{g}$ is proportional to the square root of the Schmidt number. The values are as follows. For ammonia-air at $20^{\circ} \mathrm{C}$,

$$
\begin{aligned}
\mu & =0.018 \mathrm{cP} \\
\rho & =0.0752 \mathrm{lb} / \mathrm{ft}^{3} \\
\mathcal{D} & =0.222 \mathrm{~cm}^{2} / \mathrm{s}
\end{aligned}
$$

For trichloroethylene-air at $50^{\circ} \mathrm{F}$,

$$
\begin{aligned}
\mu & =0.018 \mathrm{cP} \\
\rho & =0.0778 \mathrm{lb} / \mathrm{ft}^{3} \\
\mathcal{D} & =0.070 \mathrm{~cm}^{2} / \mathrm{s}
\end{aligned}
$$

The value of $H_{g}$ for the actual system is, accordingly,

$$
H_{g}=[0.31 \mathrm{ft}][(0.0752 / 0.0778)(0.222 / 0.070)]^{1 / 2}=0.54 \mathrm{ft}
$$

### 11.7 PACKED HEIGHT FOR ABSORPTION WITH EFFECTIVELY INSTANTANEOUS IRREVERSIBLE CHEMICAL REACTION

A tower packed with Flexipac Type 2Y structured packing (FP2Y) is to be used to remove $99.5 \%$ of the ammonia from an air stream containing an ammonia mole fraction $\left(y_{1}\right)$ of 0.005 . The tower is to operate isothermally at $100^{\circ} \mathrm{F}$ and 1 atm . The ammonia is to be absorbed in an aqueous solution of nitric acid. The tower diameter has been selected to give an $F$ factor of $2.0(\mathrm{ft} / \mathrm{s})\left(\mathrm{lb} / \mathrm{ft}^{3}\right)^{1 / 2}$ and a liquid loading of $15 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{2}\right)$. The density of the air stream is $0.0709 \mathrm{lb} / \mathrm{ft}^{3}$, and that of the water is $62.0 \mathrm{lb} / \mathrm{ft}^{3}$. What concentration of acid should be used to ensure that the maximum absorption rate is obtained throughout the entire tower? Compare the height of packing required for absorption with chemical reaction to that for physical absorption.

## Calculation Procedure

1. Identify the reaction and estimate its rate and reversibility. The absorption of ammonia with the liquid phase reaction between dissolved ammonia and a strong acid can be represented by

$$
\begin{gathered}
\mathrm{NH}_{3}(g) \longleftrightarrow \mathrm{NH}_{3}(a q) \\
\mathrm{NH}_{3}(a q)+\mathrm{H}^{+} \longleftrightarrow \mathrm{NH}_{4}^{+}
\end{gathered}
$$

In general, reactions that consist simply of the transfer of hydrogen ions can be considered to occur "instantaneously." Accordingly, the reaction rate in this example will be considered instantaneous.

All reactions are, to some extent, reversible. This is particularly true of ionic reactions that occur in aqueous solution, as is the case here. The designation of a reaction as "irreversible" (as in this example) is not to say that the reaction cannot proceed in the reverse direction. Rather, it signifies that under the conditions of the absorption, the equilibrium lies strongly in favor of the reaction products.

The criterion for a reaction being effectively irreversible with respect to the absorption of a gas is that the concentration of the unreacted gas in the solution [e.g., $\mathrm{NH}_{3}(a q)$ ] is so small that its partial pressure at the interface is much less than the partial pressure of the absorbing gas [e.g., $\mathrm{NH}_{3}(g)$ ] in the gas phase. When this criterion is satisfied, the interfacial mole fraction of the absorbing gas $y_{i}$ can be considered to be zero. This obviates the need for an equilibrium line or an $x-y$ operating diagram.

The second reaction shown above will be shifted in favor of the product by a large equilibrium constant and by a sufficient concentration of hydrogen ion in solution. For now, the reaction will be assumed to be effectively irreversible, although this assumption will be checked in step 5 .
2. Determine the gas and liquid loadings. From the loadings given for this example and the densities of air and water, calculate the molar fluxes. The superficial gas velocity is (see Example 11.1, step 2) $U_{g}=F_{s} /\left(\rho_{g}\right)^{1 / 2}=2 /(0.0709)^{1 / 2}=7.51 \mathrm{ft} / \mathrm{s}$. The molar flux of gas is $G_{M}=U_{g}(P / R T)=(7.51)(1) /[(0.73)(560)]=0.0184(\mathrm{lb} \cdot \mathrm{mol}) /\left(\mathrm{ft}^{2}\right)(\mathrm{s})$. The molar flux of liquid is $L_{M}=U_{l} \rho_{M l}=(15)(62.0) /[(7.48)(60)(18)]=0.115(\mathrm{lb} \cdot \mathrm{mol}) /\left(\mathrm{ft}^{2}\right)(\mathrm{s})$. From these values, the liquid to gas ratio is $L_{M} / G_{M}=0.115 / 0.0184=6.25$.

Note that in the calculation of the liquid molar flux, we assume that the acid concentration is so low that we can use the molecular weight of water as the liquid molecular weight. This assumption later proves to be valid.
3. Determine the HTUs for the packing at the design conditions. When corrected to the design conditions of this example, vendor data on model systems for this packing give $H_{g}=0.84 \mathrm{ft} ; H_{l}=$ 0.58 ft .
4. Calculate the required concentration of absorbent. Enough nitric acid must be used to maximize the rate of absorption throughout the tower. As the acid concentration is increased, the reaction plane moves closer and closer to the interface until, at a particular concentration, the reaction plane coincides with the interface. When this condition prevails, the concentration of unreacted $\mathrm{NH}_{3}(\mathrm{aq})$ at the interface becomes zero, the absorption becomes completely limited by the gas film, and the rate of absorption is maximized because $y_{i}$ is also zero. When this condition prevails throughout the tower, the maximum rate of absorption will be obtained.

The rate of absorption is equal to the rate of mass transfer through the gas film at the interface, which, at steady state, is equal to the rate of mass transfer through the liquid film. (The results of the film theory are used here because of their simplicity and ease of use in engineering calculations.) The rate of absorption is given by

$$
\begin{equation*}
\bar{R} \mathrm{a}=k_{g} a(P / R T)\left(y-y_{i}\right)=k_{i} a \rho_{M l} x_{i}\left[1+\left(\mathcal{D}_{B} / z \mathcal{D}_{A}\right)\left(x_{B} / x_{i}\right)\right] \tag{11.33}
\end{equation*}
$$

where $\mathcal{D}_{B}=$ diffusion coefficient of reactant (e.g., $\mathrm{H}^{+}$) in solution
$\mathcal{D}_{A}=$ diffusion coefficient of dissolved gas (e.g., $\mathrm{NH}_{3}$ ) in solution
$\rho_{M l}=$ molar density, $\mathrm{mol} / \mathrm{ft}^{3}$
$z=$ number of moles of $B$ (e.g., $\mathrm{H}^{+}$) reacting with 1 mol of $A\left(\right.$ e.g., $\mathrm{NH}_{3}$ )
$x_{B}=$ mole fraction of reactant (e.g., $\mathrm{H}^{+}$) in bulk liquid.
Other mole fractions in Eq. (11.33) refer to the absorbing gas, as with previous notation. The term in parentheses on the right of Eq. (11.33) is the enhancement factor for chemical reaction in the liquid film. As $x_{B}$ increases, $x_{i}$ and $y_{i}$ decrease until they become effectively zero.

From Eq. (11.10), $x_{i}=y_{i} P / \mathrm{He}$. Substituting for $x_{i}$ in Eq. (11.33) and solving for $y_{i}$ gives

$$
\begin{equation*}
y_{i}=\frac{k_{g} a(P / R T) y-k_{l} a \rho_{M l} \frac{\mathcal{D}_{B} x_{B}}{\mathcal{D}_{A} z}}{k_{g} a(P / R T)+k_{l} a \rho_{M l}(P / \mathrm{He})} \tag{11.34}
\end{equation*}
$$

It is clear from Eq. (11.34) that $y_{i}$ will be zero if the second term in the numerator is greater than the first. This leads to the desired criterion for $x_{B}$ :

$$
x_{B} \geq \frac{H_{l}}{H_{g}} \frac{G_{M}}{L_{M}} \frac{\mathcal{D}_{A}}{\mathcal{D}_{B}} z y
$$

where Eq. (11.18), Example 11.3, has been used to convert from mass transfer coefficients to HTUs. The liquid-phase diffusion coefficients of $\mathrm{NH}_{3}$ and $\mathrm{H}^{+}$(actually $\mathrm{H}_{3} \mathrm{O}^{+}$) are approximately equal, and the value of $z$ is 1 . The maximum value of $y$ occurs at the bottom of the tower, where $y_{1}=0.005$. Therefore, the minimum value of $x_{B}$ that will maximize the rate of absorption is $x_{B}=(0.58 / 0.84)(0.005 / 6.25)=0.000552$.

This is the minimum concentration at the bottom of the tower. The concentration of nitric acid in the liquid feed to the top of the tower must be sufficient to react with all of the ammonia absorbed in addition to providing for $x_{B 1}$ to be 0.000552 . By material balance, the mole fraction of $\mathrm{H}^{+}$in the feed to the tower is $x_{B 2}=\left[\left(0.005-2.5 \times 10^{-5}\right) / 6.25\right]+0.000552=0.00135$. This mole fraction is converted to concentration by multiplying by the liquid molar density $[55.10(\mathrm{~g} \cdot \mathrm{~mol}) / \mathrm{L}]$ to give $[B]_{2}=0.0743$ $(\mathrm{g} \cdot \mathrm{mol}) / \mathrm{L}$, which corresponds to a pH of 1.13 . At the bottom of the tower, $[B]_{1}=0.0304(\mathrm{~g} \cdot \mathrm{~mol}) / \mathrm{L}$, which gives a pH of 1.52 .
5. Check the assumption of irreversibility. For dissociation of the ammonium ion,

$$
\begin{align*}
& \mathrm{NH}_{4}^{+} \longleftrightarrow \mathrm{H}^{+}+\mathrm{NH}_{3}(a q) \\
& K_{a}=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{NH}_{3}(a q)\right]}{\left[\mathrm{NH}_{4}^{+}\right]}=5.75 \times 10^{-10}(\mathrm{~g} \cdot \mathrm{~mol}) / \mathrm{L} \quad \text { at } 25^{\circ} \mathrm{C}  \tag{11.35}\\
& {\left[\mathrm{NH}_{3}(a q)\right] }=5.75 \times 10^{-10} \frac{\left[\mathrm{NH}_{4}^{+}\right]}{\left[\mathrm{H}^{+}\right]}
\end{align*}
$$

The concentrations of $\mathrm{NH}_{4}^{+}$and $\mathrm{H}^{+}$must be such that the concentration of ammonia calculated by Eq. (11.35) exerts a partial pressure which is negligible compared to the gas-phase partial pressure of ammonia. The minimum gas-phase partial pressure occurs at the top of the tower. The maximum concentration of $\mathrm{NH}_{4}^{+}$and the minimum concentration of $\mathrm{H}^{+}$occur at the bottom of the tower. From the concentrations calculated in step $4,\left[\mathrm{H}^{+}\right]=0.0304(\mathrm{~g} \cdot \mathrm{~mol}) / \mathrm{L}$ and $\left[\mathrm{NH}_{4}^{+}\right]=0.0742-0.0304=$ $0.0438(\mathrm{~g} \cdot \mathrm{~mol}) / \mathrm{L}$, and by Eq. (11.35), $\left[\mathrm{NH}_{3}(\mathrm{aq})\right]=8.28 \times 10^{-10}(\mathrm{~g} \cdot \mathrm{~mol}) / \mathrm{L}$. Dividing by the liquid molar density gives the mole fraction $x=8.28 \times 10^{-10} / 55.10=1.50 \times 10^{-11}$. From Eq. (11.10), with $\mathrm{He}=1.724 \mathrm{~atm}$ at $100^{\circ} \mathrm{F}$, this mole fraction is equivalent to a partial pressure $p$ of $(1.724)(1.50 \times$ $10^{-11}$ ) or $2.59 \times 10^{-11} \mathrm{~atm}$. This is clearly much less than the partial pressure at either the inlet $(0.005$ $\mathrm{atm})$ or the outlet $\left(2.5 \times 10^{-5} \mathrm{~atm}\right)$ of the tower. Therefore, the reaction is effectively irreversible.

The above calculation assumes that the liquid makes only a single pass through the tower. In practice, a more effective way of treating the gas would be to recirculate the liquid with a small feed of concentrated acid to the recirculation loop and a small bleed of the recirculation loop contents. This would permit the $\mathrm{NH}_{4}^{+}$concentration to build up in the recirculation loop. However, even if this concentration built up to the solubility limit of ammonium nitrate $\left(\mathrm{NH}_{4} \mathrm{NO}_{3}\right)$, about $30(\mathrm{~g} \cdot \mathrm{~mol}) / \mathrm{L}$, the partial pressure exerted by the dissolved ammonia at the top of the tower would still be nearly two orders of magnitude below the partial pressure of ammonia in the gas at the top of the tower. Therefore, for all practical conditions, the reaction is effectively irreversible, given the acid concentrations calculated in step 4.
6. Calculate the number of gas-phase transfer units. For dilute systems in which the interfacial mole fraction $y_{i}$ is kept at zero by virtue of the chemical reaction, the expression for $N_{g}$ from Eq. (11.22), Example 11.3, becomes

$$
N_{g}=\int_{y_{2}}^{y_{1}} \frac{d y}{y}=\ln \frac{y_{1}}{y_{2}}
$$

Substituting the appropriate values for $y$ gives

$$
N_{g}=\ln \left(0.005 / 2.5 \times 10^{-5}\right)=5.30
$$

7. Calculate the height of packing required. The height of packing required is $Z=H_{g} N_{g}=$ $(0.84 \mathrm{ft})(5.30)=4.45 \mathrm{ft}$.
8. Calculate the height of packing for physical absorption at the same conditions. At $100^{\circ} \mathrm{F}$, Eq. (11.9), Example 11.3, gives $\mathrm{He}=1.72 \mathrm{~atm}$. Equation (11.11) gives $m=1.72$. By Eq. (11.17), $\lambda=$ $1.72 / 6.25=0.275$. Equation (11.19) gives $R_{D F}=0.84 /[(0.275)(0.58)]=5.27$. And Eq. (11.23) for $N_{g}$ gives

$$
N_{g}=\frac{1+(1 / 5.27)}{1-0.275} \ln \left[(1-0.275)\left(\frac{0.0050-0}{2.5 \times 10^{-5}-0}\right)+0.275\right]=8.17
$$

The required height of packing is $Z=H_{g} N_{g}=(0.84 \mathrm{ft})(8.17)=6.86 \mathrm{ft}$. The same result is obtained with Eq. (11.24).

For this example, absorption with chemical reaction gives a 34 percent reduction in the height of the packing relative to absorption without chemical reaction.

## ABSORPTION AND STRIPPING

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12.1 POWER REQUIRED TO ROTATE AN AGITATOR IMPELLER 12.1
12.2 DESIGNING AN AGITATOR TO BLEND TWO LIQUIDS 12.3
12.3 TIME REQUIRED FOR UNIFORM BLENDING 12.8
12.4 HEAT TRANSFER IN AN AGITATED TANK 12.10
12.5 SCALE-UP FOR AGITATED SOLIDS SUSPENSION 12.12

### 12.6 AGITATOR DESIGN FOR GAS DISPERSION 12.14

### 12.7 SHAFT DESIGN FOR TURBINE

 AGITATOR 12.1712.8 VISCOSITY DETERMINATION FROM IMPELLER POWER 12.20
12.9 NONGEOMETRIC SCALEUP FOR LIQUID AGITATION 12.23 REFERENCES 12.29

### 12.1 POWER REQUIRED TO ROTATE AN AGITATOR IMPELLER

For a pitched-blade turbine impeller that is $58 \mathrm{in}(1.47 \mathrm{~m})$ in diameter and has four 12 -in-wide ( $0.305-\mathrm{m}$ ) blades mounted at a $45^{\circ}$ angle, determine the power required to operate the impeller at $84 \mathrm{r} / \mathrm{min}(1.4 \mathrm{r} / \mathrm{s})$ in a liquid with a specific gravity of $1.15\left(1150 \mathrm{~kg} / \mathrm{m}^{3}\right)$ and a viscosity of $12,000 \mathrm{cP}$ ( $12 \mathrm{~Pa} \cdot \mathrm{~s}$ ). What size standard electric motor should be used to drive an agitator using this impeller?

## Calculation Procedure

1. Determine the turbulent power number for impeller geometry. Power number $N_{P}$ is a dimensionless variable [5] which relates impeller power $P$ to such operating variables as liquid density $\rho$, agitator rotational speed $N$, and impeller diameter $D$ as follows:

$$
N_{P}=\frac{P}{\rho N^{3} D^{5}}
$$

A conversion factor (see below) is used when working with English engineering units; no factor is necessary for SI metric units. For a given impeller geometry, the power number is a constant for conditions of turbulent agitation. Values of turbulent power numbers for some agitator impellers are shown in Fig. 12.1.

The pitched-blade impeller described in this example is similar to the four-blade impeller shown in the figure, except that the blade width-to-diameter ratio $W / D$ is not exactly $1 / 5$. To correct for the effect of a nonstandard $W / D$ on a four-blade impeller, a factor of actual $W / D$ to standard $W / D$ raised to the 1.25 power must be applied to the standard turbulent power number $N_{P}=1.37$. Thus


FIGURE 12.1 Values of turbulent power number $N_{P}$ for various impeller geometries. Note: $W / D$ is actual blade-width-to-impeller-diameter ratio.
the turbulent power number for a 58 -in-diameter impeller with a 12 -in blade width is

$$
N_{P}=1.37[(12 / 58) / 1 / 5]^{1.25}=1.37(1.034)^{1.25}=1.43
$$

(The correction factor for nonstandard $W / D$ on a six-blade impeller is the actual $W / D$ to standard $W / D$ raised to the 1.0 power, or simply the ratio actual to standard $W / D$.)
2. Determine the power number at process and operating conditions. Turbulence in agitation can be quantified with respect to another dimensionless variable, the impeller Reynolds number. Although the Reynolds number used in agitation is analogous to that used in pipe flow, the definition of impeller Reynolds number and the values associated with turbulent and laminar conditions are different from those in pipe flow. Impeller Reynolds number $N_{\mathrm{Re}}$ is defined as

$$
N_{\mathrm{Re}}=\frac{D^{2} N \rho}{\mu}
$$

where $\mu$ is the liquid viscosity. In agitation, turbulent conditions exist for $N_{\mathrm{Re}}>20,000$ and laminar conditions exist for $N_{\mathrm{Re}}<10$.

Power number is a function of Reynolds number as well as impeller geometry. A correction factor based on $N_{\mathrm{Re}}$ accounts primarily for the effects of viscosity on power. The Reynolds number is computed from the definition found in the previous paragraph and the conditions given in the problem statement; a factor of 10.7 makes the value dimensionless when English engineering units are used:

$$
N_{\mathrm{Re}}=\frac{10.7 D^{2} N \rho}{\mu}=\frac{10.7(58)^{2}(84)(1.15)}{12,000}=290
$$

The viscosity power factor for $N_{\mathrm{Re}}=290$ is found to be 1.2 from Fig. 12.2. The power number for the impeller described in the example is the viscosity factor times the turbulent power number (from the previous step): $N_{P}=1.2(1.43)=1.72$.
3. Compute the shaft horsepower required to rotate the impeller. Horsepower requirements can be determined by rearranging the definition of power number into $P=N_{P} \rho N^{3} D^{5}$ and using the value of the power number determined in the previous step. The result must be divided by a factor of $1.524 \times 10^{13}$ to convert units and give an answer in horsepower: $P=1.72(1.15)(84)^{3}(58)^{5} /(1.524 \times$ $\left.10^{13}\right)=50.5 \mathrm{hp}(37.7 \mathrm{~kW})$.


FIGURE 12.2 Viscosity power factor as a function of impeller Reynolds number.
4. Select a standard motor horsepower. A typical turbine impeller-type agitator consists of a motor, a specially designed gear reducer, a shaft, and one or more impellers. Although losses through the gear reducer are typically only 3 to 8 percent, slight deviations in actual speed (which enters the power calculation cubed) and fluctuations in process conditions (density and viscosity) make motor loadings in excess of 85 percent of calculated impeller power unadvisable. Therefore, the calculated impeller power of 50.5 hp and a motor loading of 85 percent would indicate a minimum motor power: $P_{\text {motor }}=50.5 / 0.85=59.4$. The next larger commercially available motor is 60 hp (or for metric sizes, 45 kW ). Thus, a $60-\mathrm{hp}$ motor should be used on an agitator designed to operate the 58 -in-diameter impeller at $84 \mathrm{r} / \mathrm{min}$ as described in the example.

Related Calculations. Impeller power requirements are relatively independent of mixing-tank diameter. However, the power numbers shown in Fig. 12.1 assume fully baffled conditions, which for a cylindrical tank would require four equally spaced (at $90^{\circ}$ ) vertical plate-type baffles. The baffles should extend the full height of the vertical wall (i.e., the straight side) of the tank and should be one-twelfth to one-tenth the tank diameter in width.

For relatively high viscosities, the liquid itself prevents uncontrolled swirling. Therefore, when the liquid viscosity is greater than $5000 \mathrm{cP}(5 \mathrm{~Pa} \cdot \mathrm{~s})$, no baffles are required for most applications. For impellers located less than one impeller diameter from the bottom of the tank, an additional correction factor for the power number may be necessary [3].

The power number provides important design information about the correct motor size necessary to operate an impeller at a given speed. However, these calculations do not give any indication of whether or not the agitation produced is adequate for process requirements. The following example shows a method for determining the horsepower and speed required to achieve a given process result.

### 12.2 DESIGNING AN AGITATOR TO BLEND TWO LIQUIDS

A process requires the addition of a concentrated aqueous solution with a 1.4 specific gravity ( 1400 $\left.\mathrm{kg} / \mathrm{m}^{3}\right)$ and a $15-\mathrm{cP}(0.015 \mathrm{~Pa} \cdot \mathrm{~s})$ viscosity to a polymer solution with a 1.0 specific gravity ( 1000 $\left.\mathrm{kg} / \mathrm{m}^{3}\right)$ and an $18,000-\mathrm{cP}(18 \mathrm{~Pa} \cdot \mathrm{~s})$ viscosity. The two liquids are completely miscible and result in a final solution with a 1.1 specific gravity $\left(1100 \mathrm{~kg} / \mathrm{m}^{3}\right)$ and a $15,000-\mathrm{cP}(15 \mathrm{~Pa} \cdot \mathrm{~s})$ viscosity. The final batch volume will be $8840 \mathrm{gal}\left(33.5 \mathrm{~m}^{3}\right)$, and the mixing will take place in a 9.5 -ft-diameter ( $2.9-\mathrm{m}$ ) flat-bottom tank. Design the agitation system.

## LIQUID AGITATION

## Calculation Procedure

1. Determine the required agitation intensity. Design of most agitation equipment is based on previous experience and a knowledge of the amount of liquid motion produced by a rotating impeller in a given situation. Although absolute rules for agitator design do not exist, good guidelines are available as a starting point for most process applications. The type of liquid motion used for most blending applications is a recirculating-flow pattern with good top-to-bottom motion. Axial-flow impellers, such as the pitched-blade turbines shown in Fig. 12.1, produce the desired liquid motion when operated in a baffled tank. Baffles are required to prevent excessive swirling of low-viscosity liquids ( $<5000 \mathrm{cP}$, or $5 \mathrm{~Pa} \cdot \mathrm{~s}$ ).

One measure of the amount of liquid motion in an agitated tank is velocity. However, by the very nature of mixing requirements, liquid velocities must be somewhat random in both direction and magnitude. Since actual velocity is difficult to measure and depends on location in the tank, an artificial, defined velocity called "bulk velocity" has been found to be a more practical measure of agitation intensity. "Bulk velocity" is defined as the impeller pumping capacity (volumetric flow rate) divided by the cross-sectional area of the tank. For consistency, the cross-sectional area is based on an "equivalent square batch tank diameter." A "square batch" is one in which the liquid level is equal to the tank diameter.

From previous design experience, the magnitude of bulk velocity can be used as a measure of agitation intensity for most problems involving liquid blending. Bulk velocities in the range from 0.1 to $1.0 \mathrm{ft} / \mathrm{s}(0.03$ to $0.3 \mathrm{~m} / \mathrm{s})$ are typical of those found in agitated tanks. An agitator that produces a bulk velocity of $0.1 \mathrm{ft} / \mathrm{s}$ is normally the smallest agitator that will move liquid throughout the tank. An agitator capable of producing a bulk velocity of $1.0 \mathrm{ft} / \mathrm{s}$ is the largest practical size for most applications. Between these typical limits of bulk velocity, increments of $0.1 \mathrm{ft} / \mathrm{s}$ provide 10 levels* of agitation intensity that are associated with typical process results, as shown in Table 12.1.

In this example, the two fluids to be mixed have a specific gravity difference of 0.4 and a viscosity ratio of 1200 . On the basis of the process capabilities associated with bulk velocities of 0.2 and 0.6 $\mathrm{ft} / \mathrm{s}$ in Table 12.1 , a bulk velocity of $0.4 \mathrm{ft} / \mathrm{s}(0.12 \mathrm{~m} / \mathrm{s})$ should be adequate for this example. Special circumstances, such as a reaction taking place or experience with a similar process, may influence the selection of a bulk velocity.
2. Compute required impeller pumping capacity. To determine the required pumping capacity, the bulk velocity ( $0.4 \mathrm{ft} / \mathrm{s}$ ) must be multiplied by the appropriate cross-sectional area. Since a "square batch" is assumed for the design basis of bulk velocity, an equivalent tank diameter $T_{\text {eq }}$ is computed by rearranging the formula for the volume of a cylinder with the height equal to the diameter, that is,

$$
\frac{\pi}{4} T_{\mathrm{eq}}^{3}=V
$$

For the final batch volume of 8840 gal and the conversion of units,

$$
\begin{aligned}
T_{\mathrm{eq}} & =\left[8840 \operatorname{gal}\left(231 \mathrm{in}^{3} / \mathrm{gal}\right) \frac{4}{\pi}\right]^{1 / 3}=6.65(8840)^{1 / 3} \\
& =137.5 \mathrm{in}(3.49 \mathrm{~m})
\end{aligned}
$$

A 137.5-in-diameter tank has a cross-sectional area of $(\pi / 4)(137.5 \mathrm{in})^{2}=14,849 \mathrm{in}^{2}$ or $103 \mathrm{ft}^{2}$, so the required impeller pumping capacity is bulk velocity times cross-sectional area: $(0.4 \mathrm{ft} / \mathrm{s})(103$ $\left.\mathrm{ft}^{2}\right)=41.2 \mathrm{ft}^{3} / \mathrm{s}$ or $2472 \mathrm{ft}^{3} / \mathrm{min}\left(1.17 \mathrm{~m}^{3} / \mathrm{s}\right)$. Geometry of the actual tank will be taken into consideration by location and number of impellers after the horsepower and speed of the agitator are determined.

[^14]TABLE 12.1 Agitation Results Associated with Bulk Velocities

| Bulk velocity, <br> $\mathrm{ft} / \mathrm{s}(\mathrm{m} / \mathrm{s})$ | Description |
| :--- | :--- |
| $0.1(0.03)$ | Bulk velocities of 0.1 and $0.2 \mathrm{ft} / \mathrm{s}(0.03 \mathrm{and} 0.06 \mathrm{~m} / \mathrm{s})$ are characteristic of applications <br> $\downarrow$ <br> $0.2(0.06)$ <br> requiring a minimum of liquid motion. Bulk velocity of $0.2 \mathrm{ft} / \mathrm{s}(0.06 \mathrm{~m} / \mathrm{s})$ will |
|  | - Blend miscible liquids to uniformity if specific gravity differences are less than 0.1 |
|  | - Blend miscible liquids to uniformity if the viscosity of the most viscous is less than 100 |
|  | - times that of any other |

Source: From Ref. 7.
3. Select impeller diameter and determine required agitator speed. The pumping capacity $Q$ for a pitched-blade impeller with four blades $\left(N_{P}=1.37\right)$ can be related to other mixing parameters by the correlation shown in Fig. 12.3. The correlation is between two dimensionless variables: pumping number $\left(Q / N D^{3}\right)$ and Reynolds number $\left(D^{2} N \rho / \mu\right)$. Since impeller diameter $D$ and rotational speed $N$ appear in both variables, an iterative solution may be required. A convenient approach to such a solution is as follows:
a. Select an impeller diameter. The impeller diameter must be some fraction of the tank diameter, typically between 0.2 and 0.6 . For this calculation, an impeller-to-tank-diameter ratio $(D / T)$ of 0.4 will be used. Based on the equivalent tank diameter ( 137.5 in ), an impeller with a $0.4(137.5$ ) $=55 \mathrm{in}(1.4 \mathrm{~m})$ diameter will be used. (Blade width will be 11 in , corresponding to a $W / D$ of $1 / \mathrm{s}$.)
b. Compute initial estimate of impeller Reynolds number. To compute impeller Reynolds number ( $D^{2} N \rho / \mu$ ), an initial estimate of rotational speed must be made to begin the iterative solution. Let us assume $100 \mathrm{r} / \mathrm{min}$. Using fluid properties for the final batch, 1.1 specific gravity, and $15,000 \mathrm{cP}$, the initial estimate of Reynolds number becomes $N_{\mathrm{Re}}=10.7(55)^{2}(100)(1.1) / 15,000=237$. (The coefficient 10.7 is a conversion factor to make the value dimensionless.)


FIGURE 12.3 Pumping number as a function of impeller Reynolds number for pitched-blade impeller ( $N_{P}=1.37$ ). (From Chemical Engineering, 1976.)
c. Determine pumping number and compute speed. From the correlation for pumping number (Fig. 12.3), at a Reynolds number of 237 and a $D / T$ of 0.4 , the pumping number is $N_{Q}=0.44$. By rearranging the definition of pumping number $\left[Q /\left(N D^{3}\right)\right]$ and using the value obtained from the correlation ( 0.44 ), we can calculate a speed for the required pumping capacity of $2472 \mathrm{ft}^{3} / \mathrm{min}$ and the impeller diameter of 55 in ( 4.583 ft ):

$$
N=\frac{Q}{N_{Q} D^{3}}=\frac{2472}{0.44(4.583)^{3}}=58.4 \mathrm{r} / \mathrm{min}
$$

The estimated and calculated speeds do not match, and the pumping number is not constant for this Reynolds number range, so an iterative solution for the speed must continue. [In the turbulent range ( $N_{\mathrm{Re}}>20,000$ ), where pumping number is constant, no iteration is required and the calculated speed is correct for the design.]
d. Perform an iterative calculation for agitator speed. Successive calculations of Reynolds number (based on the previously estimated speed), pumping number, and agitator speed, similar to steps $3 b$ and $3 c$, will converge as follows:

| Iteration | Reynolds number | Pumping number | Speed, $\mathrm{r} / \mathrm{min}$ |
| :---: | :---: | :---: | :---: |
| 2 | 139 | 0.38 | 67.6 |
| 3 | 160 | 0.40 | 64.2 |
| 4 | 152 | 0.39 | 65.8 |
| 5 | 156 | 0.395 | 65.0 |

Thus a speed of $65 \mathrm{r} / \mathrm{min}$ is necessary to provide the pumping capacity of $2472 \mathrm{ft}^{3} / \mathrm{min}$ when using a 55-in-diameter impeller.
4. Select standard speed and motor horsepower. Although design calculations have determined that an agitator speed of $65 \mathrm{r} / \mathrm{min}$ is required, only certain standard output speeds* are available with typical industrial gear reducers. The closest standard speed is $68 \mathrm{r} / \mathrm{min}$. If $68 \mathrm{r} / \mathrm{min}$ is used instead of the calculated $65 \mathrm{r} / \mathrm{min}$, the bulk velocity will increase to about $0.42 \mathrm{ft} / \mathrm{s}$, a change imperceptible with respect to agitator performance.

The horsepower required to rotate a 55 -in-diameter impeller (11-in blade width) at $68 \mathrm{r} / \mathrm{min}$ can be computed for the process fluid, using the technique described in Example 12.1. The turbulent power number is 1.37 , from Fig. 12.1. The Reynolds number at $68 \mathrm{r} / \mathrm{min}$ becomes 161. The viscosity correction factor for this value is 1.35 , from Fig. 12.2, which gives a power number $N_{P}$ of $1.37(1.35)=$ 1.85 for the design conditions. From the power number, impeller power can be computed: $P=$ $1.85(1.1)(68)^{3}(55)^{5} /\left(1.524 \times 10^{13}\right)=21.1 \mathrm{hp}$. With an 85 percent loading for the motor, a minimum motor horsepower would be $21.1 / 0.85=24.8 \mathrm{hp}$, so a $25-\mathrm{hp}(18.5-\mathrm{kW})$ motor would be required. If the next larger standard motor is substantially larger than the minimum motor horsepower, the impeller diameter may be increased by an inch or two to fully utilize the available motor capacity.
5. Specify the number and location of impellers. The calculations carried out in the previous steps show that a $25-\mathrm{hp}$ agitator operating at $68 \mathrm{r} / \mathrm{min}$ will provide sufficient agitation to solve the problem by creating a bulk velocity of $0.4 \mathrm{ft} / \mathrm{s}$. However, these calculations essentially ignore the fact that the process will be carried out in a $91 / 2$-ft-diameter tank. The idea behind this final step in the design procedure is that 25 hp at $68 \mathrm{r} / \mathrm{min}$ will provide the desired agitation if the number and location of impellers is suitable for the batch height, as related by the ratio of liquid level to tank diameter $Z / T$.

According to Table 12.2, a $91 / 2$-ft-diameter tank holds $44.1 \mathrm{gal} /$ in of liquid level. Therefore, 8840 gal will fill the tank to $8840 / 44.1=200 \mathrm{in}$. The resulting liquid-level-to-tank-diameter ratio is $Z / T=200 / 114=1.75$. The following guidelines for number and location of impellers should be applied:

| Viscosity, cP <br> $(P a \cdot s)$ | Maximum level, <br> $Z / T$ | Number of <br> impellers | Impeller clearance |  |
| :---: | :---: | :---: | :---: | :---: |
|  | 1.4 | 1 | $Z / 3$ | Lower |

Since the liquid viscosity is $15,000 \mathrm{cP}(<25,000 \mathrm{cP})$ and the liquid level gives a $Z / T$ of 1.75 , two impellers should be used to provide liquid motion throughout the tank.

To properly load the $25-\mathrm{hp}$ motor with a dual impeller system, each impeller should be sized for $25 \mathrm{hp} / 2=12.5$ motor hp , or at 85 percent loading, $0.85(12.5 \mathrm{hp})=10.6$ impeller hp . By assuming the same viscosity correction factor (1.35) for the dual impeller size, an initial estimate can be made for power number, $N_{P}=1.37(1.35)=1.85$, and impeller diameter, $D=$ $\left[1.524 \times 10^{13} P /\left(N_{P} \rho N^{3}\right)\right]^{1 / 5}=\left\{1.524 \times 10^{13}(10.6) /\left[1.85(1.1)(68)^{3}\right]\right\}^{1 / 5}=47.9 \mathrm{in}$. Using this value to compute Reynolds number gives $N_{\mathrm{Re}}=10.7(47.9)^{2}(68)(1.1) / 15,000=122$. For $N_{\mathrm{Re}}=122$, the viscosity correction factor is 1.47 from Fig. 12.2, or a power number, $N_{P}=1.37(1.47)=2.01$. Recomputing impeller diameter, that is, $D=\left\{1.524 \times 10^{13}(10.6) /\left[2.01(1.1)(68)^{3}\right]\right\}^{1 / 5}=47.1$, shows that two 47.1 -in-diameter $(1.20-\mathrm{m})$ impellers (with 9.4 -in blade width) are equivalent to one $55-\mathrm{in}$ diameter impeller. The lower impeller should be located $T / 3=114 / 3=38$ in $(0.965 \mathrm{~m})$ off bottom and the upper impeller $(2 / 3) Z=(2 / 3) 200=133$ in $(3.39 \mathrm{~m})$ off bottom. Had the tank been 11 or 12 ft in diameter, only one impeller would have been required. Liquid levels that result in $Z / T<$ 0.4 are difficult to agitate.

[^15]TABLE 12.2 Capacity Data for Cylindrical Vessels

| Vessel diameter |  | Volume of cylindrical vessel |  | Depth and volume of vessel head |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | Standard dished head |  | ASME flanged and dished head |  |
|  |  | Straight side, gal/in | Square-batch, gal |  |  |
| ft -in | in |  |  | Depth, in | Volume, gal | Depth, in | Volume, gal |
| 3 ft | 36 | 4.40 | 159 | 4.9 | 11 | 6.0 | 16 |
| 3 ft 6 in | 42 | 5.99 | 252 | 5.7 | 18 | 7.2 | 25 |
| 4 ft | 48 | 7.83 | 376 | 6.5 | 27 | 8.0 | 37 |
| 4 ft 6 in | 54 | 9.91 | 535 | 7.3 | 38 | 9.0 | 53 |
| 5 ft | 60 | 12.2 | 734 | 8.1 | 52 | 10 | 78 |
| 5 ft 6 in | 66 | 14.8 | 977 | 8.9 | 70 | 11 | 104 |
| 6 ft | 72 | 17.6 | 1269 | 9.7 | 90 | 12 | 135 |
| 6 ft 6 in | 78 | 20.7 | 1631 | 11 | 114 | 14 | 170 |
| 7 ft | 84 | 24.0 | 2041 | 11 | 142 | 15 | 212 |
| 7 ft 6 in | 90 | 27.5 | 2478 | 12 | 174 | 15 | 261 |
| 8 ft | 96 | 31.3 | 3007 | 13 | 212 | 16 | 314 |
| 8 ft 6 in | 102 | 35.3 | 3607 | 14 | 254 | 18 | 375 |
| 9 ft | 108 | 39.6 | 4287 | 15 | 301 | 19 | 446 |
| 9 ft 6 in | 114 | 44.1 | 5035 | 15 | 353 | 20 | 524 |
| 10 ft | 120 | 48.9 | 5873 | 16 | 414 | 21 | 612 |
| 10 ft 6 in | 126 | 54 | 6799 | 17 | 480 | 22 | 705 |
| 11 ft | 132 | 59 | 7817 | 18 | 560 | 23 | 806 |
| 11 ft 6 in | 138 | 65 | 8932 | 20 | 665 | 24 | 926 |
| 12 ft | 144 | 70 | 10148 | 20 | 735 | 25 | 995 |

Note: $1.0 \mathrm{ft}=0.3048 \mathrm{~m} ; 1.0 \mathrm{in}=0.0254 \mathrm{~m} ; 1.0 \mathrm{gal} / \mathrm{in}=0.149 \mathrm{~m}^{3} / \mathrm{m} ; 1.0 \mathrm{gal}=3.785 \times 10^{-3} \mathrm{~m}^{3}$.

Related Calculations. Repeating the same design calculations but starting with a different impeller diameter will result in other horsepower-speed combinations capable of producing the same bulk velocity ( $0.4 \mathrm{ft} / \mathrm{s}$ ). For instance, the following combinations also satisfy the design requirements:

| Impeller <br> diameter, in $(\mathrm{m})$ | Motor <br> horsepower | Speed, $\mathrm{r} / \mathrm{min}$ |
| :---: | :---: | :---: |
| $48(1.219)$ | 40 | 100 |
| $50(1.270)$ | 30 | 84 |
| $58(1.321)$ | 20 | 56 |
| $62(1.412)$ | 15 | 45 |

As is the case for many agitator design problems, there are several horsepower, speed, and impellerdiameter combinations that solve the problem by producing equivalent results. From the standpoint of energy conservation, large impellers usually require less horsepower to do a given job.

Agitation problems that require other process results, such as the suspension of solids or the dispersion of gas, use other design criteria $[8,9]$.

### 12.3 TIME REQUIRED FOR UNIFORM BLENDING

About $150 \mathrm{gal}\left(0.57 \mathrm{~m}^{3}\right)$ of strong acid must be added to $10,000 \mathrm{gal}\left(37.85 \mathrm{~m}^{3}\right)$ of slightly caustic waste held in a 12 -ft-diameter ( $3.66-\mathrm{m}$ ) tank. The waste has a specific gravity $\rho$ of $1.2\left(1200 \mathrm{~kg} / \mathrm{m}^{3}\right)$ and a viscosity $\mu$ of $500 \mathrm{cP}(0.5 \mathrm{~Pa} \cdot \mathrm{~s})$. Determine the time required for neutralization if the tank
is agitated by a $1-\mathrm{hp}(0.75-\mathrm{kW})$ agitator operating at a rotational speed $N$ of $68 \mathrm{r} / \mathrm{min}$ and having a pitched-blade impeller with diameter $D$ of 30 in ( 0.762 m ).

## Calculation Procedure

1. Compute the Reynolds number. Acid-base neutralizations typically are very fast reactions, so the time required for mixing is usually the limiting factor. Although both liquid motion and molecular diffusion are involved in liquid mixing, the liquid motion dominates the apparent rate of mixing. Impeller agitation creates both large-scale flow patterns and small-scale turbulence, which in combination give efficient and rapid mixing. The effect of turbulent flow patterns is to reduce the distances required for diffusion to almost the molecular scale.

One practical method for quantifying the complicated mixing process in an agitated tank is to measure the time required for a tracer material to blend to uniformity. Such measurements for blend time may use acid-base neutralization with a color-change indicator, a dye tracer, or an ionic salt with an electrode detector. Properly accounting for measurement accuracy, all these methods give essentially the same results for time required to go from extreme segregation to a high degree ( $>99$ percent) of uniformity.

This measured blend time $t_{b}$ can be expressed as a dimensionless variable by forming a product $t_{b} N$ with agitator speed. This form of dimensionless blend time, multiplied by the impeller-to-tank-diameter ratio $D / T$ to the 2.3 power, is shown as a function of impeller Reynolds number in Fig. 12.4.

The independent variable for the correlation is impeller Reynolds number ( $D^{2} N \rho / \mu$ ), which takes into account the effects of liquid properties on the blend time. To compute the value of the Reynolds number, a coefficient of 10.7 is necessary to put the given units in dimensionless form. Thus, $N_{\mathrm{Re}}=10.7(30)^{2}(68)(1.2) / 500=1572$.
2. Determine dimensionless blend time and $\boldsymbol{D} / \boldsymbol{T}$. A dimensionless blend time $t_{b} N(D / T)^{2.3}=$ 18 is found for a Reynolds number of 1600, from Fig. 12.4. This form of dimensionless blend time takes into account the main geometric effects, as embodied in the impeller-to-tank-diameter ratio, $D / T=30 / 144=0.208$.


FIGURE 12.4 Dimensionless blend time as a function of Reynolds number for pitched-blade impellers.
3. Compute blend time. Blend time can be computed directly from rearrangement of the definition and the values for dimensionless blend time, for $D / T$, and for agitator speed:

$$
\begin{aligned}
t_{b} & =\frac{18}{N(D / T)^{2.3}}=\frac{18}{68(0.208)^{2.3}} \\
& =9.80 \min (588 \mathrm{~s})
\end{aligned}
$$

The computed blend time is about 10 min , a value that is accurate to $\pm 10$ percent for successive observations of the same process and affected slightly by the location of the acid addition. A reasonable design value for the blend time might be twice the calculated value, or $20 \mathrm{~min}(1200 \mathrm{~s})$.

Related Calculations. If the waste-neutralization process were continuous and the pH adjustment were relatively small ( $<3 \mathrm{pH}$ units), a conservative design residence time in the tank might be 10 times the computed blend time, or 100 min .

### 12.4 HEAT TRANSFER IN AN AGITATED TANK

As part of the final blending operation in a continuous process, it is necessary to cool an oil product from $125^{\circ} \mathrm{F}(325 \mathrm{~K})$ to $100^{\circ} \mathrm{F}(311 \mathrm{~K})$ at the rate of $800 \mathrm{gal} / \mathrm{h}\left(0.84 \times 10^{-3} \mathrm{~m}^{3} / \mathrm{s}\right)$.

The oil has the following physical properties at $100^{\circ} \mathrm{F}$ :
Viscosity $\mu=1200 \mathrm{cP}(1.2 \mathrm{~Pa} \cdot \mathrm{~s})$
Specific gravity $\rho=0.89\left(890 \mathrm{~kg} / \mathrm{m}^{3}\right)$
Heat capacity $C_{p}=0.52 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)[2175 \mathrm{~J} /(\mathrm{kg})(\mathrm{K})]$
Thermal conductivity $k=0.079 \mathrm{Btu} /(\mathrm{h})(\mathrm{ft})\left({ }^{\circ} \mathrm{F}\right)[0.137 \mathrm{~W} /(\mathrm{m})(\mathrm{K})]$
The tank diameter $T$ is $9 \mathrm{ft}(2.74 \mathrm{~m})$, and the vessel is designed to operate at a $5000-\mathrm{gal}$ (18.9$\mathrm{m}^{3}$ ) capacity. The tank bottom is a standard dished head and the straight side of the tank is fully jacketed. The jacket-side heat-transfer coefficient is estimated to be $h_{o}=180 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)[1021$ $\left.\mathrm{W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$. The wall thickness and its heat-transfer resistance are assumed to be negligible. If the agitator is $1.5 \mathrm{hp}(1.1 \mathrm{~kW})$ [1.15 impeller hp $(0.858 \mathrm{~kW})$ ] operating at a speed $N$ of $56 \mathrm{r} / \mathrm{min}$, with a 38-in-diameter $(D)(0.97-\mathrm{m})$ impeller, estimate the average cooling water temperature required to cool the oil. Also determine what effect increasing the agitator speed to $100 \mathrm{r} / \mathrm{min}$ (assuming appropriate changes were made in the agitator) would have on the temperature of the oil if all other conditions from the first part of the problem remained unchanged.

## Procedure

1. Compute the process-side heat-transfer coefficient. The correlations for inside (process-side) heat-transfer coefficient in an agitated tank are similar to those for heat transfer in pipe flow, except that the impeller Reynolds number and geometric factors associated with the tank and impeller are used and the coefficients and exponents are different. A typical correlation for the agitated heat-transfer Nusselt number ( $N_{\mathrm{Nu}}=h_{i} T / k$ ) of a jacketed tank is expressed as

$$
N_{\mathrm{Nu}}=0.85 N_{\mathrm{Re}}^{0.66} N_{\mathrm{Pr}}^{0.33}\left(\frac{Z}{T}\right)^{-0.56}\left(\frac{D}{T}\right)^{0.13}\left(\frac{\mu}{\mu_{w}}\right)^{0.14}
$$

All terms in the expression are dimensionless.

The correlation for heat transfer is evaluated with the respective dimensionless groups. With the units stated in the example, the impeller Reynolds number ( $N_{\mathrm{Re}}=\mathrm{D}^{2} N \rho / \mu$ ) requires a conversion factor of 10.7 to make it dimensionless; thus, $N_{\mathrm{Re}}=10.7(38)^{2}(56)(0.89) / 1200=642$. The Prandtl number $\left(N_{\mathrm{Pr}}=C_{p} \mu / k\right)$ requires a conversion factor of 2.42 ; thus $N_{\mathrm{Pr}}=2.42(0.52)(1200) / 0.079=$ 19,115. The liquid-level-to-tank-diameter ratio $Z / T$ requires determination of the liquid level for a $5000-\mathrm{gal}$ batch in the tank. A standard dished head holds 301 gal and is 15 in deep, from Table 12.2. The remaining $5000-301=4699 \mathrm{gal}$ fills the cylindrical part of the tank at a rate of $39.6 \mathrm{gal} / \mathrm{in}$ of height, or to a height of $4699 / 39.6=119 \mathrm{in}$. The total liquid level is $Z=119+15=134 \mathrm{in}$ and $Z / T=$ $134 / 108=1.24$. The impeller-to-tank-diameter ratio $D / T$ is $38 / 108=0.35$. The viscosity ratio will be assumed to be unity $\left(\mu / \mu_{w}=1\right)$ because of lack of data and the very small exponent on the term.

Combining all these values according to the correlation gives a value for the Nusselt number of $N_{\mathrm{Nu}}=0.85(642)^{0.66}(19,115)^{0.33}(1.24)^{-0.56}(0.35)^{0.13}(1)^{0.14}=1212$. The value for the inside heattransfer coefficient $h_{i}$ is obtained from the Nusselt number using conductivity and tank diameter (ft); thus, $h_{i}=N_{\mathrm{Nu}} k / T=1212(0.079) / 9=10.6 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[60.1 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.
2. Compute overall heat-transfer coefficient. The overall heat-transfer coefficient $U_{o}$ is simply the series resistance to heat transfer for the inside and outside coefficients. The overall coefficient $U_{o}$ is $\left(1 / h_{i}+1 / h_{o}\right)^{-1}=(1 / 10.6+1 / 180)^{-1}=10.0 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[56.7 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$.
3. Determine total heat load for agitated heat transfer. The process requires $25^{\circ} \mathrm{F}$ cooling of 8000 $\mathrm{gal} / \mathrm{h}$ of oil. Since the oil has a specific gravity of 0.89 , its density is $(0.89)(8.337 \mathrm{lb}$ water $/ \mathrm{gal})=$ $7.42 \mathrm{lb} / \mathrm{gal}$. The product of volumetric flow, density, heat capacity, and temperature change equals the heat load for cooling the oil: $(800 \mathrm{gal} / \mathrm{h})(7.42 \mathrm{lb} / \mathrm{gal})\left[0.52 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)\right]\left(25^{\circ} \mathrm{F}\right)=77,168 \mathrm{Btu} / \mathrm{h}(22.6$ $\mathrm{kW})$. In addition, the power input of the agitator ( 1.15 hp ) also must be dissipated in the form of heat: $(1.15 \mathrm{hp})[2545 \mathrm{Btu} /(\mathrm{h})(\mathrm{hp})]=2927 \mathrm{Btu} / \mathrm{h}$. The total heat load $q$ is $77,168+2927=80,095 \mathrm{Btu} / \mathrm{h}$ ( 23.5 kW ).
4. Compute required coolant temperature. The coolant temperature can be determined from heat load and the heat-transfer coefficient because a sufficient temperature difference must exist to drive the heat-transfer rate, that is, $q=U_{o} A\left(T_{i}-T_{o}\right)$. The available heat-transfer area $A$ is the jacketed vertical wall in contact with the liquid, since the bottom head is not jacketed; thus, $A=\pi D Z_{s s}=\pi(9 \mathrm{ft})(119 / 12 \mathrm{ft})=280 \mathrm{ft}^{2}$. The temperature difference is $\left(T_{i}-T_{o}\right)=q /\left(U_{o} A\right)=$ $80,095 /[10.0(280)]=28.6^{\circ} \mathrm{F}$. To provide a temperature difference of $28.6^{\circ} \mathrm{F}$ with respect to the process temperature, the average coolant temperature must be $71.4^{\circ} \mathrm{F}(295 \mathrm{~K})$.
5. Determine the effect of increased agitator speed. Two effects must be considered when the agitator speed is increased: (1) improved heat-transfer coefficient, and (2) increased power input. The agitator speed enters the heat-transfer correlation in the Reynolds number. For $100 \mathrm{r} / \mathrm{min}$, the Reynolds number $N_{\mathrm{Re}}$ becomes $10.7(38)^{2}(100)(0.89) / 1200=1146$, which increases the Nusselt number to 1777 and the inside heat-transfer coefficient $h_{i}$ to $1777(0.079) / 9=15.6 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)$ $\left[88.5 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$. The overall coefficient $U_{o}$ becomes $(1 / 15.6+1 / 180)^{-1}=14.4 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)$ $\left[81.7 \mathrm{~W} /(\mathrm{m})^{2}(\mathrm{~K})\right]$, or a 44 percent increase from the lower speed. The horsepower increase associated with increased speed is substantial, because power is roughly proportional to speed cubed (the effect of Reynolds number on power requirement is negligible between $N_{\mathrm{Re}}=600$ and 1200 for a pitched-blade impeller; see Fig. 12.2). The horsepower at $100 \mathrm{r} / \mathrm{min}$ is approximately $(1.15 \mathrm{hp})(100 / 56)^{3}=6.55$ hp , which results in a heat load of $(6.55 \mathrm{hp})[2545 \mathrm{Btu} /(\mathrm{h})(\mathrm{hp})]=16,670 \mathrm{Btu} / \mathrm{h}$. With the increased power input, the total heat load is $q=77,168+16,670=93,838 \mathrm{Btu} / \mathrm{h}(27.5 \mathrm{~kW})$.

The combined effects of increased heat transfer and increased heat load can be seen by determining the resultant temperature difference, that is, $\left(T_{i}-T_{o}\right)=q /\left(U_{o} A\right)=93,838 /[14.4(280)]=23.3^{\circ} \mathrm{F}$. For the same jacket temperature of $71.4^{\circ} \mathrm{F}$, the process temperature would be reduced to $71.4+$ $23.3=94.7^{\circ} \mathrm{F}(307.8 \mathrm{~K})$ by doubling the agitator speed.

The cost of improved heat transfer by increased speed must be measured against the increased cooling-water requirements and increased operating power and capital cost for the agitator. In general, these increased costs more than offset the benefits of improved heat transfer. Therefore, most
agitators designed for heat transfer provide moderate blending ( 0.2 to $0.3 \mathrm{ft} / \mathrm{s}$ bulk velocity) for optimal operation.

Related Calculations. See also Section 7 for situations involving both heat transfer and mixing.

### 12.5 SCALE-UP FOR AGITATED SOLIDS SUSPENSION

An agitator must be designed for a solids-suspension operation to be carried out in a 6000-gal (22.7$\mathrm{m}^{3}$ ) tank that is $10 \mathrm{ft}(3.05 \mathrm{~m})$ in diameter and has a standard dished bottom. The material to be suspended is insoluble in the liquid and has a particle-size range from 30 to $200 \mu \mathrm{~m}$ with an actual specific gravity $\rho$ of $3.8\left(3800 \mathrm{~kg} / \mathrm{m}^{3}\right)$. The liquid is a mineral oil with a specific gravity of 0.89 $\left(890 \mathrm{~kg} / \mathrm{m}^{3}\right)$ and a viscosity of $125 \mathrm{cP}(0.125 \mathrm{~Pa} \cdot \mathrm{~s})$. The suspension is $30 \mathrm{wt} \%$ solids and must be sufficiently agitated to give particle uniformity of the large particles to at least three-fourths the liquid level.

## Calculation Procedure

1. Compute suspension density. To form 1 lb of $30 \mathrm{wt} \%$ suspension, 0.3 lb solids must be added to 0.7 lb liquid. The liquid has a density of $0.89(8.337 \mathrm{lb}$ water $/ \mathrm{gal})=7.42 \mathrm{lb} / \mathrm{gal}$. Similarly, the solids must displace liquid at $3.8(8.337)=31.68 \mathrm{lb} / \mathrm{gal}$. Thus, 1 lb of the suspension will have a volume of $0.7 / 7.42+0.3 / 31.68=0.1038$ gal, or a density of $(1 \mathrm{lb}) / 0.1038 \mathrm{gal}=9.63 \mathrm{lb} / \mathrm{gal}$, which is the same as a specific gravity of $9.63 / 8.337=1.16\left(1160 \mathrm{~kg} / \mathrm{m}^{3}\right)$.
2. Determine batch height. A 6000 -gal batch in a 10 -ft-diameter tank with a dished head will put 414 gal in the 16 -in-deep dished head (see Table 12.2). The remaining $6000-414=5586$ gal will fill the vertical-wall portion of the tank at a rate of $48.9 \mathrm{gal} / \mathrm{in}$, for a total liquid depth of ( 5586 gal )/(48.9 $\mathrm{gal} / \mathrm{in})+16$ in $=130$ in ( 3.3 m ).
3. Use an experimental model to determine required agitation intensity. Although physicalproperty data are available for solid particles, liquid, and suspension, the agitated-suspension characteristics of a relatively wide range of particle sizes in a slightly viscous liquid are almost impossible to predict without making experimental measurements in a small-scale agitated tank. The most direct approach to small-scale testing is to construct a geometrically similar model of the large-scale equipment. Assume that a 1 -ft-diameter tank ( $1 / 10 \mathrm{scale}$ ) is available for such tests. By applying the scale factor $(1 / 10)$ to the liquid level for the large tank, a $(130 \mathrm{in}) / 10=13$-in liquid level should be tested in the model.

The testing should determine the intensity of agitation necessary to obtain the desired level of suspension uniformity. Suppose that by visual observation and sample analysis, a pitched-blade impeller with a diameter $D$ of 4 in (with four blades, each 0.8 in wide) operating at a speed $N$ of 465 $\mathrm{r} / \mathrm{min}$ was found to produce the level of agitation necessary for uniform suspension to three-fourths the total liquid level. With data about impeller diameter and agitator speed in a small tank, it should be possible to scale up performance to the large-scale tank.
4. Scale-up experimental results for solids suspension. To maintain geometric similarity with scale-up, all length dimensions must remain in the same proportion between the small and large equipment. If the large tank diameter is 10 times as large as the small tank, then the impeller diameter should be $10(4 \mathrm{in})=40$ in for the large tank. Similarly, the blade width for the impeller should be $10(0.8 \mathrm{in})=8$ in for a four-blade impeller. Although geometric similarity is not strictly necessary for all agitation scale-up problems, satisfactory results are usually obtained and scale-up relationships are relatively simple.


FIGURE 12.5 Scale-up rules for geometric similarity; speed ratio as a function of length ratio.

Since impeller diameter is established by geometric similarity, the agitator speed for the largescale equipment must be determined to satisfy process requirements. Large-scale speed $N_{L}$ can be computed by the following relationship:

$$
N_{L}=N_{S}\left(\frac{D_{S}}{D_{L}}\right)^{n}
$$

where $N_{S}$ is the small-scale speed. The value of the exponent $n$ depends on the type of process result that must be duplicated, since different process results scale up differently. Some typical exponents, their effect on speed, and their scale-up significance are shown in Fig. 12.5.

For equivalent solids suspension, an exponent of $3 / 4$ will be used to scale up from the small-scale solids suspension speed of $465 \mathrm{r} / \mathrm{min}$ :

$$
N_{L}=465\left(\frac{4}{40}\right)^{3 / 4}=82.7 \mathrm{r} / \mathrm{min}
$$

5. Select standard speed and motor horsepower. Although scale-up calculations predict an 82.7 $\mathrm{r} / \mathrm{min}$ operating speed for the large-scale agitator, only certain standard output speeds are commercially available. The nearest standard speed is $84 \mathrm{r} / \mathrm{min}$. To determine power requirements, use the procedure outlined in Example 12.1. The turbulent-power number is first determined from Fig. 12.1: $N_{P}=1.37$. The Reynolds number is then computed for the process conditions: $N_{\mathrm{Re}}=10.7(40)^{2}(84)(1.16) / 125=$ 13,345, which is sufficiently turbulent that no correction factor from Fig. 12.2 need be applied to the power number. The calculated impeller power is $1.37(1.16)(84)^{3}(40)^{5} /\left(1.524 \times 10^{13}\right)=6.33 \mathrm{hp}$. Considering process variations, drive losses, and so forth, an 85 percent motor loading means that a minimum motor horsepower of ( 6.33 hp ) $/ 0.85=7.45 \mathrm{hp}$ is required. The next larger standard motor is $7.5 \mathrm{hp}(5.5 \mathrm{~kW})$, which is used to drive a 40 -in-diameter ( $1.02-\mathrm{m}$ ) impeller at $84 \mathrm{r} / \mathrm{min}$ to satisfy the solids-suspension requirements.

Related Calculations. Scale-up problems for agitator design are not always obvious with respect to which scale-up exponent should be used. Problems involving chemical reactions, where kinetics
and mixing interact, are often difficult to scale up accurately. Therefore, medium-sized pilot-plant reactors may be necessary to improve the understanding of how mixing influences performance.

### 12.6 AGITATOR DESIGN FOR GAS DISPERSION

Pilot-scale testing of an aerobic fermentation process has determined that maximum cell growth rate will consume $16.2 \mathrm{lb} \mathrm{O}_{2}$ per hour per $1000 \mathrm{gal}\left(5.4 \times 10^{-4} \mathrm{~kg} \mathrm{O} \mathrm{O}_{2}\right.$ per second per cubic meter $)$ at a temperature of $120^{\circ} \mathrm{F}(322 \mathrm{~K})$, providing the gas rate is sufficient to keep oxygen depletion of the air to less than 10 percent and the $\mathrm{O}_{2}$ concentration in the broth is at least $2.4 \mathrm{mg} / \mathrm{L}\left(2.4 \times 10^{-3} \mathrm{~kg} / \mathrm{m}^{3}\right)$. The overall mass-transfer coefficient $k_{L} a\left(s^{-1}\right)$ for the process is assumed to behave as in an ionic solution: $k_{L} a=\left(2.0 \times 10^{-3}\right)(P / V)^{0.7} u_{s}^{0.2}$, where $P / V$ is power per volume (in watts per cubic meter) and $u_{s}$ is superficial gas velocity (in meters per second). Design an agitator to carry out the fermentation in a $10,000-\mathrm{gal}\left(37.9-\mathrm{m}^{3}\right)$ batch in a $12-\mathrm{ft}$-diameter $(3.66-\mathrm{m})$ tank. The fermentation broth is initially waterlike and has a specific gravity of $1.0\left(1000 \mathrm{~kg} / \mathrm{m}^{3}\right)$ throughout the process.

## Calculation Procedure

1. Determine superficial gas velocity. The maximum oxygen uptake rate ( $16.2 \mathrm{lb} / \mathrm{h}$ per 1000 gal ) will mean that $162 \mathrm{lb} \mathrm{O}_{2}$ per hour will be required for the 10,000-gal batch. To keep oxygen depletion to less than 10 percent, 10 times the $\mathrm{O}_{2}$ demand must flow through the tank, that is, $10(162)=1620$ $\mathrm{lb} \mathrm{O}_{2}$ per hour. Water-saturated air at $120^{\circ} \mathrm{F}$ contains $21.3 \mathrm{wt} \% \mathrm{O}_{2}$ and has a density of $0.065 \mathrm{lb} / \mathrm{ft}^{3}$ at 1 atm (Handbook of Tables for Applied Engineering Science, CRC Press). To supply $1620 \mathrm{lb} \mathrm{O}_{2}$ per hour, $1620 / 0.213=7606 \mathrm{lb}$ air per hour must flow through the tank. This flow rate represents $(7606$ $\mathrm{lb} / \mathrm{h}) /\left[\left(0.065 \mathrm{lb} / \mathrm{ft}^{3}\right)(60 \mathrm{~min} / \mathrm{h})\right]=1950 \mathrm{ft}^{3} / \mathrm{min}\left(0.92 \mathrm{~m}^{3} / \mathrm{s}\right)$ at $1 \mathrm{~atm}(101.3 \mathrm{kPa})$.

To design the agitator, the gas density at the impeller location should be used for computing the superficial gas velocity. Because of liquid head, this necessitates a pressure correction. The total liquid level for $10,000 \mathrm{gal}$ in a 12 - ft -diameter tank is roughly 12 ft (see Table 12.2). If the impeller is located one-sixth of the liquid level off bottom, as it should be for gas dispersion, the additional static liquid head is 10 ft of water that must be added to the atmospheric pressure ( 34 ft of water). The pressure correction makes the actual volumetric flow rate of gas $Q_{A}$ equal ( $1950 \mathrm{ft}^{3} / \mathrm{min}$ ) ( 34 ft of water)/ $(34+10 \mathrm{ft}$ of water $)=1507 \mathrm{ft}^{3} / \mathrm{min}$. Flow rate divided by cross-sectional area of tank, that is, $\pi(12 \mathrm{ft})^{2} / 4=113 \mathrm{ft}^{2}$, gives a superficial gas velocity $u_{s}$ of $\left(1507 \mathrm{ft}^{3} / \mathrm{min}\right) / 113 \mathrm{ft}^{2}=13.3 \mathrm{ft} / \mathrm{min}$ or $0.22 \mathrm{ft} / \mathrm{s}(0.067 \mathrm{~m} / \mathrm{s})$.
2. Determine overall mass-transfer coefficient. As a design level for overall mass transfer, the coefficient should be based on the minimum concentration gradient and the maximum transfer rate. The minimum gradient will exist near the liquid surface, where the oxygen saturation concentration in the liquid is a minimum because of the minimum total pressure and the low concentration of oxygen there. The volume (mole) percent oxygen in air with 10 percent depletion is ( $18.4 \mathrm{~mol} \mathrm{O}_{2}-1.8 \mathrm{~mol}$ $\left.\mathrm{O}_{2}\right) /(100 \mathrm{~mol}$ gas -1.8 mol gas $)=0.169 \mathrm{~mol} \mathrm{O}_{2}$ per mol of gas, which gives an oxygen partial pressure of 0.169 atm . The Henry's law solubility constant $H$ for $\mathrm{O}_{2}$ at $120^{\circ} \mathrm{F}$ is $5.88 \times 10^{4}$ (Handbook of Tables for Applied Engineering Science, CRC Press) for partial pressure in atmospheres and oxygen concentration in mole fraction dissolved oxygen. Thus the mole fraction oxygen dissolved in the water is $0.169 / 5.88 \times 10^{4}=2.87 \times 10^{-6} \mathrm{~mol} \mathrm{O}_{2}$ per mole of liquid. This equals [ $2.87 \times 10^{-6} \mathrm{~mol} \mathrm{O}_{2} /$ $\left.\left.1 \mathrm{~mol} \mathrm{H} \mathrm{H}_{2} \mathrm{O}\right]\left[32 \mathrm{~g} \mathrm{O}_{2} / 1 \mathrm{~mol} \mathrm{O}_{2}\right) /\left(18 \mathrm{~g} \mathrm{H}_{2} \mathrm{O} / 1 \mathrm{~mol} \mathrm{H} \mathrm{O}\right)\right]\left[10^{3} \mathrm{mg} \mathrm{O}_{2} / 1 \mathrm{~g} \mathrm{O}_{2}\right]\left[10^{3} \mathrm{~g} \mathrm{H}_{2} \mathrm{O} / 1 \mathrm{~L} \mathrm{H}_{2} \mathrm{O}\right]=$ $5.10 \mathrm{mg} \mathrm{O}_{2}$ per liter $\left(5.10 \times 10^{-3} \mathrm{~kg} \mathrm{O}_{2}\right.$ per cubic meter $)$.

The maximum oxygen-transfer rate is $16.2 \mathrm{lb} \mathrm{O}_{2}$ per hour per $1000 \mathrm{gal}\left(5.4 \times 10^{-4} \mathrm{~kg} \mathrm{O}_{2}\right.$ per second per cubic meter) and the minimum concentration gradient between saturation $\left(5.10 \times 10^{-3} \mathrm{~kg} \mathrm{O}_{2}\right.$ per cubic meter) and bulk concentration $\left(2.4 \times 10^{-3} \mathrm{~kg} \mathrm{O}_{2}\right.$ per cubic meter) is $\left(5.1 \times 10^{-3}\right)-(2.4 \times$
$\left.10^{-3}\right)=2.7 \times 10^{-3} \mathrm{~kg} \mathrm{O}_{2}$ per cubic meter. The overall mass-transfer coefficient $k_{L} a$ is computed by dividing the transfer rate by the concentration gradient:

$$
\frac{5.4 \times 10^{-4} \mathrm{~kg} /(\mathrm{s})\left(\mathrm{m}^{3}\right) \mathrm{O}_{2}}{2.7 \times 10^{-3} \mathrm{~kg} / \mathrm{m}^{3} \mathrm{O}_{2}}=0.2 \mathrm{~s}^{-1}
$$

3. Compute required power per volume for agitation. Using the correlation for overall masstransfer coefficient, that is, $k_{L} a=2.0 \times 10^{-3}(P / V)^{0.7} u_{s}^{0.2}$, the design value for mass-transfer coefficient $\left(0.2 \mathrm{~s}^{-1}\right)$, and the superficial gas velocity $(0.067 \mathrm{~m} / \mathrm{s})$, the required agitation intensity can be computed: $P / V=\left[0.2 \mathrm{~s}^{-1} /(0.067 \mathrm{~m} / \mathrm{s})^{0.2}\left(2.0 \times 10^{-3}\right)\right]^{1 / 0.7}=1558 \mathrm{~W} / \mathrm{m}^{3}(7.91 \mathrm{hp}$ per 1000 gal ).
4. Determine minimum impeller size to prevent flooding. Flooding in an agitated gas dispersion occurs when the impeller power and pumping capacity are insufficient to control the gas flow rate. A flooding correlation for minimum power per volume and superficial gas velocity is shown in Fig. 12.6 for several impeller-to-tank-diameter ratios $(D / T)$. For a superficial gas velocity of $0.22 \mathrm{ft} / \mathrm{s}$ and 7.91 hp per 1000 gal , the minimum $D / T$ is less than 0.25 . So any impeller larger than $0.25 T=0.25$ (144 in) $=36$ in should produce sufficient agitation to overcome flooding.


FIGURE 12.6 Minimum impeller-power requirement to overcome flooding as a function of superficial gas velocity and $D / T$. (From Chemical Engineering, 1976.)


FIGURE 12.7 Gassed power factor as a function of aeration number. (From Chemical Engineering, 1976.)
5. Determine impeller size for required power input. The impeller required for the process must draw 7.91 hp per 1000 gal or 79.1 hp for the $10,000-\mathrm{gal}$ batch. This power level must be achieved at the gas flow rate required by the process, which is, $Q_{A}=1507 \mathrm{ft}^{3} / \mathrm{min}$. The power required to operate an agitator impeller for gas dispersion can be much less than the power required for a liquid without gas. The ratio of power with gas to power without $P / P_{0}$ is shown in Fig. 12.7 and is a function of the dimensionless aeration number $N_{\mathrm{Ae}}=\mathrm{Q}_{A} / N D^{3}$.

For gas-dispersion applications, a radial discharge impeller, such as the straight-blade and disk style impellers in Fig. 12.1, should be used. A straight-blade impeller with a power number $N_{P}$ of 3.86 will be used for this design. Assume that the operating speed will be $100 \mathrm{r} / \mathrm{min}$.

Since impeller diameter is unknown, aeration number and, therefore, gassed power factor cannot be determined; however, an estimate for power factor $P / P_{0}$ of 0.4 is usually a good initial estimate. By rearranging the expression for power number, that is, $N_{P}=P /\left(\rho N^{3} \mathrm{D}^{5}\right)$, an expression for impeller diameter can be derived. The factor $P / P_{0}$ must be introduced for the effect of gas and a conversion for units makes

$$
D=\left[\frac{1.524 \times 10^{13} P}{\left(P / P_{0}\right) N_{P} N^{3}}\right]^{1 / 5}=\left[\frac{1.524 \times 10^{13}(79.1)}{0.4(3.86)(100)^{3}}\right]^{1 / 5}=60.0 \mathrm{in}
$$

With a value for $D$ of 60.0 in ( 5.0 ft ), the aeration number can be computed:

$$
N_{\mathrm{Ae}}=\frac{1507 \mathrm{ft}^{3} / \mathrm{min}}{(100 \mathrm{r} / \mathrm{min})(5.0 \mathrm{ft})^{3}}=0.121
$$

The revised estimate for $P / P_{0}$ is 0.38 from Fig. 12.7, which gives an impeller diameter of 60.7 in . Therefore, a 60.7 -in-diameter ( $1.54-\mathrm{m}$ ) straight-blade impeller with a 10.1-in ( $0.257-\mathrm{m}$ ) blade width operating at $100 \mathrm{r} / \mathrm{min}$ should satisfy the process requirements.
6. Select standard size motor. A motor that is loaded to 85 percent by a 79.1 -hp impeller will require a minimum size of $(79.1 \mathrm{hp}) / 0.85=93.1 \mathrm{hp}$, which means a $100-\mathrm{hp}(75-\mathrm{kW})$ motor. This motor and impeller assembly is correctly sized for conditions with the design gas flow. However, because of the gassed power factor, that is, $P / P_{0}=0.38$, should the gas supply be lost for any reason, the impeller power would increase to $78 / 0.38=205 \mathrm{hp}$ and seriously overload the motor. To avoid this problem, some method (typically electrical control) prevents motor operation without the gas supply. When the gas supply is off, the control either stops the agitator motor or, in the case of a two-speed motor, goes to a lower speed.

Related Calculations. The majority of gas-dispersion applications are sized on the basis of power per volume. In aerobic fermentation, levels of 5 to 12 hp per $1000 \mathrm{gal}\left(1\right.$ to $\left.2.4 \mathrm{~kW} / \mathrm{m}^{3}\right)$ are typical, while for aerobic waste treatment, levels of 1 to 3 hp per $1000 \mathrm{gal}\left(0.2\right.$ to $0.6 \mathrm{~kW} / \mathrm{m}^{3}$ ) are more common, primarily because of the concentrations and oxygen requirements of the microorganisms. For more on fermentation, see Section 17.

### 12.7 SHAFT DESIGN FOR TURBINE AGITATOR

A $15-\mathrm{hp}(11.2-\mathrm{kW})$ agitator operating at $100 \mathrm{r} / \mathrm{min}$ has been selected for a process application. The vessel geometry requires two impellers, both of 36 -in $(0.91 \mathrm{~m})$ diameter, the upper one located 80 in $(2.03 \mathrm{~m})$ below the agitator drive and the lower one 130 in ( 3.30 m ) below the drive. Pitchedblade turbine impellers having four blades are to be used. The shaft is to be stainless steel, having an allowable shear stress of $6000 \mathrm{psi}(41,370 \mathrm{kPa})$, an allowable tensile stress of $10,000 \mathrm{psi}(68,950$ $\mathrm{kPa})$, a modulus of elasticity of $28,000,000 \mathrm{psi}(193,000,000 \mathrm{kPa})$, and a density of $0.29 \mathrm{lb} / \mathrm{in}^{3}(8027$ $\mathrm{kg} / \mathrm{m}^{3}$ ), which represents a weight of $0.228 d^{2}$ per linear inch, where $d$ is shaft diameter in inches. The bearing span for support of the agitator shaft is to be 16 in . What shaft diameter is required for this application?

## Calculation Procedure

1. Determine the hydraulic loads on the shaft. To rotate the agitator, the shaft must transmit torque from the drive to the impellers. The actual torque required should be found by the sum of the horsepower required by each impeller. However, process conditions can change, so it is better to assume that the full motor power can be outputted from the drive. Maximum torque $\tau$ can be found by dividing motor horsepower $P_{\text {motor }}$ by shaft speed $N$. A conversion factor of 63,025 makes the answer come out in English engineering units:

$$
\tau=P_{\text {motor }} / N=(63,025)(15) / 100=9454 \mathrm{in} \cdot \mathrm{lb}
$$

The output shaft must be large enough to transmit $9454 \mathrm{in} \cdot \mathrm{lb}(1068 \mathrm{~N} \cdot \mathrm{~m})$ at the drive. Only half the torque need be transmitted in the shaft below the first impeller, because the lower impeller should require only half the total power.

If the hydraulic forces on individual impeller blades were always uniformly distributed, torsion considerations would constitute the only significant strength requirement for the shaft. However, real loads on impeller blades fluctuate, due to the shifting flow patterns that contribute to process mixing. For shaft design, using a factor of three-tenths (0.3) approximates the imbalanced force acting at the impeller diameter. This factor (0.3) is typical for pitched-blade turbines with four blades and may be different for other types of impellers. A higher factor should be used if the mixer is subjected to external loads, such as flow from a pump return.

The imbalanced forces result in a bending moment $M$ on the shaft. Such moments must be summed for hydraulic loads at each shaft extension $L_{n}$ where an impeller is located and must be adjusted for the impeller diameter $D_{n}$ :

$$
M=\sum_{n} 0.3\left(P_{n} / N\right)\left(L_{n} / D_{n}\right)
$$

In the present example having two equal-size impellers, the motor power is split in half and the moments are calculated at each impeller location:

$$
\begin{aligned}
M & =0.3[(63,025)(15 / 2) / 100][80 / 36]+0.3[(63,025)(15 / 2) / 100][130 / 36] \\
& =8272 \mathrm{in} \cdot \mathrm{lb}
\end{aligned}
$$

Thus, a maximum bending moment of $8272 \mathrm{in} \cdot \mathrm{lb}(935 \mathrm{~N} \cdot \mathrm{~m})$ occurs just below the agitator drive, at the top of the shaft extension. The hydraulic loads on the shaft result in a torque and bending moment that the shaft must be strong enough to handle.
2. Determine the minimum shaft diameter for strength. Since the torque and bending moment may act simultaneously on the shaft, these loads must be combined and resolved into shear and tensile stresses on the shaft. The minimum shaft diameter must be the larger of the shaft diameters required by either shear- or tensile-stress limits. The shaft diameter for shear stress $d_{s}$ can be calculated as follows:

$$
d_{s}=\left[16\left(\tau^{2}+M^{2}\right)^{1 / 2} / \pi \sigma_{s}\right]^{1 / 3}
$$

where $\sigma_{s}$ is the allowable shear stress. As already noted, the $\sigma_{s}$ value recommended for carbon steel and stainless steel typically used in agitator applications is $6000 \mathrm{psi}(41,370 \mathrm{kPa})$. This stress value is low enough to prevent permanent distortions and to minimize the possibility of fatigue failures. The minimum shaft diameter for shear strength is, accordingly,

$$
d_{s}=\left[16\left(9454^{2}+8272^{2}\right)^{1 / 2} / \pi(6000)\right]^{1 / 3}=2.201 \mathrm{in}
$$

The minimum shaft diameter for tensile strength $d_{t}$ can be calculated using a similar expression:

$$
d_{t}=\left[16\left[M+\left(\tau^{2}+M^{2}\right)^{1 / 2}\right] \pi \sigma_{t}\right]^{1 / 3}
$$

where $\sigma_{t}$ is the allowable tensile stress. The minimum shaft diameter for tensile strength is, accordingly,

$$
d_{t}=\left[16\left(8272+\left(9454^{2}+8272^{2}\right)^{1 / 2}\right] / \pi(10,000)\right]^{1 / 3}=2.197 \mathrm{in}
$$

The minimum shaft diameter for shear and tensile limits is 2.201 in $(0.056 \mathrm{~m})$. The next larger standard size is 2.5 in ( 0.0635 m ), which provides an adequate initial design.
3. Calculate the natural frequency of the agitator shaft. Shaft strength is not the only limit to agitator shaft design-a long shaft may not be stiff enough to prevent uncontrolled vibrations. A given overhung shaft, of the sort typically used with top-entering agitators, will oscillate at a natural frequency, similar to the vibration of a tuning fork. If the operating speed of the agitator is too close to that frequency, destructive oscillations may occur. Most large agitator shafts are designed with the operating speed less than the first natural frequency, so that even as the agitator is started and stopped, excessive vibrations should not occur.

A typical formula for calculating the first natural frequency (critical speed) of an agitator shaft considers the shaft stiffness, the shaft length, the weights of impellers and shaft, and the rigidity of the shaft mounting:

$$
N_{c}=37.8 d^{2}\left(E_{y} / \rho_{m}\right)^{1 / 2} / L W_{e}^{1 / 2}\left(L+L_{b}\right)^{1 / 2}
$$

where $N_{c}=$ critical speed, $\mathrm{r} / \mathrm{min}$
$d=$ shaft diameter, in
$L=$ shaft extension, in
$W_{e}=$ equivalent weight (lb) of impellers and shaft at shaft extension
$L_{b}=$ spacing (in) of bearings that support shaft
$E_{y}=$ modulus of elasticity, $\mathrm{lb} / \mathrm{in}^{2}$
$\rho_{m}=$ density, $\mathrm{lb} / \mathrm{in}^{3}$
$E_{y}$ and $\rho$ are two material properties that characterize the stiffness of the shaft. Substituting the modulus and density values given in the statement of the problem reduces the expression to

$$
N_{c}=371,400 d^{2} / L W_{e}^{1 / 2}\left(L+L_{b}\right)^{1 / 2}
$$

For a two-impeller situation, $W_{e}$ can be calculated as follows:

$$
W_{e}=W_{l}+W_{u}\left(L_{u} / L\right)^{3}+w_{s}(L / 4)
$$

where $W_{l}$ and $W_{u}$ are, respectively, the weights of the lower and upper impellers, the upper impeller is located at shaft extension $L_{u}$, and $w_{s}$ is the unit weight of the shaft as given in the statement of the problem. Data on impeller weight can be furnished by the mixer vendor, measured directly by the user, or estimated from dimensions provided by the vendor. For the present case, assume that the impeller hub for a $2.5-\mathrm{in}$ shaft weighs $25 \mathrm{lb}(11.4 \mathrm{~kg})$ and a set of blades for a $36-\mathrm{in}$ impeller weighs $34.5 \mathrm{lb}(15.7 \mathrm{~kg})$, so each impeller for this agitator weighs $59.5 \mathrm{lb}(27.0 \mathrm{~kg})$. Thus,

$$
W_{e}=59.5+59.5(80 / 130)^{3}+\left[0.228(2.5)^{2}\right][130 / 4]=120 \mathrm{lb}
$$

and accordingly,

$$
N_{c}=371,400(2.5)^{2} /\left[130(120)^{1 / 2}(130+16)^{1 / 2}\right]=135 \mathrm{r} / \mathrm{min}
$$

This means that with the proposed 2.5 -in shaft, an operating speed near $135 \mathrm{r} / \mathrm{min}$ must be avoided. In practice, the design limit for operating speed should be no higher than 65 percent of critical speed. This conservative margin is necessary because of many factors that might reduce the critical speed or increase loads on the shaft. For instance, the critical-speed calculation assumes that the agitator drive support is rigid, but in fact tank nozzles and support structures have some flexibility that reduces the natural frequency. Furthermore, dynamic loads on the impeller, such as those induced by operating near the liquid level, may make the effects of natural frequency more significant.

In the present case, the $100-\mathrm{r} / \mathrm{min}$ operating speed given in the statement of the problem is 74 percent of critical speed and therefore is too close to critical speed for safe operation.
4. Redesign the shaft to avoid critical-speed problems. A larger shaft diameter should overcome critical-speed problems, provided the gear reducer will accept the larger shaft. The larger shaft diameter increases shaft stiffness and thus increases the natural frequency. However, a large shaft also means more weight in the impeller hubs and in the shaft.

For the present case, try a 3.0 -in shaft. Assume that vendor information indicates a hub weight of $40 \mathrm{lb}(18.2 \mathrm{~kg})$ for such a shaft, thus increasing the impeller weights to $74.5 \mathrm{lb}(33.8 \mathrm{~kg})$. Accordingly, the new equivalent weight is

$$
W_{e}=74.5+74.5(80 / 130)^{3}+\left[0.228(3.0)^{2}\right][130 / 4]=159 \mathrm{lb}
$$

And the new critical speed is

$$
N_{c}=371,400(3.0)^{2} /\left[(130)(159)^{1 / 2}(130+16)^{1 / 2}\right]=169 \mathrm{r} / \mathrm{min}
$$

The stated operating speed of $100 \mathrm{r} / \mathrm{min}$ is only 59 percent of this critical speed, so the 3.0 -in shaft should operate safely.
5. Explore other alternatives for solving the critical-speed problem. The seemingly obvious answer to a critical-speed problem is to reduce the operating speed of the agitator, and this option should always be checked out. However, it can introduce complications of its own. In particular, the lower speed will change the process performance of the agitator, and accordingly a larger impeller will be required for meeting performance requirements. Because larger impellers weigh more, the critical-speed determination must be made anew.

Apart from its effect on critical speed, such an impeller will affect horsepower requirements. Furthermore, the speed change may require a new gear reducer.

The critical-speed problem may in some cases be solved hand in hand with a common problem related to dynamic loads. One source of dynamic loads on an agitator shaft is the waves and vortices that occur when an impeller operates near the liquid surface, such as when a tank fills or empties.

Adding stabilizer fins to the impeller blades will help reduce some of these loads. Such fins also permit the agitator to operate closer to critical speed, perhaps at 80 percent rather than 65 percent.

Suppose, for instance, that the $2.5-\mathrm{in}$ shaft is used and stabilizer fins add $16 \mathrm{lb}(7.3 \mathrm{~kg})$ to the weight of the lower impeller. The equivalent weight increases accordingly:

$$
W_{e}=(59.5+16)+59.5(80 / 130)^{3}+\left[0.228(2.5)^{2}\right][130 / 4]=136 \mathrm{lb}
$$

and the critical speed decreases:

$$
N_{c}=371,400(2.5)^{2} /\left[130(136)^{1 / 2}(130+16)^{1 / 2}\right]=127 \mathrm{r} / \mathrm{min}
$$

The operating speed of $100 \mathrm{r} / \mathrm{min}$ is now 79 percent of critical, which is just within the aforementioned 80 percent ceiling.

Another alternative to avoid critical-speed problems is the use of a shorter shaft. Reducing the shaft length and impeller extensions by 10 in ( 0.25 m ) reduces equivalent weight to

$$
W_{e}=59.5+59.5(70 / 120)^{3}+\left[0.228(2.5)^{2}\right][120 / 4]=114 \mathrm{lb}
$$

At $114 \mathrm{lb}(51.8 \mathrm{~kg})$, the critical speed increases to

$$
N_{c}=371,400(2.5)^{2} /\left[120(114)^{1 / 2}(120+16)^{1 / 2}\right]=155 \mathrm{r} / \mathrm{min}
$$

At $155 \mathrm{r} / \mathrm{min}$, the operating speed is slightly less than 65 percent of critical speed. If the reduced shaft length can be achieved by reducing the mounting height, the impeller location and performance remain unchanged. Otherwise, review process conditions. Other design changes, such as a smaller shaft below the upper impeller, may reduce equivalent weight and increase critical speed.

The additional cost of the material for a larger-diameter shaft is rarely a major factor for carbon or stainless steel, but may be sizeable for special alloys. The additional cost of a larger mechanical seal, for pressurized applications, may add considerable cost regardless of the shaft material.

### 12.8 VISCOSITY DETERMINATION FROM IMPELLER POWER

A helical ribbon impeller, 45 in ( 1.14 m ) diameter, is operated in a 47-in (1.19-m) diameter reactor; estimate the fluid viscosity from torque readings. The impeller is a single-turn helix with a $1: 1$ pitch, so the height of the impeller is the same as the diameter, 45 in ( 1.14 m ). It is a double-flight helix, each blade of which is 4.5 in ( 0.114 m ) wide.

The agitator on the reactor is instrumented with a tachometer and torque meter. In the early stages of a polymerization, the impeller is operated at $37 \mathrm{r} / \mathrm{min}$ and the torque reading is $460 \mathrm{in} \cdot \mathrm{lb}(52 \mathrm{~N}$. $\mathrm{m})$. As the viscosity increases during polymerization, the agitator is slowed to $12 \mathrm{r} / \mathrm{min}$. The reaction is stopped when the torque reaches $27,300 \mathrm{in} \cdot \mathrm{lb}(3085 \mathrm{~N} \cdot \mathrm{~m})$. As a final check on the polymer, an additional torque reading of $20,600 \mathrm{in} \cdot \mathrm{lb}(2328 \mathrm{~N} \cdot \mathrm{~m})$ is taken at $8 \mathrm{r} / \mathrm{min}$. Assume that the polymer has a specific gravity of 0.92 throughout the polymerization. What is the apparent viscosity of the polymer at the early stage of the process and at the two final conditions?

## Calculation Procedure

1. Estimate viscous power number for the helix impeller. A helical-ribbon impeller, also called a helix impeller, is used primarily when high-viscosity fluids are being processed. Most of the power data on such impellers have been obtained in the laminar and transitional flow ranges. The effect on power of common geometry factors, i.e., impeller diameter $D$, $\operatorname{tank}$ diameter $T$, helix pitch $P$, impeller height $H$, and helix (blade) width $W$, can be incorporated into a correlation for a (dimensionless) viscous power number:

$$
N_{P}^{*}=96.9[D /(T-D)]^{0.5}[1 / P][H / D][W / D]^{0.16}
$$

For the impeller described in this problem the power number is

$$
N_{P}^{*}=96.9[45 /(47-45)]^{0.5}[1 / 1][45 / 45][4.5 / 4.5]^{0.16}=318
$$

The viscous power number is defined in terms of power $P$, viscosity $\mu$, shaft speed $N$, and impeller diameter $D$ :

$$
N_{P}^{*}=P / \mu N^{2} D^{3}=N_{P} N_{\mathrm{Re}}
$$

Thus, viscous power number $N_{P}^{*}$ is related to turbulent power number $N_{P}$ by the factor of the Reynolds number $N_{\mathrm{Re}}$. The viscous power number is chosen as a correlating value because it has a constant value in the viscous, low - Reynolds number range, less than 60 ( $N_{\mathrm{Re}}<60$ ). Using the viscous power number in the laminar range eliminates fluid density from the correlation, which is appropriate.
2. Estimate viscosity at early stages of polymerization. The torque $\tau$ measurement, combined with shaft speed, can be converted to power:

$$
P=\tau N / 63,025=(460)(37) / 63,025=0.27 \mathrm{hp}
$$

In this equation, 63,025 is a conversion factor for dimensional consistency.
At $0.27 \mathrm{hp}(0.20 \mathrm{~kW})$, a constant viscous power number can be used to predict an apparent viscosity, with the aid of a $6.11 \times 10^{-15}$ units-conversion factor:

$$
\begin{aligned}
\mu_{a} & =P / N_{P}^{*} N^{2} D^{3}=0.27 /\left(6.11 \times 10^{-15}\right)(318)(37)^{2}(45)^{3} \\
& =1114 \mathrm{cP}
\end{aligned}
$$

Now, a viscosity of 1114 cP is low for viscous (laminar) flow conditions to exist. So, it is prudent to check the magnitude of $N_{\mathrm{Re}}$ :

$$
N_{\mathrm{Re}}=D^{2} N \rho / \mu=(10.7)(45)^{2}(37)(0.92) / 1114=662
$$

where 10.7 is for dimensional consistency when $\rho$ is specific gravity.
While not fully turbulent, a Reynolds number of 662 is not laminar either. It is in the transitional range, so a correction factor from Fig. 12.8 must be applied to the viscous power number. This is done in step 3.

The term "apparent viscosity" refers to a viscosity that has been back-calculated from impeller torque or horsepower. A true-viscosity reading should be measured at a fixed and known shear rate. The effective shear rate developed by a mixing impeller is really a distribution of different shear rates. This distribution is probably most closely related to the shear between the helix blade and the tank


FIGURE 12.8 Viscosity power factor for viscous power number of a helix impeller as a function of impeller Reynolds number.
wall, but other shear rates may affect power. If viscosity is shear-dependent, as often happens with high-viscosity polymers, the velocity distribution will affect the apparent viscosity. Different impeller types may give different apparent viscosities at the same shaft speed.

Different speeds will provide different shear rates and perhaps different apparent viscosities for many viscous fluids. Apparent viscosities measured by a mixing impeller are more useful for mixer design than those obtained with a viscometer, because the appropriate distribution of shear rates are included in the measurements.
3. Reestimate viscosity for intermediate Reynolds number. In the intermediate Reynolds number range, $60<N_{\mathrm{Re}}<20,000$ (for a helix impeller), the viscous power number is not constant, nor is the turbulent power number. Figure 12.8, a graph of the viscosity power factor as a function of the Reynolds number, can be used to correct the viscous power number in the transitional range.

At a Reynolds number of 662 , the viscosity power factor $f_{\mu}$ is approximately 1.8. Applying this factor to the power number used in the apparent-viscosity calculation of step 2 enables the estimation of another apparent viscosity:

$$
\mu_{a}=0.27 /\left(6.11 \times 10^{-15}\right)(1.8)(318)(37)^{2}(45)^{3}=619 \mathrm{cP}
$$

Another estimate of Reynolds number based on a viscosity of 619 cP gives a value of 1191. At a Reynolds number of 1191 , the power factor becomes 2.3 , which leads to an apparent viscosity of 484 . A few more iterations reach an estimated viscosity of 370 cP , based on a correction factor of 3.0 at a Reynolds number of 1994.

Several iterations are required, because power becomes less dependent on viscosity as conditions approach the turbulent range, typically $N_{\mathrm{Re}}>20,000$. In the turbulent range, power is independent of viscosity, and impeller power cannot be used to estimate viscosity.
4. Determine apparent viscosities at the end of the process. As the polymerization proceeds, the viscosity increases. Higher viscosity means higher torque. Reducing the agitator speed is necessary to keep the torque and power within the capabilities of the agitator. At the end of the process, with the agitator turning at $12 \mathrm{r} / \mathrm{min}$, the torque reaches $27,300 \mathrm{in} \cdot \mathrm{lb}(3085 \mathrm{~N} \cdot \mathrm{~m})$ and the power required (see step 2) is

$$
P=(27,300)(12) / 63,025=5.20 \mathrm{hp}
$$

At $5.20 \mathrm{hp}(3.88 \mathrm{~kW})$, the apparent viscosity is

$$
\mu_{a}=5.20 /\left(6.11 \times 10^{-15}\right)(318)(12)^{2}(45)^{3}=204,000 \mathrm{cP}
$$

At 204,000 cP, the Reynolds number is only

$$
N_{\mathrm{Re}}=(10.7)(45)^{2}(12)(0.92) / 204,000=1.2
$$

which is well into the viscous (laminar) range. At these conditions, power and torque are proportional to viscosity at a set speed and the viscosity power factor is 1 .

The same calculations at $8 \mathrm{r} / \mathrm{min}$ and $20,600 \mathrm{in} \cdot \mathrm{lb}(2328 \mathrm{~N} \cdot \mathrm{~m})$ show the following:

$$
\begin{aligned}
P & =(20,600)(8) / 63,025=2.61 \mathrm{hp} \\
\text { and } \quad \mu_{a} & =2.61 /\left(6.11 \times 10^{-15}\right)(318)(8)^{2}(45)^{3}=230,000 \mathrm{cP}
\end{aligned}
$$

Thus, the fluid appears to be more viscous at the lower speed. Another view of the fluid properties is that as agitator speed increases, the shear rate increases and the viscosity decreases. This fluid behavior is called "shear thinning" and is typical of many polymers.

Thus, a properly instrumented reactor may be used as a viscometer for high-viscosity fluids.

### 12.9 NONGEOMETRIC SCALEUP FOR LIQUID AGITATION

A process involving a water-like liquid must be scaled up from an agitated 18 -in ( $0.46-\mathrm{m}$ ) diameter, $15-\mathrm{gal}\left(0.057-\mathrm{m}^{3}\right)$ pilot-scale reactor to a $120-\mathrm{in}(3.05-\mathrm{m})$ diameter, $7000-\mathrm{gal}\left(26.5-\mathrm{m}^{3}\right)$ large-scale reactor. The pilot-scale reactor has a $18-\mathrm{in}(0.46-\mathrm{m})$ straight side and the large-scale reactor will have a $168-$ in $(4.27-m)$ straight side. Both reactors have ASME dished heads on the top and bottom. Successful process performance was obtained in the pilot scale with two $6.0-\mathrm{in}$ - ( $0.15-\mathrm{m}-$ ) diameter pitched-blade turbines operating at $350 \mathrm{rev} / \mathrm{min}(5.83 \mathrm{rev} / \mathrm{s})$. It is proposed that the large-scale reactor use hydrofoil impellers instead of pitched-blade turbines, for improved liquid motion. Each pitchedblade turbine has a turbulent power number of 1.37 and each hydrofoil has a power number of 0.3 . Past scaleup experiences with similar processes, but with geometrically similar tanks, were successful when impeller tip speed was held constant.

## Calculation Procedure

1. Calculate the liquid levels. Liquid level is usually measured from the center of the bottom of the vessel head. So, the head volume must be subtracted from the total volume to calculate the straight-side liquid level; then the head depth must be added to the straight-side liquid level.

In the pilot-scale reactor, an ASME head of 18 -in $(0.46-\mathrm{m})$ diameter has a volume of 2.04 gal $\left(0.0077 \mathrm{~m}^{3}\right)$ and a depth to the straight side of 3.16 in $(0.080 \mathrm{~m})$. Tables for head depths and volumes can be found in many engineering handbooks. The straight side holds ( $15 \mathrm{gal}-2.04 \mathrm{gal}$ ), or 12.96 gal $\left(0.049 \mathrm{~m}^{3}\right)$. Working from the formula for the volume of a cylinder, which is (base area) $\times$ (height), the height is calculated by dividing the volume by the cross-sectional area. The cylindrical volume is $12.96 \mathrm{gal}\left(0.049 \mathrm{~m}^{3}\right)$, which is $(12.96 \mathrm{gal})\left(231 \mathrm{in}^{3} / \mathrm{gal}\right)$ or $2994 \mathrm{in}^{3}$. The cross-sectional area of the tank is $\pi T^{2} / 4=\pi 18^{2} / 4=254.5 \mathrm{in}^{2}\left(0.164 \mathrm{~m}^{2}\right)$. Dividing cylinder volume by cross-sectional area, $2994 \mathrm{in}^{3} / 254.5 \mathrm{in}^{2}$, gives $11.76 \mathrm{in}(0.30 \mathrm{~m})$ liquid level in the straight side of the tank. The total liquid level is the sum of the straight-side level and the head depth: $11.76+3.16=14.9$ in $(0.379 \mathrm{~m})$. Because from $5 \%$ to $10 \%$ of the calculated tank volume is typically filled by tank internals, such as impellers, shaft, and baffles, the actual liquid level may be closer to $1.10(14.9)=16.4$ in ( 0.417 m ).

Similar calculations can be done for the large-scale tank. A 120-in (3.05-m) diameter ASME head has a volume of $605 \mathrm{gal}\left(2.29 \mathrm{~m}^{3}\right)$ and a depth of $20.7 \mathrm{in}(0.53 \mathrm{~m})$. The 7000 -gal volume has $7000-605=6395 \mathrm{gal}\left(24.2 \mathrm{~m}^{3}\right)$ in the straight side, which leaves a straight-side liquid level of $(6395)(231) /\left(\pi 120^{2} / 4\right)=1,477,245 / 11,310=130.6$ in $(3.32 \mathrm{~m})$. The total liquid level is $130.6+$ $20.7=151.3$ in $(3.84 \mathrm{~m})$. If the liquid level is adjusted for tank internals, the expected liquid level is $1.10(151.3)=166$ in $(4.23 \mathrm{~m})$. This liquid depth will easily fit in a tank with a 168 -in ( 4.27 m ) straight side.

Note that the ratio of liquid level to tank diameter on the pilot scale is $16.4 / 18.0$ or 0.91 , whereas the ratio for the large-scale vessel is $166 / 120$ or 1.38 . For geometric similarity, all such length ratios should instead be equal. Since the ratios are not equal in this case, it is necessary to use nongeometric scaleup.
2. Consider the options and issues involved in direct scaleup for reactors that are not geometrically similar, and apply them to the present example. Although a direct scaleup based on equal tip speed is an option, many unanticipated changes may occur in the absence of geometric similarity. For instance, two hydrofoil impellers of $40-\mathrm{in}(1.02-\mathrm{m})$ diameter could be chosen for the large-scale reactor. A simple tip-speed scaleup would require an adjustment to the pilot-scale speed by the inverse ratio of the impeller diameters: $(350 \mathrm{rev} / \mathrm{min})(6 / 40)=52.5 \mathrm{rev} / \mathrm{min}(0.875 \mathrm{rev} / \mathrm{s})$. As a basic check, impeller tip speed for the pilot-scale reactor can be calculated by multiplying the circumference at the blade tip by the rotational speed: $\pi(6 \mathrm{in})(350 \mathrm{rev} / \mathrm{min})=6597 \mathrm{in} / \mathrm{min}$ or $550 \mathrm{ft} / \mathrm{min}(2.79 \mathrm{~m} / \mathrm{s})$. The same calculation for the large-scale reactor gives $\pi(40 \mathrm{in})(52.5 \mathrm{rev} / \mathrm{min})=6597 \mathrm{in} / \mathrm{min}$ or 550 $\mathrm{ft} / \mathrm{min}(2.79 \mathrm{~m} / \mathrm{s})$. These scaleup results have the same tip speed. Unfortunately, however, we cannot

[^16]
## LIQUID AGITATION

be sure that the arbitrarily chosen hydrofoil diameter is correct, nor whether the liquid-level ratio is important, nor whether other factors need to be considered.

One means for considering such other effects in scaleup is to calculate other basic values, such as power per volume and torque per volume, both of which can be used to describe agitation intensity. Problem 12.1 goes through some details of calculating impeller power. For the situation under consideration here, since the fluid is described as waterlike, a specific gravity of 1.0 and a viscosity of 1.0 cp are appropriate. With these characteristics, a correction for Reynolds number effects is not needed, and a constant power number can be applied in the calculations. (A more comprehensive power calculation might include effects of such factors as viscosity, density, off-bottom clearance, and impeller spacing; these additional corrections should be made at any point in the calculations when they are significant. However, in this example, and in many real applications, such corrections are not essential for scaleup.)

Using the power number of 1.37 for the pitched-blade turbine, impeller power in the pilot-scale reactor can be calculated as shown in Example 12.1 by $1.37(1.0)(350)^{3}(6)^{5} /\left(1.524 \times 10^{13}\right)=0.030 \mathrm{hp}$ ( 22.35 W ). Since two impellers are used, double this value gives a fair representation of the total power: $2(0.030)=0.060 \mathrm{hp}(44.7 \mathrm{~W})$. Power per volume in the pilot scale is $0.060 \mathrm{hp} / 15 \mathrm{gal}=0.004 \mathrm{hp} / \mathrm{gal}$ $\left(787 \mathrm{~W} / \mathrm{m}^{3}\right)$. Power per volume is often reported with respect to 1000 gal for reasonable size values: $(1000)(0.060) / 15=4.00 \mathrm{hp} / 1000 \mathrm{gal}\left(787 \mathrm{~W} / \mathrm{m}^{3}\right)$. Torque is simply power divided by speed; including a units-conversion factor $(63,025)$, the impeller torque is $63,025(0.060 \mathrm{hp}) /(350 \mathrm{rev} / \mathrm{min})=10.8$ in-lb (1.22 N-m). On a thousand-gallon basis, the torque per volume is (1000)(10.8)/15 $=720$ in-lb/1000 gal ( $21.5 \mathrm{~N}-\mathrm{m} / \mathrm{m}^{3}$ ).

The same calculations for the large-scale reactor with two 40-in hydrofoil impellers start with the power calculation. The specified hydrofoil impeller has a power number of 0.30. (Because of individual geometries, this value may differ depending on the manufacture and impeller style.) For the proposed hydrofoil impellers, the power for two impellers is $(2) 0.30(1.0)(52.5)^{3}(40)^{5} /\left(1.524 \times 10^{13}\right)=$ $0.583 \mathrm{hp}(435 \mathrm{~W})$. The power per volume is $1000(0.583) / 7000=0.08 \mathrm{hp} / 1000 \mathrm{gal}\left(16.4 \mathrm{~W} / \mathrm{m}^{3}\right)$. This scaleup results in only $0.08 / 4.0=0.02$ or only $2 \%$ of the power per volume used in the pilotscale reactor. The torque for the large scale is $63,025(0.583) / 52.5=700 \mathrm{in}-\mathrm{lb}(79 \mathrm{~N}-\mathrm{m})$. Torque per volume is $1000(700) / 7000=100 \mathrm{in}-\mathrm{lb} / 1000 \mathrm{gal}\left(2.8 \mathrm{~N}-\mathrm{m} / \mathrm{m}^{3}\right)$. In this case, large-scale torque per volume is $100 / 720=0.14$ or $14 \%$ of the value in the pilot scale.

Power per volume is often associated with agitation for mass transfer, and torque per volume is often related to liquid velocities. If these values change drastically on scaleup-as is the case in the present example-the agitation intensity will also change significantly. Admittedly, the values will change even under geometric similarity; but torque per unit volume should not be less than onethird the original value, unless the pilot scale was tested with much more than the minimum level of agitation.

The drastic changes in power and torque per unit volume experienced in the present example signal the need to adopt step-by-step nongeometric scaleup. A systematic approach, as shown in the steps that follow, will identify problems and suggest possible remedies. The order of the scaleup steps is not critical, but the one used in this example works well. Not all of the steps are required in all scaleup problems and some steps can be used for other applications.
3. Conduct a geometric-similarity scaleup. Perhaps paradoxically, a good starting point even for nongeometric scaleup is making a geometric-similarity one. For one thing, the rotational-speed changes are predictable. And, at least one key variable can be held constant. For geometric similarity, the ratios of all the length dimensions are the same from the small to the large scale. Thus a tank diameter scaleup from 18 in ( 0.46 m ) to 120 in $(3.05 \mathrm{~m})$ represents a geometric ratio of $120 / 18=6.67$. Applying this ratio to the impeller diameter gives a large-scale-impeller diameter of $(6)(120 / 18)=40$ in $(1.02 \mathrm{~m})$. For tip speed $(\pi D N)$ to remain constant, the rotational speed of the pilot scale must be adjusted in inverse proportion to the geometric ratio: $(350)(6 / 40)=52.5 \mathrm{rev} / \mathrm{min}$ ( $0.88 \mathrm{rev} / \mathrm{s}$ ).

For all of the geometric ratios to be the same, the liquid level in the large-scale vessel has to be $(16.4)(120 / 18)=109$ in $(2.77 \mathrm{~m})$. Based on the same large-scale head dimensions and volume
calculations discussed in the first step of the example (and taking into account the extra $10 \%$ for internals), the geometric-similarity volume in a $120-\mathrm{in}(3.05-\mathrm{m})$ diameter tank is calculated as 4444 gal ( $16.8 \mathrm{~m}^{3}$ ).

To verify this scaleup step, calculate tip speed as $\pi(40)(52.5) / 12=550 \mathrm{ft} / \mathrm{min}(2.79 \mathrm{~m} / \mathrm{s})$. The power required for two impellers is $(2)(1.37)(1.0)(52.5)^{3}(40)^{5} /\left(1.524 \times 10^{13}\right)=2.66 \mathrm{hp}$ $(1987 \mathrm{~W})$. Power per volume is $1000(2.66) / 4444=0.60 \mathrm{hp} / 1000 \mathrm{gal}\left(118 \mathrm{~W} / \mathrm{m}^{3}\right)$. Torque is $63,025(2.66) / 52.5=3193 \mathrm{in}-\mathrm{lb}(360 \mathrm{~N}-\mathrm{m})$ and torque per volume is $1000(3193) / 4444=720 \mathrm{in}-$ $\mathrm{lb} / 1000 \mathrm{gal}\left(21.5 \mathrm{~N}-\mathrm{m} / \mathrm{m}^{3}\right)$.

A geometric-similarity scaleup with constant tip speed also keeps the torque/volume constant. Because liquid velocities (torque/volume) are an important measure of agitation intensify in liquid agitation problems, keeping torque/volume constant is more important than keeping power/volume constant. For this scale change, power per volume is $0.6 / 4.0=0.15$ or $15 \%$ of the pilot scale. A power/volume scaleup for this scale change would be a very conservative design, but one that is potentially appropriate for certain applications.
4. Apply a volume adjustment to the results of step 3. Since geometric similarity scaleup resulted in a volume of only $4444 \mathrm{gal}\left(16.8 \mathrm{~m}^{3}\right)$ in a $120-\mathrm{in}(3.05-\mathrm{m})$ diameter tank and the design specification called for $7000 \mathrm{gal}\left(26.5 \mathrm{~m}^{3}\right)$ a higher liquid level is required. Based on the calculations in step 1 , the open-tank liquid level would be 99.1 in ( 2.52 m ). Allowing $10 \%$ for internals, the actual liquid level will be about 109 in ( 2.77 m ).

For equal tip speed and impellers with geometric similarity, the rotational speed remains the same in spite of the added liquid level. Thus, the power and torque remain the same for the same impellers, speed, and fluid properties. However, the volume change affects power per volume: $1000(2.66 \mathrm{hp}) / 7000 \mathrm{gal}=0.38 \mathrm{hp} / 1000 \mathrm{gal}\left(75.0 \mathrm{~W} / \mathrm{m}^{3}\right)$. Similarly, the torque per volume is reduced to $1000(3193 \mathrm{in}-\mathrm{lb}) / 7000 \mathrm{gal}=456 \mathrm{in}-\mathrm{lb} / 1000 \mathrm{gal}\left(13.6 \mathrm{~N}-\mathrm{m} / \mathrm{m}^{3}\right)$. Both changes represent a substantial reduction in agitation intensity from the pilot-scale results.
5. Adjust the step 4 results to gain constant torque/volume. Because equal tip speed with geometric similarity gives equal torque/volume, those two different scaleup criteria are often confused with each other when evaluating previous scaleup experience. In the present example, it seems appropriate to supplement step 4's volume adjustment with an adjustment for equal torque per unit volume. Equal torque per unit volume should keep velocity magnitudes similar, thus giving the appearance of similar liquid agitation intensity. To maintain the pilot-vessel torque per volume of $720 \mathrm{in}-\mathrm{lb} / 1000 \mathrm{gal}(21.5 \mathrm{~N}$ $\left.\mathrm{m} / \mathrm{m}^{3}\right)$ in the $7000-\mathrm{gal}\left(26.5-\mathrm{m}^{3}\right)$ vessel, the large-vessel torque must be $7000(720) / 1000=5040 \mathrm{in}-\mathrm{lb}$ ( $569 \mathrm{~N}-\mathrm{m}$ ). Combining the formulas for power and torque gives torque as $N_{P} \rho N^{2} D^{5}$, which is divided by a conversion factor of $2.418 \times 10^{8}$. Rearranging this torque formula and solving for impeller speed gives an equal-torque-per-unit-volume speed of

$$
N=\left[\frac{2.418 \times 10^{8}(5040)}{2(1.37)(1.0)(40.0)^{5}}\right]^{1 / 2}=65.9 \mathrm{rev} / \mathrm{min}(1.10 \mathrm{rev} / \mathrm{s})
$$

At $65.9 \mathrm{rev} / \mathrm{min}(1.10 \mathrm{rev} / \mathrm{s})$ the power is $(2)(1.37)(1.0)(65.9)^{3}(40.0)^{5} / 1.524 \times 10^{13}=5.27 \mathrm{hp}(3927$ $\mathrm{W})$ and power per volume is $0.75 \mathrm{hp} / 1000 \mathrm{gal}\left(148 \mathrm{~W} / \mathrm{m}^{3}\right)$. However, tip speed now becomes $\pi(65.9)(40.0 / 12)=690 \mathrm{ft} / \mathrm{min}(3.51 \mathrm{~m} / \mathrm{s})$. Whether this increase in tip speed is an advantage or disadvantage depends on the process. Without further pilot-scale testing, which will be discussed later, insufficient information is available to choose the preferred criterion.
6. Adjust the step 5 results to gain constant tip speed in addition to constant torque per unit volume. In the past two steps, the volume increase from $4444 \mathrm{gal}\left(16.8 \mathrm{~m}^{3}\right)$ to $7000 \mathrm{gal}\left(26.5 \mathrm{~m}^{3}\right)$ has been accomplished while holding either tip speed or torque per unit volume constant. However, with a change in the impeller diameter, both tip speed and torque per unit volume can be held constant simultaneously. Since turbulent conditions imply a constant power number, and since geometrically
similar impellers imply the same power number, the mathematical expressions for tip speed and torque per volume can be simplified to expressions involving rotational speeds, impeller diameters, and liquid volumes. In what follows, the subscripts 1 and 2 represent the characteristics for the small and large volumes, respectively.

Constant Tip Speed

$$
N_{1} D_{1}=N_{2} D_{2}
$$

Constant Torque per Volume

$$
\frac{N_{1}^{2} D_{1}^{5}}{V_{1}}=\frac{N_{2}^{2} D_{2}^{5}}{V_{2}}
$$

Eliminating Constant Tip Speed

$$
\begin{aligned}
N_{1}^{2} D_{1}^{2} \frac{D_{1}^{3}}{V_{1}} & =N_{2}^{2} D_{2}^{2} \frac{D_{2}^{3}}{V_{2}} \\
\frac{D_{1}^{3}}{V_{1}} & =\frac{D_{2}^{3}}{V_{2}}
\end{aligned}
$$

Solving for Impeller Diameter

$$
\begin{aligned}
D_{2} & =D_{1}\left(\frac{V_{2}}{V_{1}}\right)^{1 / 3} \\
D_{2} & =40.0\left(\frac{7000}{4444}\right)^{1 / 3} \\
& =46.5 \mathrm{in}(1.18 \mathrm{~m})
\end{aligned}
$$

## Solving for Rotational Speed

$$
\begin{aligned}
N_{2} & =N_{1}\left(\frac{D_{1}}{D_{2}}\right) \\
N_{2} & =52.5\left(\frac{40.0}{46.5}\right) \\
& =45.1 \mathrm{rev} / \mathrm{min}(0.75 \mathrm{rev} / \mathrm{s})
\end{aligned}
$$

The power required to rotate two impellers of $46.5-\mathrm{in}(1.18-\mathrm{m})$ diameter at $45.1 \mathrm{rev} / \mathrm{min}(0.75 \mathrm{rev} / \mathrm{s})$ is $(2)(1.37)(1.0)(45.1)^{3}(46.5)^{5} / 1.524 \times 10^{13}=3.59 \mathrm{hp}(2689 \mathrm{~W})$ or $1000(3.59) / 7000=0.51$ $\mathrm{hp} / 1000 \mathrm{gal}\left(102 \mathrm{~W} / \mathrm{m}^{3}\right)$. Torque is $63,025(3.59) / 45.1=5017 \mathrm{in}-\mathrm{lb}(567 \mathrm{~N}-\mathrm{m})$ and torque per volume is $1000(5,017) / 7000=717 \mathrm{in}-\mathrm{lb} / 1000 \mathrm{gal}\left(21.4 \mathrm{~N}-\mathrm{m} / \mathrm{m}^{3}\right)$. Tip speed is $\pi(45.1)(46.5 / 12)=$ $550 \mathrm{ft} / \mathrm{min}(2.79 \mathrm{~m} / \mathrm{s})$. Thus, with a small adjustment in impeller diameter, both torque per volume and tip speed can be held constant. Since liquid level has changed, geometric similarity no longer applies and an impeller diameter adjustment may be an acceptable option.
7. Investigate changing the number of impellers. When the volume changes from 4444 gal ( 16.8 $\mathrm{m}^{3}$ ) to $7000 \mathrm{gal}\left(26.5 \mathrm{~m}^{3}\right)$, the volume ratio is $7000 / 4444=1.56$. Since the volume ratio is approximately 1.5 , consider 1.5 times the number of impellers, or three impellers. More impellers in a tall tank are a good answer simply because the agitation effects are spread through the height of the vessel.

The result with three impellers looks much like the geometric similarity scaleup with an additional half tank on the top.

For three impellers with a constant-tip-speed adjustment from the geometric similarity scaleup, the power is $3(1.37)(1.0)(52.5)^{3}(40.0)^{5} / 1.524 \times 10^{13}=4.00 \mathrm{hp}(2980 \mathrm{~W})$ or $1000(4.00) / 7000=$ $0.57 \mathrm{hp} / 1000 \mathrm{gal}\left(112 \mathrm{~W} / \mathrm{m}^{3}\right)$. Torque is $63,025(4.00) / 52.5=4800 \mathrm{in}-\mathrm{lb}(542 \mathrm{~N}-\mathrm{m})$ and torque per volume is $1000(4800) / 7000=685 \mathrm{in}-\mathrm{lb} / 1000 \mathrm{gal}\left(20.5 \mathrm{~N}-\mathrm{m} / \mathrm{m}^{3}\right)$. The addition of a third impeller for the volume adjustment leaves tip speed constant and both power per volume and torque per volume almost unchanged.

This solution appears best for the initial changes using the same style impellers. However, we can still investigate the effect of changing impeller type.
8. Investigate changing impeller type while keeping tip speed constant. A change in impeller type requires a new power number for the calculations. The typical hydrofoil impeller in this problem has a power number of 0.3 , compared with the 1.37 power number for the pitched-blade turbines considered in the six previous steps. Following the success of the pitched-blade design with three impellers, consider replacing these impellers with hydrofoil impellers. To keep tip speed constant, the impeller diameters and rotational speed can remain unchanged from those of the pitched-blade-turbine case. Thus, power is $3(0.3)(1.0)(52.5)^{3}(40.0)^{5} / 1.524 \times 10^{13}=0.875 \mathrm{hp}(653 \mathrm{~W})$ and power per volume is $1000(0.875) / 7000=0.13 \mathrm{hp} / 1000 \mathrm{gal}\left(24.6 \mathrm{~W} / \mathrm{m}^{3}\right)$. Torque is $63,025(0.875) / 52.5=1050 \mathrm{in}-\mathrm{lb}$ $(119 \mathrm{~N}-\mathrm{m})$ and torque per volume is $1000(1050) / 7000=150 \mathrm{in}-\mathrm{lb} / 1000 \mathrm{gal}\left(4.5 \mathrm{~N}-\mathrm{m} / \mathrm{m}^{3}\right)$. Although hydrofoil impellers are more efficient than pitched-blade turbines for most blending problems, in this instance they are providing only one-fifth of the original torque per unit volume, which is not going to provide as much agitation intensity as was found in the pilot scale.
9. Change impeller type with equal tip speed and adjusted torque per volume. Calculations similar to those of step 6 can be used to keep both tip speed and torque per volume constant when the impeller type is changed. Because volume does not change, that factor is removed from the calculations, but the change in impeller type means that power number must be included. In addition, a hydrofoil impeller is more efficient at creating liquid motion than a pitched-blade turbine; therefore, the torque required by the hydrofoil impeller will be assumed to be half that of the pitched-blade turbine. The subscript 1 will be used for the pitched-blade turbine and the subscript 2 will be used for the hydrofoil impeller.

Constant Tip Speed

$$
N_{1} D_{1}=N_{2} D_{2}
$$

Half the Pitched-Blade Torque

$$
\frac{N_{P_{1}} N_{1}^{2} D_{1}^{5}}{2}=N_{P_{2}} N_{2}^{2} D_{2}^{5}
$$

The relative amounts of torque required by different impellers are not fixed values; they must be evaluated for individual situations. This complication demonstrates that equal values for properties or characteristics do not need to be applied in all situations.

Eliminating Constant Tip Speed

$$
\begin{aligned}
N_{1}^{2} D_{1}^{2} \frac{N_{P_{1}} D_{1}^{3}}{2} & =N_{2}^{2} D_{2}^{2} N_{P_{2}} D_{2}^{3} \\
\frac{N_{P_{1}} D_{1}^{3}}{2} & =N_{P_{2}} D_{2}^{3}
\end{aligned}
$$

## Solving for Impeller Diameter

$$
\begin{aligned}
D_{2} & =D_{1}\left(\frac{N_{P_{1}}}{2 N_{P_{2}}}\right)^{1 / 3} \\
D_{2} & =40.0\left(\frac{1.37}{2(0.3)}\right)^{1 / 3} \\
& =52.7 \mathrm{in}(1.34 \mathrm{~m})
\end{aligned}
$$

The power number for individual impellers should be used in this calculation. If different style or size impellers were used at different locations, separate calculations for each impeller would be required.

Solving for Rotational Speed

$$
\begin{aligned}
N_{2} & =N_{1}\left(\frac{D_{1}}{D_{2}}\right) \\
N_{2} & =52.5\left(\frac{40.0}{52.7}\right) \\
& =39.9 \mathrm{rev} / \mathrm{min}(0.66 \mathrm{rev} / \mathrm{s})
\end{aligned}
$$

The power for three hydrofoil impellers of $52.7-\mathrm{in}(1.34-\mathrm{m})$ diameter operating at $39.9 \mathrm{rev} / \mathrm{min}$ $(0.66 \mathrm{rev} / \mathrm{s})$ is $(3)(0.3)(1.0)(39.9)^{3}(52.7)^{5} / 1.524 \times 10^{13}=1.52 \mathrm{hp}$ (1131 W). Power per unit volume is $1000(1.52) / 7000=0.22 \mathrm{hp} / 1000 \mathrm{gal}\left(42.7 \mathrm{~W} / \mathrm{m}^{3}\right)$. Torque is $63,025(1.52) / 39.9=2399 \mathrm{in}-\mathrm{lb}$ ( $271 \mathrm{~N}-\mathrm{m}$ ) and torque per volume is $1000(2,399) / 7000=343 \mathrm{in}-\mathrm{lb} / 1000 \mathrm{gal}\left(10.2 \mathrm{~N}-\mathrm{m} / \mathrm{m}^{3}\right)$. Tip speed is $\pi(39.9)(52.7 / 12)=550 \mathrm{ft} / \mathrm{min}(2.79 \mathrm{~m} / \mathrm{s})$.

These results are consistent with a scaleup from the pilot-scale operation. Although power per volume is reduced and impeller to tank diameter ratio is increased, torque per volume is about half and tip speed is the same. With any realistic scaleup, some factors unavoidably must change, while the important ones are held constant. In a different situation and process, a different variable, such as power per volume, might be held constant. Other variables, such as blend time, could be calculated, at each step in the scaleup.

An important and practical consideration in any non-geometric-similarity scaleup is the idea of making only one change at a time, usually starting with a geometric similarity scaleup to the large-size tank diameter. Then at each step, while adjusting conditions on the large scale, relevant values should be calculated to be sure that unwanted or unacceptable changes do not occur. This process may lead to trial changes with unacceptable results. Such changes must be reexamined for possible alternatives. The solution to this example demonstrates several methods for making design change; in different situations, steps may be eliminated or added as necessary. The steps demonstrated in this problem can be used for a variety of other situations, such as changing impeller size or type in an existing application or changing operating liquid level.

No specific scaleup method can be applied to all problems. Each situation is different. Nongeometric scaleup can be done and is necessary in many situations. However, certain applications, such as solids suspension, which is geometry dependent, should follow geometric similarity scaleup.
Related Calculations. When considering whether tip speed or torque per volume was the preferred method of scaleup for this example, pilot-scale results were not available to suggest possible differences. Some simple comparisons, using different size impellers in the pilot scale, may give better insight into the process behavior. For instance, instead of making all of the tests with two 6 -in $(0.15-\mathrm{m})$ diameter impellers, additional tests could have been made with two 7 -in $(0.18-\mathrm{m})$ diameter impellers.

With a change in impeller diameter, speed adjustment based on equal tip speed, equal torque, or equal power all give different rotational speeds for comparison. Examining a change from the 6 -in
( $0.15-\mathrm{m}$ ) diameter impeller operating at $350 \mathrm{rev} / \mathrm{min}(5.83 \mathrm{rev} / \mathrm{s})$ to a $7-\mathrm{in}(0.18-\mathrm{m})$ diameter impeller shows these differences.

Equal Tip Speed

$$
\begin{aligned}
N_{1} D_{1} & =N_{2} D_{2} \\
N_{2} & =N_{1}\left(\frac{D_{1}}{D_{2}}\right) \\
N_{2} & =350\left(\frac{6}{7}\right) \\
& =300 \mathrm{rev} / \min (5.0 \mathrm{rev} / \mathrm{s})
\end{aligned}
$$

Equal Power

$$
\begin{aligned}
N_{1}^{3} D_{1}^{5} & =N_{2}^{3} D_{2}^{5} \\
N_{2} & =N_{1}\left(\frac{D_{1}}{D_{2}}\right)^{5 / 3} \\
N_{2} & =350\left(\frac{6}{7}\right)^{5 / 3} \\
& =271 \mathrm{rev} / \mathrm{min}(4.5 \mathrm{rev} / \mathrm{s})
\end{aligned}
$$

Equal Torque

$$
\begin{aligned}
N_{1}^{2} D_{1}^{5} & =N_{1}^{2} D_{1}^{5} \\
N_{1} & =N_{2}\left(\frac{D_{1}}{D_{2}}\right)^{5 / 2} \\
N_{1} & =350\left(\frac{6}{7}\right)^{5 / 2} \\
& =238 \mathrm{rev} / \min (4.0 \mathrm{rev} / \mathrm{s})
\end{aligned}
$$

All these calculations assume that all of the fluid properties are the same and the impellers are geometrically similar in turbulent conditions so that the power numbers remain constant. For conditions with variable values, more extensive calculations are necessary. Other changes may occur owing to different impeller to tank diameter ratios and the resulting change in flow patterns. Small changes to impeller diameters are strongly suggested.

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## SIZE REDUCTION*

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### 13.1 SIZE DISTRIBUTIONS OF CRUSHED OR GROUND MATERIAL 13.1

### 13.2 BREAKAGE AND SELECTION FUNCTIONS FROM BATCH BALL-MILL TESTS 13.3

13.3 PREDICTING PRODUCT SIZE DISTRIBUTION FROM FEEDSTOCK DATA 13.4
13.4 MATERIAL-BALANCE CALCULATIONS FOR CLOSED-CIRCUIT GRINDING 13.6
13.5 WORK-INDEX CALCULATIONS 13.7
13.6 POWER CONSUMPTION IN A

GRINDING MILL AS A FUNCTION OF WORK INDEX 13.7
13.7 BALL-MILL OPERATING PARAMETERS 13.8
13.8 MAXIMUM SIZE OF GRINDING MEDIA 13.8
13.9 POWER DRAWN BY A GRINDING MILL 13.9
13.10 WATER REQUIREMENTS FOR CLOSED-CIRCUIT MILL SYSTEM 13.10
REFERENCES 13.12

### 13.1 SIZE DISTRIBUTIONS OF CRUSHED OR GROUND MATERIAL

The data in the first three columns of Table 13.1 show the size distributions of a quartzgold ore obtained by sieving the material. What is the cumulative weight percent passing each sieve size? Also, construct a log-log plot of the cumulative percent versus particle size, and express the resulting relationship as an equation.

## Calculation Procedure

1. Compute the cumulative weight percent passing each sieve size. Add up the weights of samples retained on each screen (the weights are shown in the third column of Table 13.1). Express each as a percent of the total, obtaining the percents shown in the fourth column. Sum the cumulative amounts retained and subtract from 100, obtaining the cumulative percents passing. These are shown in the fifth column.
2. Express the relationship between cumulative percent passing and particle size as an equation. Plot cumulative weight percent passing $(y)$ as a function of particle size $(x)$ in microns (as denoted by size of sieve opening) on log-log paper, as in Fig. 13.1.

The straight-line portion of the plot can be expressed as $y=c x^{b}$. This can be recast into a form that is especially useful for other size-reduction calculations (e.g., see Example 13.2), namely, the

[^17]TABLE 13.1 Input Data and Calculated Results on Ore Size Distribution (Example 13.1)

| Tyler <br> mesh size | Sieve <br> opening, $\mu \mathrm{m}$ | Weight of retained <br> sample, g | Percent retained <br> (by calculation) | Cumulative percent passing <br> (by calculation) |
| :---: | :---: | :---: | :---: | :---: |
| 4 | 4950 | 0 | 0 | 100.0 |
| 6 | 3350 | 7.20 | 3.0 | 97.0 |
| 8 | 2360 | 27.84 | 11.6 | 85.4 |
| 10 | 1700 | 36.96 | 15.4 | 70.0 |
| 14 | 1180 | 43.68 | 18.2 | 51.8 |
| 20 | 850 | 34.08 | 14.2 | 37.6 |
| 28 | 600 | 27.60 | 11.5 | 26.1 |
| 35 | 425 | 16.08 | 6.7 | 19.4 |
| 48 | 300 | 15.36 | 6.4 | 13.0 |
| 65 | 212 | 8.64 | 3.6 | 9.4 |
| 100 | 150 | 6.48 | 2.7 | 6.7 |
| 150 | 106 | 4.56 | 1.9 | 4.8 |
| 200 | 75 | 3.84 | 1.6 | 3.2 |
| 270 | 53 | 2.16 | 0.9 | 2.3 |
| Pan | - | 5.52 | 2.3 | - |



FIGURE 13.1 Cumulative weight percent of particles finer than a given size as a function of the particle size (Example 13.1).

Gaudin-Schuhmann equation, that is, $y=100(x / k)^{a}$, where $a$ (the distribution modulus) is a constant for a particular size distribution, and $k$ (the size modulus) is the 100 percent size, in microns, of the extrapolated straight-line portion of the plot. By applying least-squares curve fitting to the log-log plot, the values of $a$ and $k$ can be obtained, yielding $y=100(x / 2251)^{1.003}$.

Related Calculations. Sometimes the Rosin-Rammler equation is used to represent the size distribution graphically. The dashed line on Fig. 13.1 corresponds to the Rossin-Rammler equation in the form $y=100-100 \exp \left[-(x / A)^{b}\right]$, where, in this case, $A=1558$ and $b=1.135$.

TABLE 13.2 Ball-Mill Test Data on Cement Rock (Example 13.2)

|  |  | Cumulative mass fraction finer than <br> mesh size after noted grinding time |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Tyler mesh size | Sieve opening, $\mu \mathrm{m}$ | 1 min | 2 min | 4 min | 6 min |
| 8 | 2360 | 1.000 | 1.000 | 1.000 | 1.000 |
| 10 | 1700 | 0.450 | 0.695 | 0.910 | 0.966 |
| 48 | 300 | 0.080 | 0.175 | 0.337 | 0.523 |
| 100 | 150 | 0.046 | 0.100 | 0.196 | 0.300 |
| 200 | 75 | 0.030 | 0.062 | 0.126 | 0.195 |
| 400 | 38 | 0.018 | 0.046 | 0.076 | 0.110 |
| Feed size: $-8,+10$ mesh $(8 \times 10$ mesh $)$ |  |  |  |  |  |

### 13.2 BREAKAGE AND SELECTION FUNCTIONS FROM BATCH BALL-MILL TESTS

Determine the breakage characteristics of a cement rock by using selection and breakage functions, calculating these on the basis of the ball-mill test data in Table 13.2. (A "selection function" is a parameter that represents the resistance of some size fraction to being produced during breakage. The "breakage functions" are related quantities that determine the breakage-product size distribution for material broken in this size fraction.)

## Calculation Procedure

1. Calculate the selection function that pertains to the size fraction of the feed material. This selection function $S_{1}$ is defined by the equation

$$
M_{1}(t)=M_{1}(0) \exp \left(-S_{1} t\right)
$$

where $M_{1}(t)$ is the mass fraction of feed remaining after time $t$. Referring to Table 13.2 , note that for this $8 \times 10$ mesh feedstock, $M_{1}(t)$ equals 1 minus the cumulative mass fraction finer than no. 10 mesh at time $t$. Using the data in Table 13.2, we can therefore determine $S_{1}$ by plotting log mass fraction of feed versus grinding time, determining the slope of the resulting straight line by least-squares curve fitting and multiplying the slope by -2.303 . The resulting value is $0.577 \mathrm{~min}^{-1}$.
2. Determine the production rate constant. In batch ball milling, the changes in particulate distribution with time can be characterized [1] by


FIGURE 13.2 Cumulative mass fraction of ground material as a function of grinding time (Example 13.2).

$$
\frac{d Y_{i}(t)}{d t}=\bar{F}_{i}
$$

where $t$ is time, $Y_{i}(t)$ is cumulative mass fraction finer than size $x_{i}$ at time $t$ for short grinding times, and $\bar{F}_{i}$ is cumulative zero-order production rate constant for size $x_{i}$ and the production of fine sizes much smaller than feed size. If, then, a linear plot is made of cumulative mass fraction versus (short) grinding time, the $\bar{F}_{i}$ constants can be determined for each fine size from the slopes of the curves generated. Figure 13.2 shows such a plot for the present data. From the slopes, Table 13.3 can be assembled.

TABLE 13.3 Calculated Production Rate Constants (Example 13.2)

| Particle size $x$ |  |  |
| :---: | :---: | :---: |
| Mesh | Microns | Production rate constant $\bar{F}_{i}$ |
| 48 | 300 | 0.0869 |
| 100 | 150 | 0.0500 |
| 200 | 75 | 0.0325 |
| 400 | 38 | 0.0183 |

3. Determine the breakage functions that pertain to the size fraction of the feed material. Cumulative breakage functions can be calculated [1] from the relation $B_{i, j}=\bar{F}_{i} / S_{j}$. Therefore, in the case of the feed-size selection function $S_{1}$, the equation is $B_{i, 1}=\bar{F}_{i} / S_{1}$, and the breakage functions are as follows:

$$
\begin{gathered}
B_{48 \mathrm{mesh}, 1}=\frac{\bar{F}_{48 \mathrm{mesh}}}{S_{1}}=\frac{0.0869}{0.577}=0.151 \\
B_{100 \mathrm{mesh}, 1}=\frac{0.0500}{0.577}=0.087 \\
B_{200 \mathrm{mesh}, 1}=0.056 \quad \text { and } \quad B_{400 \mathrm{mesh}, 1}=0.032
\end{gathered}
$$

4. Determine the selection and breakage functions for other size fractions of the same material. Selection functions for other size intervals may be calculated via the relation

$$
S_{j}=S_{1}\left[\frac{\left(X_{j} X_{j+1}\right)^{1 / 2}}{\left(X_{1} X_{2}\right)^{1 / 2}}\right]^{a}
$$

where $X_{1}$ and $X_{2}$ are the sieve-opening sizes that define the size fraction of the feed material, $X_{j}$ and $X_{j+1}$ are the sieve openings that define the size fraction whose selection function is now to be calculated, and $a$ is the slope of the log-log plot of the zero-order production rate constants $\bar{F}_{i}$ against particle size $x_{i}$, in microns, from Table 13.3. (That plot is not shown here.) The slope, determined by least-squares curve fitting, is 0.741 . This slope, $a$, happens to be the same as the distribution modulus in the Gaudin-Schuhmann equation (see Example 13.1).

For instance, the selection function for the size fraction, $-10,+14$ mesh (corresponding to sieve openings of 1700 and $1180 \mu \mathrm{~m}$, respectively) can be calculated thus:

$$
S_{2}=0.577\left\{\frac{[1700(1180)]^{1 / 2}}{[2360(1700)]^{1 / 2}}\right\}^{0.741}=0.446
$$

Similar calculations can be made to find selection functions for other size intervals. Then, cumulative breakage functions can be calculated by the relationship noted in step 3, namely, $B_{i, j}=\bar{F}_{i} / S_{j}$.

### 13.3 PREDICTING PRODUCT SIZE DISTRIBUTION FROM FEEDSTOCK DATA

Given the feed size distribution, the breakage functions, and the selection functions (probabilities of breakage) for a feedstock to a grinding operation, as shown in Table 13.4, predict the size distribution for the product from the operation.

TABLE 13.4 Data on Feedstock to Grinding Operation (Example 13.3)

| Size range | Size interval |  | Feed size distribution $F$, percent | Breakage matrix $B$ |  |  |  |  |  | Selection matrix $S$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Tyler mesh | Micron size |  |  |  |  |  |  |  |  |
| 1 | $-6,+8$ | $-3350,+2360$ | 24 | 0.18 | 0 | 0 | 0 | 0 | 0 | 1.00 |
| 2 | $-8,+10$ | $-2360,+1700$ | 16 | 0.22 | 0.18 | 0 | 0 | 0 | 0 | 0.81 |
| 3 | $-10,+14$ | $-1700,+1180$ | 12 | 0.16 | 0.22 | 0.18 | 0 | 0 | 0 | 0.60 |
| 4 | $-14,+20$ | $-1180,+850$ | 10 | 0.12 | 0.16 | 0.22 | 0.18 | 0 | 0 | 0.47 |
| 5 | $-20,+28$ | $-850,+600$ | 7 | 0.10 | 0.12 | 0.16 | 0.22 | 0.18 | 0 | 0.35 |
| 6 | $-28,+35$ | $-600,+425$ | 5 | 0.08 | 0.10 | 0.12 | 0.16 | 0.22 | 0.18 | 0.24 |
|  | -35 | -425 | 26 |  |  |  |  |  |  |  |

TABLE 13.5 Estimating the Percentage of Broken and Unbroken Particles (Example 13.3)

| Size range | Feed size distribution <br> $F$, percent | Selection <br> functions $S$ | Particles broken <br> $(S)(F)$, percent | Particles not broken <br> $(F)-(S)(F)$, percent |
| :---: | :---: | :---: | :---: | :---: |
| 1 | 24 | 1.00 | 24.00 | 0 |
| 2 | 16 | 0.81 | 12.96 | 3.04 |
| 3 | 12 | 0.60 | 7.20 | 4.80 |
| 4 | 10 | 0.47 | 4.70 | 5.30 |
| 5 | 7 | 0.35 | 2.45 | 4.55 |
| 6 | 5 | 0.24 | 1.20 | 3.80 |
| -35 mesh | 26 |  |  |  |

## Calculation Procedure

1. Predict the weight percentages of broken and unbroken particles within each size range. In each size range, multiply the feed size percentage $F$ by the corresponding selection function $S$; this product gives an estimate as to the percentage of feed particles within the range that become broken. Then subtract the product from the feed size percentage; this difference is an estimate as to the particles that remain unbroken. These operations are shown in Table 13.5. In matrix notation (for consistency with subsequent steps), the $S$ 's can be considered to form an $n \times n$ diagonal matrix, and the $F$ 's an $n \times 1$ matrix.
2. Predict the size distribution of the product of the breakage of broken particles. This product does not exist by itself as a separate entity, of course, because the particles that become broken remain mixed with those which stay unbroken. Even so, the distribution can be calculated by postmultiplying the $n \times n$ lower triangular matrix of breakage functions $B$ in Table 13.4 by the percentage of particles broken, the $n \times 1$ matrix $(S)(F)$, as calculated in step 1 . This postmultiplication works out as follows:

| Size range | $\quad$ Amount of breakage product in size range |
| :---: | :--- |
| 1 | $0.18(24.00)=4.32$ |
| 2 | $0.22(24.00)+0.18(12.96)=7.61$ |
| 3 | $0.16(24.00)+0.22(12.96)+0.18(7.20)=7.99$ |
| 4 | $0.12(24.00)+0.16(12.96)+0.22(7.20)+0.18(4.70)=7.38$ |
| 5 | $0.10(24.00)+0.12(12.96)+0.16(7.20)+0.22(4.70)+0.18(2.45)=6.59$ |
| 6 | $0.08(24.00)+0.10(12.96)+0.12(7.20)+0.16(4.70)+0.22(2.45)+0.18(1.20)=5.59$ |

3. Within each size range, sum up the percent of particles that remained unbroken throughout the operation (from step 1) and percent of particles in that range which resulted from breakage (from step 2). These sums work out as follows. The -35 mesh percentage is found by difference (i.e., it is the residual):

| Size interval | Total-product size <br> distribution, percent |
| :---: | :---: |
| 1 | $0 \quad+4.32=4.32$ |
| 2 | $3.04+7.61=10.65$ |
| 3 | $4.80+7.99=12.79$ |
| 4 | $5.30+7.38=12.68$ |
| 5 | $4.55+6.58=11.13$ |
| 6 | $3.80+5.59=9.39$ |
| -35 mesh | 39.04 |

Related Calculations. If the grinding system includes a classification step that recycles the larger particles (e.g., those in size ranges 1 and 2 ) to the mill instead of allowing them to leave with the product, the operation is known as "closed-circuit grinding." In such a case, the preceding sequence can be expanded into an iterative procedure. In essence, steps 1 through 3 are applied anew to the material in size ranges 1 and 2, yielding a "final product" size distribution for this second round of breakage. Steps 1 through 3 are then applied a third time to the material in size ranges 1 and 2 from the second round of breakage; the procedure is repeated until virtually no material remains in those two size ranges.

### 13.4 MATERIAL-BALANCE CALCULATIONS

 FOR CLOSED-CIRCUIT GRINDINGIn the grinding operation of Fig. 13.3, a ball mill is in closed circuit with a hydrocyclone classifier. The mass flow rates of the classifier feed, oversize, and undersize are denoted by the symbols $A, O$,


FIGURE 13.3 Ball-mill-classifier circuit (Example 13.4). and $U$, respectively. The fineness of classifier feed $a$, of oversize $o$, and of undersize $u$, all expressed as percentages passing a 200 mesh sieve, are 58.5 , 48.2 , and 96.0 percent, respectively. Undersize is produced at a rate of 20.3 tons $/ \mathrm{h}$. What is the percent circulating load? What are the flow rates of classifier feed and oversize?

## Calculation Procedure

1. Find the percent circulating load. The percent circulating load $L$ is defined by the relationship $L=100 O / U$. By material-balance algebra, then, $L=100(u-a) /(a-o)$, which is $100(96.0-58.5) /(58.5-48.2)=364$ percent.
2. Find the flow rate of oversize. From step $1, O=L U / 100$, which is $364(20.3) / 100=73.9$ tons/h.
3. Find the flow rate of classifier feed. By material-balance algebra, $A=O+U$, which is $73.9+$ $20.3=94.2$ tons $/ \mathrm{h}$.

### 13.5 WORK-INDEX CALCULATIONS

A limestone ore is to be ground in a conventional ball mill to minus 200 mesh. The Bond grindability of the ore for a mesh-of-grind of 200 mesh $(75 \mu \mathrm{~m})$ is determined by laboratory test to be 2.73 g per revolution. The 80 percent passing size of the feed to the test is $1970 \mu \mathrm{~m}$; the 80 percent passing size of the product from it is $44 \mu \mathrm{~m}$. Calculate the work index $W_{i}$ for the material at this mesh-of-grind. (The "work index," defined as the energy needed to reduce ore from infinite size to the state where 80 percent will pass a 100 mesh screen, is a parameter that is useful in calculating size-reduction power requirements; see Example 13.6.)

## Calculation Procedure

1. Employ an empirical formula that yields the work index directly. The formula [3] is

$$
W_{i}=\frac{44.5}{P_{1}^{0.23} G^{0.82}\left(\frac{10}{P^{0.5}}-\frac{10}{F^{0.5}}\right)}
$$

where $W_{i}$ is the work index, in kilowatt-hours per ton, $G$ is grindability, in grams per revolution, $P$ is the 80 percent passing size of the product of the grindability test, in microns, $F$ is the 80 percent passing size of the feed to the grindability test, in microns, and $P_{1}$ is the size of the mesh-of-grind of the grindability test, in microns. Thus,

$$
\begin{aligned}
W_{i} & =\frac{44.5}{75^{0.23} 2.73^{0.82}\left(\frac{10}{44^{0.5}}-\frac{10}{1970^{0.5}}\right)} \\
& =5.64 \mathrm{kWh} / \mathrm{ton}
\end{aligned}
$$

Related Calculations. Although the Bond grindability test is run dry, the work index calculated above is for wet grinding. For dry grinding, the work index must be multiplied by a factor of $4 / 3$.

A crushability work index can also be empirically calculated. A Bond crushability test (based on striking the specimen with weights) indicates the crushing strength $C$ per unit thickness of material, in foot pounds per inch. This is related to work index $W_{i}$, in kilowatthours per ton, by the formula $W_{i}=2.59 C / S$, where $S$ is the specific gravity.

### 13.6 POWER CONSUMPTION IN A GRINDING MILL AS A FUNCTION OF WORK INDEX

The Bond work index for a mesh-of-grind of 200 mesh for a rock consisting mainly of quartz is $17.5 \mathrm{kWh} /$ ton. How much power is needed to reduce the material in a wetgrinding ball mill from an 80 percent passing size of $1100 \mu \mathrm{~m}$ to an 80 percent passing size of $80 \mu \mathrm{~m}$ ?

## Calculation Procedure

1. Employ a formula based on the Bond third theory of comminution. The formula is

$$
W=10 W_{i}\left(P^{-0.5}-F^{-0.5}\right)
$$

where $W$ is power required, in kilowatthours per ton, $W_{i}$ is work index, in kilowatthours per ton, $P$ is 80 percent passing size of product, in microns, and $F$ is 80 percent passing size of feed, in microns.

Thus,

$$
\begin{aligned}
W & =10(17.5)\left(80^{-0.5}-1100^{-0.5}\right) \\
& =14.3 \mathrm{kWh} / \mathrm{ton}
\end{aligned}
$$

Related Calculations. The Charles-Holmes equation [4], that is,

$$
W=100^{r} W_{i}\left(P^{-r}-F^{-r}\right)
$$

is in principle more accurate than the Bond third theory formula illustrated above. However, it requires determining the parameter $r$ by running grindability tests on the rocks in question at two or more meshes-of-grind. If a single Bond grindability test is run at a mesh-of-grind close to that of the maximum product size from the proposed grinding operation, the Bond third theory equation should be almost as accurate.

### 13.7 BALL-MILL OPERATING PARAMETERS

A ball mill having an inside diameter of 12 ft and an inside length of 14 ft is to be used to grind a copper ore. Measurement shows that the distance between the top of the mill and the leveled surface of the ball charge is 6.35 ft . What is the weight of balls in the mill? What is the critical speed of the mill (the speed at which the centrifugal force on a ball in contact with the mill wall at the top of its path equals the force due to gravity)? At what percent of critical speed should the mill operate?

## Calculation Procedure

1. Calculate the volume percent of the mill occupied by the balls. The volume percent can be calculated from the relationship $V_{p}=113-126 H / D$, where $V_{p}$ is percent of mill volume occupied by grinding media, $H$ is distance from top to leveled surface, and $D$ is mill inside diameter. Thus, $V_{p}=113-126(6.35) / 12=46.3$ percent.
2. Calculate the weight of the balls in the mill. It can be assumed that loose balls weigh $290 \mathrm{lb} / \mathrm{ft}^{3}$. (Rods would weigh $390 \mathrm{lb} / \mathrm{ft}^{3}$, and silica pebbles would weigh $100 \mathrm{lb} / \mathrm{ft}^{3}$.) Then, weight of balls equals (290)(volume of mill occupied by balls) $=290 \pi(D / 2)^{2} L V_{p} / 100=$ $290(3.14)(12 / 2)^{2}(14)(46.3 / 100)=213,000 \mathrm{lb}$.
3. Calculate the proper mill speed. This can be estimated from the equation $N_{o}=57-40 \log$ $D$, where $N_{o}$ is proper speed, in $\mathrm{r} / \mathrm{min}$, and $D$ is mill inside diameter, in feet. Thus, $N_{o}=57-40 \log$ $12=57-40(1.079)=13.8 \mathrm{r} / \mathrm{min}$. [The relation $N_{o}=57-40 \log D$ is only approximate. In actual practice, it will be found that short mills $(L<2 D)$ often tend to run at slightly higher speeds, and long mills often tend to operate at slightly lower speeds.]
4. Calculate the critical mill speed. This can be estimated from the equation $N_{c}=76.6 / D^{1 / 2}$, where $N_{c}$ is critical speed, in $\mathrm{r} / \mathrm{min}$, and $D$ is mill inside diameter, in ft . Thus, $N_{c}=76.6 / 12^{1 / 2}=$ $22.1 \mathrm{r} / \mathrm{min}$.
5. Calculate the percent of critical speed at which the mill should be operated. This follows directly from steps 3 and 4 . Thus, percent of critical speed equals $100(13.8) / 22.1=62.4$ percent.

### 13.8 MAXIMUM SIZE OF GRINDING MEDIA

A taconite ore is to be ground wet in a ball mill. The mill has an internal diameter of $13 \mathrm{ft}(3.96 \mathrm{~m})$ and is run at 68 percent of critical speed. The work index of the ore is $12.2 \mathrm{kWh} / \mathrm{ton}$, and its specific gravity is 3.3 . The 80 percent passing size of the ore is $5600 \mu \mathrm{~m}$. What is the maximum size of grinding media (maximum diameter of balls) to be used for the operation?

## Calculation Procedure

1. Employ an empirical formula that yields the maximum size directly. The maximum size grinding media for a ball mill (whether for initial startup or for makeup) may be calculated from the formula

$$
M=\left(\frac{F}{K}\right)^{1 / 2}\left(\frac{S W_{i}}{100 C_{s} D^{1 / 2}}\right)^{1 / 3}
$$

where $M$ is maximum size of balls, in inches, $F$ is 80 percent passing size of feed to the mill, in microns, $S$ is specific gravity of the ore, $W_{i}$ is work index of the ore, in kilowatt-hours per ton, $D$ is inside diameter of the ball mill, in feet, $C_{s}$ is fraction of critical speed of the mill, and $K$ is a constant ( 350 for wet grinding or 330 for dry grinding).

Thus,

$$
\begin{aligned}
M & =\left(\frac{5600}{350}\right)^{1 / 2}\left[\frac{3.3(12.2)}{100(0.68)(13)^{1 / 2}}\right]^{1 / 3} \\
& =2.19 \text { in or about } 21 / 4 \operatorname{in}(0.057 \mathrm{~m})
\end{aligned}
$$

Related Calculation. The maximum-diameter rod to be fed to a rod mill can be calculated from the empirical equation

$$
R=\frac{F^{0.75}}{160\left[W_{i} S /\left(C_{s} D^{1 / 2}\right]^{1 / 2}\right.}
$$

where $R$ is maximum diameter of rod, in inches, and the other variables are as in the example.

### 13.9 POWER DRAWN BY A GRINDING MILL

A ball mill with an inside diameter of $12 \mathrm{ft}(3.66 \mathrm{~m})$ is charged with 129 tons $(117,000 \mathrm{~kg})$ of balls that have a maximum diameter of 3 in ( 0.076 m ) and occupy 46.3 percent of the mill volume. The mill is operated wet at 62.4 percent of critical speed. What is the horsepower needed to drive the mill at this percentage of critical speed?

## Calculation Procedure

1. Employ an empirical formula that yields the horsepower directly. The formula [5] is

$$
\mathrm{hp}=1.341 W_{b}\left\{D^{0.4} C_{s}\left(0.0616-0.000575 V_{p}\right)-0.1(2)^{\left[\left[C_{s}-60\right) / 10\right]-1}\right\}
$$

where hp is the required horsepower, $W_{b}$ is the weight of the ball charge, in tons, $D$ is the inside mill diameter, in feet, $C_{s}$ is the percentage of critical speed at which the mill is operated, and $V_{p}$ is the percentage of mill volume occupied by balls. Thus,

$$
\begin{aligned}
\mathrm{hp} & =1.341(129)\left\{12^{0.4}(62.4)[0.0616-0.000575(46.3)]-0.1(2)^{[(62.4-60) / 10]-1}\right\} \\
& =1.341(129)(5.84)=1010 \mathrm{hp}(753 \mathrm{~kW})
\end{aligned}
$$

Related Calculations. For large-diameter mills using makeup balls of relatively small maximum size, it is often necessary to subtract a "slump correction" [4] from the braced term of the empirical
relation above. The formula for this correction is $[12 D-60 B(D-8)] / 240 B$, where $D$ is inside mill diameter, in feet, and $B$ is the largest size of makeup ball, in inches. For the present example, the slump correction is $[12(12)-60(3)(12-8] / 240(3)=-0.8$. Thus the required horsepower becomes $1.341(129)[5.84-(-0.8)]=1150 \mathrm{hp}(858 \mathrm{~kW})$.

### 13.10 WATER REQUIREMENTS FOR CLOSED-CIRCUIT MILL SYSTEM

A closed-circuit grinding system employs a high-efficiency air classifier wherein the classifier feed (i.e., the mill discharge) is exposed to outside air rather than recirculated air, thus reducing the product-cooling load. The system is shown in Fig. 13.4.

Fresh-feed rate $N$ and mill production rate $P$ are each $200,000 \mathrm{lb} / \mathrm{h}(90,900 \mathrm{~kg} / \mathrm{h})$. The circulating load $L$ is 150 percent (i.e., 1.5). The flow rate of $80^{\circ} \mathrm{F}(300 \mathrm{~K})$ ambient air to the classifier $A$ is $221,000 \mathrm{lb} / \mathrm{h}(100,500 \mathrm{~kg} / \mathrm{h})$. The fresh feed enters the mill at $160^{\circ} \mathrm{F}(344 \mathrm{~K})$. The flow rate of $80^{\circ} \mathrm{F}$ $(300 \mathrm{~K})$ sweep air $S$ to the mill is $53,000 \mathrm{lb} / \mathrm{h}(24,100 \mathrm{~kg} / \mathrm{h})$. Mill power input is 4000 hp .

How much $70^{\circ} \mathrm{F}(294 \mathrm{~K})$ cooling water must be sprayed into the mill to keep the product temperature from exceeding $150^{\circ} \mathrm{F}(339 \mathrm{~K})$ ?


FIGURE 13.4 Closed-circuit grinding system with high-efficiency air classifier (Example 13.10).

Use $0.25 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)$ as the specific heat of the air, and $0.19 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)$ as the specific heat of the fresh feed, mill discharge $D$, tailings $T$, and product. Assume that the fractional heat losses in the mill and classifier circuits are 20 percent and 12 percent, respectively. Assume that the tailings are 15 degrees hotter than the product (i.e., that they are $165^{\circ} \mathrm{F}$ ), that the classifier exhaust $E$ is 2 degrees cooler than the product (i.e., that the exhaust is $148^{\circ} \mathrm{F}$ ), and that the mill vent is 20 degrees cooler than the mill discharge. Assume that the water achieves its cooling via vaporization in the mill, and that amount of water vapor leaving with the mill vent is negligibly small.

## Calculation Procedure

1. Determine the mill-discharge flow rate $\boldsymbol{D}$. Use the equation $D=P(1+L)$ where, as noted in the statement of the problem, $L$ is the circulating load. Thus, $D=200,000(1+1.5)=500,000 \mathrm{lb} / \mathrm{h}$.
2. Calculate the tailings flow rate T. The equation is $T=P L$. Thus, $T=200,000(1.5)=$ $300,000 \mathrm{lb} / \mathrm{h}$.
3. Determine the enthalpies of the fresh feed $N$, product P, tailings $T$, ambient air to classifier $A$, and classifier exhaust $\boldsymbol{E}$. For all of these streams, use the general formula $H=c m\left(t-t_{o}\right)$, where $H$ is enthalpy in Btu's per hour, $c$ is specific heat as given in the statement of the problem, $m$ is mass flow rate, and $t$ and $t_{o}$ are, respectively, the stream temperature and reference temperature in degrees Fahrenheit. For arithmetical simplicity, use $0^{\circ} \mathrm{F}$ as the reference temperature throughout. Then

$$
\begin{aligned}
& H_{N}=0.19(200,000)(160-0)=6.1 \times 10^{6} \mathrm{Btu} / \mathrm{h} \\
& H_{P}=0.19(200,000)(150-0)=5.7 \times 10^{6} \mathrm{Btu} / \mathrm{h} \\
& H_{T}=0.19(300,000)(165-0)=9.4 \times 10^{6} \mathrm{Btu} / \mathrm{h} \\
& H_{A}=0.25(221,000)(80-0)=4.4 \times 10^{6} \mathrm{Btu} / \mathrm{h} \\
& H_{E}=0.25(221,000)(148-0)=8.2 \times 10^{6} \mathrm{Btu} / \mathrm{h}
\end{aligned}
$$

4. Estimate the heat loss $\boldsymbol{H}_{K}$ from the classifier circuit. Use the equation $H_{K}=\left[p_{K} /(1-\right.$ $\left.\left.p_{K}\right)\right]\left(H_{E}-H_{A}\right)$, where $p_{K}$ is the fractional heat loss ( 12 percent, or 0.12 ). Thus,

$$
H_{K}=[0.12 /(1-0.12)]\left[(8.2-4.4) \times 10^{6}\right]=0.5 \times 10^{6} \mathrm{Btu} / \mathrm{h}
$$

5. Estimate the heat loss $\boldsymbol{H}_{\boldsymbol{M}}$ from the mill circuit. The equation is $H_{M}=\left(p_{M}\right)$ (power input to mill), where $p_{M}$ is the fractional heat loss ( 20 percent, or 0.2 ). Thus,

$$
H_{M}=(0.2)(4000 \mathrm{hp})(2545 \mathrm{Btu} /(\mathrm{h})(\mathrm{hp}))=2.0 \times 10^{6} \mathrm{Btu} / \mathrm{h}
$$

6. Determine $H_{D}$, the enthalpy of the mill-discharge stream. This is done by making an energy balance around the classifier and solving it for $H_{D}$. The energy balance is $H_{D}+H_{A}=H_{P}+H_{T}+$ $H_{E}+H_{K}$. Accordingly, $H_{D}=(5.7+9.4+8.2+0.5-4.4) \times 10^{6}=19.4 \times 10^{6} \mathrm{Btu} / \mathrm{h}$.
7. Calculate the mill-discharge temperature $t_{D}$. Solve the general enthalpy equation (step 3 ) for $t$. Thus, $t_{D}=H_{D} / \mathrm{cm}=\left(19.4 \times 10^{6}\right) /(0.19)\left(0.5 \times 10^{6}\right)=204^{\circ} \mathrm{F}$, with $m$ being the mill discharge rate determined in step 1 .
8. Estimate $\boldsymbol{H}_{V}$, the mill-vent enthalpy. The mill-vent rate equals the sweep-air rate, $53,000 \mathrm{lb} / \mathrm{h}$. From the statement of the problem, the mill-vent temperature is $204-20$, i.e., $184^{\circ}$ F. Accordingly, $H_{V}=0.25(53,000)(184-0)=2.4 \times 10^{6} \mathrm{Btu} / \mathrm{h}$.
9. Determine $H_{W}$, the enthalpy of the water sprayed into the mill. The water must remove the heat introduced via the fresh feed, the tailings, the sweep air, and the mill power input $H_{I}$, less the heat removed via the mill discharge and the mill vent and less the mill heat losses. Thus, $H_{W}=H_{N}+$ $H_{T}+H_{S}+H_{I}-H_{D}-H_{V}-H_{M}$. Now, $H_{I}=(4000 \mathrm{hp})(2545 \mathrm{Btu} /(\mathrm{h})(\mathrm{hp}))=10.2 \times 10^{6} \mathrm{Btu} / \mathrm{h}$, and $H_{S}=(0.25)(53,000)(80-0)=1.1 \times 10^{6} \mathrm{Btu} / \mathrm{h}$. Accordingly, $H_{W}=(6.1+9.4+1.1+10.2-$ $19.4-2.4-2.0) \times 10^{6}=3.0 \times 10^{6} \mathrm{Btu} / \mathrm{h}$.
10. Calculate the required water rate $\boldsymbol{W}$. From enthalpy tables, determine the enthalpy difference between the water entering the mill and the vapor leaving. For the purpose of this example, assume that the difference is $1100 \mathrm{Btu} / \mathrm{lb}$. Then the amount of water needed to satisfy the enthalpy requirement calculated in step 9 is

$$
\left(3.0 \times 10^{6} \mathrm{Btu} / \mathrm{h}\right) /(1100 \mathrm{lb} / \mathrm{h})=2700 \mathrm{lb} / \mathrm{h}(1225 \mathrm{~kg} / \mathrm{h})
$$

This is significantly lower cooling duty than would be the case with a conventional closed-circuit grinding system.

Related Calculations. Three related problems are (1) How much will the product temperature change during the hottest part of the year if the water flow rate is substantially raised at the same time? (2) Determine the required water rate assuming that the mill vent $V$ is sent to the classifier instead of being discharged to the atmosphere; (3) Assume that the water rate determined in Problem 2 is at a maximum; how much will the product temperature increase during the hottest period of the year? All three of these call for trial-and-error solution.

Note: This example is adapted from an article by Ivan Klumpar of Badger Engineers, Inc., in Chemical Engineering, March 1992.

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## SECTION 14

## FILTRATION*

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### 14.1 BASIS FOR FILTRATION CALCULATIONS 14.1 <br> 14.2 CONSTANT-PRESSURE FILTRATION 14.2 <br> 14.3 CENTRIFUGAL-PUMP FILTRATION 14.7 <br> 14.4 FILTER-CAKE WASHING 14.11

14.5 ROTARY-VACUUM-DRUM FILTERS 14.13
14.6 DESIGN OF A ROTARY-VACUUMDRUM FILTER 14.17
14.7 PRESSURE DROP AND SPECIFIC DEPOSIT FOR A GRANULAR-BED FILTER 14.19
REFERENCES 14.22

### 14.1 BASIS FOR FILTRATION CALCULATIONS

## Mass Balance

An overall filtration material balance based on a unit area is
Mass of slurry $=$ mass of cake + mass of filtrate
or

$$
\frac{w_{c}}{s}=\frac{w_{c}}{s_{c}}+\rho v
$$

where $w_{c}$ is total mass of dry-cake solids per unit area, $v$ is filtrate volume per unit area, $s$ and $s_{c}$ are, respectively, the mass fraction and average mass fraction of solids in the slurry and cake, and $\rho$ is the density of filtrate. Solving for $w_{c}$ yields

$$
\begin{equation*}
w_{c}=\frac{\rho s}{1-s / s_{c}} v=c v \tag{14.1}
\end{equation*}
$$

where $c$ is concentration expressed by mass of dry cake per unit volume of filtrate.
*Example 14.7 is from Chemical Engineering magazine, September 1998, pp. 159ff.

The value of $c$ can be obtained from Eq. (14.1) (that is, $c=w_{c} / v$ ) if it is possible to obtain the mass of solids in the cake. However, draining the slurry can often lead to difficulties in accurate determination of the cake mass. An alternative approach is to consider the cake thickness.

The cake thickness $L$ can be related to the cake mass $w_{c}$ by

$$
w_{c}=\rho_{s}\left(1-\epsilon_{\mathrm{av}}\right) L
$$

where $\rho_{s}$ is the true density of the solid and $\epsilon_{\mathrm{av}}$ is the average porosity of the cake. Combining the two $w_{c}$ equations produces

$$
\begin{equation*}
L=\frac{c}{\rho_{s}\left(1-\epsilon_{\mathrm{av}}\right)} v=c_{L} v \tag{14.2}
\end{equation*}
$$

where $c_{L}$ is the ratio of cake thickness $L$ to the per-unit area filtrate volume $v$. The thickness $L$ is in fact the primary parameter related to filter design. Spacing of leaves, frame thickness, and minimum cake thickness for removal from vacuum drum filters all depend on a knowledge of $L$.

## Rate Equations

In filtration theory, Darcy's law is used in the form

$$
\frac{d p_{L}}{d w}=\frac{-d p_{s}}{d w}=\mu \alpha q
$$

or

$$
\frac{d p_{L}}{d x}=\frac{-d p_{s}}{d x}=\mu \rho_{s}(1-\epsilon) \alpha q
$$

where $p_{L}$ is hydraulic pressure, $p_{s}$ is solid compressive or effective pressure, $w$ is mass of cake per unit area in the cake-thickness range from 0 to $x, \mu$ is viscosity of the filtrate, $\alpha$ is local specific filtration resistance, and $q$ is superficial velocity of liquid. Solid compressive pressure is defined by $p_{s}=p-p_{L}$, where $p$ is filtration pressure.

With respect to the cake cross section, $p_{s}$ is zero at the cake-slurry interface and reaches its maximum at the cake-medium interface. Conversely, $p_{L}$ has its maximum value (equal to $p$ ) at the cake-slurry interface, whereas at the cake-medium interface it consists solely of $p_{1}$, the pressure required to overcome the resistance $R_{m}$ of the medium.

Integration of the preceding $d p_{L} / d w$ expression with the assumption that $q$ is constant throughout the cake gives

$$
\begin{equation*}
\mu q w_{c}=\mu c q v=\frac{\Delta p_{c}}{\alpha_{\mathrm{av}}} \tag{14.3}
\end{equation*}
$$

where $\Delta p_{c}=p-p_{1}=p-\mu q R_{m}$. Substitution and rearrangement give

$$
\begin{equation*}
\frac{d v}{d t}=q=\frac{p}{\mu\left(\alpha_{\mathrm{av}} w_{c}+R_{m}\right)} \tag{14.4}
\end{equation*}
$$

The latter equation can be used to calculate $v$ or $L$ as a function of time $t$, once the filtration mode is specified, e.g., constant-pressure filtration, with $p$ constant; constant-rate filtration, with $q$ constant; or centrifugal-pump filtration, with $q$ as a function of $p$.

### 14.2 CONSTANT-PRESSURE FILTRATION

The first two columns of Table 14.1 show laboratory data* on filtering calcium silicate with an average particle size of $6.5 \mu \mathrm{~m}$ in a $0.04287-\mathrm{m}^{2}\left(0.460-\mathrm{ft}^{2}\right)$ plate-and-frame filter press operating at a pressure

[^18]TABLE 14.1 Data and Calculated Values for Constant-Pressure Filtration (Example 14.2)

| Elapsed time $t$, <br> S <br> (1) | Filtrate volume $V$, $\mathrm{m}^{3}$ (2) | Volume per unit area $v$, $\mathrm{m}^{3} / \mathrm{m}^{2}$ <br> (3) | Interpolated $v, \mathrm{~m}^{3} / \mathrm{m}^{2}$ <br> (4) | $w_{c}=c v$, <br> $\mathrm{kg} / \mathrm{m}^{2}$ <br> (5) | $q=\frac{\Delta v}{\Delta t}, \mathrm{~m} / \mathrm{s}$ | $\frac{p}{\mu q_{\mathrm{av}}}=\frac{p t}{\mu v},$ <br> 1/m <br> (7) | $\frac{p}{\mu q}=\frac{p \Delta t}{\mu \Delta v},$ <br> $1 / \mathrm{m}$ <br> (8) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 0 | 0 | 0 |  | 0 |  | - |  |
|  |  |  | 0.012 | 0.06 | $2.56 \times 10^{-3}$ |  | $2.69 \times 10^{10}$ |
| 9 | $10 \times 10^{-4}$ | 0.023 |  | 0.12 |  | $2.70 \times 10^{10}$ |  |
|  |  |  | 0.035 | 0.18 | 2.40 |  | 2.87 |
| 19 | 20 | 0.047 |  | 0.24 |  | 2.79 |  |
|  |  |  | 0.059 | 0.30 | 1.84 |  | 3.74 |
| 31.5 | 30 | 0.070 |  | 0.35 |  | 3.10 |  |
|  |  |  | 0.082 | 0.41 | 1.28 |  | 5.38 |
| 49.5 | 40 | 0.093 |  | 0.47 |  | 3.67 |  |
|  |  |  | 0.105 | 0.53 | 1.17 |  | 5.89 |
| 70 | 50 | 0.117 |  | 0.59 |  | 4.12 |  |
|  |  |  | 0.129 | 0.65 | 1.00 |  | 6.89 |
| 93 | 60 | 0.140 |  | 0.71 |  | 4.58 |  |
|  |  |  | 0.152 | 0.77 | $8.52 \times 10^{-4}$ |  | 8.09 |
| 120 | 70 | 0.163 |  | 0.82 |  | 5.07 |  |
|  |  |  | 0.175 | 0.88 | 7.50 |  | 9.19 |
| 152 | 80 | 0.187 |  | 0.94 |  | 5.60 |  |
|  |  |  | 0.199 | 1.00 | 6.57 |  | $1.05 \times 10^{11}$ |
| 187 | 90 | 0.210 |  | 1.06 |  | 6.14 |  |
|  |  |  | 0.222 | 1.12 | 5.75 |  | 1.20 |
| 227 | 100 | 0.233 |  | 1.17 |  | 6.71 |  |
|  |  |  | 0.245 | 1.23 | 5.58 |  | 1.23 |
| 270 | 110 | 0.257 |  | 1.30 |  | 7.24 |  |

$p$ of $68.9 \mathrm{kPa}\left(10 \mathrm{lbf} / \mathrm{in}^{2}\right)$ and a slurry-solid mass fraction $s$ of 0.00495 . The cake had an average moisture content corresponding to a cake mass fraction of solids $S_{c}$ of 0.2937 . Viscosity of the water $\mu$ was $0.001 \mathrm{~Pa} \cdot \mathrm{~s}(1.0 \mathrm{cP})$. The densities of liquid and solid $\rho$ and $\rho_{s}$, respectively, were 1000 and $1950 \mathrm{~kg} / \mathrm{m}^{3}$. Calculate the average specific and medium resistances, and set up an equation relating cake thickness $L$ to filtration time $t$.

## Calculation Procedure

1. Calculate $v$, the filtrate volume per unit filtration area, and plot $v$ versus $t$ and $\log v$ versus $\log t$. Values of $v$ based on a $0.04287-\mathrm{m}^{2}$ area are shown in col. 3 of Table 14.1. The plots are presented in Figs. 14.1 and 14.2. (These figures also include 16 data points that are omitted from the table for simplicity.) The slope of the logarithmic plot can be taken as essentially 0.5 when $t$ exceeds


FIGURE 14.1 Filtrate volume versus elapsed time (Example 14.2).


FIGURE 14.2 Filtrate volume versus elapsed time (logarithmic scales) (Example 14.2).

120 s . Beyond 120 s , the curve of $p /\left(\rho q_{\mathrm{av}}\right)$ versus $w_{c}$ in step 5 below should be straight enough to give an adequate value of $\alpha_{\mathrm{av}}$ at the full applied pressure.
2. Calculate $w_{c}$, the total mass of dry-cake solids per unit area. Use Eq. (14.1). Thus,

$$
w_{c} \frac{1000(0.00495)}{1-0.00495 / 0.2937} v=5.04 v
$$

The values of $w_{c}$ thus calculated are shown in col. 5 of Table 14.1.
3. Calculate $\boldsymbol{p} /\left(\boldsymbol{\mu} \boldsymbol{q}_{\boldsymbol{a} v}\right)$. The average rate is simply $q_{\mathrm{av}}=v / t$. Then, $p /\left(\mu q_{\mathrm{av}}\right)=\left(6.89 \times 10^{7}\right) t / v$. Values are listed in col. 7 of Table 14.1.
4. Calculate $\boldsymbol{p} /(\boldsymbol{\mu q})$. The instantaneous rate $q=d v / d t$ must be obtained. Inasmuch as $v$ versus $t$ data pertaining to constant-pressure filtration are parabolic, use the following property of parabolas to obtain the slope:

$$
\left(\frac{d v}{d t}\right)_{\left(v_{1}+v_{2}\right) / 2}=\frac{\Delta v}{\Delta t}
$$

This equation states that the angle of the tangent taken at the midpoint $(v+\Delta v / 2)$ of a volume interval (not midpoint with respect to time) equals the angle of the secant. The rule is valid regardless of the size of $\Delta v$ and is generally best applied to smoothed data.

Between 9 and $19 \mathrm{~s}, \Delta v / \Delta t=(0.047-0.023) / 10=0.00240 \mathrm{~m} / \mathrm{s}$. This value corresponds to $d v / d t$ at $v=(0.047+0.023) / 2=0.035 \mathrm{~m}$. Since any size interval can be used, we find that between 93 and $270 \mathrm{~s}, \Delta v / \Delta t=(0.257-0.140) / 177=0.00066 \mathrm{~m} / \mathrm{s}$. The value of $v$ to be used is $(0.257+$ $0.140) / 2=0.199 \mathrm{~m}$.

In Table 14.1, values of $\left(v_{1}+v_{2}\right) / 2$ and the corresponding derivatives are shown in cols. 4 and 6 , respectively. The $p /(\mu q)$ values in col. 8 are obtained from the expression $6.89 \times 10^{7} / q$.
5. Plot $\boldsymbol{p} /(\boldsymbol{\mu q})$ and $\boldsymbol{p} /\left(\boldsymbol{\mu}_{\boldsymbol{a} \boldsymbol{v}}\right)$ versus $\boldsymbol{w}_{\boldsymbol{c}}$. These plots are shown in Fig. 14.3. They enable the calculation of the medium resistance $R_{m}$ and the specific filtration resistance $\alpha_{\text {av }}$ because Eq. (14.4) can be rearranged into the form $p /(\mu q)=\alpha_{\mathrm{av}} w_{c}+R_{m}$, and there also can be written a similar expression (valid only when $\alpha_{\mathrm{av}}$ and $R_{m}$ are constant): $p /\left(\mu q_{\mathrm{av}}\right)=\left(\alpha_{\mathrm{av}} / 2\right) w_{c}+R_{m}$. Both equations have the same $y$ intercept, namely, $R_{m}$. The slope of the first is twice that of the second. It is advisable to plot both lines in order to reach a compromise on the slopes and intercept.

It is important to take enough $v$ and $t$ data to generate the initial curved portions of the plots. The specific filtration resistance is smaller at the start of filtration, and the slopes of both plots have their minimum value when $t$ and $w_{c}$ equal zero. If the first four points taken during the first 50 s were


FIGURE 14.3 Determination of medium resistance $R_{m}$ (Example 14.2).
omitted, only the straight-line portions of the plots would be present; if these were extrapolated along the dotted lines to $w_{c}=0$, the resulting value of the $y$ intercept would be false.
6. Determine the medium resistance $\boldsymbol{R}_{\boldsymbol{m}} . \quad R_{m}$ is the (true) $y$ intercept in Fig. 14.3, approximately $0.24 \times 10^{11} \mathrm{~m}^{-1}$. (However, use this result with caution, because it is hard to establish operating conditions at $t=0$.) It frequently happens that the intercept of the $p /(\mu q)$ line is negative. Such a result generally implies (1) migration of fine particles, with subsequent blinding of medium or cake, or (2) sedimentation on a horizontal filter surface facing up.
7. Calculate $\boldsymbol{\alpha}_{a v}$. In this step, do not rely on finding a single, constant slope of either of the plots in Fig. 14.3. Such a method would be correct only if the entire plot (including its initial portion) were straight and the false medium resistance were the true medium resistance. Instead, use the first equation in step 5 , rearranged into the form $\alpha_{\mathrm{av}}=\left[p /(\mu q)-R_{m}\right] / w_{c}$. The resulting value of $\alpha_{\mathrm{av}}$ will vary, with the difference from value to value being greatest when $w_{c}$ is small. As $w_{c}$ increases, the value of $\alpha_{\mathrm{av}}$ does approach the slope of the $p /(\mu q)$ plot in its straight-line portion, namely, $0.97 \times 10^{11}$.

Thus when $w_{c}=0.88 \mathrm{~kg} / \mathrm{m}^{2}$ and $p /(\mu q)=0.92 \times 10^{11} \mathrm{~m}^{-1}, \alpha_{\mathrm{av}}=\left[\left(0.92 \times 10^{11}\right)-(0.24 \times\right.$ $\left.\left.10^{11}\right)\right] / 0.88=0.77 \times 10^{11} \mathrm{~m} / \mathrm{kg}\left(1.15 \times 10^{11} \mathrm{ft} / \mathrm{lb}\right)$. And when $w_{c}=3.0 \mathrm{~kg} / \mathrm{m}^{2}, \alpha_{\mathrm{av}}=[(3.03 \times$ $\left.\left.10^{11}\right)-\left(0.24 \times 10^{11}\right)\right] / 3.0=0.93 \times 10^{11} \mathrm{~m} / \mathrm{kg}$.

The pressure drop across the cake is given by the equation $\Delta p_{c}=p-\mu q R_{m}$. Thus, at these two points, it equals 50.9 and $63.4 \mathrm{kPa}\left(7.38\right.$ and $\left.9.20 \mathrm{lbf} / \mathrm{in}^{2}\right)$, respectively.
8. Calculate the average porosity $\epsilon_{a v}$. Average porosity can be calculated from the equation

$$
\begin{aligned}
\epsilon_{\mathrm{av}} & =\frac{1}{1+\left(\rho / \rho_{s}\right) s_{c} /\left(1-s_{c}\right)}=\frac{1}{1+(1000 / 1950) 0.2937 /(1-0.2937)} \\
& =0.824
\end{aligned}
$$

9. Obtain equations for versus tand L versus t. In Fig. 14.3, the $p /\left(\mu q_{\mathrm{av}}\right)$ plot is an excellent straight line for $w_{c}$ values greater than about $0.8 \mathrm{~kg} / \mathrm{m}^{2}$, that is, for filtration times greater than about 120 s . Therefore, data in this range can be accurately represented by an equation based on the assumption that $\alpha_{\mathrm{av}}$ and $R_{m}$ are constant and are the slope and intercept of the straight-line portion of the plot. Thus, $\alpha_{\mathrm{av}}=0.97 \times 10^{11} \mathrm{~m} / \mathrm{kg}$, and $R_{m}$, found by extending the straight line leftward until it intercepts the vertical axis, is $0.10 \times 10^{11} \mathrm{~m}^{-1}$. Then, substituting $w_{c}=c v$ and integrating Eq. (14.4) yields the parabola

$$
v^{2}+\frac{2 R_{m}}{c \alpha_{\mathrm{av}}} v=\frac{2 p}{\mu c \alpha_{\mathrm{av}}} t
$$

Noting from step 2 that $c=5.04 \mathrm{~kg} / \mathrm{m}^{3}$ and substituting and rearranging, we obtain the relationship $t=3548 v^{2}+145 v$. And relating $L$ to $v$ via Eq. (14.2), where $c_{L}=5.04 / 1950(1-0.824)=0.0147$, we obtain $t=\left(1.64 \times 10^{7}\right) L^{2}+\left(9.9 \times 10^{3}\right) L$. In these equations, $v$ is in cubic meters per square meter and $L$ is in meters.

As for filtration times of less than 120 s-for instance, with continuous drum or disk filters, where filtration time would normally be less than 60 s -the initial $\alpha_{\text {av }}$ of $0.11 \times 10^{11} \mathrm{~m} / \mathrm{kg}$ and the true $R_{m}$ of $0.24 \times 10^{11} \mathrm{~m}^{-1}$ will yield a reasonable representation of the data. Thus the equations become $t=402 v^{2}+348 v$ and $t=\left(1.86 \times 10^{6}\right) L^{2}+\left(2.4 \times 10^{4}\right) L$.

Related Calculations. In constant-rate (as opposed to constant-pressure) filtration, $v=q t$ and $w_{c}=$ $c q t$. Then, from Eq. (14.3), the average specific filtration resistance $\alpha_{\mathrm{av}}=\left(p-p_{1}\right) /\left(\mu c q^{2} t\right)$, where $p_{1}$ is the pressure at the interface of the filter medium and the cake. Constant-rate filtrations are usually operated at above $10 \mathrm{lbf} / \mathrm{in}^{2}(69 \mathrm{kPa})$, and this equation is accurate enough for most purposes. At


FIGURE 14.4 Average specific filtration resistance and average porosity (Example 14.3). (Note: $1 \mathrm{lbf} / \mathrm{in}^{2}=6.895 \mathrm{kPa} ; 1 \mathrm{ft} / \mathrm{lb}$ $=6.72 \mathrm{~m} / \mathrm{kg}$.)
higher and higher pressures, it becomes more and more acceptable to neglect $p_{1}$, which leads to the pressure-time relationship $p=\alpha_{\mathrm{av}} \mu c q^{2} t$.

Constant-rate filtration is employed sometimes when an improperly used centrifugal pump may break down the slurry particles. In fact, however, centrifugal pumps are most often chosen for filtration operations. The following example shows the relevant calculations.

### 14.3 CENTRIFUGAL-PUMP FILTRATION

A $2 \%$ (by weight) aqueous slurry containing solids with an average density of $202.6 \mathrm{lb} / \mathrm{ft}^{3}(3244 \mathrm{~kg} /$ $\mathrm{m}^{3}$ ) is to be filtered in a $500-\mathrm{ft}^{2}\left(46.45-\mathrm{m}^{2}\right)$ filter using a centrifugal pump having the following performance characteristics:

| Pressure: |  |  |  |  |  |  |  |  |  |  |
| :--- | ---: | ---: | ---: | ---: | ---: | ---: | ---: | ---: | ---: | ---: |
| lbf/in | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 | 55 | 60 |
| kPa | 103 | 138 | 172 | 207 | 241 | 276 | 310 | 345 | 379 | 414 |
| Flow rate: |  |  |  |  |  |  |  |  |  |  |
| gal/min | 500 | 482 | 457 | 420 | 375 | 308 | 232 | 155 | 78 | 0 |
| $\mathrm{~m}^{3} / \mathrm{s}$ | 0.0315 | 0.0304 | 0.0288 | 0.0265 | 0.0237 | 0.0194 | 0.0146 | 0.0098 | 0.0049 | 0 |

The pump has a throttling valve that relates pressure drop to flow rate $Q$ as follows: $\Delta p$ (throttling) $=$ $15(Q / 500)^{2}$. The temperature varies from 20 to $27^{\circ} \mathrm{C}\left(68\right.$ to $\left.80.6^{\circ} \mathrm{F}\right)$. A series of constant-pressure tests yielded the data on $\alpha_{\mathrm{av}}$ and ( $1-\epsilon_{\mathrm{av}}$ ) shown in Fig. 14.4, $\alpha_{\mathrm{av}}$ being the average specific filtration resistance and $\epsilon_{\mathrm{av}}$ the average porosity of the cake. Find cake thickness as a function of time.

## Calculation Procedure

1. Select the approach to be used. If both pressure and filtration rate vary, as in this case, it is necessary to impose the pump characteristics on the filtration equations. No simple formulas can be obtained to relate $p$ to $t$; instead, a relatively easy numerical integration is used.

Equation (14.3) can be rearranged into the form

$$
v=\frac{\Delta p_{c}}{\mu c q \alpha_{\mathrm{av}}}
$$



FIGURE 14.5 Centrifugal-pump curves (Example 14.3).
the terms being defined as at the beginning of this section. Now $q$ is a function of $p$, and $\alpha_{\mathrm{av}}$ is a function of $\Delta p_{c}$. Once $v$ has been obtained as a function of $p$ and $q, t$ can be obtained by integration:

$$
t=\int_{0}^{v} \frac{d v}{q}
$$

If data from a series of constant-pressure tests yield values of $\alpha_{\mathrm{av}}$ and the average solid fraction $s_{c}$, the first equation in this paragraph can be used to find the volume-versus-rate relationship, which can then be used to find the time by integration.
2. Construct a modified pump curve. The characteristic pump curve is plotted as the upper line in Fig. 14.5. Below point $U$, the pump is unstable and must be throttled so that the pressure does not fall to too low a value. Inasmuch as the throttling pressure is not available to the filter, it must be subtracted from the characteristic curve to give the modified pump curve. From the equation in the statement of the problem, plot the throttling curve. Then, assuming a negligible filter-medium resistance, the pressure drop $\Delta p_{c}$ across the cake equals the difference between the characteristic and throttling curves. Plot this difference, labeling it the "modified pump curve."

## 3. Calculate $c$, the concentration of cake, that is, the mass of dry cake per unit volume of filtrate.

 As indicated in Eq. (14.1), $c=\rho s /\left(1-s / s_{c}\right)$, or in the present case, $c=62.3(0.02) /\left(1-0.02 / s_{c}\right)$, where 62.3 is the density of water in $1 \mathrm{bm} / \mathrm{ft}^{3}$. Now, $s_{c}=\rho_{s}\left(1-\epsilon_{\mathrm{av}}\right) /\left[\rho_{s}\left(1-\epsilon_{\mathrm{av}}\right)+\rho \epsilon_{\mathrm{av}}\right]$, or in the present case, since $\rho_{s}$ is given as $202.6 \mathrm{lbm} / \mathrm{ft}^{3}, s_{c}=1 /\left[1+0.308 \epsilon_{\mathrm{av}} /\left(1-\epsilon_{\mathrm{av}}\right)\right]$.Select various values for $\Delta p_{c}$; from Fig. 14.4, determine $\epsilon_{\mathrm{av}}$. From the equations in the preceding paragraph, calculate $s_{c}$ and $c$. The results are shown in the fourth, fifth, and sixth columns of Table 14.2.
4. Calculate $c_{L}$, the ratio of cake thickness $L$ to the filtrate volume per unit filter area $v$. The values of $c_{L}$ can be calculated from the equation

$$
c_{L}=\frac{c}{\rho_{s}\left(1-\epsilon_{\mathrm{av}}\right)}
$$

Note that both $c$ and $c_{L}$ thus vary with $\Delta p_{c}$. The calculated values of $c_{L}$ appear in Table 14.2.

TABLE 14.2 Data and Calculated Results for Centrifugal-Pump Filtration (Example 14.3)

| $\Delta p_{c}$, <br> $\mathrm{bf} / \mathrm{in}^{2}$ | $Q$, <br> $\mathrm{gal} / \mathrm{min}$ | $q, \mathrm{ft} / \mathrm{s}$ | $\epsilon_{\mathrm{av}}$ | $s_{c}$ | $c$, <br> $\mathrm{lbm} / \mathrm{ft}^{3}$ | $c_{L}$ | $\alpha_{\mathrm{av}} \times 10^{-9}$, <br> $\mathrm{ft} / \mathrm{lbm}$ | $v$, <br> $\mathrm{ft}^{3} / \mathrm{ft}^{2}$ | $L$, <br> in | $1 / q$, <br> $\mathrm{s} / \mathrm{ft}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 0.5 | 499 | 0.00224 | 0.915 | 0.232 | 1.364 | 0.0792 | 2.1 | 0.54 | 0.51 | 446 |
| 1 | 498 | 0.00222 | 0.905 | 0.254 | 1.352 | 0.0702 | 2.2 | 1.04 | 0.88 | 450 |
| 5 | 487 | 0.00217 | 0.880 | 0.307 | 1.332 | 0.0548 | 3.8 | 3.14 | 2.06 | 461 |
| 10 | 469 | 0.00209 | 0.869 | 0.329 | 1.327 | 0.0500 | 5.7 | 4.36 | 2.62 | 478 |
| 15 | 446 | 0.00199 | 0.860 | 0.346 | 1.322 | 0.0466 | 7.2 | 5.46 | 3.05 | 503 |
| 20 | 418 | 0.00186 | 0.853 | 0.359 | 1.319 | 0.0443 | 9.0 | 6.24 | 3.32 | 538 |
| 25 | 384 | 0.00171 | 0.849 | 0.366 | 1.318 | 0.0431 | 10.0 | 7.65 | 3.96 | 585 |
| 30 | 345 | 0.00154 | 0.846 | 0.371 | 1.317 | 0.0422 | 12.0 | 8.50 | 4.30 | 649 |

Note: $\quad 1 \mathrm{lbf} / \mathrm{in}^{2}=6.895 \mathrm{kPa} ; 1 \mathrm{gal} / \mathrm{min}=6.3 \times 10^{-5} \mathrm{~m}^{3} / \mathrm{s} ; 1 \mathrm{ft} / \mathrm{s}=0.3048 \mathrm{~m} / \mathrm{s} ; 1 \mathrm{lbm} / \mathrm{ft}^{3}=16.02 \mathrm{~kg} / \mathrm{m}^{3} ; 1 \mathrm{ft} / \mathrm{lbm}=$ $0.67 \mathrm{~m} / \mathrm{kg} ; 1 \mathrm{ft}^{3} / \mathrm{ft}^{2}=0.3048 \mathrm{~m}^{3} / \mathrm{m}^{2} ; 1$ in $=0.0254 \mathrm{~m} ; 1 \mathrm{~s} / \mathrm{ft}=3.28 \mathrm{~s} / \mathrm{m}$.
5. Calculate $q$, the superficial velocity (velocity based on unit filter area) corresponding to the values of $\Delta p_{c}$ selected in step 3. This operation employs Fig. 14.3. The modified pump curve relates $\Delta p_{c}$ to $Q$, the flow rate in gallons per minute. For a given $\Delta p_{c}$, find $Q$ and multiply it by ( $1 \mathrm{~min} / 60 \mathrm{~s}$ ) $\times\left(1 \mathrm{ft}^{3} / 7.481 \mathrm{gal}\right)\left(1 / 500 \mathrm{ft}^{2}\right.$ of filter area) to find $q$. The calculated values of $q$ appear in Table 14.2.
6. Calculate v, the volume of filtrate per unit of filter area. Use the first equation in step 1. Thus,

$$
\begin{aligned}
v & =\frac{\Delta p_{c}}{\mu c q \alpha_{\mathrm{av}}} \\
& =\frac{\left(144 \mathrm{in}^{2} / \mathrm{ft}^{2}\right)\left[32.17 \mathrm{lbm} \cdot \mathrm{ft} /\left(\mathrm{lbf} \cdot \mathrm{~s}^{2}\right)\right]\left(\Delta p_{c} \mathrm{lbf} / \mathrm{in}^{2}\right)}{[0.000672 \mathrm{lbm} /(\mathrm{ft} \cdot \mathrm{~s})]\left(c \mathrm{lbm} / \mathrm{ft}^{3}\right)(q \mathrm{ft} / \mathrm{s})\left(\alpha_{\mathrm{av}} \mathrm{ft} / \mathrm{lbm}\right)} \\
& =6.893 \times 10^{6} \frac{\Delta p_{c}}{c q \alpha_{\mathrm{av}}}
\end{aligned}
$$

Use Fig. 14.4 to obtain $\alpha_{\mathrm{av}}$ for each value of $\Delta p_{c}$. These values of $\alpha_{\mathrm{av}}$ are shown in Table 14.2, and so are the calculated values of $v$.
7. Calculate L, the cake thickness. The equation is $L=c_{L} v$. The values of $L$ thus calculated are shown in Table 14.2, in inches.
8. Plot $L, \Delta p_{c}$, and $1 / q$ against $v$. The values are taken from Table 14.2. The resulting smoothed plots appear in Fig. 14.6.
9. Find filtration time $t$. The time is found by taking the area under the curve of $1 / q$ versus $v$. The result of this integration is shown in the third and fourth columns of Table 14.3. Values of $\Delta p_{c}$ and $L$ are repeated in the table for convenience.
10. Show cake thickness as a function of time. This relationship is shown graphically in Fig. 14.7. The figure also shows $\Delta p_{c}$ as a function of time.

Related Calculations. Filtrate volume as a function of time can be calculated by dividing each value of $L$ in Fig. 14.7 by $c_{L}$ and multiplying by the filter area.

Note that this pump proves to be somewhat large for the filter. If the cake thickness is restricted to 2.5 in $(0.064 \mathrm{~m})$, the rate would never drop below 95 percent of the initial pump rate.

TABLE 14.3 Determination of Filtration Time for Centrifugal-Pump Filtration (Example 14.3)

| $v, \mathrm{ft}^{3} / \mathrm{ft}^{2}$ | Incremental <br> area, s | $t, \mathrm{~s}$ | $t, \mathrm{~min}$ | $\Delta p_{c}, \mathrm{lbf} / \mathrm{in}^{2}$ | $L$, in |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 446 | 446 | 7.4 | 0.9 | 0.80 |
| 2 | 451 | 897 | 15.0 | 2.6 | 1.47 |
| 3 | 457 | 1354 | 22.6 | 5.0 | 2.00 |
| 4 | 466 | 1820 | 30.3 | 8.3 | 2.47 |
| 5 | 482 | 2302 | 38.4 | 12.6 | 2.90 |
| 6 | 507 | 2809 | 46.8 | 17.2 | 3.32 |
| 7 | 540 | 3349 | 55.8 | 22.3 | 3.70 |
| 8 | 582 | 3931 | 65.5 | 27.5 | 4.10 |

 centrifugal-pump filtration (Example 14.3).


FIGURE 14.7 Cake thickness and pressure drop as a function of time; centrifugalpump filtration (Example 14.3).

TABLE 14.4 Data on Filter-Cake Washing (Example 14.4)

| Time $t$, min | Volume of wash <br> $v_{w}$, gal/ft | Wash concentration <br> $C_{w}$, lbm solute/gal |
| :---: | :---: | :---: |
| 0 | 0 | 0.740 |
| 1 | 0.2 | 0.739 |
| 2 | 0.4 | 0.740 |
| 3 | 0.6 | 0.687 |
| 4 | 0.8 | 0.480 |
| 5 | 1.0 | 0.266 |
| 6 | 1.2 | 0.144 |
| 8 | 1.6 | 0.0575 |
| 10 | 2.0 | 0.0313 |
| 15 | 3.0 | 0.0158 |
| 20 | 4.0 | 0.0115 |
| 40 | 8.0 | 0.00624 |
| 60 | 12.0 | 0.00312 |
| 90 | 18.0 | 0.00119 |
| 120 | 24.0 | 0.00070 |

[^19]
### 14.4 FILTER-CAKE WASHING

A filter cake was washed at a rate of $0.2 \mathrm{gal} /\left(\mathrm{ft}^{2}\right)(\mathrm{min})\left[0.0081 \mathrm{~m}^{3} /\left(\mathrm{m}^{2}\right)(\mathrm{min})\right]$ with pure water to remove the soluble salts present in the voids. The cake had a thickness of 2.0 in . $(0.051 \mathrm{~m})$ and the following compositions:

|  | Mass fraction | Density, $\mathrm{lbm} / \mathrm{ft}^{3}\left(\mathrm{~kg} / \mathrm{m}^{3}\right)$ |
| :--- | :---: | :---: |
| Inert solids | 0.4789 | $88.6(1420)$ |
| Water | 0.4641 | $62.4(1000)$ |
| Soluble salts | 0.0570 | $85.1(1363)$ |

Data for instantaneous wash concentration versus time were taken as shown in Table 14.4. At the end of the washing period the cake was analyzed and found to have mass fraction $0.24 \%$ of salts on a moisture-free basis. How much water must be used if it is permissible to leave mass fraction $0.67 \%$ of soluble material on a moisture-free basis?

## Calculation Procedure

1. Convert mass fractions into volume fractions and find average porosity. The volume fraction $x_{i}$ of component $i$ (inert solid, water, or soluble salts) can be calculated by

$$
x_{i}=\frac{y_{i} / \rho_{i}}{\sum\left(y_{i} / \rho_{i}\right)}
$$

where $y_{i}$ and $\rho_{i}$ are the mass fraction and density of component $i$, respectively. Then, the initial composition of cake is $40.00 \%$ inert solid, $55.04 \%$ water, and $4.96 \%$ soluble salts by volume. The average porosity $\epsilon_{\mathrm{av}}$ of the cake is thus also known to be $0.5504+0.0496=0.6$.

The volume fraction of soluble material on a moisture free-basis $\psi_{v}$ can be obtained from

$$
\psi_{v}=\frac{\psi_{m} / \rho_{\text {salt }}}{\psi_{m} / \rho_{\text {salt }}+\left(1-\psi_{m}\right) / \rho_{s}}
$$

where $\psi_{m}$ is the mass fraction of soluble material on a moisture-free basis and the subscript $s$ refers to the inert solids. Thus the volume fractions of salts on a moisture-free basis are $0.25 \%$ at the end of 120 min and $0.70 \%$ permissible.

## 2. Calculate the average density of the cake, mass of dry inert solid, initial and final mass of soluble salts, and void volume

Average cake density $=\Sigma($ density of component $i)$ (volume of fraction of component $i)$

$$
\begin{aligned}
& =88.6(0.4000)+62.4(0.5504)+85.1(0.0496) \\
& =74.0 \mathrm{lbm} / \mathrm{ft}^{3}\left(1186 \mathrm{~kg} / \mathrm{m}^{3}\right)
\end{aligned}
$$

Mass of dry inert solid per unit area of filtration $=$ (inert solid density)(cake thickness) $\times$ (volume fraction of dry inert solid)

$$
=88.6(2 / 12)(0.4)
$$

$$
=5.91 \mathrm{lbm} / \mathrm{ft}^{2}\left(28.8 \mathrm{~kg} / \mathrm{m}^{2}\right)
$$

Initial mass of solute per unit area of filtration $=($ solute density $)($ cake thickness $)$

$$
\times \text { (volume fraction of solute) }
$$

$$
=85.1(2 / 12)(0.0496)
$$

$$
=0.703 \mathrm{lbm} / \mathrm{ft}^{2}\left(3.43 \mathrm{~kg} / \mathrm{m}^{2}\right)
$$

Final mass of solute per unit area of filtration $=($ mass of dry inert solid $)\left[\psi_{m} /\left(1-\psi_{m}\right)\right]$

$$
\begin{aligned}
& =5.91(0.0024) / 0.9976 \\
& =0.0142 \mathrm{bm} / \mathrm{ft}^{2}\left(0.0692 \mathrm{~kg} / \mathrm{m}^{2}\right)
\end{aligned}
$$

Void volume per unit area of filtration $=\left(\epsilon_{\mathrm{av}}\right)($ cake thickness $)$

$$
\begin{aligned}
& =0.6(2 / 12)=0.1 \mathrm{ft}^{3} / \mathrm{ft}^{2} \\
& =0.748 \mathrm{gal} / \mathrm{ft}^{2}\left(0.0305 \mathrm{~m}^{3} / \mathrm{m}^{2}\right)
\end{aligned}
$$

3. Calculate the average wash concentration $\boldsymbol{C}_{w, a v}$. The instantaneous wash concentration $C_{w}$, shown as the third column in Table 14.4, is plotted against volume of wash (the second column in Table 14.4) in Fig. 14.8. Now, by a material balance for the solute in the cake,

$$
\epsilon_{\mathrm{av}} L\left(C_{0}-C_{\mathrm{av}}\right)=\int_{0}^{v_{w}} C_{w} d v_{w}=C_{w, \mathrm{av}} v_{w}
$$

where $L$ is cake thickness (and therefore $\epsilon_{\mathrm{av}} L$ is void volume per unit area of filtration, calculated in step 2 ), $C_{0}$ is initial concentration of solute in the cake, and $v_{w}$ is volume of wash per unit area of filtration. Therefore, the total (cumulative) amount of solute removed from the cake may be determined by integrating the instantaneous-concentration-versus-volume data as shown in the first three columns of Table 14.5. Dividing the cumulative amount of solute removed by the cumulative volume of wash


FIGURE 14.8 Wash concentration and percent of soluble material versus volume of wash (Example 14.4).
used yields the average wash concentration, shown as the fourth column in Table 14.5 and plotted in Fig. 14.8.
4. Calculate the mass of solute remaining in the cake at each moment. Since $24 \mathrm{gal} / \mathrm{ft}^{2}\left(0.98 \mathrm{~m}^{3} /\right.$ $\mathrm{m}^{2}$ ) of wash was used in the run, the total amount of solute removed was $0.8296 \mathrm{lb} / \mathrm{ft}^{2}$, as shown in Table 14.5. The amount remaining in the cake is $0.0142 \mathrm{lb} / \mathrm{ft}^{2}$, from step 2 . Thus the total amount present in the system initially must have been $0.8296+0.0142=0.8438 \mathrm{lb} / \mathrm{ft}^{2}\left(4.11 \mathrm{~kg} / \mathrm{m}^{2}\right)$. (Since step 2 shows that only $0.703 \mathrm{lb} / \mathrm{ft}^{2}$ was present in the cake initially, the rest must have been in the feed lines to the filter press; it is important to keep this complication in mind when dealing with problems of this kind.)

Then the initial cake concentration $C_{0}$ may be calculated from the true initial amount of solute divided by void volume, that is, $0.8438 / 0.1=8.438 \mathrm{lbm} / \mathrm{ft}^{3}\left(135 \mathrm{~kg} / \mathrm{m}^{3}\right)$, and the mass of solute remaining in the cake may be calculated by subtracting the cumulative amount of solute removed from the true initial mass of solute, $0.8438 \mathrm{lbm} / \mathrm{ft}^{2}$, as shown in the fifth column of Table 14.5. Since the mass of solid remaining equals $5.91 \psi_{m} /\left(1-\psi_{m}\right)$, the values in that column can be employed to calculate $\psi_{m}$; the results (on a percentage basis) appear as the sixth column in the table.

Thus, if it is permissible to retain 0.67 percent of soluble material, on a moisture-free basis, the table shows that slightly over 10 gal of wash water must be used per square foot (slightly over $0.41 \mathrm{~m}^{3} / \mathrm{m}^{2}$ ).

Related Calculations. The average concentration of solute in the cake consists of mass of solute remaining divided by void volume. These values appear as the final column in Table 14.5.

### 14.5 ROTARY-VACUUM-DRUM FILTERS

The salient features of rotary-drum filtration are illustrated in Fig. 14.9, where a cylindrical drum having a permeable surface is revolving counterclockwise partially submerged in a slurry. A pressure differential is usually maintained between the outer and inner surfaces by means of a vacuum pump. However, the drum might be enclosed and operated under pressure. In addition to the vacuum or pressure, each point on the periphery of the drum is subjected to a hydrostatic head of slurry.

TABLE 14.5 Results of Cake Washing (Example 14.4)

| Range of wash volume, gal/ft ${ }^{2}$ | Solute removed, $\mathrm{lbm} / \mathrm{ft}^{2}$ | Conditions at the end of the interval of wash volume |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | Cumulative solute removed, $\mathrm{lbm} / \mathrm{ft}^{2}$ | Average wash concentration, lbm/gal | Mass of solute remaining, $\mathrm{lbm} / \mathrm{ft}^{2}$ | Present solute on moisture-free basis | Average cake concentration, lbm/gal |
| 0 | 0 | 0 | - | 0.8438 | 12.49 | 1.128 |
| 0.0-0.1 | 0.0740 | 0.0740 | 0.740 | 0.7698 | 11.52 | 1.029 |
| 0.1-0.2 | 0.0740 | 0.1480 | 0.740 | 0.6958 | 10.53 | 0.930 |
| 0.2-0.3 | 0.0740 | 0.2220 | 0.740 | 0.6218 | 9.52 | 0.831 |
| 0.3-0.4 | 0.0740 | 0.2960 | 0.740 | 0.5478 | 8.48 | 0.732 |
| $0.4-0.5$ | 0.0730 | 0.3690 | 0.738 | 0.4748 | 7.44 | 0.635 |
| 0.5-0.6 | 0.0705 | 0.4395 | 0.733 | 0.4043 | 6.40 | 0.541 |
| 0.6-0.7 | 0.0650 | 0.5045 | 0.721 | 0.3393 | 5.43 | 0.454 |
| 0.7-0.8 | 0.0545 | 0.5590 | 0.699 | 0.2848 | 4.60 | 0.381 |
| 0.8-0.9 | 0.0420 | 0.6010 | 0.669 | 0.2428 | 3.95 | 0.325 |
| 0.9-1.0 | 0.0315 | 0.6325 | 0.633 | 0.2113 | 3.45 | 0.282 |
| 1.0-1.1 | 0.0226 | 0.6551 | 0.596 | 0.1887 | 3.09 | 0.252 |
| 1.1-1.2 | 0.0163 | 0.6714 | 0.560 | 0.1724 | 2.83 | 0.230 |
| 1.2-1.3 | 0.0126 | 0.6840 | 0.526 | 0.1598 | 2.63 | 0.214 |
| 1.3-1.4 | 0.0100 | 0.6940 | 0.496 | 0.1498 | 2.47 | 0.200 |
| 1.4-1.5 | 0.0079 | 0.7019 | 0.468 | 0.1419 | 2.34 | 0.190 |
| 1.5-1.6 | 0.0063 | 0.7082 | 0.443 | 0.1356 | 2.24 | 0.181 |
| 1.6-1.7 | 0.0050 | 0.7132 | 0.420 | 0.1306 | 2.16 | 0.175 |
| 1.7-1.8 | 0.0042 | 0.7174 | 0.399 | 0.1264 | 2.09 | 0.169 |
| 1.8-1.9 | 0.0036 | 0.7210 | 0.379 | 0.1228 | 2.04 | 0.164 |
| 1.9-2.0 | 0.0032 | 0.7242 | 0.362 | 0.1196 | 1.98 | 0.160 |
| 2.0-3.0 | 0.02190 | 0.7461 | 0.249 | 0.0977 | 1.63 | 0.131 |
| 3.0-4.0 | 0.01350 | 0.7596 | 0.190 | 0.0842 | 1.40 | 0.113 |
| 4.0-5.0 | 0.01035 | 0.7700 | 0.154 | 0.0738 | 1.23 | 0.099 |
| 5.0-6.0 | 0.00888 | 0.7788 | 0.130 | 0.0650 | 1.09 | 0.087 |
| 6.0-7.0 | 0.00762 | 0.7864 | 0.112 | 0.0574 | 0.96 | 0.077 |
| 7.0-8.0 | 0.00662 | 0.7931 | 0.099 | 0.0507 | 0.85 | 0.068 |
| 8.0-9.0 | 0.00575 | 0.7988 | 0.089 | 0.0450 | 0.76 | 0.060 |
| 9.0-10.0 | 0.00490 | 0.8037 | 0.080 | 0.0401 | 0.67 | 0.054 |
| 10.0-11.0 | 0.00425 | 0.8080 | 0.073 | 0.0358 | 0.60 | 0.048 |
| 11.0-12.0 | 0.00350 | 0.8115 | 0.068 | 0.0323 | 0.54 | 0.043 |
| 12.0-13.0 | 0.00302 | 0.8145 | 0.063 | 0.0293 | 0.49 | 0.039 |
| 13.0-14.0 | 0.00258 | 0.8171 | 0.058 | 0.0267 | 0.45 | 0.036 |
| 14.0-15.0 | 0.00222 | 0.8193 | 0.055 | 0.0245 | 0.41 | 0.033 |
| 15.0-16.0 | 0.00182 | 0.8211 | 0.051 | 0.0227 | 0.38 | 0.030 |
| 16.0-17.0 | 0.00152 | 0.8226 | 0.048 | 0.0212 | 0.36 | 0.028 |
| 17.0-18.0 | 0.00132 | 0.8240 | 0.046 | 0.0198 | 0.33 | 0.026 |
| 18.0-19.0 | 0.00118 | 0.8252 | 0.043 | 0.0186 | 0.31 | 0.025 |
| 19.0-20.0 | 0.00102 | 0.8262 | 0.041 | 0.0176 | 0.30 | 0.024 |
| 20.0-21.0 | 0.00100 | 0.8272 | 0.039 | 0.0166 | 0.28 | 0.022 |
| 21.0-22.0 | 0.00092 | 0.8281 | 0.038 | 0.0157 | 0.26 | 0.021 |
| 22.0-23.0 | 0.00080 | 0.8289 | 0.036 | 0.0149 | 0.25 | 0.020 |
| 23.0-24.0 | 0.00075 | 0.8296 | 0.035 | 0.0142 | 0.24 | 0.019 |

Note: $1.0 \mathrm{gal} / \mathrm{ff}^{2}=0.041 \mathrm{~m}^{3} / \mathrm{m}^{2} ; 1.0 \mathrm{lbm} / \mathrm{ft}^{2}=4.88 \mathrm{~kg} / \mathrm{m}^{2} ; 1.0 \mathrm{lbm} / \mathrm{gal}=119.8 \mathrm{~kg} / \mathrm{m}^{3}$.


FIGURE 14.9 Rotary vacuum drum filter (Example 14.6).

Continuous multicompartment drum filters, as illustrated in Fig. 14.9, are normally used on materials that are relatively concentrated and easy to filter. Rates of cake buildup are in the range of $0.05 \mathrm{in} / \mathrm{min}(0.0013 \mathrm{~m} / \mathrm{min})$ to $0.05 \mathrm{in} / \mathrm{s}(0.0013 \mathrm{~m} / \mathrm{s})$. Submergence normally runs from 25 to 75 percent ( 40 percent being quite common), with rotation speeds from 0.1 to $3 \mathrm{r} / \mathrm{min}$. With these conditions, filtration times could range from 5 s to 7.5 min , the great majority of industrial filtration falling within these limits.

Drum diameters typically are 6 to 12 ft ( 1.83 to 3.66 m ), although larger values may be encountered. With 40 percent submergence and a $12-\mathrm{ft}$ diameter, the hydrostatic head ranges up to $5.7 \mathrm{ft}(1.74 \mathrm{~m})$, which is a significant fraction of the driving force in vacuum filtration. Since the slurry will have a density greater than water, the effective head may be as high as $7 \mathrm{ft}(2.13 \mathrm{~m})$.

The drum of radius $r$ rotates at an angular


FIGURE 14.10 Dry-cake mass as a function of filtration time (Example 14.6). [Note: $1 \mathrm{lbm} /\left(\mathrm{ft}^{2}\right)(\mathrm{r})=4.88 \mathrm{~kg} /$ $\left(\mathrm{m}^{2}\right)(\mathrm{r})$.] velocity of $\omega \mathrm{rad} / \mathrm{s}(N \mathrm{r} / \mathrm{s})$. The portion of the drum submerged in the slurry is subtended by an arc $\phi_{0}$. The remaining part of the drum is utilized for washing, drying, and discharge. Filtration through a given portion of the drum is assumed to begin at the instant that that portion enters the slurry; in practice, however, there is a time lag in establishing the full vacuum because of the need to maintain a vacuum seal as each compartment enters the slurry.

Dry-cake mass per area is shown in Fig. 14.10 as a function of elapsed time during a given revolution of the drum.

## Cake Washing

Experimental wash curves represented as fraction of solute remaining versus the wash ratio $j$ (ratio of wash to void volume of cake) can be plotted semilogarithmically as in Fig. 14.11 (the solid line). No experimental point will fall on the left of the maximum theoretical curve (the dotted line), which represents perfect displacement.

Cake wash time is the most difficult variable to correlate. Filtration theory suggests three possible correlations: (1) wash time versus $w_{c} v_{w}$; where $w_{c}$ and $v_{w}$ are total mass of dry solids and volume of wash, each per area of filtration; (2) wash time versus $j w_{c}$; and (3) wash time per form time versus


FIGURE 14.11 Cake-washing curves (Example 14.6).


FIGURE 14.12 Cake-wash time correlation with mass of dry solids $w_{c}$ and volume of wash $v_{w}$ per unit of area (Example 14.6).
wash volume per form volume. Fortunately, the easiest correlation (no. 1) usually gives satisfactory results. This curve starts as a straight line, but often falls off as the volume of wash water increases, as in Fig. 14.12.

## Cake Moisture Content, Air Rate

Experience has shown that the following factor is useful in correlating cake-moisture-content data [1]:

$$
\text { Correlating factor }=\frac{\mathrm{ft}^{3} / \min }{\mathrm{ft}^{2}} \frac{\Delta p_{c}}{w_{c}} \frac{t_{d}}{\mu}
$$

where $\mathrm{ft}^{3} /(\mathrm{min})\left(\mathrm{ft}^{2}\right)$ is air rate through the filter cake, $t_{d}$ is drying time, $\Delta p_{c}$ is pressure drop across the cake, and $\mu$ is liquid viscosity.

Figure 14.13 shows the general shape of the curve. The correlating factor chosen for design should be somewhere past the knee of the curve. Values to the left approach an unstable operating range, wherein a small change in operating conditions can result in a relatively drastic change in cake moisture content.

If runs are made at constant temperature and vacuum, the pressure drop and viscosity terms can be dropped from the expression. Often air-rate data are not available, but correlations can be obtained without air rates, particularly if the cakes are relatively non-porous. The correlating factor is then reduced to the simplified term $t_{d} / w_{c}$, which involves only drying time and cake weight per unit area per revolution. A substantial degree of data scatter is normally encountered in the moisture-content correlation. Any point selected on the correlation will represent an average operating condition. To ensure that cake moisture content will not exceed a particular value, the correlating factor at the desired minimum should be multiplied by 1.2 before calculating the required drying time.

Air rate through the cake-and thus, vacuum-pump capacity-can be determined from measurements of flow rate as a function of time. Integration of these data over the times involved in the first and second stages of drying in continuous filters yields vacuum-pump-capacity data.


FIGURE 14.13 Correlating factor for cake moisture content and air rate (Example 14.6).

### 14.6 DESIGN OF A ROTARY-VACUUM-DRUM FILTER

A drum filter as illustrated in Fig. 14.9 is to be used for filtering, washing, and drying a cake having the properties given by Figs. 14.10 through 14.13. Air rate through the cake is determined from measurements of flow rate as a function of time with a rotameter as follows:

|  | Time, $\min$ |  |  |  |  |  |  |  |  |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
|  | 0.05 | 0.1 | 0.2 | 0.3 | 0.4 | 0.6 | 0.8 | 1.0 | 1.5 |
| $\mathrm{ft}^{3} /(\mathrm{min})\left(\mathrm{ft}^{2}\right)$ | 2.5 | 4.2 | 5.9 | 6.8 | 7.45 | 8.2 | 8.6 | 8.75 | 9.2 |
| $\mathrm{~m}^{3} /(\mathrm{min})\left(\mathrm{m}^{2}\right)$ | 0.762 | 1.28 | 1.80 | 2.07 | 2.27 | 2.50 | 2.62 | 2.67 | 2.80 |

These data are also plotted in Fig. 14.14.
The following conditions and specifications are assumed: slurry contains $40 \%$ solids by weight; solute in the liquid is $2 \%$; final cake moisture is $25 \%$; wash ratio (wash volume per void volume) is 1.5 ;


FIGURE 14.14 Air rate as a function of time (Example 14.6).
cake mass $w_{c}$ (in lbm/ft ${ }^{2}$ ) is $7.2 L$, where $L$ is cake thickness in inches; maximum submergence is 35 percent or $126^{\circ}$; effective submergence is 30 percent or $108^{\circ}$; maximum washing arc is 29 percent or $104^{\circ}$; suction (initial drying) arc is 7.5 percent or $27^{\circ}$; discharge and resubmergence arc is 25 percent or $90^{\circ}$; and minimum cake thickness is $1 / 8$ in $(0.0032 \mathrm{~m})$. Determine the relevant design parameters for the filter.

## Calculation Procedure

1. Calculate the cake mass, find the filtration time for a thickness of 0.25 in ( 0.0064 m ), and determine the minimum cycle needed for cake formation. The cake mass is given by $w_{c}=7.2(0.25)=1.8 \mathrm{lbm} / \mathrm{ft}^{2}$. From Fig. 14.10, filtration time is found to be 0.22 min , and so the filtration rate is $(1.8 / 0.22)(60)=491 \mathrm{lbm} / \mathrm{h}$ per square foot of drum surface. With an effective submergence of 30 percent, the minimum cycle based on cake formation is $0.22 / 0.3=0.73 \mathrm{~min} / \mathrm{r}$, which corresponds to $1.37 \mathrm{r} / \mathrm{min}$.
2. Check to see if initial drying or washing can be done within the time available during the minimum cycle from step 1. Minimum suction time elapses during passage through $27^{\circ}$ ( 7.5 percent) of the perimeter. Therefore, drying time is $0.075(0.73)=0.06 \mathrm{~min}$, and the correlating factor is $t_{d} / w_{c}=0.06 / 1.8=0.033$. Based on Fig. 14.13, the dewatered but unwashed $(D / u)$ cake will have a moisture content of $30 \%$. Then with a wash ratio of 1.5 , liquid in $D / u$ cake equals $(30 / 70)(1.8)=$ $0.77 \mathrm{lbm} /\left(\mathrm{ft}^{2}\right)(\mathrm{r})$, and quantity of wash equals $1.5(0.77)=1.155 \mathrm{lbm} /\left(\mathrm{ft}^{2}\right)(\mathrm{r})$, or, at $8.33 \mathrm{lbm} / \mathrm{gal}$, $0.14 \mathrm{gal} /\left(\mathrm{ft}^{2}\right)(\mathrm{r})$. To calculate wash time, $w_{c} v_{w}=1.8(0.14)=0.25$. From Fig. 14.12, the required wash time is 0.15 min . This corresponds to an arc of $0.15 / 0.73=0.21$; that is, to 21 percent of the circumference. Since up to 29 percent of the circumference can be used, washing offers no problems.
3. Check the drying time and determine the cycle time. For a final moisture content of $25 \%$, the simplified correlating factor $t_{d} / w_{c}$ from Fig. 14.13 (taking into account the 1.2 factor mentioned above) is approximately $1.2(0.25)=0.3$ (the $25 \%$ moisture content is employed to enter the graph along the ordinate; the 0.25 is read from the graph along its abscissa). With $w_{c}=1.8, t_{d}=0.54 \mathrm{~min}$ and $0.54 / 0.73=0.739$, which takes up nearly three-quarters of the circumference for drying, so a lower speed must be used.

As a first estimate, note that since 25 percent of the arc is needed for discharge and resubmergence, the maximum arc for washing plus final drying is given by 75 - (cake-formation arc) - (suction arc) $=75-30-7.5=37.5$ percent. Using the originally calculated washing plus drying times of $0.54+0.15=0.69 \mathrm{~min}$, then $0.69 / 0.375=1.84 \mathrm{~min} / \mathrm{r}$ and the washing arc is $0.15 / 1.84$, which is 8.15 percent or $29^{\circ}$.
4. Repeat the calculations of step 2. Minor adjustments can be made by recalculating each quantity with each change in conditions. Thus initial drying time equals $1.84(0.075)=0.14 \mathrm{~min}$, so $t_{d} / w_{c}=0.14 / 1.8=0.08$. From Fig. $14.13, D / u$ moisture is $27 \%$, and accordingly, the liquor in the $D / u$ cake is $(27 / 73)(1.8)=0.67 \mathrm{lbm} /\left(\mathrm{ft}^{2}\right)(\mathrm{r})$. The quantity of wash becomes $1.5(0.67)=1.0 \mathrm{lbm} /$ $\left(\mathrm{ft}^{2}\right)(\mathrm{r})$, or $0.12 \mathrm{gal} /\left(\mathrm{ft}^{2}\right)(\mathrm{r})$. Then $w_{c} v_{w}=1.8(0.12)=0.22$, and from Fig. 14.12, the wash time becomes 0.14 min .
5. Summarize the filtration cycle. The cycle time is now $(0.14+0.54) / 0.375=1.81 \mathrm{~min} / \mathrm{r}$, equivalent to $0.55 \mathrm{r} / \mathrm{min}$. The required effective submergence is $(0.22 / 1.81)(100)=12.2$ percent. This is much less than the 30 percent available. The filter valve bridge must delay the start of vacuum or the slurry level can be reduced. If the level is reduced, additional initial drying time will be available, thereby reducing the angle required for washing. The design cycle is as follows:

| Operation | Minutes |
| :--- | :---: |
| Form | 0.22 |
| Initial dry | 0.14 |
| Wash | 0.14 |
| Final dry | 0.54 |
| Discharge and resubmergence | $\underline{0.77}$ |
| Total time | 1.81 |

6. Calculate cake thickness and filtration rate. Cake thickness is given by $L$ (in inches) $=$ $w_{c} / 7.2=1.8 / 7.2=0.25 \mathrm{in}$. Taking into account the effective submergence of 12.2 percent, we calculate the filtration rate as $491(0.122)=59.9 \mathrm{lbm} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left[0.081 \mathrm{~kg} /(\mathrm{s})\left(\mathrm{m}^{2}\right)\right]$. Experience suggests applying a scaleup factor of $0.8: 0.8(59.9)=47.9 \mathrm{lbm} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left[0.065 \mathrm{~kg} /(\mathrm{s})\left(\mathrm{m}^{2}\right)\right]$. This is not intended as a safety factor to allow for increased production; instead, it corrects for deviation owing to the size of the test equipment, to media blinding, and to similar factors.
7. Calculate the efficiency of solute recovery. Assume that Fig. 14.11 applies. With $j=1.5$, the fraction remaining is 0.145 . To be on the safe side, use a value of 0.2 . The following calculations are needed:

Solute in feed $=(60 / 40)(0.02)=0.03 \mathrm{lb}$ solute per pound of feed
Solute in $D / u$ cake $=(27 / 73)(0.02)=0.0074 \mathrm{lb}$ solute per pound of cake
Solute in washed cake $=0.0074(0.2)=0.0015 \mathrm{lb}$ solute per pound of washed cake

The fractional recovery, then, equals $(0.030-0.0015) / 0.03=0.95$. Using 0.145 instead of 0.2 would have yielded a figure of 0.964 .
8. Calculate the air rate. The air rate can be calculated based on the data previously presented and shown in Fig. 14.14. During the 0.14 min of initial drying, the average rate is found to be 2.95 $\left(\mathrm{ft}^{3} / \mathrm{min}\right) /\left(\mathrm{ft}^{2}\right)(\mathrm{r})$. The average rate during the final 0.54 min of drying is $5.85\left(\mathrm{ft}^{3} / \mathrm{min}\right) /\left(\mathrm{ft}^{2}\right)(\mathrm{r})$. The total air rate is given by $0.14(2.95)+0.54(5.85)=3.57\left(\mathrm{ft}^{3} / \mathrm{min}\right) /\left(\mathrm{ft}^{2}\right)(\mathrm{r})$. Since there are $1.81 \mathrm{~min} / \mathrm{r}$, the air rate is $3.57 / 1.81=1.97\left(\mathrm{ft}^{3} / \mathrm{min}\right) / \mathrm{ft}^{2}\left[0.01\left(\mathrm{~m}^{3} / \mathrm{s}\right) / \mathrm{m}^{2}\right]$.

### 14.7 PRESSURE DROP AND SPECIFIC DEPOSIT FOR A GRANULAR-BED FILTER

For filtering dust streams, a fixed-granular-bed filter with a length, $L$, of 1 m is filled with glass spheres of $5-\mathrm{mm}(0.005-\mathrm{m})$ diameter, $d_{m}$. The dust to be captured is limestone with a $0.1-\mathrm{mm}$ mean diameter, $d_{d}$. The limestone density, $\rho_{d}$, is $2700 \mathrm{~kg} / \mathrm{m}^{3}$, and the gas velocity, $u$, is $0.5 \mathrm{~m} / \mathrm{s}$. The initial porosity, $\epsilon_{0}$, of the filter is 0.4 , and the filtration process stops when the porosity has dropped to a level, $\epsilon$, of 0.3. The gas has a viscosity, $\mu_{g}$, of $17.2 \times 10^{-6} \mathrm{~N}-\mathrm{s} / \mathrm{m}^{2}$ and a density, $\rho_{g}$, of $1.293 \mathrm{~kg} / \mathrm{m}^{3}$. Determine the pressure drop through the filter, $\Delta P$, and the mass of deposited dust per unit volume (also known as the specific deposit), $m$.

## Calculation Procedure

1. Calculate the direct interception number, $N_{I}$, as well as $\left(\boldsymbol{1}-\boldsymbol{\epsilon}_{\mathbf{0}}\right) /(\mathbf{1}-\boldsymbol{\epsilon}) . \quad N_{I}$ is defined as $d_{d} / d_{m}$. In this case, it equals $0.1 \mathrm{~mm} / 5 \mathrm{~mm}$, or 0.02 . And $\left(1-\epsilon_{0}\right) /(1-\epsilon)=(1-0.4) /(1-0.3)=$ 0.857 .


FIGURE 14.15 Chart for determining parameter $f$ for use in $\Delta P$ calculation.


FIGURE 14.16 Chart for determining parameter $F$ for use in $\Delta P$ calculation.
2. Find the parameter $f$. Use Fig. 14.15. From an abscissa of 0.857 and the line corresponding to $N_{I}$ of 0.02 , read along the ordinate a value of 8 for $f$.

Caution: Do not use Fig. 14.15, nor Fig. 14.16, if the gas velocity is greater than $1 \mathrm{~m} / \mathrm{s}$, because the dust particles may tend to "bounce" off the surface of the granular medium.
3. Calculate the Reynolds particle number, $\boldsymbol{R e}_{\boldsymbol{m}}$. The relationship is as follows:

$$
\operatorname{Re}_{m}=\left(u \rho_{g} d_{m}\right) / \mu_{g}
$$

So,

$$
\operatorname{Re}_{m}=(0.5)(1.293)(0.005) /\left(17.2 \times 10^{-6}\right)=188
$$

4. Find the parameter $\boldsymbol{F}$. Use Fig. 14.16. From an abscissa of $188 / 8$, or 23.5 , and the line corresponding to an $\epsilon$ of 0.3 , read along the ordinate a value of 190 for $F$.
5. Calculate the pressure drop through the filter. Use the relationship $\Delta P=L \rho_{g} u^{2} f F / d_{m}$. Thus,

$$
\Delta P=(1)(1.293)(0.5) 3(8)(190) / 0.005=96,200 \mathrm{~Pa}
$$

6. Calculate the specific deposit. Use the relationship

$$
m=\rho_{d}\left(\epsilon_{0}-\epsilon\right)=2700(0.4-0.3)=270 \mathrm{~kg} / \mathrm{m}^{3}
$$

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## SECTION 15

# AIR POLLUTION CONTROL* 

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15.1 EFFICIENCY OF PARTICULATE- SETTLING CHAMBER 15.1
15.2 EFFICIENCY OF CYCLONE SEPARATOR 15.3
15.3 SIZING AN ELECTROSTATICPRECIPITATOR 15.5
15.4 EFFICIENCY OF A VENTURISCRUBBING OPERATION 15.6
15.5 SELECTING A FILTER BAGSYSTEM 15.8
15.6 SIZING A CONDENSERFOR ODOR-CARRYINGSTEAM 15.9
15.7 AMOUNT OF ADSORBENT FOR A VOC ADSORBER 15.10
15.8 PERFORMANCE OF AN AFTERBURNER 15.11
15.9 PRELIMINARY SIZING OF ANABSORBER FOR GASCLEANUP 15.13
15.10 ESTIMATING HAZARD DISTANCESFROM ACCIDENTAL RELEASES 15.14
15.11 GROUND-LEVEL CONCENTRATIONOF UNBURNED FLAMMABLEGAS 15.15

### 15.1 EFFICIENCY OF PARTICULATE-SETTLING CHAMBER

A particulate-settling chamber is installed in a small heating plant that uses a traveling grate stoker. Determine the overall collection efficiency of the chamber, given the following operating conditions, chamber dimensions, and particle-size distribution:

Chamber width: $10.8 \mathrm{ft}(3.29 \mathrm{~m})$
Chamber height: $\quad 2.46 \mathrm{ft}(0.75 \mathrm{~m})$
Chamber length: $\quad 15.0 \mathrm{ft}(4.57 \mathrm{~m})$
Volumetric flow rate of contaminated air stream: $70.6 \mathrm{std} \mathrm{ft}^{3} / \mathrm{s}\left(2.00 \mathrm{~m}^{3} / \mathrm{s}\right)$
Flue-gas temperature: $446^{\circ} \mathrm{F}$
Viscosity of air stream at $446^{\circ} \mathrm{F}: \quad 1.75 \times 10^{-5} \mathrm{lb} /(\mathrm{ft})(\mathrm{s})\left[2.60 \times 10^{-5}(\mathrm{~N})(\mathrm{s}) / \mathrm{m}^{2}\right]$
Flue-gas pressure: $1 \mathrm{~atm}(101.3 \mathrm{kPa})$
Particle concentration: 0.23 grains $/ \mathrm{std} \mathrm{ft}^{3}\left(8.13\right.$ grains $\left./ \mathrm{m}^{3}\right)$
Particle specific gravity: 2.65
Standard operating conditions: $\quad 32^{\circ} \mathrm{F}, 1 \mathrm{~atm}(273 \mathrm{~K}, 101.3 \mathrm{kPa})$
*Examples 15.10 and 15.11 are adapted from Chemical Engineering magazine.

Particle-size distribution on the inlet dust:

| Particle size range, <br> $\mu \mathrm{m}$ | Average particle <br> diameter, $\mu \mathrm{m}$ | grains $/ \mathrm{std} \mathrm{ft}^{3}$ | grains $/ \mathrm{m}^{3}$ | Weight $\%$ |
| :---: | :---: | :---: | :---: | ---: |
| $0-20$ | 10 | 0.0062 | 0.219 | 2.7 |
| $20-30$ | 25 | 0.0159 | 0.562 | 6.9 |
| $30-40$ | 35 | 0.0216 | 0.763 | 9.4 |
| $40-50$ | 45 | 0.0242 | 0.855 | 10.5 |
| $50-60$ | 55 | 0.0242 | 0.855 | 10.5 |
| $60-70$ | 65 | 0.0218 | 0.770 | 9.5 |
| $70-80$ | 75 | 0.0161 | 0.569 | 7.0 |
| $80-94$ | 87 | 0.0218 | 0.770 | 9.5 |
| $94+$ | $94+$ | 0.0782 | 2.763 | 34.0 |

Assume that the actual terminal settling velocity is one-half of the velocity given by Stokes’ law.

## Calculation Procedure

1. Express the collection efficiency $E$ in terms of the particle diameter $d_{p}$ by employing the terminal settling velocity for Stokes' law. Since the actual terminal settling velocity is assumed to be one-half of the Stokes' law velocity,

$$
v_{t}=g d_{p}^{2} \rho_{p} / 36 \mu
$$

and

$$
E=v_{t} B L / q=g \rho_{p} B L d_{p}^{2} / 36 \mu q_{a}
$$

where $v_{t}=$ terminal velocity, $\mathrm{ft} / \mathrm{s}$
$g=$ gravitational constant, $32.2(\mathrm{lbm})(\mathrm{ft}) /\left(\mathrm{s}^{2}\right)(\mathrm{lbf})$
$d_{p}=$ particle diameter, ft
$\rho_{p}=$ particle density, $\mathrm{lb} / \mathrm{ft}^{3}$
$\mu=$ air viscosity, $\mathrm{lb} /(\mathrm{ft})(\mathrm{s})$
$B=$ chamber width, ft
$L=$ chamber length, ft
$q=$ volumetric flow rate for the gas, actual $\mathrm{ft}^{3} / \mathrm{s}$
2. Determine the particle density. As the specific gravity is 2.65 , the density is $(2.65)\left(62.4 \mathrm{lb} / \mathrm{ft}^{3}\right)=$ $165.4 \mathrm{lb} / \mathrm{ft}^{3}\left(2648 \mathrm{~kg} / \mathrm{m}^{3}\right)$.
3. Determine the actual volumetric flow rate. Use Charles' law to convert from $q_{s}$, the flow rate at the standard-conditions temperature $T_{s}$, to $q_{a}$, the flow rate at the actual temperature $T_{a}$ :

$$
q_{a}=a_{s}\left(T_{a} / T_{s}\right)=70.6[(446+460) /(32+460)]=130 \text { actual } \mathrm{ft}^{3} / \mathrm{s}
$$

4. Express the collection efficiency in terms of $\boldsymbol{d}_{\boldsymbol{p}}$ in micrometers. The efficiency equation set out in step 1 is for $d_{p}$ in feet. To adapt it for $d_{p}$ in micrometers, note that there are $304,800 \mu \mathrm{~m}$ in a
foot and accordingly divide the equation by the conversion factor $(304,800)^{2}$. Thus,

$$
\begin{aligned}
E & =g \rho_{p} B L d_{p}^{2} / 36 \mu q_{a} \\
& =(32.2)(165.4)(10.8)(15) d_{p}^{2} /(36)\left(1.75 \times 10^{-5}(130)(304,800)^{2}\right. \\
& =1.14 \times 10^{-4} d_{p}^{2}
\end{aligned}
$$

5. Calculate the collection efficiency at each average particle size given in the statement of the problem. Applying the equation from step 4 and multiplying the answer by 100 (to convert the efficiency from a decimal fraction to a percent) gives the following results:

| Average particle <br> diameter, $\mu \mathrm{m}$ | Efficiency, \% |
| :---: | :---: |
| 10 | 1.1 |
| 25 | 7.1 |
| 35 | 14 |
| 45 | 23 |
| 55 | 34 |
| 65 | 48 |
| 75 | 64 |
| 87 | 86 |
| 94 | 100 |

6. Calculate the overall collection efficiency. This is the sum of each of the efficiencies from the previous step multiplied by the weight fraction of the corresponding particle size in the mixture; in other words,

$$
E=\Sigma w_{i} E_{i}
$$

Thus, from the weight fractions given in the statement of the problem,

$$
\begin{aligned}
E= & (0.027)(1.1)+(0.069)(7.1)+(0.094)(14)+(0.105)(23)+(0.105)(34) \\
& +(0.095)(48)+(0.070)(64)+(0.095)(86)+(0.34)(100)=59.0 \%
\end{aligned}
$$

Related Calculations. Instead of following steps 5 and 6 as stated, one can calculate the efficiency at a variety of arbitrary particle diameters, graph the results, and then read the efficiencies for the actual particle diameters from the graph.

### 15.2 EFFICIENCY OF CYCLONE SEPARATOR

A cyclone separator $2 \mathrm{ft}(0.62 \mathrm{~m})$ in diameter, with an inlet width of $0.5 \mathrm{ft}(0.15 \mathrm{~m})$ and rated at providing 4.5 effective turns is being considered for removing particulates from offgases from a gravel dryer. Gases to the cyclone have a loading of 0.5 grains $/ \mathrm{ft}^{3}\left(17.7\right.$ grains $\left./ \mathrm{m}^{3}\right)$, with an average particle diameter of $7.5 \mu \mathrm{~m}$. Specific gravity of the particles is 2.75 . Operating temperature is $70^{\circ} \mathrm{F}$ $(294 \mathrm{~K})$ at which the air viscosity is $1.21 \times 10^{-5} \mathrm{lb} /(\mathrm{ft})(\mathrm{s})\left[1.80 \times 10^{-5}(\mathrm{~N})(\mathrm{s}) / \mathrm{m}^{2}\right]$. Inlet velocity to the cyclone is $50 \mathrm{ft} / \mathrm{s}(15.2 \mathrm{~m} / \mathrm{s})$. The local air-pollution authority requires that the maximum total loading of the cyclone effluent be 0.1 grains $/ \mathrm{ft}^{3}$ ( 3.53 grains $/ \mathrm{m}^{3}$ ). Can this cyclone meet that criterion?

## Calculation Procedure

1. Calculate the particle density. As the specific gravity of the particles is 2.75 , the particle density $\rho_{p}$ is (2.75)(62.4) or $171.6 \mathrm{lb} / \mathrm{ft}^{3}\left(2747 \mathrm{~kg} / \mathrm{m}^{3}\right)$.
2. Calculate the cut diameter. The cut diameter $d_{p c}$ for a given cyclone and given gas to be treated is the diameter of the particle that would be collected at 50 percent efficiency by the cyclone. It can be found from the equation

$$
d_{p c}=\left[9 \mu B_{c} / 2 \pi n_{t} v_{i}\left(\rho_{p}-\rho\right)\right]^{0.5}
$$

where $\mu=$ air viscosity, $\mathrm{lb} /(\mathrm{ft})(\mathrm{s})$
$B_{c}=$ cyclone inlet width, ft
$n_{t}=$ number of effective turns provided by cyclone
$v_{i}=$ inlet gas velocity, $\mathrm{ft} / \mathrm{s}$
$\rho_{p}=$ particle density, $\mathrm{lb} / \mathrm{ft}^{3}$
$\rho=$ gas density, $\mathrm{lb} / \mathrm{ft}^{3}$
In this example, the gas density can be assumed negligible in comparison with the particle density, so use $\rho_{p}$ instead of the density difference.

Thus,

$$
\begin{aligned}
d_{p c} & =\left[9\left(1.21 \times 10^{-5}\right)(0.5) / 2 \pi(4.5)(50)(171.6)\right]^{0.5}=1.5 \times 10^{-5} \mathrm{ft} \\
& =4.57 \mu \mathrm{~m}
\end{aligned}
$$

3. Calculate the ratio of average particle diameter to the cut diameter. Thus, $d_{p} / d_{p c}=$ $7.5 / 4.57=1.64$
4. Determine the collection efficiency using Lapple's curve. Refer to Fig. 15.1. For the particlesize ratio of 1.64 on the abscissa, the curve yields an efficiency of 0.72 , or 72 percent, on the ordinate.


FIGURE 15.1 Collection efficiency as a function of particle size ratio.
5. Determine the collection efficiency required by the air-pollution-control authority. This efficiency is, simply, (inlet loading - outlet loading)/(inlet loading). In the present example, it equals $(0.5-0.1) /(0.5)$, i.e., 0.8 , or 80 percent.
6. Does the cyclone meet the requirements of the pollution-control authority? As an 80 percent efficiency is required whereas the cyclone achieves only a 72 percent efficiency, the cyclone does not meet the requirements.

Related Calculations. If the cyclone is of conventional design and its inlet width is not given, it is relatively safe to assume that the width is one-quarter the cyclone diameter.

Instead of using Lapple's curve, one can solve for cyclone efficiency by using the equation

$$
E=1.0 /\left[1.0+\left(d_{p c} / d_{p}\right)^{2}\right]
$$

where $d_{p c}$ is the cut diameter and $d_{p}$ the average particle diameter.

### 15.3 SIZING AN ELECTROSTATIC PRECIPITATOR

A duct-type electrostatic precipitator is to be used to clean 100,000 actual $\mathrm{ft}^{3} / \mathrm{min}$ (47.2 actual $\mathrm{m}^{3} / \mathrm{s}$ ) of an industrial gas stream containing particulates. The proposed design of the precipitator consists of three bus sections (fields) arranged in series, each having the same amount of collection surface. The inlet loading has been measured as 17.78 grains $/ \mathrm{ft}^{3}\left(628\right.$ grains $\left./ \mathrm{m}^{3}\right)$, and a maximum outlet loading of 0.08 grains $/ \mathrm{ft}^{3}$ ( 2.8 grains $/ \mathrm{m}^{3}$ ) (both volumes corrected to dry standard conditions and 50 percent excess air) is allowed by the local air-pollution regulations. The drift velocity for the particulates has been experimentally determined in a similar installation, with the following results:

First section (inlet): $0.37 \mathrm{ft} / \mathrm{s}(0.11 \mathrm{~m} / \mathrm{s})$
Second section (middle): $0.35 \mathrm{ft} / \mathrm{s}(0.107 \mathrm{~m} / \mathrm{s})$
Third section (outlet): $0.33 \mathrm{ft} / \mathrm{s}(0.10 \mathrm{~m} / \mathrm{s})$
Calculate the total collecting surface required. And find the total mass flow rate of particulates captured in each section.

## Calculation Procedure

1. Calculate the required total collection efficiency $\mathbf{E}$ based on the given inlet and outlet loading. The equation is

$$
E=1-(\text { outlet loading }) /(\text { inlet loading })
$$

Thus,

$$
E=1-0.08 / 17.78=0.9955, \text { or } 99.55 \%
$$

2. Calculate the average drift velocity $\boldsymbol{w}$. Thus, $w=(0.37+0.35+0.33) / 3=0.35 \mathrm{ft} / \mathrm{s}(0.107$ $\mathrm{m} / \mathrm{s}$ ).
3. Calculate the total surface area required. Use the Deutsch-Anderson equation:

$$
E=1-\exp (-w A / q)
$$

where $E=$ collection efficiency
$w=$ average drift velocity
$A=$ required surface area
$q=$ gas flow rate
Rearrange the equation as follows:

$$
A=\ln (1-E) /(w / q)
$$

For consistency between $w$ and $q$, convert $q$ from $\mathrm{ft}^{3} / \mathrm{min}^{\text {to }} \mathrm{ft}^{3} / \mathrm{s}$ :

$$
100,000 / 60=1666.7 \mathrm{ft}^{3} / \mathrm{s}
$$

Then

$$
A=-\ln (1-0.9955) /(0.35 / 1666.7)=25,732 \mathrm{ft}^{2}\left(2393 \mathrm{~m}^{2}\right)
$$

4. Calculate the collection efficiencies of each section. Use the Deutsch-Anderson equation (from step 3) directly. For the first section, $E_{1}=1-\exp [-(25,732)(0.37) /(3)(1666.7)]=0.851$. Similarly, $E_{2}$ for the second section is found to be 0.835 , and $E_{3}$ for the third section 0.817 .
5. Calculate the mass flow rate $\dot{m}$ of particulates captured by each section. For the first section, the equation is

$$
\dot{m}=\left(E_{1}\right)(\text { inlet loading })(q)
$$

Thus,

$$
\dot{m}=(0.851)(17.78)(100,000)=1.513 \times 10^{6} \text { grains } / \mathrm{min}=216.1 \mathrm{lb} / \mathrm{min}(1.635 \mathrm{~kg} / \mathrm{s})
$$

For the second section, the equation is

$$
\dot{m}=\left(1-E_{1}\right)\left(E_{2}\right)(\text { inlet loading })(q)
$$

Thus,

$$
\begin{aligned}
\dot{m} & =(1-0.851)(0.835)(17.78)(100,000)=2.212 \times 10^{5} \text { grains } / \mathrm{min} \\
& =31.6 \mathrm{lb} / \mathrm{min}(0.239 \mathrm{~kg} / \mathrm{s})
\end{aligned}
$$

And for the third section, the equation is

$$
\dot{m}=\left(1-E_{1}\right)\left(1-E_{2}\right)\left(E_{3}\right)(\text { inlet loading })(q)
$$

which yields $5.10 \mathrm{lb} / \mathrm{min}(0.039 \mathrm{~kg} / \mathrm{s})$.
The total mass captured is the sum of the amounts captured in each section, i.e., $252.8 \mathrm{lb} / \mathrm{min}$ $(1.91 \mathrm{~kg} / \mathrm{s})$. It is not surprising that a full 85 percent of the mass is captured in the first section.

### 15.4 EFFICIENCY OF A VENTURI SCRUBBING OPERATION

A gas stream laden with fly ash is to be cleaned by a venturi scrubber using a liquid-to-gas ratio $\left(q_{L} / q_{G}\right)$ of 8.5 gal per 1000 actual cubic feet. The fly ash has a particle density of $43.7 \mathrm{lb} / \mathrm{ft}^{3}$ ( $700 \mathrm{~kg} / \mathrm{m}^{3}$ ). The collection-efficiency $k$ factor equals $200 \mathrm{ft}^{3} / \mathrm{gal}$. The throat velocity is $272 \mathrm{ft} / \mathrm{s}$ $(82.9 \mathrm{~m} / \mathrm{s})$, and the gas viscosity is $1.5 \times 10^{-5} \mathrm{lb} /(\mathrm{ft})(\mathrm{s})\left[2.23 \times 10^{-5}(\mathrm{~N})(\mathrm{s}) / \mathrm{m}^{2}\right]$. The particle-size
distribution is as follows:

|  | Percent by weight, <br> $d_{p i}, \mu \mathrm{~m}$ |
| :---: | :---: |
| $<0.10$ | 0.01 |
| $0.1-0.5$ | 0.21 |
| $0.6-1.0$ | 0.78 |
| $1.1-5.0$ | 13.0 |
| $6.0-10.0$ | 16.0 |
| $11.0-15.0$ | 12.0 |
| $16.0-20.0$ | 8.0 |
| $>20.0$ | 50.0 |

## Calculation Procedure

1. Determine the mean droplet diameter $d_{0}$. Use the Nukiyama-Tanasawa equation:

$$
d_{o}=(16,400 / v)+1.45\left(q_{L} / q_{G}\right)^{1.5}
$$

where $d_{o}$ is the mean droplet diameter in micrometers and $v$ is the throat velocity in feet per second. Thus,

$$
d_{o}=(16,400 / 272)+1.45(8.5)^{1.5}=96.23 \mu \mathrm{~m}=3.16 \times 10^{-4} \mathrm{ft}\left(9.63 \times 10^{-5} \mathrm{~m}\right)
$$

2. Express the inertial impaction number $\psi_{1}$ in terms of particle diameter $d_{p}$. The relationship is

$$
\psi_{1}=d_{p}^{2} \rho_{p} v / 9 \mu d_{o}
$$

where $\rho_{p}$ is particle density in $\mathrm{lb} / \mathrm{ft}^{3}$ and $\mu$ is gas viscosity in $\mathrm{lb} /(\mathrm{ft})(\mathrm{s})$. Thus,

$$
\begin{aligned}
\psi_{1} & =d_{p}^{2}(43.7)(272) /(9)\left(1.5 \times 10^{-5}\right)\left(3.16 \times 10^{-4}\right) \\
& =2.78 \times 10^{11} d_{p}^{2} \quad \text { with } d_{p} \text { in feet }
\end{aligned}
$$

To make the expression suitable for the steps that follow, express it with $d_{p}$ in micrometers, by dividing by the feet-to-micrometers conversion factor squared (because $d_{p}$ is squared):

$$
2.78 \times 10^{11} d_{p}^{2} /\left(3.048 \times 10^{5}\right)^{2}=3.002 d_{p}^{2} \quad \text { with } d_{p} \text { in micrometers }
$$

3. Express the individual collection efficiency in terms of $d_{p}$. Use the Johnstone equation:

$$
\begin{aligned}
E_{i} & =1-\exp \left(-k q_{L} \psi_{1}^{0.5} / q_{G}\right) \\
& =1-\exp \left(-2.94 d_{p i}\right)
\end{aligned}
$$

4. Calculate the overall collection efficiency. This is done by (a) determining the midpoint size of each of the particle-size ranges in the statement of the problem, (b) using the expression from step 3 to calculate the collection efficiency corresponding to that midpoint size, (c) multiplying each collection
efficiency by the percent representation $w_{i}$ for that size range in the statement of the problem, and (d) summing the results. These steps are embodied in the following table:

| $d_{p i}, \mu \mathrm{~m}$ | $E_{i}$ | $w_{i}, \%$ | $E_{i} w_{i}, \%$ |
| :---: | :--- | :---: | :---: |
| 0.05 | 0.1367 | 0.01 | 0.001367 |
| 0.30 | 0.586 | 0.21 | 0.123 |
| 0.80 | 0.905 | 0.78 | 0.706 |
| 3.0 | 0.9998 | 13.0 | 12.998 |
| 8.0 | 0.9999 | 16.0 | 16.0 |
| 13.0 | 0.9999 | 12.0 | 12.0 |
| 18.0 | 0.9999 | 8.0 | 8.0 |
| 20.0 | 0.9999 | 50.0 | 50.0 |

Then $E=\Sigma E_{i} w_{i}=99.83$ percent.
Related Calculations. In situations where the particles are so small that their size approaches the length of the mean free path of the fluid molecules, the fluid can no longer be regarded as a continuum; that is, the particles can "fall between" the molecules. That problem can be offset by applying a factor, the Cunningham correction factor, to the calculation of the inertial-impact-number expression in step 2.

### 15.5 SELECTING A FILTER BAG SYSTEM

It is proposed to install a pulse-jet fabric-filter system to remove particulates from an air stream. Select the most appropriate bag from the four proposed below. The volumetric flow rate of the air stream is $10,000 \mathrm{std} \mathrm{ft}^{3} / \mathrm{min}\left(4.72 \mathrm{~m}^{3} / \mathrm{s}\right)$ (standard conditions being $60^{\circ} \mathrm{F}$ and 1 atm ), the operating temperature is $250^{\circ} \mathrm{F}(394 \mathrm{~K})$, the concentration of pollutants is 4 grains $/ \mathrm{ft}^{3}\left(141 \mathrm{grains} / \mathrm{m}^{3}\right)$, the average air-to-cloth ratio is $\left(2.5 \mathrm{ft}^{3} / \mathrm{min}\right) / \mathrm{ft}^{2}$, and the required collection efficiency is 99 percent.

Information on the four proposed bags is as follows:

| Bag designation | A | B | C | D |
| :--- | :--- | :--- | :--- | :--- |
| Tensile strength <br> Recommended maximum <br> temperature, ${ }^{\circ} \mathrm{F}$ | Excellent | 260 | Above average | Fair |$⿻$| Excellent |
| :--- |
| Cost per bag |
| Standard size |

Note: No bag has an advantage from the standpoint of durability.

## Procedure

1. Eliminate from consideration any bags that are patently unsatisfactory. $\quad \mathrm{Bag} \mathrm{D}$ is eliminated because its recommended maximum temperature is below the operating temperature for this application. Bag C is also eliminated, because a pulse-jet fabric-filter system requires that the tensile strength of the bag be at least above average.
2. Convert the given flow rate to actual cubic feet per minute. The flow rate as stated corresponds to flow at $60^{\circ} \mathrm{F}$, whereas the actual flow $q$ will be at $250^{\circ} \mathrm{F}$. Accordingly,

$$
q=(10,000)(250+460) /(60+460)=13,654 \text { actual } \mathrm{ft}^{3} / \mathrm{min}\left(6.44 \text { actual } \mathrm{m}^{3} / \mathrm{s}\right)
$$

3. Establish the filtering velocity $\boldsymbol{v}_{f}$. The air-to-cloth ratio is $\left(2.5 \mathrm{ft}^{3} / \mathrm{min}\right) / \mathrm{ft}^{2}$. Dimensional simplification converts this to $2.5 \mathrm{ft} / \mathrm{min}(0.0127 \mathrm{~m} / \mathrm{s})$.
4. Calculate the total filtering area required. This equals the actual volumetric flow rate (from step 2 ) divided by the filtering velocity (from step 3). Thus,

$$
\text { Total filtering area }=13,654 / 2.5=5461.6 \mathrm{ft}^{2}\left(507.9 \mathrm{~m}^{2}\right)
$$

5. Calculate the filtering area available per bag. Consider the operating bag to be in the form of a cylinder, whose wall constitutes the filtering area. This is accordingly calculated from the formula $A=\pi D h$, where $A$ is area, $D$ is bag diameter, and $h$ is bag height. The two bags still under consideration are Bag A and Bag B. The area of each is as follows:

For Bag A,

$$
A=\pi(8 / 12)(16)=33.5 \mathrm{ft}^{2}\left(3.12 \mathrm{~m}^{2}\right)
$$

For Bag B,

$$
A=\pi(10 / 12)(16)=41.9 \mathrm{ft}^{2}\left(3.90 \mathrm{~m}^{2}\right)
$$

6. Determine the number of bags required. The total filtering area required is $5461.6 \mathrm{ft}^{2}$. Accordingly, if Bag A is selected, the number of bags needed is $5461.6 / 33.5$, i.e., 163 bags. If instead Bag B is selected, the number needed is $5461.6 / 41.9$, i.e., 130 bags.
7. Determine the total bag cost. If Bag A is used, the total cost is (163)(\$26.00), i.e., \$4238. If instead Bag B is used, the total cost is (130)(\$38.00), i.e., $\$ 4940$.
8. Select the most appropriate bag. Since the total cost for Bag A is less than that for Bag B, select Bag A.

### 15.6 SIZING A CONDENSER FOR ODOR-CARRYING STEAM

The discharge gases from a meat-rendering plant consist mainly of atmospheric steam, plus a small fraction of noncondensable odor-carrying gases. The stream is to pass through a condenser to remove the steam before the noncondensable gases go to an incinerator or adsorber. Estimate the size of a condenser to treat $60,000 \mathrm{lb} / \mathrm{h}(7.55 \mathrm{~kg} / \mathrm{s})$ of this discharge stream. Assume that the overall heattransfer coefficient is $135 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[765 \mathrm{~W} /\left(\mathrm{m}^{2}\right)(\mathrm{K})\right]$, that the enthalpy of vaporization for the steam is $1000 \mathrm{Btu} / \mathrm{lb}$, and that the cooling water enters the condenser at $80^{\circ} \mathrm{F}(300 \mathrm{~K})$ and leaves at $115^{\circ} \mathrm{F}$ (319 K).

## Calculation Procedure

1. Determine the heat load $Q$ for the condenser. This equals the flow rate times the enthalpy of vaporization:

$$
Q=(60,000)(1000)=6.0 \times 10^{7} \mathrm{Btu} / \mathrm{h}\left(17.6 \times 10^{6} \mathrm{~W}\right)
$$

2. Estimate the log-mean temperature temperature-difference driving force. The formula is LMTD $=\left(t_{g}-t_{l}\right) / \ln \left(t_{g}-t_{l}\right)$, where LMTD is log-mean temperature difference, $t_{g}$ is the maximum temperature difference between steam and cooling water, and $t_{l}$, is the minimum temperature difference between them. The maximum difference is $(212-80)$, or 132 ; the minimum is $(212-115)$, or 97. Accordingly, LMTD $=(132-97) / \ln (132 / 97)=113.6^{\circ} \mathrm{F}$.
3. Calculate the required area of the condenser. The formula is $A=Q / U(\mathrm{LMTD})$, where $A$ is area, $Q$ is heat load, and $U$ is overall heat-transfer coefficient. Thus, $A=\left(6.0 \times 10^{7}\right) /(135)(113.6)$, i.e., $3912 \mathrm{ft}^{2}\left(363.8 \mathrm{~m}^{2}\right)$.

Related Calculations. A comprehensive design procedure for condensers, including several examples of its application, was originally developed by the author and can be found in several of the author's Theodore Tutorials. Refer also to Section 7 of this handbook, which deals with heat transfer.

Note: This material is original to the author. Some of it has been published elsewhere without authorization.

### 15.7 AMOUNT OF ADSORBENT FOR A VOC ADSORBER

Determine the required height of adsorbent in an adsorption column that treats a degreaser-ventilation stream contaminated with trichloroethylene (TCE). Design and operating data are as follows:

Volumetric flow rate of contaminated air: $\quad 10,000 \mathrm{std} \mathrm{ft}^{3} / \mathrm{min}$ $\left(4.72 \mathrm{~m}^{3} / \mathrm{s}\right)$, standard conditions being $60^{\circ} \mathrm{F}$ and 1 atm

Operating temperature: $70^{\circ} \mathrm{F}(294 \mathrm{~K})$
Operating pressure: $20 \mathrm{psia}(138 \mathrm{kPa})$
Adsorbent: activated carbon
Bulk density $\rho_{B}$ of activated carbon: $36 \mathrm{lb} / \mathrm{ft}^{3}\left(576 \mathrm{~kg} / \mathrm{m}^{3}\right)$
Working capacity of activated carbon: 28 lb TCE per 100 lb carbon
Inlet concentration of TCE: 2000 ppm (by volume)
Molecular weight of TCE: 131.5
The adsorption column is a vertical cylinder with an inside diameter of $6 \mathrm{ft}(1.8 \mathrm{~m})$ and a height of $15 \mathrm{ft}(4.57 \mathrm{~m})$. It operates on the following cycle: 4 h in the adsorption mode, 2 h for heating and desorbing, 1 h for cooling, 1 h for standby. An identical column treats the contaminated gas while the first one is not in the adsorption mode. The system is required to recover 99.5 percent of the TCE by weight.

## Procedure

1. Determine the actual volumetric flow rate of the contaminated gas stream. The flow rate as stated corresponds to flow at $60^{\circ} \mathrm{F}$ and 1 atm, whereas the actual flow $q$ is at $70^{\circ} \mathrm{F}$ and 20 psia . Accordingly,

$$
\begin{aligned}
q & =10,000[(70+460) /(60+460)][14.7 / 20] \\
& =7491 \text { actual } \mathrm{ft}^{3} / \mathrm{min}, \text { or } 4.5 \times 10^{5} \text { actual } \mathrm{ft}^{3} / \mathrm{h}\left(3.54 \text { actual } \mathrm{m}^{3} / \mathrm{s}\right)
\end{aligned}
$$

2. Calculate the volumetric flow rate of TCE. This flow rate $q_{\mathrm{TCE}}$ equals the inlet concentration $y_{\mathrm{TCE}}$ of TCE in the gas times the gas flow rate. Thus,

$$
\begin{aligned}
q_{\mathrm{TCE}} & =\left(y_{\mathrm{TCE}}\right)(q)=\left(2000 \times 10^{-6}\right)\left(4.5 \times 10^{5}\right) \\
& =900 \text { actual } \mathrm{ft}^{3} / \mathrm{h}\left(0.007 \mathrm{~m}^{3} / \mathrm{s}\right)
\end{aligned}
$$

3. Convert the volumetric flow rate of TCE into mass flow rate. For the conversion, rearrange the ideal-gas law, bearing in mnd that mass equals the number of moles times the molecular weight. Thus $\dot{m}$, the mass flow rate in pounds per hour, equals $q_{\text {TCE }}(P M / R T)$, where $P$ is the pressure, $M$ the molecular weight, $T$ the absolute temperature, and $R$ the gas constant. Accordingly,

$$
\dot{m}=(900)(131.5) /(10.73)(70+460)=416.2 \mathrm{lb} / \mathrm{h}(0.052 \mathrm{~kg} / \mathrm{s})
$$

4. Determine the mass of TCE to be adsorbed during the 4-h period. This equals, simply, the required degree of adsorption times the amount of TCE that will pass through the system in 4 h :

$$
\text { TCE adsorbed }=(416.2 \mathrm{lb} / \mathrm{h})(4 \mathrm{~h})(0.995)=1656.6 \mathrm{lb}
$$

5. Calculate the volume of activated carbon required. To obtain this volume $v_{\mathrm{AC}}$, divide the amount of TCE to be adsorbed by the adsorption capacity of the carbon, and convert from mass to volume by taking into account the bulk density of the carbon:

$$
\begin{aligned}
v_{\mathrm{AC}} & =(\mathrm{TCE} \text { to be adsorbed }) /(28 \mathrm{lb} \mathrm{TCE} / 100 \mathrm{lb} \text { carbon })(\text { bulk density }) \\
& =(1656.6) /(28 / 100)(36)=164 \mathrm{ft}^{3}\left(4.64 \mathrm{~m}^{3}\right)
\end{aligned}
$$

6. Find the required height of the carbon in the adsorber. This height $z$ equals the volume of carbon divided by the cross-sectional area of the column:

$$
z=164 /\left[\pi\left(D^{2} / 4\right)\right]=164 /\left[\pi\left(6^{2} / 4\right)\right]=5.8 \mathrm{ft}(1.77 \mathrm{~m})
$$

Note: This material is original to the author. Some of it has been published elsewhere without authorization.

### 15.8 PERFORMANCE OF AN AFTERBURNER

It is proposed to use a natural-gas-fired, direct-flame afterburner to incinerate toluene in the effluent gases from a lithography plant. The afterburner system is as shown in Fig. 15.2. The flow rate of the $300^{\circ} \mathrm{F}(422 \mathrm{~K})$ effluent is $7000 \mathrm{std} \mathrm{ft}^{3} / \mathrm{min}\left(3.30 \mathrm{~m}^{3} / \mathrm{s}\right)$, standard conditions being $60^{\circ} \mathrm{F}$ and 1 atm ; its toluene content is $30 \mathrm{lb} / \mathrm{h}(0.0038 \mathrm{~kg} / \mathrm{s})$. After passing through the afterburner preheater, the gas enters the afterburner at $738^{\circ} \mathrm{F}(665 \mathrm{~K})$. The afterburner is essentially a horizontal cylinder, 4.2 ft $(1.28 \mathrm{~m})$ in diameter and $14 \mathrm{ft}(4.27 \mathrm{~m})$ long; it can be assumed to incur heat losses at 10 percent in excess of the calculated heat load. Gases leaving the afterburner are at $1400^{\circ} \mathrm{F}(1033 \mathrm{~K})$.


FIGURE 15.2 Natural-gas-fired afterburner (Example 15.8).

When reviewing plans for such an installation, the local air-pollution-control agency knows from experience that in order to meet emission standards, the afterburner must operate at 1300 to $1500^{\circ} \mathrm{F}$, that the residence time in the vessel must be 0.3 to 0.5 s , and that the velocity within it must be 20 to $40 \mathrm{ft} / \mathrm{s}$. Can this afterburner satisfy those three criteria?

Use the following data:
Gross heating value of natural gas: $1059 \mathrm{Btu} / \mathrm{std} \mathrm{ft}^{3}$
Volume of combustion products produced per standard cubic foot of natural gas burned: 11.5 std $\mathrm{ft}^{3}\left(11.5 \mathrm{~m}^{3}\right.$ per standard cubic meter)
Average available heat from natural gas between 738 and $1400^{\circ} \mathrm{F}$ : $600 \mathrm{Btu} / \mathrm{std} \mathrm{ft}^{3}\left(22,400 \mathrm{~kJ} / \mathrm{m}^{3}\right)$
Molecular weight of toluene: 92
Average heat capacity $C_{p 1}$ of effluent gases between 0 and $738^{\circ} \mathrm{F}$ : $7.12 \mathrm{Btu} /(\mathrm{lb} \cdot \mathrm{mol})\left({ }^{\circ} \mathrm{F}\right)[29.8 \mathrm{~kJ} /$ $(\mathrm{kg} \cdot \mathrm{mol})(\mathrm{K})]$

Average heat capacity $C_{p 2}$ of effluent gases between 0 and $1400^{\circ} \mathrm{F}$ : $7.38 \mathrm{Btu} /(\mathrm{lb} \cdot \mathrm{mol})\left({ }^{\circ} \mathrm{F}\right)[30.9 \mathrm{~kJ} /$ $(\mathrm{kg} \cdot \mathrm{mol})(\mathrm{K})]$

Volume of air required to combust natural gas: $10.33 \mathrm{std} \mathrm{ft}^{3}$ air $/ \mathrm{std}_{\mathrm{ft}^{3}}$ natural gas $\left(10.33 \mathrm{~m}^{3} / \mathrm{m}^{3}\right.$ natural gas)

## Calculation Procedure

1. Convert the gas flow rate to the molar basis. Since $1 \mathrm{lb}-\mathrm{mol}$ of gas at $32^{\circ} \mathrm{F}$ and 1 atm occupies $359 \mathrm{ft}^{3}$, at $60^{\circ} \mathrm{F}$ it will occupy $(359)[(460+60) /(460+32)]$, i.e., $379 \mathrm{ft}^{3}$. Accordingly, the molar gas flow rate $\dot{n}$ is $\left(7000\right.$ actual $\left.\mathrm{ft}^{3} / \mathrm{min}\right) /\left(379\right.$ actual $\left.\mathrm{ft}^{3} / \mathrm{lb} \cdot \mathrm{mol}\right)$, i.e., $18.47 \mathrm{lb} \cdot \mathrm{mol} / \mathrm{min}(0.139 \mathrm{~kg} \cdot \mathrm{~mol} / \mathrm{s})$.
2. Calculate the total heat load (heating rate) required to raise the gas stream from 738 to $1400^{\circ} \mathrm{F}$. Since the heat capacity data are given with $0^{\circ} \mathrm{F}$ as a basis, this heat load $Q$ must be based on first cooling the gases from 738 to $0^{\circ} \mathrm{F}$, then heating them from 0 to $1400^{\circ} \mathrm{F}$. Thus,

$$
\begin{aligned}
Q & =\dot{n}\left[C_{p 2}(1400-0)-C_{p 1}(738-0)\right] \\
& =18.47[(7.38)(1400)-(7.12)(738)]=93,790 \mathrm{Btu} / \min (1648 \mathrm{~kW})
\end{aligned}
$$

3. Determine the actual required heat load, taking into account the 10 percent heat loss. Thus, actual heat load $=1.1 Q=(1.1)(93,790)=103,169 \mathrm{Btu} / \mathrm{min}(1813 \mathrm{~kW})$.
4. Find the rate of natural gas needed to satisfy this heat load. This is, simply, the heat load divided by the available heat. Thus,

$$
\text { Rate of natural gas }=103,169 / 600=171.9 \mathrm{std} \mathrm{ft}^{3} / \mathrm{min}\left(0.081 \mathrm{~m}^{3} / \mathrm{s}\right)
$$

5. Determine the volumetric flow rate of the combustion products of the natural gas. This flow rate $q_{1}$ equals the natural gas rate times the volume of combustion products produced per standard cubic foot of natural gas. Thus,

$$
q_{1}=(171.9)(11.5)=1976 \mathrm{std} \mathrm{ft}^{3} / \min \left(0.932 \mathrm{~m}^{3} / \mathrm{s}\right)
$$

Note that the 11.5 figure already takes into account the air needed to burn the natural gas.
6. Calculate the total volumetric flow rate through the afterburner. This flow rate $q_{T}$ equals that of the effluent from the lithography plant plus that of the combustion products from step 5. Thus,

$$
q_{T}=7000+1976=8976 \mathrm{std} \mathrm{ft}^{3} / \mathrm{min}\left(4.233 \mathrm{~m}^{3} / \mathrm{s}\right)
$$

For the subsequent steps, this figure must be converted to actual cubic feet per minute. Since the afterburner operates at $1400^{\circ} \mathrm{F}$, this equals $(8976)[(1400+460) /(60+460)]$, or $32,106 \mathrm{actual} \mathrm{ft}^{3} / \mathrm{min}$ ( $15.14 \mathrm{~m}^{3} / \mathrm{s}$ ).
7. Determine the cross-sectional area of the afterburner. As the cross section is circular, this area $S$ equals $\pi D^{2} / 4$, where $D$ is the diameter of the afterburner. Thus, $S=\pi(4.2)^{2} / 4=13.85 \mathrm{ft}^{2}$ (4.22 $\mathrm{m}^{2}$ ).
8. Calculate the velocity through the afterburner. This residence time $t$ equals the length of the vessel divided by the velocity. Thus, $t=14 / 38.6=0.363 \mathrm{~s}$.
9. Find the residence time within the afterburner. This residence time $t$ equals the length of the vessel divided by the velocity. Thus, $t=14 / 38.6=0.363 \mathrm{~s}$.
10. Ascertain whether the afterburner meets the agency's criteria. The afterburner operates at $1400^{\circ} \mathrm{F}(1033 \mathrm{~K})$, so it meets the temperature criterion. The residence time of 0.363 s meets the residence-time criterion. And the gases pass through the vessel at $38.6 \mathrm{ft} / \mathrm{s}(11.8 \mathrm{~m} / \mathrm{s})$, which satisfies the velocity criterion. Thus, all three criteria are satisfied.

Related Calculations. The determination of the natural gas rate is discussed in more detail in the Wiley-Interscience text Introduction to Hazardous Waste Incineration by Theodore and Reynolds.

Note: This material is original to the author. Some of it has been published elsewhere without authorization.

### 15.9 PRELIMINARY SIZING OF AN ABSORBER FOR GAS CLEANUP

Describe how one can make a rough estimate of the required diameter and height for a randomly packed absorption tower to achieve a given degree of gas cleanup without detailed information on the properties of the dirty gas, knowing only that the absorbent is water (or has properties similar to those of water) and that the pollutant has a strong affinity with the absorbent.

## Calculation Procedure

1. Estimate a diameter for the tower. Use the rule of thumb that superficial gas velocity through the tower (i.e., velocity assuming that the tower is empty) should be about 3 to $6 \mathrm{ft} / \mathrm{s}$ ( 1 to $2 \mathrm{~m} / \mathrm{s}$ ). If we assume, for instance, a velocity of $4 \mathrm{ft} / \mathrm{s}$, then the tower cross section $S$ equals the actual volumetric flow rate of the dirty gas divided by 4 . Then the diameter $D$ can be found from the formula $D=(4 S / \pi)^{0.5}$.

To illustrate, assume that the volumetric flow rate is 60 actual $\mathrm{ft}^{3} / \mathrm{s}\left(1.7 \mathrm{~m}^{3} / \mathrm{s}\right)$. Then a suitable cross section would be about $60 / 4$, i.e., $15 \mathrm{ft}^{2}\left(1.4 \mathrm{~m}^{2}\right)$, and a suitable diameter about $[(4)(15) / \pi]^{0.5}$, i.e., about $4.4 \mathrm{ft}(1.3 \mathrm{~m})$. Given the imprecision of the superficial-gas-velocity guideline, it is appropriate to round this figure off to 4 ft .
2. Choose a packing size for the tower. If $D$ is about $3 \mathrm{ft}(1 \mathrm{~m})$, use a packing whose diameter is 1 in . If $D$ is under 3 ft , use smaller packing; if $D$ is greater than 3 ft , use larger.

Continuing the illustration from step 1 , since the tower is to be about 4 ft , use packing larger than 1 in , for instance, 1.5 in .

## AIR POLLUTION CONTROL*

3. Estimate a height for the tower. The height of an absorption tower equals the product of $H_{O G}$, the height of a gas transfer unit, and $N_{O G}$, the number of transfer units needed. It is also prudent to multiply this product by a safety factor of 1.25 to 1.50 .

Since equilibrium data are not available, assume that the slope of the equilibrium curve (see Section 11 for discussion of this curve) approaches zero. This is not an unreasonable assumption for most solvents that preferentially absorb (or react with) the pollutant. For that condition, the value of $N_{O G}$ approaches $\ln \left(y_{1} / y_{2}\right)$, where $y_{1}$ and $y_{2}$ represent the inlet and outlet concentrations, respectively. Accordingly, if for instance the required degree of gas cleanup is 99 percent, then $N_{O G}=\ln [1 /(1-0.99)]=4.61$.

As for $H_{O G}$, since the solvent is either water or similar to it, use the values that are normally encountered for aqueous systems:

| Packing diameter, in | $H_{O G}$ for plastic <br> packing, ft | $H_{O G}$ for ceramic <br> packing, ft |
| :---: | :---: | :---: |
| 1.0 | 1.0 | 2.0 |
| 1.5 | 1.25 | 2.5 |
| 2.0 | 1.5 | 3.0 |
| 3.0 | 2.25 | 4.5 |
| 3.5 | 2.75 | 5.5 |

Continue the illustration from step 2. Assume that the required cleanup is in fact 90 percent, that $1-5$-in ceramic packing is to be used, and that a safety factor of 1.4 is to be used in the height calculation. Then the estimated height equals (safety factor) $\left(N_{O G}\right)\left(H_{O G}\right)$, i.e., $(1.4)(4.61)(2.5)$, or $16 \mathrm{ft}(4.9 \mathrm{~m})$.

Related Calculations. Apart from the rule of thumb concerning superficial velocity (see step 1), be aware of similar guidelines that pertain to mass flow rate through the absorption tower. For plastic packing, the liquid and gas flow rates are both typically around 1500 to $2000 \mathrm{lb} / \mathrm{h}$ per square foot of tower cross-sectional area; for ceramic packing, the corresponding range is about 500 to $1000 \mathrm{lb} / \mathrm{h}$.

As a rough estimate of pressure drop for the gas flow through the packing, it is about 0.15 to 0.4 in of water per foot of packing.

For more detail on absorption, see Section 11.
Note: This material is original to the author. Some of it has been published elsewhere without authorization.

## ESTIMATING HAZARD DISTANCES ACCIDENTAL RELEASES

Hydrogen sulfide is accidentally released at the rate of $2 \mathrm{~kg} / \mathrm{s}$ from a $15-\mathrm{m}$ vent at night, from a plant located in an urban area. The wind speed is $3 \mathrm{~m} / \mathrm{s}$. Estimate the hazard distance for this release if the hazard level of concern for hydrogen sulfide is $0.042 \mathrm{mg} / \mathrm{L}\left(42 \mathrm{mg} / \mathrm{m}^{3}\right)$.

## Calculation Procedure

1. Determine the hazard distance, HD, without taking vent height nor wind speed into account. Use the formula: $H D=16,800\left(Q_{1} / C_{1}\right)^{0.73}$, where $Q_{1}$ is the release rate in kilograms per second, $C_{1}$ is the ground-level concentration of concern in milligrams per cubic meter, and $H D$ is in meters. Thus, $H D=16,800(2 / 42)^{0.73}=1820 \mathrm{~m}$.
2. Determine the correction factor to take into account the elevation of the vent. The height correction factor is $1.12-0.014 H$, where $H$ is the height in meters, assuming that $H$ lies between 10 and 20 m . In this case, the correction factor is $1.12-0.014(15)=0.91$.
3. Determine the correction factor for wind speed. The result in step 1 assumes a (nighttime) wind speed of $1.5 \mathrm{~m} / \mathrm{s}$. For correcting for other wind speeds, the correction factor equals $1.32 U^{-0.68}$, where $U$ is the wind speed. In this case, the correction factor is $1.32(3)^{-0.68}=0.62$.
4. Determine the hazard distance corrected for height and wind speed. The result is, from steps 1,2 , and 3 , as follows:

$$
1,820(0.91)(0.62)=1027 \mathrm{~m}
$$

Related Calculations. For daytime releases from elevated vents, the equation for step 1 is $H D=$ $2431\left(Q_{1} / C_{1}\right)^{0.65}$ and the height correction factor (for heights of 10 to 20 m ) is $1.09-0.0096 \mathrm{H}$; and for wind speeds other than $5 \mathrm{~m} / \mathrm{s}$ (not other than $1.5 \mathrm{~m} / \mathrm{s}$ ), the correction factor is $2.85(U)-0.65$. For more information, see Chemical Engineering, August 1998, pp. 121ff. For information on calculating ground-level concentrations of unburned gas released from flares, see Example 15.11.

### 15.11 GROUND-LEVEL CONCENTRATION OF UNBURNED FLAMMABLE GAS

Estimate the maximum ground-level concentration, $C$, if a flammable gas is accidentally released unburned from a flare, if the release rate to the atmosphere, $Q$, is $200,000 \mathrm{lb} / \mathrm{h}(25,200 \mathrm{~g} / \mathrm{s})$, the exit velocity, $V_{\mathrm{ex}}$, is $275 \mathrm{ft} / \mathrm{s}(83.8 \mathrm{~m} / \mathrm{s})$, and flare tip diameter, $d$, is $1.5 \mathrm{ft}(0.46 \mathrm{~m})$. The flare stack height, $H$, is $200 \mathrm{ft}(61 \mathrm{~m})$. Assume that the wind speed, $U$, is $10 \mathrm{ft} / \mathrm{s}(3.1 \mathrm{~m} / \mathrm{s})$. The molecular weight, $M W$, of the gas is 54 .

## Calculation Procedure

1. Calculate the momentum plume rise (the plume rise due to gas exit velocity), $\Delta H$. Use the formula, $\Delta H=3 d V_{\text {ex }} / U$. Thus,

$$
\Delta H=3(0.46)(83.8) / 3.1=37.3 \mathrm{~m}
$$

2. Calculate the effective flare stack height, $H^{\prime}$. Use the formula

$$
H^{\prime}=H+\Delta H=61+37.3=98.3 \mathrm{~m}
$$

3. Estimate the maximum ground-level concentration in grams per cubic meter. Use the approximation formula $C=0.23 Q / U\left(H^{\prime}\right)^{2}$, where $C$ is in grams per cubic meter, $Q$ is in grams per second, $U$ is in meters per second, and $H^{\prime}$ is in meters. Thus,

$$
C=0.23(25,200) /(3.1)(98.3)^{2}=19 \mathrm{~g} / \mathrm{m}^{3}, \text { or } 190 \mathrm{mg} / \mathrm{m}^{3}
$$

4. Convert the result to parts per million. Use the formula
parts per million $=[$ milligrams per cubic meter $][24.45 /($ molecular weight $)]$
Thus,

$$
\text { parts per million }=190(24.45 / 54)=86 \mathrm{ppm}
$$

Related Calculations. For more information, see Chemical Engineering, December 1998, pp. 133ff. For a method to calculate ground-level hazard distances for accidental releases of hazardous pollutants, see Example 15.10.

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16.1 ANALYSIS OF SOLIDS DATA 16.1
16.2 CONVERSION OF GAS CONCENTRATION UNITS 16.3
16.3 SATURATION CONCENTRATION OF OXYGEN IN WATER 16.3
16.4 DETERMINATION OF BIOCHEMICAL OXYGEN DEMAND (BOD) FROM LABORATORY DATA 16.5
16.5 CALCULATION OF THEORETICAL OXYGEN DEMAND (ThOD) 16.5
16.6 DEVELOPMENT OF BOD SUSTAINED MASS-LOADING VALUES 16.6
16.7 HEADLOSS BUILDUP IN COARSE SCREENS 16.8
16.8 DETERMINATION OF FLOWRATE EQUALIZATION VOLUME REQUIREMENTS AND EFFECTS ON BOD MASS LOADING 16.9
16.9 POWER REQUIREMENTS AND PADDLE AREA FOR A WASTEWATER FLOCCULATOR 16.14
16.10 SIZING AN ACTIVATED-SLUDGE SETTLING TANK 16.14
16.11 STRIPPING OF BENZENE IN THE ACTIVATED-SLUDGE PROCESS 16.16
16.12 ESTIMATION OF SLUDGE VOLUME FROM CHEMICAL PRECIPITATION OF UNTREATED WASTEWATER 16.19
16.13 DETERMINATION OF ALUM DOSAGE FOR PHOSPHORUS REMOVAL 16.20
16.14 ESTIMATION OF SLUDGE VOLUME FROM THE CHEMICAL PRECIPITATION OF PHOSPHORUS

WITH LIME IN A PRIMARY SEDIMENTATION TANK 16.22 16.15 DETERMINATION OF REACTION POTENTIAL 16.25
16.16 OBSERVED BIOMASS YIELD AND OXYGEN CONSUMPTION 16.26
16.17 DETERMINATION OF BIOMASS AND SOLIDS YIELDS 16.27
16.18 PREDICTING METHANE PRODUCTION FROM AN ANAEROBIC REACTOR 16.29
16.19 WASTEWATER CHARACTERIZATION EVALUATION 16.30
16.20 TRICKLING FILTER SIZING USING NRC EQUATIONS 16.33
16.21 DETERMINATION OF FILTER-MEDIUM SIZES 16.35
16.22 DETERMINATION OF MEMBRANE AREA REQUIRED FOR DEMINERALIZATION 16.36
16.23 AREA AND POWER REQUIREMENTS FOR ELECTRODIALYSIS 16.37
16.24 ANALYSIS OF ACTIVATED-CARBON ADSORPTION DATA 16.38
16.25 ESTIMATE THE REQUIRED OZONE DOSE FOR A TYPICAL SECONDARY EFFLUENT 16.40
16.26 DESIGN OF A UV DISINFECTION SYSTEM 16.42
16.27 ESTIMATION OF BLOWDOWN WATER COMPOSITION 16.44
16.28 DESIGN A GRAVITY THICKENER FOR COMBINED PRIMARY AND WASTE-ACTIVATED SLUDGE 16.46
16.29 BELT-FILTER PRESS DESIGN 16.48 REFERENCES 16.50

### 16.1 ANALYSIS OF SOLIDS DATA

The following test results were obtained for a wastewater sample taken at the headworks to a wastewater-treatment plant:

Tare mass of evaporating dish $=53.5433 \mathrm{~g}$
Mass of evaporating dish plus residue after evaporation at $105^{\circ} \mathrm{C}=53.5794 \mathrm{~g}$
*The material in this section is adapted from Metcalf and Eddy, Wastewater Engineering, 4th Edition, McGraw-Hill.

Mass of evaporating dish plus residue after ignition at $550^{\circ} \mathrm{C}=53.5625 \mathrm{~g}$
Tare mass of Whatman GF/C filter after drying at $105^{\circ} \mathrm{C}=1.5433 \mathrm{~g}$
Mass of Whatman GF/C filter and residue after drying at $105^{\circ} \mathrm{C}=1.5554 \mathrm{~g}$
Mass of Whatman GF/C filter and residue after ignition at $550^{\circ} \mathrm{C}=1.5476 \mathrm{~g}$

All of the tests were performed using a sample size of 50 mL . Determine the concentration of total solids, total volatile solids, suspended solids, volatile suspended solids, total dissolved solids, and total volatile dissolved solids. The samples used in the solids analyses were all evaporated, dried, or ignited to constant weight.

## Calculation Procedure

## 1. Determine total solids

$$
\begin{aligned}
\mathrm{TS} & =\frac{\binom{\text { mass of evaporating }}{\text { dish plus residue, } \mathrm{g}}-\left(\begin{array}{c}
\text { mass of evaporating } \\
\text { dish, } \mathrm{g}
\end{array}\right.}{\text { sample size, } \mathrm{L}} \\
& =\frac{[(53.5794-53.5433) \mathrm{g}]\left(10^{3} \mathrm{mg} / \mathrm{g}\right)}{0.050 \mathrm{~L}}=722 \mathrm{mg} / \mathrm{L}
\end{aligned}
$$

## 2. Determine total volatile solids

$$
\begin{aligned}
\text { TVS } & =\frac{\binom{\text { mass of evaporating }}{\text { dish plus residue, } \mathrm{g}}-\binom{\text { mass of evaporating dish }}{\text { plus residue after ignition, } \mathrm{g}}}{\text { sample size, } \mathrm{L}} \\
& =\frac{[(53.5794-53.5625) \mathrm{g}]\left(10^{3} \mathrm{mg} / \mathrm{g}\right)}{0.050 \mathrm{~L}}=338 \mathrm{mg} / \mathrm{L}
\end{aligned}
$$

## 3. Determine the total suspended solids

$$
\begin{aligned}
\mathrm{TSS} & =\frac{\binom{\text { residue on filter }}{\text { after drying, } \mathrm{g}}-\binom{\text { tare mass of filter }}{\text { after drying, } \mathrm{g}}}{\text { sample size, } \mathrm{L}} \\
& =\frac{[(1.5554-1.5433) \mathrm{g}]\left(10^{3} \mathrm{mg} / \mathrm{g}\right)}{0.050 \mathrm{~L}}=242 \mathrm{mg} / \mathrm{L}
\end{aligned}
$$

## 4. Determine the volatile suspended solids

$$
\begin{aligned}
\text { VSS } & =\frac{\binom{\text { residue on filter }}{\text { after drying, } \mathrm{g}}-\binom{\text { residue on filter }}{\text { after ignition, } \mathrm{g}}}{\text { sample size, } \mathrm{L}} \\
& =\frac{[(1.5554-1.5476) \mathrm{g}]\left(10^{3} \mathrm{mg} / \mathrm{g}\right)}{0.050 \mathrm{~L}}=156 \mathrm{mg} / \mathrm{L}
\end{aligned}
$$

5. Determine the total dissolved solids

$$
\mathrm{TDS}=\mathrm{TS}-\mathrm{TSS}=722-242=480 \mathrm{mg} / \mathrm{L}
$$

## 6. Determine the volatile dissolved solids

$$
\mathrm{VDS}=\mathrm{TVS}-\mathrm{VSS}=338-156=182 \mathrm{mg} / \mathrm{L}
$$

### 16.2 CONVERSION OF GAS CONCENTRATION UNITS

The off gas from a wastewater force main (i.e., pressure sewer) was found to contain $9 \mathrm{ppm}_{\mathrm{v}}$ (by volume) of hydrogen sulfide ( $\mathrm{H}_{2} \mathrm{~S}$ ). Determine the concentration in $\mu \mathrm{g} / \mathrm{m}^{3}$ and in $\mathrm{mg} / \mathrm{L}$ at standard conditions ( $0^{\circ} \mathrm{C}, 101.325 \mathrm{kPa}$ ). The molecular weight of $\mathrm{H}_{2} \mathrm{~S}$ is 34.08 .

## Calculation Procedure

1. Compute the concentration in $\mu \mathrm{g} / \mathrm{L}$. The following relationship, based on the ideal gas law, is used to convert between gas concentrations expressed in $\mathrm{ppm}_{\mathrm{v}}$ and $\mu \mathrm{g} / \mathrm{m}^{3}$ :

$$
\left.\left.\mu \mathrm{g} / \mathrm{m}^{3}=\frac{(\text { concentration, } \mathrm{ppm}}{\mathrm{v}}\right)(\mathrm{mw}, \mathrm{~g} / \mathrm{mole} \text { of gas })\left(10^{6} \mu \mathrm{~g} / \mathrm{g}\right)\right)
$$

Now, $9 \mathrm{ppm}_{\mathrm{v}}=9 \mathrm{~m}^{3} / 10^{6} \mathrm{~m}^{3}$, so

$$
\mu \mathrm{g} / \mathrm{m}^{3}=\left(\frac{9 \mathrm{~m}^{3}}{10^{6} \mathrm{~m}^{3}}\right)\left(\frac{\left(34.08 \mathrm{~g} / \text { mole } \mathrm{H}_{2} \mathrm{~S}\right)}{\left(22.4 \times 10^{-3} \mathrm{~m}^{3} / \mathrm{mole}^{\text {of } \left.\mathrm{H}_{2} \mathrm{~S}\right)}\right.}\right)\left(\frac{10^{6} \mu \mathrm{~g}}{\mathrm{~g}}\right)=13,693 \mu \mathrm{~g} / \mathrm{m}^{3}
$$

2. Compute the concentration in $m g / L$. The concentration in $m g / L$ is

$$
\left(\frac{13,693 \mu \mathrm{~g}}{\mathrm{~m}^{3}}\right)\left(\frac{1 \mathrm{mg}}{10^{3} \mu \mathrm{~g}}\right)\left(\frac{1 \mathrm{~m}^{3}}{10^{3} \mathrm{~L}}\right)=0.0137 \mathrm{mg} / \mathrm{L}
$$

Related Calculations. If gas measurements, expressed in $\mu \mathrm{g} / \mathrm{L}$, are made at other than standard conditions, the concentration must be corrected to standard conditions, using the ideal gas law, before converting to ppm .

### 16.3 SATURATION CONCENTRATION OF OXYGEN IN WATER

What is the saturation of oxygen in water in contact with dry air at 1 atm and $20^{\circ} \mathrm{C}$ ?

## Calculation Procedure

1. Establish the partial pressure of oxygen in air, $\boldsymbol{p}_{g}$. Dry air contains about 21 percent oxygen by volume. Therefore, $p_{g}=0.21 \mathrm{~mole} \mathrm{O}_{2} / \mathrm{mole}$ air.
2. Find the mole fraction of oxygen in the water, $\boldsymbol{x}_{\boldsymbol{g}}$. From the Table 16.1 , at $20^{\circ} \mathrm{C}$, Henry's constant is

$$
H=4.11 \times 10^{4} \frac{\mathrm{~atm}(\text { mole gas } / \mathrm{mole} \text { air })}{(\text { mole gas } / \mathrm{mole} \text { water })}
$$

TABLE 16.1 Henry's Law Constants at $20^{\circ} \mathrm{C}$, Unitless Henry's Law Constants at $20^{\circ} \mathrm{C}$, and Temperature-Dependent Coefficients

|  |  |  | Temperature coefficients |  |
| :--- | :---: | :---: | :---: | :---: |
| Parameter | Henry's constant, atm | Henry's constant, unitless | A | B |
| Air | 66,400 | 49.68 | 557.60 | 6.724 |
| Ammonia | 0.75 | $5.61 \times 10^{-4}$ | 1887.12 | 6.315 |
| Carbon dioxide | 1420 | 1.06 | 1012.40 | 6.606 |
| Carbon monoxide | 53,600 | 40.11 | 554.52 | 6.621 |
| Chlorine | 579 | 0.43 | 875.69 | 5.75 |
| Chlorine dioxide | 1500 | 1.12 | 1041.77 | 6.73 |
| Hydrogen | 68,300 | 51.10 | 187.04 | 5.473 |
| Hydrogen sulfide | 483 | 0.36 | 884.94 | 5.703 |
| Methane | 37,600 | 28.13 | 675.74 | 6.880 |
| Nitrogen | 80,400 | 60.16 | 537.62 | 6.739 |
| Oxygen | 41,100 | 30.75 | 595.27 | 6.644 |
| Ozone | 3.97 | 1268.24 | 8.05 |  |
| Sulfur dioxide | 36 | $2.69 \times 10^{-2}$ | 1207.85 | 5.68 |

Source: Adapted in part from Montgomery (1985), Cornwell (1990), and Hand et al. (1998).

The value of $x_{g}$ is

$$
x_{g}=\frac{P_{T}}{H} p_{g}
$$

where $P_{T}$ equals the total pressure. So,

$$
\begin{aligned}
x_{g} & =\frac{1.0 \mathrm{~atm}}{4.11 \times 10^{4} \frac{\mathrm{~atm}(\mathrm{~mole} \text { gas } / \mathrm{mole} \text { air })}{(\mathrm{mole} \text { gas } / \mathrm{mole} \text { water })}}(0.21 \mathrm{~mole} \text { gas } / \mathrm{mole} \mathrm{air}) \\
& =5.11 \times 10^{-6} \mathrm{~mole} \text { gas } / \mathrm{mole} \text { water }
\end{aligned}
$$

3. Find the number of moles of oxygen per liter, $\boldsymbol{n}_{\boldsymbol{g}}$. One liter of water contains $1000 \mathrm{~g} /$ $(18 \mathrm{~g} / \mathrm{mole})=55.6 \mathrm{~mole}$, thus

$$
\frac{n_{g}}{n_{g}+55.6}=5.11 \times 10^{-6}
$$

Because the number of moles of dissolved gas in a liter of water is much less than the number of moles of water,

$$
n_{g}+55.6 \approx 55.6
$$

and so

$$
\begin{aligned}
n_{g} & \approx(55.6) 5.11 \times 10^{-6} \\
& \approx 2.84 \times 10^{-4} \mathrm{~mole} \mathrm{O}_{2} / \mathrm{L}
\end{aligned}
$$

## 4. Determine the saturation concentration of oxygen

$$
\begin{aligned}
C_{s} & \approx \frac{\left(2.84 \times 10^{-4} \mathrm{~mole}_{2} / \mathrm{L}\right)\left(32 \mathrm{~g} / \mathrm{mole}_{2}\right)}{\left(1 \mathrm{~g} / 10^{3} \mathrm{mg}\right)} \\
& \approx 9.09 \mathrm{mg} / \mathrm{L}
\end{aligned}
$$

### 16.4 DETERMINATION OF BIOCHEMICAL OXYGEN DEMAND (BOD) FROM LABORATORY DATA

In a seeded five-day BOD test conducted on a wastewater sample, 15 mL of the waste sample was added directly into a $300-\mathrm{mL}$ BOD incubation bottle. The initial dissolved oxygen level, $D_{1}$, of the diluted sample was $8.8 \mathrm{mg} / \mathrm{L}$, and the final level, $D_{2}$, after five days was $1.9 \mathrm{mg} / \mathrm{L}$. The corresponding initial and final dissolved oxygen levels of the seeded dilution water, $B_{1}$ and $B_{2}$, were 9.1 and 7.9 , respectively. What is the five-day $\mathrm{BOD}\left(\mathrm{BOD}_{5}\right)$ of the wastewater sample?

## Calculation Procedure

Use the equation

$$
\mathrm{BOD}_{5}, \mathrm{mg} / \mathrm{L}=\frac{\left(D_{1}-D_{2}\right)-\left(B_{1}-B_{2}\right) f}{P}
$$

where $f$ is the fraction of seeded dilution waster volume in the sample to the volume or seeded dilution water in the seed control, and $P$ is the wastewater sample volume divided by the combined volume. Then

$$
\begin{aligned}
f & =[(300-15) / 300]=0.95 \\
P & =15 / 300=0.05 \\
\mathrm{BOD}_{5}, \mathrm{mg} / \mathrm{L} & =\frac{(8.8-1.9)-(9.1-7.9) 0.95}{0.05}=115.2 \mathrm{mg} / \mathrm{L}
\end{aligned}
$$

### 16.5 CALCULATION OF THEORETICAL OXYGEN DEMAND (ThOD)

Determine the ThOD for glycine $\left(\mathrm{CH}_{2}\left(\mathrm{NH}_{2}\right) \mathrm{COOH}\right)$ using the following assumptions:

1. In the first step, the organic carbon and nitrogen are converted to carbon dioxide $\left(\mathrm{CO}_{2}\right)$ and ammonia $\left(\mathrm{NH}_{3}\right)$, respectively.
2. In the second and third steps, the ammonia is oxidized sequentially to nitrite and nitrate.
3. The ThOD is the sum of the oxygen required for all three steps.

## Calculation Procedure

1. Write a balanced reaction for the carbonaceous oxygen demand

$$
\mathrm{CH}_{2}\left(\mathrm{NH}_{2}\right) \mathrm{COOH}+\frac{3}{2} \mathrm{O}_{2} \rightarrow \mathrm{NH}_{3}+2 \mathrm{CO}_{2}+\mathrm{H}_{2} \mathrm{O}
$$

2. Write balanced reactions for the nitrogenous oxygen demand

$$
\begin{aligned}
& \mathrm{NH}_{3}+\frac{3}{2} \mathrm{O}_{2} \rightarrow \mathrm{HNO}_{2}+\mathrm{H}_{2} \mathrm{O} \\
& \mathrm{HNO}_{2}+\frac{1}{2} \mathrm{O}_{2} \rightarrow \mathrm{HNO}_{3} \\
& \frac{\mathrm{NH}_{3}+2 \mathrm{O}_{2} \rightarrow \mathrm{HNO}_{3}+\mathrm{H}_{2} \mathrm{O}}{}
\end{aligned}
$$

## 3. Determine the ThOD

$$
\begin{aligned}
\text { ThOD } & =(3 / 2+4 / 2){\text { mole } \mathrm{O}_{2} / \text { mole glycine }} \\
& =7 / 2 \text { mole } \mathrm{O}_{2} / \text { mole glycine } \times 32 \mathrm{~g} / \text { mole } \mathrm{O}_{2} \\
& =112 \mathrm{~g} \mathrm{O}_{2} / \text { mole glycine }
\end{aligned}
$$

### 16.6 DEVELOPMENT OF BOD SUSTAINED MASS-LOADING VALUES

Develop a sustained BOD peak mass-loading curve for a treatment plant with a design flowrate of $1 \mathrm{~m}^{3} / \mathrm{s}(22.8 \mathrm{Mgal} / \mathrm{d})$. Assume that the long-term daily average BOD concentration is $200 \mathrm{~g} / \mathrm{m}^{3}$.

## Calculation Procedure

## 1. Compute the daily mass-loading value for BOD

$$
\text { Daily BOD mass loading, } \mathrm{kg} / \mathrm{d}=\frac{\left(200 \mathrm{~g} / \mathrm{m}^{3}\right)\left(1 \mathrm{~m}^{3} / \mathrm{s}\right)(86,400 \mathrm{~s} / \mathrm{d})}{\left(10^{3} \mathrm{~g} / \mathrm{kg}\right)}=17,280 \mathrm{~kg} / \mathrm{d}
$$

2. Construct a computation table. Set up a computation table for the development of the necessary information for the peak sustained BOD mass-loading curve (see following table).
3. Get peaking factors and mass loading rates. Obtain peaking factors for the sustained peak BOD loading rate from Fig. 16.1a, and determine the sustained mass-loading rates for various time periods [see table, columns (1), (2), and (3)].
4. Develop data for the sustained mass-loading curve and prepare a plot of the resulting data. See Fig. 16.2.

| Length of sustained <br> peak, d <br> $(1)$ | Peaking factor <br>  <br> a | Peak BOD mass <br> loading, kg/d <br> $(2)$ | Total mass <br> loading, $\mathrm{kg}^{b}$ <br> $(4)$ |
| :---: | :---: | :---: | :---: |
| 1 | 2.4 | 41,472 | 41,472 |
| 2 | 2.1 | 36,288 | 72,576 |
| 3 | 1.9 | 32,832 | 98,496 |
| 4 | 1.8 | 31,104 | 124,416 |
| 5 | 1.7 | 29,376 | 146,880 |
| 10 | 1.4 | 24,192 | 241,920 |
| 15 | 1.3 | 22,464 | 336,960 |
| 20 | 1.25 | 21,600 | 432,000 |
| 30 | 1.21 | 19,872 | 596,160 |
| 365 | 1.0 | 17,280 |  |

${ }^{a}$ From Fig. 16.1a.
${ }^{b}$ Col. $1 \times \operatorname{Col} .3=\operatorname{Col} .4$.

The interpretation of the curve plotted for this example is as follows. If the sustained peak loading period were to last for 10 days, the total amount of BOD that would be received at a treatment facility during the 10-day period would be $241,695 \mathrm{~kg}$. The corresponding amounts for sustained peak periods


FIGURE 16.1 Typical information on the ratio of averaged peak and low-constituent mass loadings to average mass loadings for (a) BOD, (b) TSS, and (c) nitrogen and phosphorus.


FIGURE 16.2 Peaking factor and total BOD versus length of sustained peak loading.
of 1 and 2 days would be 41,401 and $72,451 \mathrm{~kg}$, respectively. Computations for an example of this type can be facilitated by using a personal computer spreadsheet program.

### 16.7 HEADLOSS BUILDUP IN COARSE SCREENS

Determine the buildup of headloss, $h$, through a bar screen when 50 percent of the flow area is blocked off by the accumulation of coarse solids. Assume the following conditions apply:
approach velocity, $v=0.6 \mathrm{~m} / \mathrm{s}$
velocity through clean bar screen, $V=0.9 \mathrm{~m} / \mathrm{s}$
open area for flow through clean bar screen $=0.19 \mathrm{~m}^{2}$
headloss coefficient for a clean bar screen, $C=0.7$

## Procedure

1. Compute the clean water headloss through bar screen. Use the equation

$$
h_{L}=\frac{1}{C}\left(\frac{V^{2}-v^{2}}{2 g}\right)
$$

where $g$ is the acceleration due to gravity, to get

$$
h_{L}=\frac{1}{0.7}\left[\frac{(0.9 \mathrm{~m} / \mathrm{s})^{2}-(0.6 \mathrm{~m} / \mathrm{s})^{2}}{2\left(9.81 \mathrm{~m} / \mathrm{s}^{2}\right)}\right]=0.033 \mathrm{~m}
$$

2. Estimate the headloss through the clogged bar screen. Reducing the screen area by 50 percent results in a doubling of the velocity.

The velocity through the clogged bar screen is

$$
V_{c}=0.9 \mathrm{~m} / \mathrm{s} \times 2=1.8 \mathrm{~m} / \mathrm{s}
$$

Assuming the flow coefficient for the clogged bar screen is approximately 0.6 , the estimated headloss is

$$
h_{L}=\frac{1}{0.6}\left[\frac{(1.8 \mathrm{~m} / \mathrm{s})^{2}-(0.6 \mathrm{~m} / \mathrm{s})^{2}}{2(9.81 \mathrm{~m} / \mathrm{s})^{2}}\right]=0.24 \mathrm{~m}
$$

Related Calculations. Where mechanically cleaned coarse screens are used, the cleaning mechanism typically is actuated by the buildup of headloss. Headloss is determined by measuring the water level before and after the screen. In some cases, the screen is cleaned at predetermined time intervals, as well as at a maximum head differential.

### 16.8 DETERMINATION OF FLOWRATE EQUALIZATION VOLUME REQUIREMENTS AND EFFECTS ON BOD MASS LOADING

For the flowrate and BOD concentration data given in the following table, determine (1) the in-line storage volume required to equalize the flowrate and (2) the effect of flow equalization on the BOD mass-loading rate.

|  | Given data |  |  | Derived data |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | Average <br> flowrate during <br> time period, <br> $\mathrm{m}^{3} / \mathrm{s}$ | Average BOD <br> concentration <br> during time period, <br> Time period |  |  | Cumulative <br> volume of <br> flow at end of <br> time period, $\mathrm{m}^{3}$ |

[^20]
## Calculation Procedure

1. Determine the volume of the basin required for the flow equalization. The first step is to develop a cumulative volume curve of the wastewater flowrate expressed in cubic meters. The cumulative volume curve is obtained by converting the average flowrate $\left(q_{i}\right)$ during each hourly period to cubic meters, using the expression

$$
\text { volume, } \mathrm{m}^{3}=\left(q_{i}, \mathrm{~m}^{3} / \mathrm{s}\right)(3600 \mathrm{~s} / \mathrm{h})(1.0 \mathrm{~h})
$$

and then cumulatively summing the hourly values to obtain the cumulative flow volume. For example, for the first two time periods shown in the data table, the corresponding hourly volumes are as follows:

$$
\begin{aligned}
V_{\mathrm{M}-1} & =\left(0.275 \mathrm{~m}^{3} / \mathrm{s}\right)(3600 \mathrm{~s} / \mathrm{h})(1.0 \mathrm{~h})=990 \mathrm{~m}^{3} \\
V_{1-2} & =\left(0.220 \mathrm{~m}^{3} / \mathrm{s}\right)(3600 \mathrm{~s} / \mathrm{h})(1.0 \mathrm{~h})=792 \mathrm{~m}^{3}
\end{aligned}
$$

The cumulative flow, expressed in $\mathrm{m}^{3}$, at the end of each time period is determined as follows:

$$
\begin{aligned}
& V_{1}=990 \mathrm{~m}^{3}(\text { at the end of the first time period } \mathrm{M}-1) \\
& V_{2}=990+792=1782 \mathrm{~m}^{3}(\text { at the end of the second time period } 1-2)
\end{aligned}
$$

The cumulative flows for all the hourly time periods are computed in a similar manner (see derived data in data table).

The second step is to prepare a plot of the cumulative flow volume, as shown in the following diagram. As will be noted, the slope of the line drawn from the origin to the endpoint of the inflow mass diagram represents the average flowrate for the day, which in this case is equal to $0.307 \mathrm{~m}^{3} / \mathrm{s}$.


The third step is to determine the required storage volume. The required storage volume is determined by drawing a line parallel to the average flowrate tangent to the low point of the inflow mass
diagram. The required volume is represented by the vertical distance from the point of tangency to the straight line representing the average flowrate. Thus, the required volume is

$$
V=4110 \mathrm{~m}^{3}\left(145,100 \mathrm{ft}^{3}\right)
$$

2. Determine the effect of the equalization basin on the BOD mass-loading rate. Although there are alternative computation methods, perhaps the simplest way is to perform the necessary computations starting with the time period when the equalization basin is empty. Because the equalization basin is empty at about 8:30 A.m. the necessary computations will be performed starting with the $8-9$ time period.

The first step is to compute the liquid volume in the equalization basin at the end of each time period. The volume required is obtained by subtracting the equalized hourly flowrate expressed as a volume from the inflow flowrate also expressed as a volume. The volume corresponding to the equalized flowrate for a period of 1 h is $0.307 \mathrm{~m}^{3} / \mathrm{s} \times 3600 \mathrm{~s} / \mathrm{h}=1106 \mathrm{~m}^{3}$. Using this value, the volume in storage is computed using the following expression:

$$
V_{\mathrm{sc}}=V_{\mathrm{sp}}+V_{\mathrm{ic}}-V_{\mathrm{oc}}
$$

where $V_{\mathrm{sc}}=$ volume in the equalization basin at the end of current time period
$V_{\mathrm{sp}}=$ volume in the equalization basin at the end of previous time period
$V_{\text {ic }}=$ volume of inflow during the current time period
$V_{\mathrm{oc}}=$ volume of outflow during the current time period
Thus, using the values in the original data table, the volume in the equalization basin for the time period $8-9$ is as follows:

$$
V_{\mathrm{sc}}=0+1278 \mathrm{~m}^{3}-1106 \mathrm{~m}^{3}=172 \mathrm{~m}^{3}
$$

For time period 9-10:

$$
V_{\mathrm{sc}}=172 \mathrm{~m}^{3}+1476 \mathrm{~m}^{3}-1106 \mathrm{~m}^{3}=542 \mathrm{~m}^{3}
$$

The volume in storage at the end of each time period has been computed in a similar way (see the following computation table).
\(\left.$$
\begin{array}{cccccc}\hline & \begin{array}{c}\text { Volume } \\
\text { of flow } \\
\text { during time } \\
\text { period, } \mathrm{m}^{3}\end{array} & \begin{array}{c}\text { Volume } \\
\text { in storage at } \\
\text { end of time } \\
\text { period, } \mathrm{m}^{3}\end{array} & \begin{array}{c}\text { Average BOD } \\
\text { concentration } \\
\text { during time } \\
\text { period, } \mathrm{mg} / \mathrm{L}\end{array} & \begin{array}{c}\text { Equalized BOD } \\
\text { concentration } \\
\text { during time } \\
\text { period, } \mathrm{mg} / \mathrm{L}\end{array} & \begin{array}{c}\text { Equalized BOD } \\
\text { mass loading } \\
\text { during time }\end{array}
$$ <br>

\hline 8-9 \& 1278 \& 172 \& 175 \& 175 \& period, \mathrm{kg} / \mathrm{h}\end{array}\right]\)| 193 |
| :---: |
| $9-10$ |


| Time <br> period | Volume <br> of flow <br> during time <br> period, $\mathrm{m}^{3}$ | Volume <br> in storage at <br> end of time <br> period, $\mathrm{m}^{3}$ | Average BOD <br> concentration <br> during time <br> period, $\mathrm{mg} / \mathrm{L}$ | Equalized BOD <br> concentration <br> during time <br> period, $\mathrm{mg} / \mathrm{L}$ | Equalized BOD <br> mass loading <br> during time <br> period, $\mathrm{kg} / \mathrm{h}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $9-10$ | 1440 | 3704 | 305 | 245 | 271 |
| $10-11$ | 1368 | 3966 | 245 | 245 | 271 |
| $11-\mathrm{M}$ | 1242 | 4102 | 180 | 230 | 254 |
| M-1 | 990 | 3986 | 150 | 214 | 237 |
| $1-2$ | 792 | 3972 | 115 | 196 | 217 |
| $2-3$ | 594 | 3160 | 75 | 179 | 198 |
| $3-4$ | 468 | 2522 | 50 | 162 | 179 |
| $4-5$ | 378 | 1794 | 45 | 147 | 162 |
| $5-6$ | 360 | 1048 | 60 | 132 | 146 |
| $6-7$ | 432 | 374 | 90 | 126 | 132 |
| $7-8$ | 738 | 0 | 130 |  | 139 |
| Average |  |  |  |  | 213 |

```
Note: \(\mathrm{m}^{3} \times 35.3147=\mathrm{ft}^{3}\).
\(\mathrm{kg} \times 2.2046=\mathrm{l}\).
\(\mathrm{g} / \mathrm{m}^{3}=\mathrm{mg} / \mathrm{L}\).
```

The second step is to compute the average concentration leaving the storage basin. Using the following expression, which is based on the assumption that the contents of the equalization basin are mixed completely, the average concentration leaving the storage basin is

$$
X_{\mathrm{oc}} \frac{\left(V_{\mathrm{ic}}\right)\left(X_{\mathrm{ic}}\right)+\left(V_{\mathrm{sp}}\right)\left(X_{\mathrm{sp}}\right)}{V_{\mathrm{ic}}+V_{\mathrm{sp}}}
$$

where $X_{\mathrm{oc}}=$ average concentration of BOD in the outflow from the storage basin during the current time period, $\mathrm{g} / \mathrm{m}^{3}(\mathrm{mg} / \mathrm{L})$
$V_{\text {ic }}=$ volume of wastewater inflow during the current period, $\mathrm{m}^{3}$
$X_{\text {ic }}=$ average concentration of BOD in the inflow wastewater volume, $\mathrm{g} / \mathrm{m}^{3}$
$V_{\mathrm{sp}}=$ volume of wastewater on storage basin at the end of the previous time period, $\mathrm{m}^{3}$
$X_{\mathrm{sp}}=$ concentration of BOD in wastewater in storage basin at the end of the previous time period, $\mathrm{g} / \mathrm{m}^{3}$

Using the data given in column 2 of the previous computation table, the effluent concentration is computed as follows:

$$
\begin{aligned}
& X_{\mathrm{oc}}=\frac{\left(1278 \mathrm{~m}^{3}\right)\left(175 \mathrm{~g} / \mathrm{m}^{3}\right)+(0)(0)}{1278 \mathrm{~m}^{3}}=175 \mathrm{~g} / \mathrm{m}^{3} \quad(\text { for the time period } 8-9) \\
& X_{\mathrm{oc}}=\frac{\left(1476 \mathrm{~m}^{3}\right)\left(200 \mathrm{~g} / \mathrm{m}^{3}\right)+\left(172 \mathrm{~m}^{3}\right)\left(175 \mathrm{~g} / \mathrm{m}^{3}\right)}{(1476+172) \mathrm{m}^{3}}=197 \mathrm{~g} / \mathrm{m}^{3} \quad(\text { for the time period } 9-10)
\end{aligned}
$$

All the concentration values computed in a similar manner are reported in the previous computation table.

The third step is to compute the hourly mass-loading rate using the following expression:

$$
\text { mass-loading rate, } \mathrm{kg} / \mathrm{h}=\frac{\left(X_{\mathrm{oc}}, \mathrm{~g} / \mathrm{m}^{3}\right)\left(q_{i}, \mathrm{~m}^{3} / \mathrm{s}\right)(3600 \mathrm{~s} / \mathrm{h})}{\left(10^{3} \mathrm{~g} / \mathrm{kg}\right)}
$$

For example, for the time period 8-9, the mass-loading rate is

$$
\frac{\left(175 \mathrm{~g} / \mathrm{m}^{3}\right)\left(0.307 \mathrm{~m}^{3} / \mathrm{s}\right)(3600 \mathrm{~s} / \mathrm{h})}{\left(10^{3} \mathrm{~g} / \mathrm{kg}\right)}=193 \mathrm{~kg} / \mathrm{h}
$$

All hourly values are summarized in the computation table. The corresponding values without flow equalization are reported in the original data table.

The effect of flow equalization can be shown best graphically by plotting the hourly unequalized and equalized BOD mass loading (see the following plot). The following flowrate ratios, derived from the data presented in the table given in the problem statement and the computation table prepared in this step, are also helpful in assessing the benefits derived from flow equalization:

|  | BOD mass loading |  |
| :--- | :--- | :--- |
| Ratio | Unequalized | Equalized |
| $\frac{\text { Peak }}{\text { Average }}$ | $\frac{439}{213}=2.06$ | $\frac{271}{213}=1.27$ |
| $\frac{\text { Minimum }}{\text { Average }}$ | $\frac{17}{213}=0.08$ | $\frac{132}{213}=0.62$ |
| $\frac{\text { Peak }}{\text { Minimum }}$ | $\frac{439}{17}=25.82$ | $\frac{271}{132}=2.05$ |



Related Calculations. Where in-line equalization basins are used, additional damping of the BOD mass-loading rate can be obtained by increasing the volume of the basins. Although the flow to a treatment plant was equalized in this example, flow equalization would be used, more realistically, in locations with high infiltration or inflow or peak stormwater flows.

### 16.9 POWER REQUIREMENTS AND PADDLE AREA FOR A WASTEWATER FLOCCULATOR

Determine the theoretical power requirement, $P$, and paddle area, $A$, theoretically required to achieve an average velocity gradient, $G$, of $50 / \mathrm{s}$ in a $3000 \mathrm{~m}^{3}$ tank. The water temperature is $15^{\circ} \mathrm{C}$, the dynamic viscosity, $\mu$, is $1.139 \times 10^{-3} \mathrm{~N} \cdot \mathrm{~s} / \mathrm{m}^{2}$, the density is $999.1 \mathrm{~kg} / \mathrm{m}^{3}$, the coefficient of drag, $C_{D}$, for rectangular paddles is 1.8 , the paddle-tip velocity, $v$, is $0.6 \mathrm{~m} / \mathrm{s}$, and the relative velocity, $v_{p}$, of the paddles with respect to the fluid is $0.75 v$.

## Calculation Procedure

1. Determine the theoretical power requirement. Use the equation

$$
\begin{aligned}
P & =G^{2} \mu V \\
& =(50 / \mathrm{s})^{2}\left(1.139 \times 10^{-3} \mathrm{~N} \cdot \mathrm{~s} / \mathrm{m}^{2}\right)\left(3000 \mathrm{~m}^{3}\right) \\
& =8543 \mathrm{~kg} \cdot \mathrm{~m}^{2} / \mathrm{s}^{3}=8543 \mathrm{~W} \\
& =8.543 \mathrm{~kW}
\end{aligned}
$$

2. Determine the required paddle area. Use the equation

$$
\begin{aligned}
A & =\frac{2 P}{C_{D} \rho v_{p}^{3}} \\
& =\frac{2\left(8543 \mathrm{~kg} / \mathrm{m}^{2} \cdot \mathrm{~s}^{3}\right)}{1.8\left(999.1 \mathrm{~kg} / \mathrm{m}^{3}\right)(0.75 \times 0.6 \mathrm{~m} / \mathrm{s})^{3}} \\
& =104.3 \mathrm{~m}^{2}
\end{aligned}
$$

## SIZING AN ACTIVATED-SLUDGE TANK

The settling curve shown in the following diagram was obtained for an activated sludge with an initial solids concentration, $C_{0}$, of $3000 \mathrm{mg} / \mathrm{L}$. The initial height of the interface in the settling column was at $0.75 \mathrm{~m}(2.5 \mathrm{ft})$. Determine the area required to yield a thickened solids concentration, $C_{\mu}$, of 12,000 $\mathrm{mg} / \mathrm{L}$ with a total flow of $3800 \mathrm{~m}^{3} / \mathrm{d}(1 \mathrm{Mgal} / \mathrm{d})$. Determine also the solids loading $\left(\mathrm{kg} / \mathrm{m}^{2} \cdot \mathrm{~d}\right)$ and the overflow rate $\left(\mathrm{m}^{3} / \mathrm{m}^{2} \cdot \mathrm{~d}\right)$.


## Calculation Procedure

1. Determine the area required for thickening. Determine the value of $H_{u}$, the depth at which the solids are at the desired thickened-solids concentration:

$$
H_{u}=\frac{C_{0} H_{0}}{C_{u}}
$$

where $H_{0}$ is the initial height of the interface, so

$$
H_{u}=\frac{(3000 \mathrm{mg} / \mathrm{L})(0.75 \mathrm{~m})}{(12,000 \mathrm{mg} / \mathrm{L})}=0.188 \mathrm{~m}
$$

On the settling curve, a horizontal line is constructed at $H_{u}=0.188 \mathrm{~m}$. A tangent is constructed to the settling curve at $C_{2}$, the midpoint of the region between hindered and compression settling. Bisecting the angle formed where the two tangents meet determines point $C_{2}$. The intersection of the tangent at $C_{2}$ and the line $H_{u}=0.188 \mathrm{~m}$ determines $t_{u}$. Thus $t_{u}=47 \mathrm{~min}$, and the required area is

$$
A=\frac{Q t_{u}}{H_{0}}=\left[\frac{\left(3800 \mathrm{~m}^{3} / \mathrm{d}\right)}{(24 \mathrm{~h} / \mathrm{d})(60 \mathrm{~min} / \mathrm{h})}\right]\left(\frac{47 \mathrm{~min}}{0.75 \mathrm{~m}}\right)=165 \mathrm{~m}^{2}
$$

2. Determine the area required for clarification. First determine the interface subsidence velocity, $v$. The subsidence velocity is determined by computing the slope of the tangent drawn from the initial portion of the interface settling curve. The computed velocity represents the unhindered settling rate of the sludge.

$$
v=\left(\frac{0.75 \mathrm{~m}-0.3 \mathrm{~m}}{29.5 \mathrm{~m}}\right)\left(\frac{60 \mathrm{~min}}{\mathrm{~h}}\right)=0.92 \mathrm{~m} / \mathrm{h}
$$

Then determine the clarification rate. Because the clarification rate is proportional to the liquid volume above the critical sludge zone, it may be computed as follows:

$$
Q=3800 \mathrm{~m}^{3} / \mathrm{d}\left(\frac{0.75 \mathrm{~m}-0.188 \mathrm{~m}}{0.75 \mathrm{~m}}\right)=2847 \mathrm{~m}^{3} / \mathrm{d}
$$

The required area is obtained by dividing the clarification rate by the settling velocity:

$$
A=\frac{Q_{c}}{v}=\frac{\left(2847 \mathrm{~m}^{3} / \mathrm{d}\right)}{(24 \mathrm{~h} / \mathrm{d})(0.91 \mathrm{~m} / \mathrm{h})}=129 \mathrm{~m}^{2}
$$

3. Determine the controlling area. The controlling area is the thickening area $\left(165 \mathrm{~m}^{2}\right)$ because it exceeds the area required for clarification ( $129 \mathrm{~m}^{2}$ ).
4. Determine the solids loading. The solids loading is computed as follows:

$$
\begin{aligned}
& \text { solids, } \mathrm{kg} / \mathrm{d}=\frac{\left(3800 \mathrm{~m}^{3} / \mathrm{d}\right)\left(3000 \mathrm{~g} / \mathrm{m}^{3}\right)}{\left(10^{3} \mathrm{~g} / \mathrm{kg}\right)}=11,400 \mathrm{~kg} / \mathrm{d} \\
& \text { solids loading }=\frac{(11,400 \mathrm{~kg} / \mathrm{d})}{165 \mathrm{~m}^{2}}=69.1 \mathrm{~kg} / \mathrm{m}^{2} \cdot \mathrm{~d}
\end{aligned}
$$

## 5. Determine the hydraulic loading rate.

$$
\text { Hydraulic loading rate }=\frac{\left(3800 \mathrm{~m}^{3} / \mathrm{d}\right)}{165 \mathrm{~m}^{2}}=23.0 \mathrm{~m}^{3} / \mathrm{m}^{2} \cdot \mathrm{~d}
$$

### 16.11 STRIPPING OF BENZENE IN THE

 ACTIVATED-SLUDGE PROCESSDetermine the amount of benzene that can be stripped in a complete-mix activated-sludge reactor equipped with a diffused-air aeration system. Assume the following conditions apply:

```
wastewater flowrate, \(Q=4000 \mathrm{~m}^{3} / \mathrm{d}\)
aeration tank volume, \(V=1000 \mathrm{~m}^{3}\)
depth of aeration tank \(=6 \mathrm{~m}\)
air flowrate \(=50 \mathrm{~m}^{3} / \mathrm{min}\) at standard conditions
oxygen mass transfer rate \(=6.2 / \mathrm{h}\)
influent concentration of benzene \(=100 \mu \mathrm{~g} / \mathrm{m}^{3}\)
\(H\), Henry's constant \(=5.49 \times 10^{-3} \mathrm{~m}^{3} \cdot \mathrm{~atm} /\) mole (see Table 16.2 )
\(n\), coefficient for mass transfer equation in step \(3=1.0\)
temperature \(=20^{\circ} \mathrm{C}\)
oxygen diffusivity, \(D_{\mathrm{O}_{2}}=2.11 \times 10^{-5} \mathrm{~cm}^{2} / \mathrm{s}\)
benzene diffusivity, \(D_{v o c}=0.96 \times 10^{-5} \mathrm{~cm}^{2} / \mathrm{s}\)
```


## Calculation Procedure

1. Determine the quantity of air referenced to the middepth of the aeration tank. This represents the depth for an average bubble size:

$$
Q_{g}=\left(50 \mathrm{~m}^{3} / \mathrm{min}\right) \times \frac{10.33}{10.33+3}=38.7 \mathrm{~m}^{3} / \mathrm{min}
$$

TABLE 16.2 Physical Properties of Selected Volatile and Semivolatile Organic Compounds ${ }^{a}$

| Compounds | mw | $\mathrm{mp},{ }^{\circ} \mathrm{C}$ | bp, ${ }^{\circ} \mathrm{C}$ | vp, mmHg | vd | sg | Sol, mg/L | $C, \mathrm{~g} / \mathrm{m}^{3}$ | $H, \mathrm{~m}^{3} \cdot \mathrm{~atm} / \mathrm{mole}$ | $\log K_{\text {ow }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Benzene | 78.11 | 5.5 | 80.1 | 76 | 2.77 | 0.8786 | 1780 | 319 | $5.49 \times 10^{-3}$ | 2.1206 |
| Chlorobenzene | 112.56 | -45 | 132 | 8.8 | 3.88 | 1.1066 | 500 | 54 | $3.70 \times 10^{-3}$ | 2.18-3.79 |
| $o$-Dichlorobenzene | 147.01 | 18 | 180.5 | 1.60 | 5.07 | 1.036 | 150 | N/A | $1.7 \times 10^{-3}$ | 3.3997 |
| Ethylbenzene | 106.17 | -94.97 | 136.2 | 7 | 3.66 | 0.867 | 152 | 40 | $8.43 \times 10^{-3}$ | 3.13 |
| 1,2-Dibromoethane | 187.87 | 9.8 | 131.3 | 10.25 | 0.105 | 2.18 | 2699 | 93.61 | $6.29 \times 10^{-4}$ | N/A |
| 1,1-Dichloroethane | 98.96 | -97.4 | 57.3 | 297 | 3.42 | 1.176 | 7840 | 160.93 | $5.1 \times 10^{-3}$ | N/A |
| 1,2-Dichloroethane | 98.96 | -35.4 | 83.5 | 61 | 3.4 | 1.25 | 8690 | 350 | $1.14 \times 10^{-3}$ | 1.4502 |
| 1,1,2,2-Tetrachloroethane | 167.85 | -36 | 146.2 | 14.74 | 5.79 | 1.595 | 2800 | 13.10 | $4.2 \times 10^{-4}$ | 2.389 |
| 1,1,1-Trichloroethane | 133.41 | -32 | 74 | 100 | 4.63 | 1.35 | 4400 | 715.9 | $3.6 \times 10^{-3}$ | 2.17 |
| 1,1,2-Trichloroethane | 133.4 | -36.5 | 133.8 | 19 | N/A | N/A | 4400 | 13.89 | $7.69 \times 10^{-4}$ | N/A |
| Chloroethene | 62.5 | -153 | $-13.9$ | 2548 | 2.15 | 0.912 | 6000 | 8521 | $6.4 \times 10^{-2}$ | N/A |
| 1,1-Dichloroethene | 96.94 | -122.1 | 31.9 | 500 | 3.3 | 1.21 | 5000 | 2640 | $1.51 \times 10^{-2}$ | N/A |
| $c$-1,2-Dichloroethene | 96.95 | -80.5 | 60.3 | 200 | 3.34 | 1.284 | 800 | 104.39 | $4.08 \times 10^{-3}$ | N/A |
| $t$-1,2-Dichloroethene | 96.95 | -50 | 48 | 269 | 3.34 | 1.26 | 6300 | 1428 | $4.05 \times 10^{-3}$ | N/A |
| Tetrachloroethene | 165.83 | -22.5 | 121 | 15.6 | N/A | 1.63 | 160 | 126 | $2.85 \times 10^{-2}$ | 2.5289 |
| Trichloroethene | 131.5 | -87 | 86.7 | 60 | 4.54 | 1.46 | 1100 | 415 | $1.17 \times 10^{-2}$ | 2.4200 |
| Bromodichloromethane | 163.8 | $-57.1$ | 90 | N/A | N/A | 1.971 | N/A | N/A | $2.12 \times 10^{-3}$ | N/A |
| Chlorodibromomethane | 208.29 | <-20 | 120 | 50 | N/A | 2.451 | N/A | N/A | $8.4 \times 10^{-4}$ | N/A |
| Dichloromethane | 84.93 | -97 | 39.8 | 349 | 2.93 | 1.327 | 20,000 | 1702 | $3.04 \times 10^{-3}$ | N/A |
| Tetrachloromethane | 153.82 | -23 | 76.7 | 90 | 5.3 | 1.59 | 800 | 754 | $2.86 \times 10^{-2}$ | 2.7300 |
| Tribromomethane | 252.77 | 8.3 | 149 | 5.6 | 8.7 | 2.89 | 3130 | 7.62 | $5.84 \times 10^{-4}$ | N/A |
| Trichloromethane | 119.38 | -64 | 62 | 160 | 4.12 | 1.49 | 7840 | 1027 | $3.10 \times 10^{-3}$ | 1.8998 |
| 1,2-Dichloropropane | 112.99 | $-100.5$ | 96.4 | 41.2 | 3.5 | 1.156 | 2600 | 25.49 | $2.75 \times 10^{-3}$ | N/A |
| 2,3-Dichloropropene | 110.98 | -81.7 | 94 | 135 | 3.8 | 1.211 | insol. | 110 | N/A | N/A |
| $t$-1,3-Dichloropropene | 110.97 | N/A | 112 | 99.6 | N/A | 1.224 | 515 | 110 | N/A | N/A |
| Toluene | 92.1 | -95.1 | 110.8 | 22 | 3.14 | 0.867 | 515 | 110 | $6.44 \times 10^{-3}$ | 2.2095 |

Note $: \quad \mathrm{mw}=$ molecular weight, $\mathrm{mp}=$ melting point, $\mathrm{bp}=$ boiling point, $\mathrm{vd}=$ vapor density, $\mathrm{sg}=$ specific gravity, Sol $=$ solubility, $C_{5}=\mathrm{saturation}$ concentration in air,
$H=$ Henry's law constant, $\log K_{o w}=$ logarithm of the octanol-water partition coefficient, $\mathrm{N} / \mathrm{A}=$ not available.
2. Determine the air/liquid ratio $Q_{g} / Q$

$$
\begin{aligned}
Q & =\frac{\left(4000 \mathrm{~m}^{3} / \mathrm{d}\right)}{(1440 \mathrm{~min} / \mathrm{d})}=2.78 \mathrm{~m}^{3} / \mathrm{min} \\
\frac{Q_{g}}{Q} & =\frac{\left(38.7 \mathrm{~m}^{3} / \mathrm{min}\right)}{\left(2.78 \mathrm{~m}^{3} / \mathrm{min}\right)}=13.9
\end{aligned}
$$

3. Estimate the mass transfer coefficient for benzene. Use the equation

$$
K_{L} a_{\mathrm{VOC}}=K_{L} a_{\mathrm{O}_{2}}\left(\frac{D_{\mathrm{voc}}}{D_{\mathrm{O}_{2}}}\right)^{n}
$$

where $K_{L} a_{\mathrm{voc}}$ is the system mass-transfer coefficient and $K_{L} a_{\mathrm{O}_{2}}$ is the system oxygen mass-transfer coefficient. Then

$$
\begin{aligned}
K_{L} a_{\mathrm{VOC}} & =(6.2 / \mathrm{h})\left[\frac{\left(0.96 \times 10^{-5} \mathrm{~cm}^{2} / \mathrm{S}\right)}{\left(2.11 \times 10^{-5} \mathrm{~cm}^{2} / \mathrm{S}\right)}\right]^{1.0} \\
& =2.82 / \mathrm{h}=0.047 / \mathrm{min}
\end{aligned}
$$

4. Determine the dimensionless value of Henry's constant. Use the equation

$$
H_{u}=\frac{H}{R T}
$$

to get

$$
H_{u}=\frac{\left(0.00549 \mathrm{~m}^{3} \cdot \mathrm{~atm} / \mathrm{mole}\right)}{\left(0.000082057 \mathrm{~atm} \cdot \mathrm{~m}^{3} / \mathrm{mole} \cdot \mathrm{~K}\right)[(273.15+20) \mathrm{K}]}=0.228
$$

5. Determine the saturation parameter $\phi$. Use the equation

$$
\phi=\frac{\left(K_{L} a\right)_{\mathrm{voc}} V}{H_{u} Q_{g}}
$$

to get

$$
\phi=\frac{\left(0.047 / \mathrm{min} \times 1000 \mathrm{~m}^{3}\right)}{\left(0.228 \times 38.7 \mathrm{~m}^{3} / \mathrm{min}\right)}=5.33
$$

6. Determine the fraction of benzene removed from the liquid phase. Use the equation

$$
1-\frac{C_{e}}{C_{i}}=1-\left[1+\frac{Q_{g}}{Q}\left(H_{u}\right)\left(1-e^{-\phi}\right)\right]^{-1}
$$

where $C_{e}$ is the benzene concentration in the effluent and $C_{i}$ is its concentration in the influent. Then

$$
\begin{aligned}
1-\frac{C_{e}}{C_{i}} & =1-\left[1+13.9(0.228)\left(1-e^{-5.33}\right)\right]^{-1} \\
& =1-0.32=0.68
\end{aligned}
$$

### 16.12 ESTIMATION OF SLUDGE VOLUME FROM CHEMICAL PRECIPITATION OF UNTREATED WASTEWATER

Estimate the mass and volume of sludge produced from untreated wastewater without and with the use of ferric chloride for the enhanced removal of total suspended solids (TSS). Also estimate the amount of lime required for the specified ferric chloride dose. Assume that 60 percent of the TSS is removed in the primary settling tank without the addition of chemicals, and that the addition of ferric chloride results in an increased removal of TSS to 85 percent. Also, assume that the following data apply to this situation:

| Wastewater flowrate, $\mathrm{m}^{3} / \mathrm{d}$ | 1000 |
| :--- | :---: |
| Wastewater TSS, $\mathrm{mg} / \mathrm{L}$ | 220 |
| Wastewater alkalinity as $\mathrm{CaCO}_{3}, \mathrm{mg} / \mathrm{L}$ | 136 |
| Ferric chloride $\left(\mathrm{FeCl}_{3}\right)$ added, $\mathrm{kg} / 1000 \mathrm{~m}^{3}$ | 40 |
| Raw sludge properties |  |
| $\quad$ Specific gravity | 1.03 |
| $\quad$ Moisture content, $\%$ | 94 |
| Chemical sludge properties |  |
| $\quad$ Specific gravity | 1.05 |
| $\quad$ Moisture content, $\%$ | 92.5 |

## Calculation Procedure

1. Compute the mass of TSS removed without and with chemicals. Determine the mass of TSS removed without chemicals:

$$
M_{\mathrm{TSS}}=\frac{0.6\left(220 \mathrm{~g} / \mathrm{m}^{3}\right)\left(1000 \mathrm{~m}^{3} / \mathrm{d}\right)}{\left(10^{3} \mathrm{~g} / \mathrm{kg}\right)}=132.0 \mathrm{~kg} / \mathrm{d}
$$

Determine the mass of TSS removed with chemicals:

$$
M_{\mathrm{TSS}}=\frac{0.85\left(220 \mathrm{~g} / \mathrm{m}^{3}\right)\left(1000 \mathrm{~m}^{3} / \mathrm{d}\right)}{\left(10^{3} \mathrm{~g} / \mathrm{kg}\right)}=187.0 \mathrm{~kg} / \mathrm{d}
$$

2. Determine the mass of ferric hydroxide $\left[\mathrm{Fe}(\mathrm{OH})_{3}\right]$ produced from the addition of $40 \mathrm{~kg} / \mathbf{1 0 0 0}$ $\boldsymbol{m}^{3}$ of ferrous sulfate $\left(\mathrm{FeCl}_{3}\right)$. The relevant reaction is

where $162.2,100$, and 106.9 are molecular weights.
So,

$$
\mathrm{Fe}(\mathrm{OH})_{3} \text { formed }=40 \times\left(\frac{2 \times 106.9}{2 \times 162.2}\right)=26.4 \mathrm{~kg} / 1000 \mathrm{~m}^{3}
$$

3. Determine the mass of lime required to convert the ferric chloride to ferric hydroxide $\mathrm{Fe}(\mathrm{OH})_{3}$. The relevant equation is

| $2 \times 162.2$ | $3 \times 56(\mathrm{as} \mathrm{CaO})$ |  | $2 \times 106.9$ | $3 \times 111$ |
| :---: | :---: | :---: | :---: | :---: |
| $2 \mathrm{FeCl}_{3}+$ | $3 \mathrm{Ca}(\mathrm{OH})_{2}$ | $\leftrightarrow$ | $2 \mathrm{Fe}(\mathrm{OH})_{3}$ | $+3 \mathrm{CaCl}_{2}$ |
| Ferric | Calcium |  | Ferric | Calcium |
| oride | hydroxide |  | hydroxide | chloride |
| (soluble) | (slightly |  | (insoluble) | (soluble) |

So,

$$
\text { lime required }=40 \times\left(\frac{3 \times 56}{2 \times 162.2}\right)=20.7 \mathrm{~kg} / 1000 \mathrm{~m}^{3}
$$

Because there is sufficient natural alkalinity no lime addition will be required.

## 4. Determine the total amount of sludge on a dry basis resulting from chemical precipitation

$$
\text { Total dry solids }=187+26.4=213.4 \mathrm{~kg} / 1000 \mathrm{~m}^{3}
$$

5. Determine the total volume of sludge resulting from chemical precipitation. Assume that the sludge has a specific gravity of 1.05 and a moisture content of 92.5 percent. Then

$$
V_{s}=\frac{(213.4 \mathrm{~kg} / \mathrm{d})}{(1.05)\left(1000 \mathrm{~kg} / \mathrm{m}^{3}\right)(0.075)}=2.71 \mathrm{~m}^{3} / \mathrm{d}
$$

6. Determine the total volume of sludge without chemical precipitation. Assume that the sludge has a specific gravity of 1.03 and a moisture content of 94 percent. Then

$$
V_{s}=\frac{(132 \mathrm{~kg} / \mathrm{d})}{(1.03)\left(1000 \mathrm{~kg} / \mathrm{m}^{3}\right)(0.06)}=2.1 \mathrm{~m}^{3} / \mathrm{d}
$$

## 7. Prepare a summary table of sludge masses and volumes without and with chemical precipitation

|  | Sludge |  |
| :--- | :---: | :---: |
| Treatment | Mass, $\mathrm{kg} / \mathrm{d}$ | Volume, $\mathrm{m}^{3} / \mathrm{d}$ |
| Without chemical precipitation | 132.0 | 2.13 |
| With chemical precipitation | 213.4 | 2.71 |

Related Calculations. The magnitude of the sludge disposal problem when chemicals are used is evident from a review of the data presented in the summary table given in step 7. Even larger volumes of sludge are produced when lime is used as the primary precipitant.

### 16.13 DETERMINATION OF ALUM DOSAGE FOR PHOSPHORUS REMOVAL

Determine the amount of liquid alum required to precipitate phosphorus in a wastewater that contains 8 mg P/L. Also determine the required alum storage capacity if a $30-\mathrm{d}$ supply is to be stored at the
treatment facility. Based on laboratory testing, 1.5 mole of Al will be required per mole of P . The flowrate is $12,000 \mathrm{~m}^{3} / \mathrm{d}$. The following data are for the liquid alum supply:

Formula for liquid alum $\mathrm{Al}_{2}\left(\mathrm{SO}_{4}\right)_{3} \cdot 18 \mathrm{H}_{2} \mathrm{O}$
Alum strength $=48$ percent
Density of liquid alum solution $=1.2 \mathrm{~kg} / \mathrm{L}$

## Calculation Procedure

1. Determine the weight of aluminum (Al) available per liter of liquid alum. The weight of alum per liter is

$$
\text { alum } / \mathrm{L}=(0.48)(1.2 \mathrm{~kg} / \mathrm{L})=0.576 \mathrm{~kg} / \mathrm{L}
$$

The weight of aluminum per liter is calculated as follows:

$$
\begin{aligned}
& \text { molecular weight of alum }=666.5 \\
& \text { aluminum } / \mathrm{L}=(0.58 \mathrm{~kg} / \mathrm{L})(2 \times 26.98 / 666.5)=0.0466 \mathrm{~kg} / \mathrm{L}
\end{aligned}
$$

2. Determine the weight of Al required per unit weight of $\boldsymbol{P}$. The relevant equation is

$$
\mathrm{Al}^{3}+\mathrm{H}_{n} \mathrm{PO}_{4}^{3-n} \leftrightarrow \mathrm{AlPO}_{4}+n \mathrm{H}^{+}
$$

So,

$$
\begin{aligned}
\text { theoretical dosage } & =1.0 \mathrm{~mole} \mathrm{Al} \text { per } 1.0 \text { mole } \mathrm{P} \\
\text { aluminum required } & =1.0 \mathrm{~kg} \times(\mathrm{mw} \mathrm{Al} / \mathrm{mw} \mathrm{P}) \\
& =1.0 \mathrm{~kg} \times(26.98 / 30.97)=0.87 \mathrm{~kg} \mathrm{Al} / \mathrm{kg} \mathrm{P}
\end{aligned}
$$

3. Determine the amount of alum solution required per kg $P$

$$
\begin{aligned}
\text { Alum dose } & =1.5 \times\left(\frac{0.87 \mathrm{~kg} \mathrm{Al}}{1.0 \mathrm{~kg} \mathrm{P}}\right)\left(\frac{\mathrm{L} \text { alum solution }}{0.0466 \mathrm{~kg}}\right) \\
& =28.0 \mathrm{~L} \text { alum solution } / \mathrm{kg} \mathrm{P}
\end{aligned}
$$

4. Determine the amount of alum solution required per day

$$
\begin{aligned}
\text { Alum } & =\frac{\left(12,000 \mathrm{~m}^{3} / \mathrm{d}\right)\left(8 \mathrm{~g} \mathrm{P} / \mathrm{m}^{3}\right)(28.0 \mathrm{~L} \text { alum } / \mathrm{kg} \mathrm{P})}{\left(10^{3} \mathrm{~g} / \mathrm{kg}\right)} \\
& =2688 \mathrm{~L} \text { alum solution } / \mathrm{d}
\end{aligned}
$$

5. Determine the required alum solution storage capacity based on average flow

$$
\begin{aligned}
\text { Storage capacity } & =(2688 \mathrm{~L} \text { alum solution/d })(30 \mathrm{~d}) \\
& =80,640 \mathrm{~L}=80.6 \mathrm{~m}^{3}
\end{aligned}
$$

### 16.14 ESTIMATION OF SLUDGE VOLUME FROM THE CHEMICAL PRECIPITATION OF PHOSPHORUS WITH LIME IN A PRIMARY SEDIMENTATION TANK

Estimate the mass and volume of sludge produced in a primary sedimentation tank from the precipitation of phosphorus with lime. Assume that 60 percent of the total suspended solids (TSS) is removed without the addition of lime and that the addition of $400 \mathrm{mg} / \mathrm{L}$ of $\mathrm{Ca}(\mathrm{OH})_{2}$ results in an increased removal of TSS to 85 percent. Assume the following data apply:

| Wastewater flowrate, $\mathrm{m}^{3} / \mathrm{d}$ | 1000 |
| :--- | :---: |
| Wastewater TSS, $\mathrm{mg} / \mathrm{L}$ | 220 |
| Wastewater volatile TSS, $\mathrm{mg} / \mathrm{L}$ | 150 |
| Wastewater $\mathrm{PO}_{4}^{3-}$ as $\mathrm{P}, \mathrm{mg} / \mathrm{L}$ | 10 |
| Wastewater total hardness as $\mathrm{CaCO}_{3}, \mathrm{mg} / \mathrm{L}$ | 241.3 |
| Wastewater $\mathrm{Ca}^{2+}, \mathrm{mg} / \mathrm{L}$ | 80 |
| Wastewater $\mathrm{Mg}^{2+}, \mathrm{mg} / \mathrm{L}$ | 10 |
| Effluent $\mathrm{PO}_{4}^{3-}$ as $\mathrm{P}, \mathrm{mg} / \mathrm{L}$ | 0.5 |
| Effluent $\mathrm{Ca}^{2+}, \mathrm{mg} / \mathrm{L}$ | 60 |
| Effluent $\mathrm{Mg}^{2+}, \mathrm{mg} / \mathrm{L}$ | 0 |
| Chemical sludge properties |  |
| $\quad$ Specific gravity | 1.07 |
| $\quad$ Moisture content, $\%$ | 92.5 |

## Calculation Procedure

1. Compute the mass and volume of solids removed without chemicals. Assume that the sludge contains 94 percent moisture and has a specific gravity of 1.03 .

Determine the mass of TSS removed:

$$
M_{\mathrm{TSS}}=\frac{0.6\left(220 \mathrm{~g} / \mathrm{m}^{3}\right)\left(1000 \mathrm{~m}^{3} / \mathrm{d}\right)}{\left(10^{3} \mathrm{~g} / \mathrm{kg}\right)}=132 \mathrm{~kg} / \mathrm{d}
$$

Determine the volume of sludge produced:

$$
V_{s}=\frac{(132 \mathrm{~kg} / \mathrm{d})}{(1.03)\left(1000 \mathrm{~kg} / \mathrm{m}^{3}\right)(0.06)}=2.14 \mathrm{~m}^{3} / \mathrm{d}
$$

2. Using the equations summarized in the Table, determine the mass of $\mathrm{Ca}_{5}\left(\mathrm{PO}_{4}\right)_{3} \mathrm{OH}, \mathrm{Mg}(\mathrm{OH})_{2}$, and $\mathrm{CaCO}_{3}$ produced from the addition of $400 \mathrm{mg} / \mathrm{L}$ of lime. First determine the mass of $\mathrm{Ca}_{5}\left(\mathrm{PO}_{4}\right)_{3} \mathrm{OH}$ formed.
I. Determine the moles of P removed:

$$
\begin{aligned}
\text { moles P removed } & =\frac{(10-0.5) \mathrm{mg} / \mathrm{L}}{(30.97 \mathrm{~g} / \mathrm{mole})\left(10^{3} \mathrm{mg} / \mathrm{g}\right)} \\
& =0.307 \times 10^{-3} \mathrm{~mole} / \mathrm{L}
\end{aligned}
$$

| Reaction | Chemical species <br> in sludge |
| :--- | :---: |
| Lime, $\mathrm{CaCO}_{3}$ |  |
| $1.10 \mathrm{Ca}^{2+}+6 \mathrm{PO}_{4}^{3-}+2 \mathrm{OH}^{-} \leftrightarrow \mathrm{Ca}_{10}\left(\mathrm{PO}_{4}\right)_{6}(\mathrm{OH})_{2}$ | $\mathrm{Ca}_{10}\left(\mathrm{PO}_{4}\right)_{6}(\mathrm{OH})_{2}$ |
| 2. $\mathrm{Mg}^{2+}+2 \mathrm{OH}^{-} \leftrightarrow \mathrm{Mg}(\mathrm{OH})_{2}$ | $\mathrm{Mg}(\mathrm{OH})_{2}$ |
| $3 . \mathrm{Ca}^{2+}+\mathrm{CO}_{3}^{2-} \leftrightarrow \mathrm{CaCO}_{3}$ | $\mathrm{CaCO}_{3}$ |
| $\mathrm{Alum}, \mathrm{Al}(\mathrm{III})$ |  |
| 1. $\mathrm{Al}^{3-}+\mathrm{PO}_{4}^{3-} \leftrightarrow \mathrm{AlPO}_{4}$ | $\mathrm{AlPO}_{4}$ |
| 2. $2 \mathrm{Al}^{3-}+3 \mathrm{OH}^{-} \leftrightarrow \mathrm{Al}(\mathrm{OH})_{3}$ | $\mathrm{Al}(\mathrm{OH})_{3}$ |
| $\mathrm{Iron}, \mathrm{Fe}^{(\mathrm{III})}$ |  |
| 1. $\mathrm{Fe}^{3+}+\mathrm{PO}_{4}^{3-} \leftrightarrow \mathrm{FePO}_{4}$ | FePO |
| 2. $\mathrm{Fe}^{3+}+3 \mathrm{OH}^{-} \leftrightarrow \mathrm{Fe}(\mathrm{OH})_{3}$ | $\mathrm{Fe}(\mathrm{OH})_{3}$ |

II. Determine the moles of $\mathrm{Ca}_{5}\left(\mathrm{PO}_{4}\right)_{3} \mathrm{OH}$ formed:

$$
\text { moles } \begin{aligned}
\mathrm{Ca}_{5}\left(\mathrm{PO}_{4}\right)_{3} \mathrm{OH} \text { formed } & =1 / 3 \times 0.307 \times 10^{-3} \mathrm{~mole} / \mathrm{L} \\
& =0.102 \times 10^{-3} \mathrm{~mole} / \mathrm{L}
\end{aligned}
$$

III. Determine the mass of $\mathrm{Ca}_{5}\left(\mathrm{PO}_{4}\right)_{3} \mathrm{OH}$ formed:

$$
\begin{aligned}
\operatorname{mass} \mathrm{Ca}_{5}\left(\mathrm{PO}_{4}\right)_{3} \mathrm{OH} & =0.102 \times 10^{-3} \mathrm{~mole} / \mathrm{L} \times 502 \mathrm{~g} / \mathrm{mole} \times 10^{3} \mathrm{mg} / \mathrm{g} \\
& =51.3 \mathrm{mg} / \mathrm{L}
\end{aligned}
$$

Then determine the mass of $\mathrm{Mg}(\mathrm{OH})_{2}$ formed.
I. Determine the moles of $\mathrm{Mg}^{2+}$ removed:

$$
\begin{aligned}
\text { moles } \mathrm{Mg}^{2+} \text { removed } & =\frac{(10 \mathrm{mg} / \mathrm{L})}{(24.31 \mathrm{~g} / \mathrm{mole})\left(10^{3} \mathrm{mg} / \mathrm{g}\right)} \\
& =0.411 \times 10^{-3} \mathrm{~mole} / \mathrm{L}
\end{aligned}
$$

II. Determine the mass of $\mathrm{Mg}(\mathrm{OH})_{2}$ formed:

$$
\begin{aligned}
\text { moles } \mathrm{Mg}(\mathrm{OH})_{2} & =0.411 \times 10^{-3} \mathrm{~mole} / \mathrm{L} \times 58.3 \mathrm{~g} / \mathrm{mole} \times 10^{3} \mathrm{mg} / \mathrm{g} \\
& =24.0 \mathrm{mg} / \mathrm{L}
\end{aligned}
$$

Then determine the mass of $\mathrm{CaCO}_{3}$ formed.
I. Determine the mass of $\mathrm{Ca}^{2+}$ in $\mathrm{Ca}_{5}\left(\mathrm{PO}_{4}\right)_{3}(\mathrm{OH})$ :

$$
\begin{aligned}
& \text { mass } \mathrm{Ca}^{2+} \text { in } \mathrm{Ca}_{5}\left(\mathrm{PO}_{4}\right)_{3}(\mathrm{OH}) \\
& =5(40 \mathrm{~g} / \mathrm{mole})\left(0.102 \times 10^{-3} \mathrm{~mole} / \mathrm{L}\right)\left(10^{3} \mathrm{mg} / \mathrm{g}\right) \\
& =20.4 \mathrm{mg} / \mathrm{L}
\end{aligned}
$$

II. Determine the mass of $\mathrm{Ca}^{2+}$ added in the original dosage:

$$
\begin{aligned}
\text { mass } \mathrm{Ca}^{2+} \text { in } \mathrm{Ca}(\mathrm{OH})_{2} & =\frac{(40 \mathrm{~g} / \mathrm{mole})(400 \mathrm{mg} / \mathrm{L})}{(74 \mathrm{~g} / \mathrm{mole})} \\
& =216.2 \mathrm{mg} / \mathrm{L}
\end{aligned}
$$

III. Determine the mass of Ca present as $\mathrm{CaCO}_{3}$ :

$$
\begin{aligned}
\mathrm{Ca}^{2+} \text { in } \mathrm{CaCO}_{3}= & \mathrm{Ca} \text { in } \mathrm{Ca}(\mathrm{HO})_{2}+\left(\mathrm{Ca}^{2+} \text { in influent wastewater }\right) \\
& -\left(\mathrm{Ca}^{2+} \text { in } \mathrm{Ca}_{5}\left(\mathrm{PO}_{4}\right)_{3} \mathrm{OH}\right)-\left(\mathrm{Ca}^{2+} \text { in effluent wastewater }\right) \\
= & 216.2+80-20.4-60 \\
= & 215.8 \mathrm{mg} / \mathrm{L}
\end{aligned}
$$

IV. Determine the mass of $\mathrm{CaCO}_{3}$ :

$$
\begin{aligned}
\text { mass } \mathrm{CaCO}_{3} & =\frac{(100 \mathrm{~g} / \mathrm{mole})(215.8 \mathrm{mg} / \mathrm{L})}{(40 \mathrm{~g} / \mathrm{mole})} \\
& =540 \mathrm{mg} / \mathrm{L}
\end{aligned}
$$

3. Determine the total mass of solids removed as a result of the lime dosage. The mass of TSS in wastewater is

$$
M_{\mathrm{TSS}}=\frac{0.85\left(220 \mathrm{~g} / \mathrm{m}^{3}\right)\left(1000 \mathrm{~m}^{3} / \mathrm{d}\right)}{\left(10^{3} \mathrm{~g} / \mathrm{kg}\right)}=187 \mathrm{~kg} / \mathrm{d}
$$

The masses of the chemical solids are

$$
\begin{aligned}
M_{\mathrm{Ca}_{5}\left(\mathrm{PO}_{4}\right)_{3} \mathrm{OH}} & =\frac{\left(51.2 \mathrm{~g} / \mathrm{m}^{3}\right)\left(1000 \mathrm{~m}^{3} / \mathrm{d}\right)}{\left(10^{3} \mathrm{~g} / \mathrm{kg}\right)}=51.2 \mathrm{~kg} / \mathrm{d} \\
M_{\mathrm{Mg}(\mathrm{OH})_{2}} & =\frac{\left(24 \mathrm{~g} / \mathrm{m}^{3}\right)\left(1000 \mathrm{~m}^{3} / \mathrm{d}\right)}{\left(10^{3} \mathrm{~g} / \mathrm{kg}\right)}=24.0 \mathrm{~kg} / \mathrm{d} \\
M_{\mathrm{CaCO}_{3}} & =\frac{\left(540 \mathrm{~g} / \mathrm{m}^{3}\right)\left(1000 \mathrm{~m}^{3} / \mathrm{d}\right)}{\left(10^{3} \mathrm{~g} / \mathrm{kg}\right)}=540 \mathrm{~kg} / \mathrm{d}
\end{aligned}
$$

Hence the total mass of solids removed is

$$
\begin{aligned}
M_{T} & =(187+51.3+24+540) \mathrm{kg} / \mathrm{d} \\
& =802.3 \mathrm{~kg} / \mathrm{d}
\end{aligned}
$$

4. Determine the total volume of sludge resulting from chemical precipitation. Assume that the sludge has a specific gravity of 1.07 and a moisture content of 92.5 percent. Then

$$
V_{s}=\frac{(802.3 \mathrm{~kg} / \mathrm{d})}{(1.07)\left(1000 \mathrm{~kg} / \mathrm{m}^{3}\right)(0.075)}=10.0 \mathrm{~m}^{3} / \mathrm{d}
$$

## 5. Prepare a summary table of sludge masses and volumes without and with chemical precipitation

|  | Sludge |  |
| :--- | :---: | :---: |
| Treatment | Mass, $\mathrm{kg} / \mathrm{d}$ | Volume, $\mathrm{m}^{3} / \mathrm{d}$ |
| Without chemical precipitation | 132.0 | 2.14 |
| With chemical precipitation | 802.3 | 10.0 |

### 16.15 DETERMINATION OF REACTION POTENTIAL

Determine whether hydrogen sulfide $\left(\mathrm{H}_{2} \mathrm{~S}\right)$ can be oxidized with hydrogen peroxide $\left(\mathrm{H}_{2} \mathrm{O}_{2}\right)$. The pertinent half reactions from Table 16.3 are as follows:

$$
\begin{aligned}
\mathrm{H}_{2} \mathrm{~S} & \leftrightarrow \mathrm{~S}+2 \mathrm{H}^{+}+2 \mathrm{e}^{-} \quad E^{\circ}=-0.14 \\
\mathrm{H}_{2} \mathrm{O}_{2} & +2 \mathrm{H}^{+}+2 \mathrm{e}^{-} \leftrightarrow 2 \mathrm{H}_{2} \mathrm{O} \quad E^{\circ}=+1.776
\end{aligned}
$$

TABLE 16.3 Selected Standard Electrode Potentials for Oxidation-Reduction Half Reactions

| Half reaction | Oxidation potential, ${ }^{\text {a }}$ V |
| :---: | :---: |
| $\mathrm{Li}^{+}+\mathrm{e}^{-} \rightarrow \mathrm{Li}$ | -3.03 |
| $\mathrm{K}^{+}+\mathrm{e}^{-} \rightarrow \mathrm{K}$ | -2.92 |
| $\mathrm{Ba}^{2+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Ba}$ | -2.90 |
| $\mathrm{Ca}^{2+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Ca}$ | -2.87 |
| $\mathrm{Na}^{+}+\mathrm{e}^{-} \rightarrow \mathrm{Na}$ | -2.71 |
| $\mathrm{Mg}(\mathrm{OH})_{2}+2 \mathrm{e}^{-} \rightarrow \mathrm{Mg}+2 \mathrm{OH}^{-}$ | -2.69 |
| $\mathrm{Mg}^{2+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Mg}$ | -2.37 |
| $\mathrm{Al}^{3+}+3 \mathrm{e}^{-} \rightarrow \mathrm{Al}$ | -1.66 |
| $\mathrm{MnO}_{4}^{-}+8 \mathrm{H}^{+}+5 \mathrm{e}^{-} \rightarrow \mathrm{Mn}^{2+}+4 \mathrm{H}_{2} \mathrm{O}$ | -1.51 |
| $\mathrm{Mn}^{2+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Mn}$ | -1.18 |
| $2 \mathrm{H}_{2} \mathrm{O}+2 \mathrm{e}^{-} \rightarrow \mathrm{H}_{2}+2 \mathrm{OH}^{-}$ | -0.828 |
| $\mathrm{Zn}^{2+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Zn}$ | -0.763 |
| $\mathrm{Fe}^{2+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Fe}$ | -0.440 |
| $\mathrm{Cd}^{2+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Cd}$ | -0.40 |
| $\mathrm{Ni}^{2+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Ni}$ | -0.250 |
| $\mathrm{S}+2 \mathrm{H}^{+}+2 \mathrm{e}^{-} \rightarrow \mathrm{H}_{2} \mathrm{~S}$ | -0.14 |
| $\mathrm{Pb}^{2+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Pb}$ | -0.126 |
| $2 \mathrm{H}^{+}+2 \mathrm{e}^{-} \rightarrow \mathrm{H}_{2}$ | 0.000 |
| $\mathrm{Cu}^{2+}+\mathrm{e}^{-} \rightarrow \mathrm{Cu}^{+}$ | +0.15 |
| $\mathrm{N}_{2}+4 \mathrm{H}^{+}+3 \mathrm{e}^{-} \rightarrow \mathrm{NH}_{4}^{+}$ | +0.27 |
| $\mathrm{Cu}^{2+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Cu}$ | +0.34 |
| $\mathrm{I}_{2}+2 \mathrm{e}^{-} \rightarrow 2 \mathrm{I}^{-}$ | $+0.54$ |
| $\mathrm{O}_{2}+2 \mathrm{H}^{+}+2 \mathrm{e}^{-} \rightarrow \mathrm{H}_{2} \mathrm{O}_{2}$ | +0.68 |
| $\mathrm{Fe}^{3+}+\mathrm{e}^{-} \rightarrow \mathrm{Fe}^{2+}$ | +0.771 |
| $\mathrm{Ag}^{+}+\mathrm{e}^{-} \rightarrow \mathrm{Ag}$ | +0.799 |
| $\mathrm{ClO}^{-}+\mathrm{H}_{2} \mathrm{O}+2 \mathrm{e}^{-} \rightarrow \mathrm{Cl}^{-}+2 \mathrm{OH}^{-}$ | +0.90 |
| $\mathrm{Br}_{2}(\mathrm{aq})+2 \mathrm{e}^{-} \rightarrow 2 \mathrm{Br}^{-}$ | +1.09 |
| $\mathrm{O}_{2}+4 \mathrm{H}^{+}+4 \mathrm{e}^{-} \rightarrow 2 \mathrm{H}_{2} \mathrm{O}$ | +1.229 |
| $\mathrm{Cl}_{2}(\mathrm{~g})+2 \mathrm{e}^{-} \rightarrow 2 \mathrm{Cl}^{-}$ | +1.360 |
| $\mathrm{H}_{2} \mathrm{O}_{2}+2 \mathrm{H}^{+}+2 \mathrm{e}^{-} \rightarrow 2 \mathrm{H}_{2} \mathrm{O}$ | +1.776 |
| $\mathrm{O}_{3}+2 \mathrm{H}^{+}+2 \mathrm{e}^{-} \leftrightarrow \mathrm{O}_{2}+\mathrm{H}_{2} \mathrm{O}$ | +2.07 |
| $\mathrm{F}_{2}+2 \mathrm{H}^{+}+2 \mathrm{e}^{-} \rightarrow 2 \mathrm{HF}$ | +2.87 |

Source: Adapted in part from Bard (1996) and Benefield et al. (1982). ${ }^{a}$ Reported values will vary depending on source.

## Calculation Procedure

## 1. Determine the overall reaction by adding the two half reactions.

$$
\begin{gathered}
\mathrm{H}_{2} \mathrm{~S} \leftrightarrow \mathrm{~S}+2 \mathrm{H}^{+}+2 \mathrm{e}^{-} \\
\frac{\mathrm{H}_{2} \mathrm{O}_{2}+2 \mathrm{H}^{+}+2 \mathrm{e}^{-} \leftrightarrow 2 \mathrm{H}_{2} \mathrm{O}}{\mathrm{H}_{2} \mathrm{~S}+\mathrm{H}_{2} \mathrm{O}_{2} \leftrightarrow \mathrm{~S}+2 \mathrm{H}_{2} \mathrm{O}}
\end{gathered}
$$

2. Determine the $E_{\text {reaction }}^{\circ}$ for the overall reaction

$$
\begin{aligned}
E_{\text {reaction }}^{\circ} & =E_{\mathrm{H}_{2} \mathrm{O}_{2}{ }^{2+}, \mathrm{H}_{2} \mathrm{O}}^{\circ}-E_{\mathrm{s}^{2}, \mathrm{~s}}^{\circ} \\
& =(1.78)-(-0.14)=+1.92 \text { volts }
\end{aligned}
$$

Because the $E_{\text {reaction }}^{\circ}$ for the reaction is positive, the reaction will proceed as written.

### 16.16 OBSERVED BIOMASS YIELD AND OXYGEN CONSUMPTION

The aerobic complete-mix biological treatment process without recycle, as shown in the drawing, receives wastewater with a biodegradable soluble COD (bsCOD) concentration of $500 \mathrm{~g} / \mathrm{m}^{3}$. The flowrate is $1000 \mathrm{~m}^{3} / \mathrm{d}$ and the reactor effluent bsCOD and suspended volatile solids (VSS) concentrations are 10 and $200 \mathrm{~g} / \mathrm{m}^{3}$, respectively. Based on these data:

What is the observed yield in g VSS/g COD removed?
What is the amount of oxygen used in $\mathrm{g} \mathrm{O}_{2} / \mathrm{g}$ COD removed and in $\mathrm{g} / \mathrm{d}$ ?


## Procedure

1. Determine the observed yield. Assume the following general reaction is applicable:

$$
\underset{500 \mathrm{~g} \mathrm{COD} / \mathrm{m}^{3}}{\text { organic matter }}+\mathrm{O}_{2}+\text { nutrients } \rightarrow \underset{200 \mathrm{~g} \mathrm{VSS} / \mathrm{m}^{3}}{\mathrm{C}_{5} \mathrm{H}_{7} \mathrm{NO}_{2}}+\mathrm{CO}_{2}+\mathrm{H}_{2} \mathrm{O}
$$

The g VSS/d produced is

$$
\mathrm{g} \mathrm{VSS} / \mathrm{d}=200 \mathrm{~g} / \mathrm{m}^{3}\left(1000 \mathrm{~m}^{3} / \mathrm{d}\right)=200,000 \mathrm{~g} \mathrm{VSS} / \mathrm{d}
$$

The g bsCOD/d removed is

$$
\begin{aligned}
\mathrm{g} \mathrm{COD} / \mathrm{d} & =(500-10) \mathrm{g} \mathrm{COD} / \mathrm{m}^{3}\left(1000 \mathrm{~m}^{3} / \mathrm{d}\right) \\
& =490,000 \mathrm{~g} \mathrm{COD} / \mathrm{d}
\end{aligned}
$$

The observed yield is then

$$
Y_{\mathrm{obs}}=\frac{(200,000 \mathrm{~g} \mathrm{VSS} / \mathrm{d})}{(490,000 \mathrm{~g} \mathrm{COD} / \mathrm{d})}=0.41 \mathrm{~g} \mathrm{VSS} / \mathrm{g} \mathrm{COD} \text { removed }
$$

2. Determine the amount of oxygen used per g bsCOD removed. Prepare a steady-state COD mass balance around the reactor:

$$
\text { accumulation }=\text { inflow }- \text { outflow }+ \text { conversion }
$$

$$
0=\mathrm{COD}_{\text {in }}-\mathrm{COD}_{\text {out }}-\text { oxygen used (expressed as COD) }
$$

Now,

$$
\text { oxygen used }=\mathrm{COD}_{\text {in }}-\mathrm{COD}_{\text {out }}
$$

and

$$
\begin{aligned}
\mathrm{COD}_{\text {in }} & =500 \mathrm{~g} \mathrm{COD}^{2} \mathrm{~m}^{3}\left(1000 \mathrm{~m}^{3} / \mathrm{d}\right)=500,000 \mathrm{~g} \mathrm{COD} / \mathrm{d} \\
\mathrm{COD}_{\text {out }} & =\mathrm{bsCOD}_{\text {out }}+\text { biomass } \mathrm{COD}_{\text {out }}
\end{aligned}
$$

where

$$
\mathrm{bsCOD}
$$

$$
\begin{aligned}
\text { biomass } \mathrm{COD}_{\text {out }} & =200,000 \mathrm{~g} \mathrm{VSS} / \mathrm{d}(1.42 \mathrm{~g} \mathrm{COD} / \mathrm{g} \mathrm{VSS}) \\
& =284,000 \mathrm{~g} \mathrm{COD} / \mathrm{d}
\end{aligned}
$$

So,

$$
\text { total } \mathrm{COD}_{\text {out }}=10,000 \mathrm{~g} / \mathrm{d}+284,000 \mathrm{~g} / \mathrm{d}=294,000 \mathrm{~g} \mathrm{COD} / \mathrm{d}
$$

The oxygen used is

$$
\begin{aligned}
\text { oxygen used } & =500,000 \mathrm{~g} \mathrm{COD} / \mathrm{d}-294,000 \mathrm{~g} \mathrm{COD} / \mathrm{d} \\
& =206,000 \mathrm{~g} \mathrm{COD} / \mathrm{d}=206,000 \mathrm{~g} \mathrm{O}_{2} / \mathrm{d}
\end{aligned}
$$

The amount of oxygen used per unit COD removed is then

$$
\text { oxygen } / \mathrm{COD}=(206,000 \mathrm{~g} / \mathrm{d}) /(490,000 \mathrm{~g} / \mathrm{d})=0.42 \mathrm{~g} \mathrm{O}_{2} / \mathrm{g} \mathrm{COD}
$$

Related Calculations. The general COD balance that accounts for cell production and COD oxidation is
g COD cells +g COD oxidized $=\mathrm{g}$ COD removed
$(0.41 \mathrm{~g} \mathrm{VSS} / \mathrm{g} \mathrm{COD})\left(1.42 \mathrm{~g} \mathrm{O}_{2} / \mathrm{g} \mathrm{VSS}\right)+0.42 \mathrm{~g} \mathrm{O}_{2} / \mathrm{g} \mathrm{COD}=1.0 \mathrm{~g} \mathrm{O}_{2} / \mathrm{g} \mathrm{COD}$

### 16.17 DETERMINATION OF BIOMASS AND SOLIDS YIELDS

For an industrial wastewater activated-sludge process, the amount of bsCOD in the influent wastewater is $300 \mathrm{~g} / \mathrm{m}^{3}$ and the influent nonbiodegradable suspended volatile solids ( nbVSS ) concentration is $50 \mathrm{~g} / \mathrm{m}^{3}$. The influent flowrate is $1000 \mathrm{~m}^{3} / \mathrm{d}$, the biomass concentration is $2000 \mathrm{~g} / \mathrm{m}^{3}$, the reactor bsCOD concentration is $15 \mathrm{~g} / \mathrm{m}^{3}$, and the reactor volume is $105 \mathrm{~m}^{3}$. If the cell debris fraction, $f_{d}$,
is 0.10 , determine the net biomass yield, the observed solids yield, and the biomass fraction in the mixed-liquor volatile suspended solids (MLVSS). Use the kinetic coefficients given in the table that follow.

|  |  | Value $^{a}$ |  |
| :---: | :---: | :---: | :---: |
| Coefficient | Unit | Range | Typical |
| $k$ | g bs COD/g VSS $\cdot \mathrm{d}$ | $2-10$ | 5 |
| $K_{s}$ | $\mathrm{mg} / \mathrm{L} \mathrm{BOD}$ | $25-100$ | 60 |
|  | $\mathrm{mg} / \mathrm{L}$ bsCOD | $10-60$ | 40 |
| $Y$ | mg VSS/mg BOD | $0.4-0.8$ | 0.6 |
|  | mg VSS/mg bsCOD | $0.3-0.6$ | 0.4 |
| $k_{d}$ | g VSS/g VSS $\cdot \mathrm{d}$ | $0.06-0.15$ | 0.10 |

${ }^{a}$ Values reported are for $20^{\circ} \mathrm{C}$.

## Calculation Procedure

1. Determine the net biomass yield. Use the equation

$$
Y_{b i o}=-r_{g} / r_{s u},
$$

where $r_{g}$ and $r_{s u}$ are rates of biomass growth and substrate utilizatization.
First, solve for $r_{s u}$ using the information given in the table and the following equation, in which $X$ is biomass concentration, $S$ is growth-limiting substrate concentration, and $K_{s}$ is the substrate concentration at one-half the maximum specific substrate-utilization rate:

$$
\begin{aligned}
r_{s u} & =-\frac{k X S}{K_{S}+S} \\
& =-\frac{(5 / \mathrm{d})\left(2000 \mathrm{~g} / \mathrm{m}^{3}\right)\left(15 \mathrm{~g} \mathrm{bsCOD} / \mathrm{m}^{3}\right)}{(40+15) \mathrm{g} / \mathrm{m}^{3}} \\
& =-2727 \mathrm{~g} \mathrm{bsCOD} / \mathrm{m}^{3} \cdot \mathrm{~d}
\end{aligned}
$$

Then determine the net biomass production rate $r_{g}$ using the equation

$$
r_{g}=-Y r_{s u}-k_{d} X
$$

where $k_{d}$ is endogenous decay coefficient. This gives

$$
\begin{aligned}
r_{g}= & -(0.40 \mathrm{~g} \mathrm{VSS} / \mathrm{g} \mathrm{bsCOD})\left(-2727 \mathrm{~g} \mathrm{bsCOD} / \mathrm{m}^{3} \cdot \mathrm{~d}\right) \\
& -(0.10 \mathrm{~g} \mathrm{VSS} / \mathrm{g} \mathrm{VSS} \cdot \mathrm{~d})\left(2000 \mathrm{~g} \mathrm{VSS} / \mathrm{m}^{3}\right) \\
= & 891 \mathrm{~g} \mathrm{VSS} / \mathrm{m}^{3} \cdot \mathrm{~d}
\end{aligned}
$$

Now calculate the net biomass yield:

$$
\begin{aligned}
Y_{\text {bio }} & =-r_{g} / r_{s u}=\left(891 \mathrm{~g} \mathrm{VSS} / \mathrm{m}^{3} \cdot \mathrm{~d}\right) /\left(2727 \mathrm{~g} \mathrm{bsCOD} / \mathrm{m}^{3} \cdot \mathrm{~d}\right) \\
& =0.33 \mathrm{~g} \text { VSS } / \mathrm{g} \mathrm{bsCOD}
\end{aligned}
$$

2. Determine VSS production rate. Use the equation

$$
r_{X_{T}, \mathrm{VSS}}=-Y r_{s u}-k_{d} X+f_{d}\left(k_{d}\right) X+Q X_{o, i} / V
$$

where $f_{d}$ is the fraction of biomass that remains as cell debris, $Q$ is the influent flowrate, $X_{o, 1}$ is the influent nbVSS concentration, and $V$ is the reactor volume. Then,

$$
\begin{aligned}
r_{X_{T}, \mathrm{VSS}}= & 891 \mathrm{~g} \mathrm{VSS} / \mathrm{m}^{3} \cdot \mathrm{~d} \\
& +(0.10 \mathrm{~g} \mathrm{VSS} / \mathrm{g} \mathrm{VSS})(0.10 \mathrm{~g} \mathrm{VSS} / \mathrm{g} \mathrm{VSS} \cdot \mathrm{~d})\left(2000 \mathrm{~g} \mathrm{VSS} / \mathrm{m}^{3}\right) \\
& +\left(1000 \mathrm{~m}^{3} / \mathrm{d}\right)\left(50 \mathrm{~g} \mathrm{VSS} / \mathrm{m}^{3}\right) / 105 \mathrm{~m}^{3} \\
= & (891+20+476) \mathrm{g} \mathrm{VSS} / \mathrm{m}^{3} \cdot \mathrm{~d} \\
= & 1387 \mathrm{~g} \mathrm{VSS} / \mathrm{m}^{3} \cdot \mathrm{~d}
\end{aligned}
$$

3. Calculate the observed solids yield. Use the equation

$$
Y_{\mathrm{obs}}=-r_{X_{T}, \mathrm{VSS}} / r_{s u}
$$

Then

$$
\begin{aligned}
Y_{\text {obs }} & =-\left(1387 \mathrm{~g} \mathrm{VSS} / \mathrm{m}^{3} \cdot \mathrm{~d}\right) /\left(-2727 \mathrm{~g} \mathrm{bsCOD} / \mathrm{m}^{3} \cdot \mathrm{~d}\right) \\
& =0.51 \mathrm{~g} \text { VSS } / \mathrm{g} \text { bsCOD }
\end{aligned}
$$

4. Calculate the active biomass fraction in the MLVSS. Use the equation

$$
F_{X, \text { act }}=\left(-Y r_{s u}-k_{d} X\right) / r_{X_{T}, \mathrm{vss}}
$$

to get

$$
\begin{aligned}
F_{X, \text { act }} & =\left(891 \mathrm{~g} \mathrm{VSS} / \mathrm{m}^{3} \cdot \mathrm{~d}\right) /\left(1387 \mathrm{~g} \mathrm{VSS} / \mathrm{m}^{3} \cdot \mathrm{~d}\right) \\
& =0.64
\end{aligned}
$$

Thus, accounting for the nbVSS in the wastewater influent and cell debris produced, the MLVSS contains 64 percent active biomass.

### 16.18 PREDICTING METHANE PRODUCTION FROM AN ANAEROBIC REACTOR

An anaerobic reactor, operated at $35^{\circ} \mathrm{C}$, processes a wastewater stream with a flow of $3000 \mathrm{~m}^{3} / \mathrm{d}$ and a bsCOD concentration of $5000 \mathrm{~g} / \mathrm{m}^{3}$. At 95 percent bsCOD removal and a net biomass synthesis yield of $0.04 \mathrm{~g} \mathrm{VSS} / \mathrm{g}$ COD used, what is the amount of methane produced in $\mathrm{m}^{3} / \mathrm{d}$ ?

## Calculation Procedure

1. Prepare a steady-state mass balance for COD to determine the amount of the influent COD converted to methane. The required steady-state mass balance is

$$
\begin{aligned}
& \text { Influent portion of influent COD influent COD } \\
& 0=\mathrm{COD} \text { - influent COD - converted to - converted to } \\
& \text { in effluent cell tissue methane } \\
& \mathrm{COD}_{\text {in }}=\mathrm{COD}_{\text {eff }}+\mathrm{COD}_{\mathrm{VSS}}+\mathrm{COD}_{\text {methane }}
\end{aligned}
$$

Determine the values of the individual mass balance terms:

$$
\begin{aligned}
\mathrm{COD}_{\text {in }} & =\left(5000 \mathrm{~g} / \mathrm{m}^{3}\right)\left(3000 \mathrm{~m}^{3} / \mathrm{d}\right)=15,000,000 \mathrm{~g} / \mathrm{d} \\
\mathrm{COD}_{\text {eff }} & =(1-0.95)\left(5000 \mathrm{~g} / \mathrm{m}^{3}\right)\left(3000 \mathrm{~m}^{3} / \mathrm{d}\right)=750,000 \mathrm{~g} / \mathrm{d} \\
\mathrm{COD}_{\text {vSS }} & =(1.42 \mathrm{~g} \mathrm{COD} / \mathrm{g} \text { VSS })(0.04 \mathrm{~g} \mathrm{VSS} / \mathrm{g} \mathrm{COD})(0.95)(15,000,000 \mathrm{~g} / \mathrm{d}) \\
& =809,400 \mathrm{~g} / \mathrm{d}
\end{aligned}
$$

Solve for the COD converted to methane:

$$
\mathrm{COD}_{\text {methane }}=15,000,000-750,000-809,400=13,440,600 \mathrm{~g} / \mathrm{d}
$$

2. Determine the amount of methane produced at $35^{\circ} \mathrm{C}$. Determine the volume of gas occupied by 1 mole of gas at $35^{\circ} \mathrm{C}$ :

$$
\begin{aligned}
V & =\frac{n R T}{P} \\
& =\frac{(1 \mathrm{~mole})(0.082057 \mathrm{~atm} \cdot \mathrm{~L} / \mathrm{mole} \cdot \mathrm{~K})[(273.15+35) \mathrm{K}]}{1.0 \mathrm{~atm}} \\
& =25.29 \mathrm{~L}
\end{aligned}
$$

The $\mathrm{CH}_{4}$ equivalent of COD converted under anaerobic conditions is $(25.29 \mathrm{~L} / \mathrm{mole}) /(64 \mathrm{~g} \mathrm{COD} / \mathrm{mole}$ $\left.\mathrm{CH}_{4}\right)=0.40 \mathrm{LCH}_{4} / \mathrm{g}$ COD.

The amount of methane produced is then

$$
\begin{aligned}
\mathrm{CH}_{4} \text { production } & =(13,440,600 \mathrm{~g} \mathrm{COD} / \mathrm{d})\left(0.40 \mathrm{~L} \mathrm{CH}_{4} / \mathrm{g} \mathrm{COD}\right)\left(1 \mathrm{~m}^{3} / 10^{3} \mathrm{~L}\right) \\
& =5376 \mathrm{~m}^{3} / \mathrm{d}
\end{aligned}
$$

At 65 percent methane

$$
\begin{aligned}
\text { total gas flow } & =\left(5376 \mathrm{~m}^{3} / \mathrm{d}\right) / 0.65 \\
& =8271 \mathrm{~m}^{3} / \mathrm{d}
\end{aligned}
$$

It is important to determine the volume occupied by the gas at the actual operating temperature.

### 16.19 WASTEWATER CHARACTERIZATION EVALUATION

Given the following wastewater characterization results, determine concentrations for the following:

1. bCOD (biodegradable COD)
2. nbpCOD (nonbiodegradable particulate COD)
3. sbCOD (slowly biodegradable COD)
4. nbVSS (nonbiodegradable volatile suspended solids)
5. iTSS (inert total suspended solids)
6. nbpON (nonbiodegradable particulate organic nitrogen)
7. total degradable TKN (Kjeldahl nitrogen)

The influent wastewater characteristics are as follows:

| Constituent | Concentration, <br> $\mathrm{mg} / \mathrm{L}$ |
| :--- | :---: |
| BOD | 195 |
| sBOD | 94 |
| COD | 465 |
| sCOD (soluble COD) | 170 |
| rbCOD (readily biodegradable COD) | 80 |
| TSS | 220 |
| VSS | 200 |
| TKN | 40 |
| NH | 26 |
| Alkalinity | $260\left(\mathrm{as} \mathrm{CaCO}_{3}\right)$ |

The activated-sludge effluent data are as follows:

| Constituent | Concentration, <br> $\mathrm{mg} / \mathrm{L}$ |
| :--- | :---: |
| sCODe | 30 |
| sON | 1.2 |

## Calculation Procedure

1. Determine biodegradable (bCOD). Use the equation

$$
\mathrm{bCOD}=\sim 1.6(\mathrm{BOD})
$$

to get

$$
\mathrm{bCOD}=1.6(195 \mathrm{mg} / \mathrm{L})=312 \mathrm{mg} / \mathrm{L}
$$

2. Determine the nbpCOD. First determine the nbCOD using the equation

$$
\mathrm{nbCOD}=\mathrm{COD}-\mathrm{bCOD}
$$

So,

$$
\mathrm{nbCOD}=(465-312) \mathrm{mg} / \mathrm{L}=153 \mathrm{mg} / \mathrm{L}
$$

Then determine the nbpCOD using the equation

$$
\mathrm{nbpCOD}=\mathrm{nbCOD}-\mathrm{sCODe}
$$

to get

$$
\mathrm{nbpCOD}=(153-30) \mathrm{mg} / \mathrm{L}=123 \mathrm{mg} / \mathrm{L}
$$

3. Determine the sbCOD. Use the equation

$$
\mathrm{sbCOD}=\mathrm{bCOD}-\mathrm{rbCOD}
$$

to get

$$
\mathrm{sbCOD}=(312-80) \mathrm{mg} / \mathrm{L}=232 \mathrm{mg} / \mathrm{L}
$$

4. Determine the nbVSS. First determine the bpCOD/pCOD ratio using the equation

$$
\frac{\mathrm{bpCOD}}{\mathrm{pCOD}}=\frac{(\mathrm{bCOD} / \mathrm{BOD})(\mathrm{BOD}-\mathrm{sBOD})}{\mathrm{COD}-\mathrm{sCOD}}
$$

where bpCOD is biodegradable particulate COD. So,

$$
\frac{\mathrm{bpCOD}}{\mathrm{pCOD}}=\frac{1.6(195-94) \mathrm{mg} / \mathrm{L}}{(465-170) \mathrm{mg} / \mathrm{L}}=0.55
$$

Then determine the nbVSS using

$$
\mathrm{nbVSS}=\left[1-\left(\frac{\mathrm{bpCOD}}{\mathrm{pCOD}}\right)\right] \mathrm{VSS}
$$

which gives

$$
\mathrm{nbVSS}=(1-0.55)(200 \mathrm{mg} / \mathrm{L})=90 \mathrm{mg} / \mathrm{L}
$$

## 5. Determine the inert TSS

$$
\mathrm{iTSS}=\mathrm{TSS}-\mathrm{VSS}=(220-200) \mathrm{mg} / \mathrm{L}=20 \mathrm{mg} / \mathrm{L}
$$

6. Determine the nbpON. First determine the organic N content of VSS using the equation

$$
f_{N}=\frac{\left(\mathrm{TKN}-\mathrm{sON}-\mathrm{NH}_{4}-\mathrm{N}\right)}{\mathrm{VSS}}
$$

So,

$$
f_{N}=\frac{(40-1.2-26) \mathrm{mg} / \mathrm{L}}{(200 \mathrm{mg} / \mathrm{L})}=0.064
$$

Then determine the nbpON using

$$
\mathrm{nbpON}=f_{N}(\mathrm{nbVSS})
$$

which gives

$$
\mathrm{nbpON}=0.064(90 \mathrm{mg} / \mathrm{L})=5.8 \mathrm{mg} / \mathrm{L}
$$

## 7. Determine total degradable TKN

$$
\begin{aligned}
\mathrm{bTKN} & =\mathrm{TKN}-\mathrm{nbpON}-\mathrm{sON} \\
& =(40-5.8-1.2) \mathrm{mg} / \mathrm{L} \\
& =33 \mathrm{mg} / \mathrm{L}
\end{aligned}
$$

### 16.20 TRICKLING FILTER SIZING USING NRC EQUATIONS

A municipal wastewater having a BOD of $250 \mathrm{~g} / \mathrm{m}^{3}$ is to be treated by a two-stage trickling filter. The desired effluent quality is $25 \mathrm{~g} / \mathrm{m}^{3}$ of BOD. If both of the filter depths, $D_{e}$, are to be 1.83 m and the recirculation ratio, $R$, is $2: 1$, find the required filter diameters. Assume the following design assumptions apply.

$$
\begin{aligned}
& \text { flowrate }=7570 \mathrm{~m}^{3} / \mathrm{d} \\
& \text { wastewater temperature }=20^{\circ} \mathrm{C}
\end{aligned}
$$

BOD removal in primary sedimentation $=35$ percent

$$
E_{1}=E_{2}
$$

## Calculation Procedure

1. Compute $E_{1}$ and $E_{2}$

$$
\begin{aligned}
& \text { Overall efficiency }=\left\{\frac{\left[(200-25) \mathrm{g} / \mathrm{m}^{3}\right]}{\left(200 \mathrm{~g} / \mathrm{m}^{3}\right)}\right\}(100)=87.5 \% \\
& E_{1}+E_{2}\left(1-E_{1}\right)=0.875 \\
& E_{1}=E_{2}=0.646
\end{aligned}
$$

2. Compute the recirculation factor $\boldsymbol{F}$. Use the equation

$$
F=\frac{1+R}{(1+R / 10)^{2}}=\frac{1+2}{(1.2)^{2}}=2.08
$$

3. Compute the BOD loading for the first filter, $W_{1}$

Primary effluent $\mathrm{BOD}=(1.0-0.35)\left(250 \mathrm{~g} / \mathrm{m}^{3}\right)=163 \mathrm{~g} / \mathrm{m}^{3}$

$$
W_{1}=\left(163 \mathrm{~g} / \mathrm{m}^{3}\right)\left(7570 \mathrm{~m}^{3} / \mathrm{d}\right)\left(1 \mathrm{~kg} / 10^{3} \mathrm{~g}\right)=1234 \mathrm{~kg} \mathrm{BOD} / \mathrm{d}
$$

4. Compute the volume for the first stage, $V_{1}$. Use the equation

$$
E_{1}=\frac{100}{1+0.4432 \sqrt{\frac{W_{1}}{V_{1} F}}}
$$

So

$$
64.6=\frac{100}{1+0.4432 \sqrt{\frac{1234}{V_{1}(2.08)}}}
$$

and

$$
V_{1}=388 \mathrm{~m}^{3}
$$

5. Compute the diameter of the first filter, $D_{1}$, from the cross-section area, $A_{1}$

$$
\begin{aligned}
A_{1} & =\frac{V_{1}}{D_{e}}=\frac{388 \mathrm{~m}^{3}}{1.83 \mathrm{~m}}=212 \mathrm{~m}^{2}=\frac{\pi}{4} D_{1}^{2} \\
D_{1} & =16.4 \mathrm{~m}
\end{aligned}
$$

6. Compute the BOD loading for the second-stage filter, $W_{2}$

$$
W_{2}=\left(1-E_{1}\right) W_{1}=(1-0.646)(1234 \mathrm{~kg} \mathrm{BOD} / \mathrm{d})=437 \mathrm{~kg} \mathrm{BOD} / \mathrm{d}
$$

7. Compute $V_{2}$, the volume of the second-stage filter. Use the equation

$$
E_{2}=\frac{100}{1+\frac{0.4432}{1-E_{1}} \sqrt{\frac{W_{2}}{V_{2} F}}}
$$

So

$$
64.6=\frac{100}{1+\frac{0.4432}{1-0.646} \sqrt{\frac{437}{V_{2}(2.08)}}}
$$

and

$$
V_{2}=1096 \mathrm{~m}^{3}
$$

8. Compute the diameter of the second filter, $D_{2}$

$$
\begin{aligned}
& A_{2}=\frac{V_{2}}{D_{e}}=\frac{1096 \mathrm{~m}^{3}}{1.83 \mathrm{~m}}=599 \mathrm{~m}^{2} \\
& D_{2}=27.6 \mathrm{~m}
\end{aligned}
$$

9. Compute the BOD loading to each filter. For the first-stage filter:

$$
\mathrm{BOD} \text { loading }=\frac{(1234 \mathrm{~kg} / \mathrm{d})}{388 \mathrm{~m}^{3}}=3.18 \mathrm{~kg} / \mathrm{m}^{3} \cdot \mathrm{~d}
$$

For the second-stage filter:

$$
\mathrm{BOD} \text { loading }=\frac{(437 \mathrm{~kg} / \mathrm{d})}{1096 \mathrm{~m}^{3}}=0.40 \mathrm{~kg} / \mathrm{m}^{3} \cdot \mathrm{~d}
$$

10. Compute the hydraulic loading to each filter. For the first-stage filter:

$$
\begin{aligned}
\text { hydraulic loading } & =\frac{(1+2)\left(7570 \mathrm{~m}^{3} / \mathrm{d}\right)}{(1440 \mathrm{~min} / \mathrm{d})\left(212 \mathrm{~m}^{2}\right)} \\
& =0.0744 \mathrm{~m}^{3} / \mathrm{m}^{2} \cdot \mathrm{~min}
\end{aligned}
$$

For the second-stage filter:

$$
\begin{aligned}
\text { hydraulic loading } & =\frac{(1+2)\left(7570 \mathrm{~m}^{3} / \mathrm{d}\right)}{(1440 \mathrm{~m} / \mathrm{d})\left(599 \mathrm{~m}^{2}\right)} \\
& =0.0263 \mathrm{~m}^{3} / \mathrm{m}^{2} \cdot \mathrm{~min}
\end{aligned}
$$

Related Calculations. To accommodate standard rotary distributor mechanisms, the diameters of the two filters should be rounded to the nearest $1.5 \mathrm{~m}(5 \mathrm{ft})$. To reduce construction costs, the two trickling filters are often made the same size. Where two filters of equal diameter are used, the removal efficiencies will be unequal. In many cases, the hydraulic loading rate will be limited by state standards.

### 16.21 DETERMINATION OF FILTER-MEDIUM SIZES

A dual-medium filter bed composed of sand and anthracite is to be used for the filtration of settled secondary effluent. If the effective size of the sand in the dual-medium filter is to be 0.55 mm , determine the effective size of the anthracite to avoid significant intermixing.

## Calculation Procedure

1. Summarize the properties of the filter media. For sand,

$$
\begin{aligned}
& \text { effective size }=0.55 \mathrm{~mm} \\
& \text { specific gravity }=2.65(\text { see table })
\end{aligned}
$$

For anthracite,

> effective size $=$ to be determined, mm specific gravity $=1.7($ see Table $)$

| Filter material | Specific gravity | Porosity, $\alpha$ | Sphericity $^{a}$ |
| :--- | :---: | :---: | :---: |
| Anthracite | $1.4-1.75$ | $0.56-0.60$ | $0.40-0.60$ |
| Sand | $2.55-2.65$ | $0.40-0.46$ | $0.75-0.85$ |
| Garnet | $3.8-4.3$ | $0.42-0.55$ | $0.60-0.80$ |
| Ilmenite | 4.5 | $0.40-0.55$ |  |
| Fuzzy filter medium |  | $0.87-0.89$ |  |

Source: Adapted in part from Cleasby and Logsdon (1999).
${ }^{a}$ Sphericity is defined as the ratio of the surface area of an equal volume sphere to the surface area of the filter medium particle.
2. Compute the effective size of the anthracite. Use the equation

$$
d_{1}=d_{2}\left(\frac{\rho_{2}-\rho_{w}}{\rho_{1}-\rho_{w}}\right)^{0.667}
$$

where $\rho$ is density. The result is identical if the densities are replaced by the numerical values for the specific gravities. Thus,

$$
\begin{aligned}
d_{1} & =0.55 \mathrm{~mm}\left(\frac{2.65-1}{1.7-1}\right)^{0.667} \\
& =0.97 \mathrm{~mm}
\end{aligned}
$$

Related Calculations. Another approach that can be used to assess whether intermixing will occur is to compare the fluidized bulk densities of the two adjacent layers (e.g., upper 450 mm of sand and lower 100 mm of anthracite).

### 16.22 DETERMINATION OF MEMBRANE AREA REQUIRED FOR DEMINERALIZATION

A brackish water having a TDS concentration of $3000 \mathrm{~g} / \mathrm{m}^{3}$ is to be desalinized using a thin-film composite membrane having a flux rate coefficient, $k_{w}$, of $1.5 \times 10^{-6} \mathrm{~s} / \mathrm{m}$ and a mass transfer rate coefficient, $k_{i}$, of $1.8 \times 10^{-6} \mathrm{~m} / \mathrm{s}$. The product water is to have a TDS of no more than $200 \mathrm{~g} / \mathrm{m}^{3}$. The flowrate, $Q_{p}$, is to be $0.010 \mathrm{~m}^{3} / \mathrm{s}$. The net operating pressure ( $\Delta P_{a}-\Delta \Pi$ ) will be 2500 kPa . Assume the recovery rate, $r$, will be 90 percent. Estimate the rejection rate and the concentration of the concentrate stream.

## Calculation Procedure

1. Set out the basis for solving the problem. The problem involves determination of the membrane area required to produce $0.010 \mathrm{~m}^{3} / \mathrm{s}$ of water and the TDS concentration of the permeate. If the permeate TDS concentration is well below $200 \mathrm{~g} / \mathrm{m}^{3}$, blending of feed and permeate will reduce the required membrane area.
2. Estimate membrane area $\boldsymbol{A}$. Use the equation

$$
F_{w}=k_{w}\left(\Delta P_{a}-\Delta \Pi\right)
$$

where $F_{w}$ is the flux of water to get

$$
F_{w}=\left(1.5 \times 10^{-6} \mathrm{~s} / \mathrm{m}\right)\left(2500 \mathrm{~kg} / \mathrm{m}^{2}\right)=3.75 \times 10^{-3} \mathrm{~kg} / \mathrm{m}^{2} \cdot \mathrm{~s}
$$

Since $Q_{p}=F_{w} \times A$, then

$$
A=\frac{\left(0.010 \mathrm{~m}^{3} / \mathrm{s}\right)\left(10^{3} \mathrm{~kg} / \mathrm{m}^{3}\right)}{\left(3.75 \times 10^{-3} \mathrm{~kg} / \mathrm{m}^{2} \cdot \mathrm{~s}\right)}=2667 \mathrm{~m}^{2}
$$

3. Estimate permeate TDS concentration, $\boldsymbol{C}_{p}$. Use the equation

$$
F_{i}=k_{i} \Delta C_{i}=\frac{Q_{p} C_{p}}{A}
$$

where $\Delta C_{i}$ is the solution concentration gradient

$$
Q_{p} C_{p}=k_{i}\left(\left[\frac{C_{f}+C_{c}}{2}\right]-C_{p}\right) A
$$

Assume $C_{c} \approx C_{f}$ where $C_{\mathrm{f}}$ is solute concentration in feed, and solve for $C_{p}$ :

$$
C_{p}=\frac{k_{i} A C_{f}}{Q_{p}+k_{i} A}
$$

Assume $Q_{p}=r Q_{f}$. Then

$$
C_{p}=\frac{\left(1.8 \times 10^{-6} \mathrm{~m} / \mathrm{s}\right)\left(2667 \mathrm{~m}^{2}\right)\left(3.0 \mathrm{~kg} / \mathrm{m}^{3}\right)}{(0.01)(0.9)+\left(1.8 \times 10^{-6} \mathrm{~m} / \mathrm{s}\right)\left(2667 \mathrm{~m}^{3}\right)}=0.152 \mathrm{~kg} / \mathrm{m}^{3}
$$

The permeate solute concentration is lower than necessary. It may be possible to reduce the area by blending.
4. Estimate the rejection rate $\boldsymbol{R}$. Use the equation

$$
R, \%=\frac{C_{f}-C_{p}}{C_{f}} \times 100
$$

Then

$$
R=\frac{\left(3.0 \mathrm{~kg} / \mathrm{m}^{3}-0.152 \mathrm{~kg} / \mathrm{m}^{3}\right)}{\left(3.0 \mathrm{~kg} / \mathrm{m}^{3}\right)} \times 100=95 \%
$$

5. Estimate the concentrate stream TDS. Use the equation

$$
C_{c}=\frac{Q_{f} C_{f}-Q_{p} C_{p}}{Q_{c}}
$$

Then

$$
C_{c}=\frac{(0.1 \mathrm{~L})\left(3.0 \mathrm{~kg} / \mathrm{m}^{3}\right)-(0.9 \mathrm{~L})\left(0.152 \mathrm{~kg} / \mathrm{m}^{3}\right)}{0.1 \mathrm{~L}}=31.4 \mathrm{~kg} / \mathrm{m}^{3}
$$

### 16.23 AREA AND POWER REQUIREMENTS FOR ELECTRODIALYSIS

Determine the area and power required to demineralize $4000 \mathrm{~m}^{3} / \mathrm{d}$ of treated wastewater to be used for industrial cooling water using an electrodialysis unit composed of 240 cells. Assume the following data apply:

$$
\begin{aligned}
& \text { TDS concentration }=2500 \mathrm{mg} / \mathrm{L} \\
& \text { cation and anion concentration }=0.010 \mathrm{~g}-\mathrm{eq} / \mathrm{L} \\
& \text { efficiency of salt removal } \eta=50 \text { percent } \\
& \text { current efficiency } E_{c}=90 \text { percent } \\
& C D / N \text { ratio }=500 \mathrm{~mA} / \mathrm{cm}^{2}
\end{aligned}
$$

where $C D$ is current density and $N$ is the normality of the solution,

$$
\text { resistance } R=5.0 \Omega
$$

## Calculation Procedure

1. Calculate the current. Use the equation

$$
I=\frac{F Q N \eta}{\eta E_{c}}
$$

where $F$ is Faraday's constant and $Q$ is flowrate. Then

$$
\begin{aligned}
Q & =\left(4000 \mathrm{~m}^{3} / \mathrm{d}\right)\left(10^{3} \mathrm{~L} / \mathrm{m}^{3}\right) /(86,400 \mathrm{~s} / \mathrm{d})=46.3 \mathrm{~L} / \mathrm{s} \\
I & =\frac{(96,485 \mathrm{~A} \cdot \mathrm{~s} / \mathrm{g}-\mathrm{eq})(46.3 \mathrm{~L} / \mathrm{s})(0.010 \mathrm{~g}-\mathrm{eq} / \mathrm{L})(0.50)}{240 \times 0.90} \\
& =103.4 \mathrm{~A}
\end{aligned}
$$

2. Determine the power required. Use the equation

$$
P=R(I)^{2}
$$

to get

$$
P=(5.0 \Omega)(103.4 \mathrm{~A})^{2}=53,477 \mathrm{~W}=53.5 \mathrm{~kW}
$$

3. Determine the required surface area. First determine the current density:

$$
C D=(500)(\text { normality })=500 \mathrm{~mA} / \mathrm{cm}^{2} \times 0.010=50 \mathrm{~mA} / \mathrm{cm}^{2}
$$

The required area is

$$
\text { area }=\frac{(103.4 \mathrm{~A})\left(10^{3} \mathrm{~mA} / \mathrm{A}\right)}{\left(50 \mathrm{~mA} / \mathrm{cm}^{2}\right)}=2068 \mathrm{~cm}^{2}
$$

Then determine area of membrane assuming a square configuration will be used:

$$
\text { area per membrane }=\sqrt{2068 \mathrm{~cm}^{2}} \approx 45 \mathrm{~cm}^{2}
$$

Comment. The actual performance will have to be determined from pilot tests.

### 16.24 ANALYSIS OF ACTIVATED-CARBON ADSORPTION DATA

Determine the Freundlich and Langmuir isotherm coefficients for the following adsorption test data on granular activated carbon (GAC). The liquid volume used in the batch adsorption tests was 1 L . The initial concentration of the adsorbate in solution was $3.37 \mathrm{mg} / \mathrm{L}$. Equilibrium was obtained after 7 days.

| Mass of GAC, | Equilibrium concentration <br> of adsorbate in solution, <br> $C_{e}, \mathrm{gg} / \mathrm{L}$ |
| :---: | :---: |
| 0.0 | 3.37 |
| 0.001 | 3.27 |
| 0.010 | 2.77 |
| 0.100 | 1.86 |
| 0.500 | 1.33 |

The Freundlich isotherm is defined as follows:

$$
\frac{x}{m}=K_{f} C_{e}^{1 / n}
$$

where $x / m=$ mass of adsorbate adsorbed per unit mass of adsorbent, mg adsorbate/g activated carbon
$K_{f}=$ Freundlich capacity factor, (mg absorbate/g activated carbon)(L water/mg adsorbate) ${ }^{1 / n}$
$C_{e}=$ equilibrium concentration of adsorbate in solution after adsorption, $\mathrm{mg} / \mathrm{L}$
$1 / n=$ Freundlich intensity parameter
The constants in the Freundlich isotherm can be determined by plotting $\log (x / m)$ versus $\log C_{e}$ and making use of the equation

$$
\log \left(\frac{x}{m}\right)=\log K_{f}+\frac{1}{n} \log C_{e}
$$

The Langmuir adsorption isotherm is defined as

$$
\frac{x}{m}=\frac{a b C_{e}}{1+b C_{e}}
$$

where $x / m=$ mass of adsorbate adsorbed per unit mass of adsorbent, mg adsorbate/g activated carbon
$a, b=$ empirical constants
$C_{e}=$ equilibrium concentration of adsorbate in solution after adsorption, $\mathrm{mg} / \mathrm{L}$
The constants in the Langmuir isotherm can be determined by plotting $C_{e} /(x / m)$ versus $C_{e}$ and making use of the equation

$$
\frac{C_{e}}{(x / m)}=\frac{1}{a b}+\frac{1}{a} C_{e}
$$

## Calculation Procedure

## 1. Derive the values needed to plot the Freundlich and Langmuir adsorption isotherms using the batch adsorption test data

| Adsorbate concentration, <br> $\mathrm{mg} / \mathrm{L}$ |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | $C_{e}$ | $C_{o}-C_{e}$ | $m, \mathrm{~g}$ | $x / m,{ }^{a} \mathrm{mg} / \mathrm{g}$ | $C_{e} /(x / m)$ |
| $C_{o}$ | 3.37 | 0.00 | 0.000 | - | - |
| 3.37 | 3.27 | 0.10 | 0.001 | 100 | 0.0327 |
| 3.37 | 2.77 | 0.60 | 0.010 | 60 | 0.0462 |
| 3.37 | 1.51 | 0.100 | 15.1 | 0.1232 |  |
| 3.37 | 1.86 | 1.51 | 4.08 | 0.3260 |  |
| 3.37 | 1.33 | 2.04 | 0.500 |  |  |

$$
{ }^{a} q_{e}=\frac{x}{m}=\frac{\left(C_{o}-C_{e}\right) V}{m}
$$

2. Plot the Freundlich and Langmuir adsorption isotherms. Use the data developed in step 1 (see following figures).

3. Determine the adsorption isotherm coefficients. For the Freundlich coefficients, when $x / m$ versus $C_{e}$ is plotted on $\log -\log$ paper, the intercept when $C_{e}=1.0$ is the value of $(x / m)$ and the slope of the line is equal to $1 / n$. Thus, $x / m=1.55$, and $K_{f}=1.55$. When $x / m=1.0, C_{e}=0.9$ and $1 / n=0.26$. Thus,

$$
\frac{x}{m}=1.5 C_{e}^{0.26}
$$

Because the plot for the Langmuir isotherm is curvilinear, use of the Langmuir adsorption isotherm is inappropriate.

### 16.25 ESTIMATE THE REQUIRED OZONE DOSE FOR A TYPICAL SECONDARY EFFLUENT

Estimate the ozone dose needed to disinfect a filtered secondary effluent to an MPN (most probable number) value of $240 / 100 \mathrm{~mL}$ using the following disinfection data obtained from pilot-scale
installation. Assume the starting coliform concentration will be $1 \times 10^{6} / 100 \mathrm{~mL}$ and that the ozone transfer efficiency is 80 percent.

| Test <br> number | Initial coliform <br> count $N_{o}$, <br> MPN $/ 100 \mathrm{~mL}$ | Ozone <br> transferred, <br> $\mathrm{mg} / \mathrm{L}$ | Final coliform <br> count $N$, <br> MPN $/ 100 \mathrm{~mL}$ | $-\log \left(N / N_{o}\right)$ |
| :---: | :---: | :---: | :---: | :---: |
| 1 | 95,000 | 3.1 | 1500 | 1.80 |
| 2 | 470,000 | 4.0 | 1200 | 2.59 |
| 3 | $3,500,000$ | 4.5 | 730 | 3.68 |
| 4 | 820,000 | 5.0 | 77 | 4.03 |
| 5 | $9,200,000$ | 6.5 | 92 | 5.00 |

The relevant equations are

$$
\begin{align*}
& N / N_{o}=1 \quad \text { for } U<q  \tag{16.1}\\
& N / N_{o}=[(U) / q]^{-n} \quad \text { for } U>q \tag{16.2}
\end{align*}
$$

where $N=$ number of organisms remaining after disinfection
$N_{o}=$ number of organisms present before disinfection
$U=$ utilized (or transferred) ozone dose, $\mathrm{mg} / \mathrm{L}$
$n=$ slope of dose response curve
$q=$ value of $x$ intercept when $N / N_{o}=1$ or $\log N / N_{o}=0$ (assumed to be equal to the initial ozone demand)

The required ozone dosage must be increased to account for the transfer of the applied ozone to the liquid. The required dosage can be computed with the following expression:

$$
\begin{equation*}
D=U\left(\frac{100}{T E}\right) \tag{16.3}
\end{equation*}
$$

where $D=$ total required ozone dosage, $\mathrm{mg} / \mathrm{L}$
$U=$ utilized (or transferred) ozone dose, $\mathrm{mg} / \mathrm{L}$
$T E=$ ozone transfer efficiency, \%
Typical ozone transfer efficiencies vary from about 80 to 90 percent.

## Calculation Procedure

1. Determine the coefficients in Eq. (16.1) using the pilot-plant data. Linearize Eq. (16.1) and plot the $\log$ inactivation data versus the ozone dose on $\log -\log$ paper to determine the constants in

$$
\begin{aligned}
& N / N_{o}=[(U) / q]^{-n} \\
& \log \left(N / N_{o}\right)=-n \log (U / q)
\end{aligned}
$$

The required $\log -\log$ plot is as follows:


The required coefficients are

$$
\begin{aligned}
q & =0.23 \mathrm{mg} / \mathrm{L} \\
n & =2.78
\end{aligned}
$$

2. Determine the ozone dose required to achieve an effluent coliform concentration of 240 MPN/100 mL. Rearrange Eq. (16.2) to solve for $U$ :

$$
U=q\left(N / N_{o}\right)^{-1 / n}
$$

Then

$$
U=(0.23 \mathrm{mg} / \mathrm{L})\left(240 / 10^{6}\right)^{-1 / 2.78}=4.61 \mathrm{mg} / \mathrm{L}
$$

3. Determine the dose that must be applied. Use Eq. (16.3), and assume a transfer efficiency of 80 percent. Then

$$
D=U\left(\frac{100}{T E}\right)=(4.61 \mathrm{mg} / \mathrm{L})\left(\frac{100}{80}\right)=5.76 \mathrm{mg} / \mathrm{L}
$$

## DESIGN OF A UV DISINFECTION SYSTEM

Design a UV disinfection system that will deliver a minimum design dose of $100 \mathrm{~mJ} / \mathrm{cm}^{2}$. Assume for the purpose of this example that the following data apply:

Wastewater characteristics:

- Minimum design flow $=6000 \mathrm{~m}^{3} / \mathrm{d}=4167 \mathrm{~L} / \mathrm{min}$ (diurnal low flow).
- Maximum design flow $=21,000 \mathrm{~m}^{3} / \mathrm{d}=14,584 \mathrm{~L} / \mathrm{min}$ (peak hour flow with recycle streams).
- Minimum transmittance $=55$ percent.

System characteristics:

- Lamp configuration is horizontal.
- Validated system performance $=100 \mathrm{~mJ} / \mathrm{cm}^{2}$ within range of $20-43 \mathrm{~L} / \mathrm{min} \cdot$ lamp.
- System headloss coefficient $=1.8$ (manufacturer-specific).
- Lamp/sleeve diameter $=23 \mathrm{~mm}$.
- Cross-sectional area of quartz sleeve $=4.15 \times 10^{-4} \mathrm{~m}^{2}$.
- Lamp spacing $=75 \mathrm{~mm}$ (center to center).
- One standby UV bank will be required per channel.


## Calculation Procedure

1. Determine the number of UV channels. The manufacturer has provided validated information for a three-bank system at a flow range of 20 to $80 \mathrm{~L} / \mathrm{min}$. lamp. The system is capable of applying a dose of $100 \mathrm{~mJ} / \mathrm{cm}^{2}$ within the range of 20 to $43 \mathrm{~L} / \mathrm{min}$ • lamp.

Therefore, the system has an approximate $2: 1$ flow variation capacity for the design dose under consideration.

Use two channels. From 4167 to $8000 \mathrm{~L} / \mathrm{min}$ use one channel. From 8000 to $14,584 \mathrm{~L} / \mathrm{min}$ split the flow between two channels such that each channel is loaded between 4000 and $7300 \mathrm{~L} / \mathrm{min}$.
2. Determine the number of lamps required per channel. At $8000 \mathrm{~L} / \mathrm{min}$, the total number of required lamps is

$$
\text { lamps required at } 8000 \mathrm{~L} / \mathrm{min}=\frac{(8000 \mathrm{~L} / \mathrm{min})}{(43 \mathrm{~L} / \mathrm{lamp} \cdot \mathrm{~min})}=186 \mathrm{lamps}
$$

## 3. Determine the minimum number of lamps per bank

$$
\frac{186 \text { lamps }}{3 \text { banks }}=62 \frac{\text { lamps }}{\text { bank }}
$$

4. Configure the UV disinfection system. Typically, 2, 4, 8, or 16 lamps per module are available. For an 8-lamp module, eight modules are required per bank for a total of 64 lamps per bank.
5. Check that the design falls within the manufacturer recommended range. At low flow,

$$
\frac{(4167 \mathrm{~L} / \mathrm{min})}{192 \mathrm{lamps}}=21.7 \mathrm{~L} / \mathrm{lamp} \cdot \min
$$

At high flow,

$$
\frac{(14,584 \mathrm{~L} / \mathrm{min})}{384 \mathrm{lamps}}=38.0 \mathrm{~L} / \mathrm{lamp} \cdot \mathrm{~min}
$$

Both of these hydraulic loading rates fall within the acceptable range for the UV disinfection system provided by the manufacturer.
6. Check whether the headloss for the selected configuration is acceptable. First determine the channel cross-sectional area:

$$
\begin{aligned}
\text { cross-sectional area of channel } & =(8 \times 0.075 \mathrm{~m}) \times(8 \times 0.075 \mathrm{~m}) \\
& =0.36 \mathrm{~m}^{2}
\end{aligned}
$$

Then determine the net channel cross-sectional area by subtracting the cross-sectional area of the quartz sleeves ( $4.15 \times 10^{-4} \mathrm{~m}^{2} / \mathrm{lamp}$ ):

$$
\begin{aligned}
A_{\text {channel }} & =0.36 \mathrm{~m}^{2}-[(8 \times 8) \text { lamps } / \mathrm{bank}] \times\left(4.15 \times 10^{-4} \mathrm{~m}^{2} / \mathrm{lamp}\right) \\
& =0.33 \mathrm{~m}^{2}
\end{aligned}
$$

Now determine the maximum velocity in each channel:

$$
v_{\text {channel }}=\frac{(14,584 \mathrm{~L} / \mathrm{min})}{(2 \text { channel })\left(0.33 \mathrm{~m}^{2}\right)\left(10^{3} \mathrm{~L} / \mathrm{m}^{3}\right)(60 \mathrm{~s} / \mathrm{min})}=0.37 \mathrm{~m} / \mathrm{s}
$$

The headloss per UV channel is then

$$
\begin{aligned}
h_{\text {channel }} & =1.8 \frac{v^{2}}{2 g} \\
& =1.8 \frac{(0.37 \mathrm{~m} / \mathrm{s})^{2}\left(10^{3} \mathrm{~mm} / \mathrm{m}\right)}{2\left(9.81 \mathrm{~m} / \mathrm{s}^{2}\right)}(4 \text { banks })=50 \mathrm{~mm}
\end{aligned}
$$

Note that four banks were used to determine system headloss. Use of four banks includes a redundant bank of lamps in each channel. Because the clear spacing between quartz sleeves is 52 mm $(75 \mathrm{~mm}-23 \mathrm{~mm}$ ), the headloss cannot exceed 26 mm total (one-half the clear spacing between the quartz sleeves) without exposing the uppermost row of lamps to the air. To allow for the calculated 50 mm of total headloss, each UV channel will require a stepped channel bottom. A $24-\mathrm{mm}$ step between the second and third bank of lamps is required to allow for the expected headloss and to allow the third and fourth banks of lamps to be set lower.
7. Summarize the system configuration. The minimum required system utilizes two channels, each channel containing four banks of lamps in series, three operational banks and one redundant bank. Each bank contains eight modules, each of which contains eight lamps.

### 16.27 ESTIMATION OF BLOWDOWN WATER COMPOSITION

Reclaimed water with the chemical characteristics given in the table is being considered for use as makeup water for a cooling tower. Calculate the composition of the blowdown flow if five cycles of concentration are to be used. Assume that the temperature of the hot water entering the cooling tower is $50^{\circ} \mathrm{C}\left(120^{\circ} \mathrm{F}\right)$ and the solubility of $\mathrm{CaSO}_{4}$ is about $2200 \mathrm{mg} / \mathrm{L}$ as $\mathrm{CaCO}_{3}$ at this temperature.

| Constituent | Concentration, $\mathrm{mg} / \mathrm{L}$ |
| :--- | :---: |
| Total hardness $\left(\right.$ as $\left.\mathrm{CaCO}_{3}\right)$ | 118 |
| $\mathrm{Ca}^{2+}\left(\right.$ as $\left.\mathrm{CaCO}_{3}\right)$ | 85 |
| $\mathrm{Mg}^{2+}\left(\right.$ as $\left.\mathrm{CaCO}_{3}\right)$ | 33 |
| Total alkalinity $\left(\mathrm{as} \mathrm{CaCO}_{3}\right)$ | 90 |
| $\mathrm{SO}_{4}^{2-}$ | 20 |
| $\mathrm{Cl}^{-}$ | 19 |
| $\mathrm{SiO}_{2}$ | 2 |
| Note: Molecular weights- $\mathrm{CaCO}_{3}=100, \mathrm{CaSO}_{4}=136$ |  |
| $\mathrm{H}_{2} \mathrm{SO}_{4}=98$, and $\mathrm{SO}_{4}=96$. |  |

## Calculation Procedure

1. Determine the total hardness in the circulating water. When the total alkalinity is less than the total hardness, Ca and Mg are also present in forms other than carbonate hardness.

Setting the cycles of concentration equal to 5 , we obtain the total hardness in circulating water of

$$
C_{b}=(\text { cycles of concentration })\left(C_{m}\right)
$$

where $C_{b}$ and $C_{m}$ are salt concentration in blowdown and makeup water, respectively. Thus,

$$
C_{b}=5 \times 118=590 \mathrm{mg} / \mathrm{L} \mathrm{CaCO}_{3}
$$

2. Determine the total amount of $\mathrm{H}_{2} \mathrm{SO}_{4}$ that must be added to convert the $\mathrm{CaCO}_{3}$ to $\mathrm{CaSO}_{4}$. To convert from $\mathrm{CaCO}_{3}$ to $\mathrm{CaSO}_{4}$, sulfuric acid is injected into the circulating water and the following reaction occurs:

$$
\underset{100}{\mathrm{CaCO}_{3}}+\underset{98}{\mathrm{H}_{2} \mathrm{SO}_{4}} \rightarrow \underset{136}{\mathrm{CaSO}_{4}}+\mathrm{H}_{2} \mathrm{O}+\mathrm{CO}_{2}
$$

where 100,98 , and 136 are the molecular weights.
The alkalinity in the circulating water, if not converted into sulfates, is $5 \times 90=450 \mathrm{mg} / \mathrm{L}$ as $\mathrm{CaCO}_{3}$. If 10 percent of the alkalinity is left unconverted to avoid corrosion, the amount of alkalinity remaining is $0.1 \times 450=45 \mathrm{mg} / \mathrm{L}$ as $\mathrm{CaCO}_{3}$. The amount of alkalinity that must be converted is $450-(0.1 \times 450)=405 \mathrm{mg} / \mathrm{L}$ as $\mathrm{CaCO}_{3}$.

The amount of sulfate that must be added for the conversion is

$$
\mathrm{SO}_{4}^{2-}=(405 \mathrm{mg} / \mathrm{L})\left(\frac{96}{100}\right)=389 \mathrm{mg} / \mathrm{L}
$$

Converting to $\mathrm{mg} / \mathrm{LCaSO}_{4}$ yields

$$
\mathrm{CaSO}_{4}=(389 \mathrm{mg} / \mathrm{L})\left(\frac{136}{96}\right)=551 \mathrm{mg} / \mathrm{L}
$$

## 3. Determine the required sulfuric acid concentration in the circulating water

$$
\mathrm{H}_{2} \mathrm{SO}_{4}=\left(389 \mathrm{mg} / \mathrm{L} \mathrm{SO}_{4}\right)\left(\frac{98}{96}\right)=397 \mathrm{mg} / \mathrm{L}
$$

4. Determine the sulfate concentration in the circulating water contributed by the makeup water. Sulfate from makeup water is $5 \times 20=100 \mathrm{mg} / \mathrm{L}$ as $\mathrm{SO}_{4}$. If combined with $\mathrm{Ca}^{2+}$, the concentration is

$$
\mathrm{CaSO}_{4}=(100 \mathrm{mg} / \mathrm{L})\left(\frac{136}{96}\right)=142 \mathrm{mg} / \mathrm{L}
$$

5. Determine amount of additional CaSO $_{4}$ formation that is permissible. The solubility of $\mathrm{CaSO}_{4}$ at $50^{\circ} \mathrm{C}\left(120^{\circ} \mathrm{F}\right)$ is about $2200 \mathrm{mg} / \mathrm{L}$. In the circulating water, $142 \mathrm{mg} / \mathrm{LCaSO}_{4}$ was originally present after five cycles of concentration and $551 \mathrm{mg} / \mathrm{L}$ was formed by the addition of sulfuric acid. Therefore, an additional $1507 \mathrm{mg} / \mathrm{L}$ of $\mathrm{CaSO}_{4}$ formation is theoretically permissible before the solubility limit is exceeded. The cycles of concentration could have been carried out much higher before $\mathrm{CaSO}_{4}$ would precipitate in the system.
6. Determine the concentrations of Cl and $\mathrm{SiO}_{2}$ in the circulating water. For chloride,

$$
\mathrm{Cl}^{-}=5 \times 19=95 \mathrm{mg} / \mathrm{L}
$$

For silica,

$$
\mathrm{SiO}_{2}=5 \times 2=10 \mathrm{mg} / \mathrm{L}
$$

7. Summarize the composition of the blowdown flow after five cycles of concentration

|  | Concentration, <br> $\mathrm{mg} / \mathrm{L}$ |  |
| :--- | :---: | :---: |
| Parameter | Initial | Final |
| Total hardness $\left(\mathrm{as} \mathrm{CaCO}_{3}\right)$ | 118 | 590 |
| Total alkalinity $\left(\mathrm{as} \mathrm{CaCO}_{3}\right)$ | 90 | 45 |
| $\mathrm{SO}_{4}^{2-}$ | 20 | 489 |
| $\mathrm{Cl}^{-}$ | 19 | 95 |
| $\mathrm{SiO}_{2}$ | 2 | 10 |

### 16.28 DESIGN A GRAVITY THICKENER FOR COMBINED PRIMARY AND WASTE-ACTIVATED SLUDGE

Design a gravity thickener for a wastewater treatment plan having primary and waste-activated sludge with the following characteristics:

| Type of sludge | Specific gravity | Solids, $\%$ | Flowrate, $\mathrm{m}^{3} / \mathrm{d}$ |
| :---: | :---: | :---: | :---: |
| Average design conditions: |  |  |  |
| Primary sludge | 1.03 | 3.3 | 400 |
| Waste activated | 1.005 | 0.2 | 2250 |
| Peak design conditions: |  |  |  |
| Primary sludge | 1.03 | 3.4 | 420 |
| Waste activated | 1.005 | 0.23 | 2500 |

## Procedure

1. Compute the dry solids at peak design conditions. For the primary sludge,

$$
\begin{aligned}
\mathrm{kg} / \mathrm{dry} \text { solids } & =\left(420 \mathrm{~m}^{3} / \mathrm{d}\right)(1.03)(0.034 \mathrm{~g} / \mathrm{g})\left(10^{3} \mathrm{~kg} / \mathrm{m}^{3}\right) \\
& =14,708 \mathrm{~kg} / \mathrm{d}
\end{aligned}
$$

For the waste-activated sludge,

$$
\begin{aligned}
\mathrm{kg} / \mathrm{dry} \text { solids } & =\left(2500 \mathrm{~m}^{3} / \mathrm{d}\right)(1.005)(0.0023 \mathrm{~g} / \mathrm{g})\left(10^{3} \mathrm{~kg} / \mathrm{m}^{3}\right) \\
& =5779 \mathrm{~kg} / \mathrm{d}
\end{aligned}
$$

TABLE 16.4 Typical Concentrations of Unthickened and Thickened Sludges and Solids Loadings for Gravity Thickeners

|  | Solids concentration, $\%$ |  |  | Solids loading |  |
| :--- | :---: | :---: | :---: | :---: | :---: |
| Type of sludge or biosolids | Unthickened | Thickened |  | $\mathrm{lb} / \mathrm{ft}^{2} \cdot \mathrm{~d}$ | $\mathrm{~kg} / \mathrm{m}^{2} \cdot \mathrm{~d}$ |
| Separate: |  |  |  |  |  |
| Primary sludge | $2-6$ | $5-10$ |  | $20-30$ | $100-150$ |
| Trickling-filter humus sludge | $1-4$ | $3-6$ |  | $8-10$ | $40-50$ |
| Rotating biological contactor | $1-3.5$ | $2-5$ |  | $7-10$ | $35-50$ |
| Air-activated sludge | $0.5-1.5$ | $2-3$ |  | $4-8$ | $20-40$ |
| High-purity oxygen-activated sludge | $0.5-1.5$ | $2-3$ |  | $4-8$ | $20-40$ |
| Extended aeration-activated sludge | $0.2-1.0$ | $2-3$ |  | $5-8$ | $25-40$ |
| Anaerobically digested primary sludge | 8 | 12 |  | 25 | 120 |
| $\quad$ from primary digester |  |  |  |  |  |
| Combined: |  |  |  |  |  |
| Primary and trickling-filter humus sludge | $2-6$ | $5-9$ |  | $12-20$ | $60-100$ |
| Primary and rotating biological contactor | $2-6$ | $5-8$ |  | $10-18$ | $50-90$ |
| Primary and waste-activated sludge | $0.5-1.5$ | $4-6$ |  | $5-14$ | $25-70$ |
|  | $2.5-4.0$ | $4-7$ |  | $8-16$ | $40-80$ |
| Waste-activated sludge and trickling-filter | $0.5-2.5$ | $2-4$ |  | $4-8$ | $20-40$ |
| $\quad$ humus sludge |  |  |  |  |  |
| Chemical (tertiary) sludge: |  |  |  |  |  |
| High lime | $3-4.5$ | $12-15$ |  | $24-61$ | $120-300$ |
| Low lime | $3-4.5$ | $10-12$ |  | $10-30$ | $50-150$ |
| Iron | $0.5-1.5$ | $3-4$ |  | $2-10$ | $10-50$ |

Source: Adapted from WEF (1996).

Therefore,

$$
\begin{aligned}
& \text { combined sludge mass }=14,708+5779=20,487 \mathrm{~kg} / \mathrm{d} \\
& \text { combined sludge flowrate }=2500+420=2920 \mathrm{~m}^{3} / \mathrm{d}
\end{aligned}
$$

2. Compute solids concentration of the combined sludge. Assume the specific gravity of the combined sludge is 1.02 . Then

$$
\% \text { solids }=\frac{(20,487 \mathrm{~kg} / \mathrm{d})}{\left(2920 \mathrm{~m}^{3} / \mathrm{d}\right)(1.02)\left(10^{3} \mathrm{~kg} / \mathrm{m}^{3}\right)} \times 100 \%=0.69 \%
$$

3. Compute surface area based on solids loading rate. Because the solids concentration is between $0.5 \%$ and $1.5 \%$, select a solids loading rate of $50 \mathrm{~kg} / \mathrm{m}^{2} \cdot \mathrm{~d}$ from Table 16.4. Then

$$
\text { area }=\frac{(20,487 \mathrm{~kg} / \mathrm{d})}{\left(50 \mathrm{~kg} / \mathrm{m}^{2} \cdot \mathrm{~d}\right)}=409.7 \mathrm{~m}^{2}
$$

## 4. Compute hydraulic loading rate

$$
\text { Hydraulic loading }=\frac{\left(2920 \mathrm{~m}^{3} / \mathrm{d}\right)}{409.7 \mathrm{~m}^{2}}=7.13 \mathrm{~m}^{3} / \mathrm{m}^{2} \cdot \mathrm{~d}
$$

5. Compute diameter of thickener. Assume two thickeners. Then

$$
\text { diameter }=\sqrt{\frac{4 \times 409.7 \mathrm{~m}^{2}}{2 \times \pi}}=16.15 \mathrm{~m}
$$

Related Calculations. The hydraulic loading rate of $7.13 \mathrm{~m}^{3} / \mathrm{m}^{2} \cdot \mathrm{~d}$ at peak design flow is at the lower end of the recommended rate. To prevent septicity and odors, dilution water should be provided. Calculation of the dilution water requirements for average design flow is a homework problem. The thickener size of 16.15 m is within the maximum size of 20 m customarily recommended by thickener equipment manufacturers for use in municipal wastewater treatment. In actual design, round the thickener diameter to the nearest 0.5 m , or, in this case, 16 m .

### 16.29 BELT-FILTER PRESS DESIGN

A wastewater treatment plant produces $72,000 \mathrm{~L} / \mathrm{d}$ of thickened biosolids containing 3 percent solids. A belt-filter press installation is to be designed based on a normal operation of $8 \mathrm{~h} / \mathrm{d}$ and $5 \mathrm{~d} /$ week, a belt-filter press loading rate of $275 \mathrm{~kg} / \mathrm{m} \cdot \mathrm{h}$, and the following data:

Total solids in dewatered sludge $=25$ percent.
Total suspended solids concentration in filtrate $=900 \mathrm{mg} / \mathrm{L}=0.09$ percent.
Washwater flowrate $=90 \mathrm{~L} / \mathrm{min}$ per m of belt width.
Sepcific gravities of sludge feed, dewatered cake, and filtrate are $1.02,1.07$, and 1.01 , respectively.
Compute the number and size of belt-filter presses required and the expected solids capture, in percent. Determine the daily hours of operation required if a sustained 3-d peak solids load occurs.

## Calculation Procedure

## 1. Compute average weekly sludge production rate

$$
\begin{aligned}
\text { Wet biosolids } & =(72,000 \mathrm{~L} / \mathrm{d})(7 \mathrm{~d} / \text { week })\left(10^{3} \mathrm{~g} / \mathrm{L}\right)\left(1 \mathrm{~kg} / 10^{3} \mathrm{~g}\right)(1.02) \\
& =514,080 \mathrm{~kg} / \text { week } \\
\text { dry solids } & =514,080 \times 0.03=15,422 \mathrm{~kg} / \text { week }
\end{aligned}
$$

## 2. Compute daily and hourly dry solids-processing requirements

$$
\begin{aligned}
\text { Daily rate } & =15,442 \mathrm{~kg} / \text { week } / 5 \text { operating d/week } \\
& =3084 \mathrm{~kg} / \mathrm{d} \\
\text { hourly rate } & =3084 / 8=385.5 \mathrm{~kg} / \mathrm{h} \text { (per } 8 \mathrm{~h} \text { operating d) }
\end{aligned}
$$

## 3. Compute belt-filter press size

$$
\text { Belt width }=\frac{(385.5 \mathrm{~kg} / \mathrm{h})}{(275 \mathrm{~kg} / \mathrm{m} \cdot \mathrm{~h})}=1.40 \mathrm{~m}
$$

Use one $1.5-\mathrm{m}$ belt-filter press and provide one of identical size for standby.
4. Compute filtrate flowrate by developing solids balance and flow balance equations. First, develop the daily solids balance equation:

$$
\text { solids in sludge feed }=\text { solids in sludge cake }+ \text { solids in filtrate }
$$

$$
\begin{aligned}
& 3084=(S \mathrm{~L} / \mathrm{d})(1.07)(0.25)+(F \mathrm{~L} / \mathrm{d})(1.01) \times(0.0009) \\
& 3084=0.2675 S+0.00091 F
\end{aligned}
$$

where $S=$ sludge cake flowrate, $\mathrm{L} / \mathrm{d}$
$F=$ filtrate flowrate, $\mathrm{L} / \mathrm{d}$
Then develop the flowrate equation:

$$
\begin{aligned}
& \text { sludge flowrate }+ \text { washwater flowrate }=\text { filtrate flowrate }+ \text { cake flowrate } \\
& \text { daily sludge flowrate }=(72,000 \mathrm{~L} / \mathrm{d})(7 / 5)=100,800 \mathrm{~L} / \mathrm{d} \\
& \begin{aligned}
\text { washwater flowrate } & =(90 \mathrm{~L} / \mathrm{min} \cdot \mathrm{~m})(1.5 \mathrm{~m})(60 \mathrm{~min} / \mathrm{h})(8 \mathrm{~h} / \mathrm{d}) \\
& =64,800 \mathrm{~L} / \mathrm{d}
\end{aligned}
\end{aligned}
$$

So

$$
100,800+64,800=165,600=F+S
$$

Now solve the mass balance and flowrate equations simultaneously to get

$$
F=154,600 \mathrm{~L} / \mathrm{d}
$$

## 5. Determine solids capture

$$
\begin{aligned}
\text { Solids capture } & =\frac{\text { solids in feed }- \text { solids in filtrate }}{\text { solids in feed }} \times 100 \% \\
& =\frac{(3084 \mathrm{~kg} / \mathrm{d})-\left[(154,600 \mathrm{~L} / \mathrm{d})(1.01)(0.0009)\left(10^{3} \mathrm{~g} / \mathrm{L}\right)\left(1 \mathrm{~kg} / 10^{3} \mathrm{~g}\right)\right]}{(3084 \mathrm{~kg} / \mathrm{d})} \times 100 \% \\
& =95.4 \%
\end{aligned}
$$



Hour of the day
FIGURE 16.3 Illustration of diurnal wastewater flow, BOD, and massloading variability.
6. Determine operating requirements for sustained peak biosolids load. First determine the peak 3-d load. From Fig. 16.3, the ratio of peak to average mass loading for three consecutive days is 2. The peak load is $72,000(2)=144,000 \mathrm{~L} / \mathrm{d}$.

Then determine the daily operating time requirements, neglecting sludge in storage:

$$
\begin{aligned}
\text { dry solids } / \mathrm{d} & =144,000 / \mathrm{d}(1.02)(0.03) \\
& =4406 \mathrm{~kg} / \mathrm{d} \\
\text { operating time } & =\frac{(4406 \mathrm{~kg} / \mathrm{d})}{(275 \mathrm{~kg} / \mathrm{m} \cdot \mathrm{~h})(1.5 \mathrm{~m})}=10.7 \mathrm{~h}
\end{aligned}
$$

The operating time can be accomplished by running the standby belt-filter press in addition to the duty press or by operating the duty press for an extended shift.

Comment. The value of sludge storage is important in dewatering applications because of the ability to schedule operations to suit labor availability most efficiently. Scheduling sludge dewatering operations during the day shift is also desirable if sludge has to be hauled off-site.

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# BIOTECHNOLOGY 

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17.1 DETERMINING THE LABORATORY-
REACTOR SIZE NEEDED FOR SEEDING
A BIOLOGICAL REACTION 17.1
17.2 ESTIMATING THE HOLDING TIME
NEEDED FOR STERILIZING A
BIOREACTOR 17.2
17.3 DETERMINING THE REQUIRED SIZE
FOR A STERILIZER 17.4
17.4 FINDING THE MASS TRANSFER
COEFICIENT FOR DISSOLVING
OXYGEN IN WATER 17.5
17.5 MAKING ESTIMATES FOR

DIFFUSIVITY OF OXYGEN IN WATER, AND ASSESSING THE RESULTS 17.6
17.6 CALCULATING PARAMETERS FOR SPARGED BIOCHEMICAL VESSELS 17.7
17.7 SIZING A FILTER FOR MICROFILTRATION OF A PROTEIN SOLUTION 17.9
17.8 ESTIMATING THE CAPACITY OF A WESTFALIA SEPARATOR TO REMOVE BACTERIA FROM BROTH 17.12
REFERENCES 17.13

### 17.1 DETERMINING THE LABORATORY-REACTOR SIZE NEEDED FOR SEEDING A BIOLOGICAL REACTION

Assuming a minimum $12 \%$ inoculum volume, what size of laboratory vessel would be required to initiate the seeding of a $20,000-\mathrm{L}$ full-scale cell-culture bioreactor?

## Calculation Procedure

1. Determine the size of reactor that would be required to seed the 20,000-L bioreactor. Since the seed volume must represent $12 \%$ of the vessel before reaction starts, the bioreactor being specified in this step would have to have a size $12 \%$ that of the $20,000-\mathrm{L}$ bioreactor, or $(0.12)(20,000)$, or 2400 L .
2. Determine the size of bioreactor needed to seed the 2400-L bioreactor of Step 1. Applying the same logic as in step 1, we see that the bioreactor being sought in this second step must be sized at $12 \%$ of 2400 L , or $(0.12)(2400)$, or 288 L .
3. Repeat Step 2 successively until a bioreactor of reasonable laboratory volume is reached. Twelve percent of 288 L is 34.6 L ; then, $12 \%$ of 34.6 is 4.15 L ; and $12 \%$ of 4.15 L is 500 ml . Thus, a 4.15-L laboratory vessel can be used if available. Otherwise, use a $500-\mathrm{ml}$ vessel. The contents of the $500-\mathrm{ml}$ vessel provide seeding for the $4.15-\mathrm{L}$ vessel; the contents of the latter vessel then seed the $34.6-\mathrm{L}$ bioreactor; the contents of this latter then seed the 288 -L bioreactor; and so on.

### 17.2 ESTIMATING THE HOLDING TIME NEEDED FOR STERILIZING A BIOREACTOR

A bioreactor containing $20 \mathrm{~m}^{3}$ of medium at room temperature $\left(25^{\circ} \mathrm{C}\right)$ is ready for sterilization by direct injection of saturated clean steam. The typical bacterial count of the medium is about $10 \times 10^{12} / \mathrm{m}^{3}$, which needs to be reduced to a level so that the chance for contaminant surviving the sterilization is 1 in 1000 , that is, a level of $1 \times 10^{-3}$ for the vessel.

The steam ( 345 kPa , absolute pressure) will be injected with a flowrate of $2500 \mathrm{~kg} / \mathrm{h}$, which will be stopped when the medium temperature reaches $122^{\circ} \mathrm{C}$. During the holding time, the heat loss through the vessel is assumed negligible. After an appropriate holding time, the bioreactor will be cooled by passing $200 \mathrm{~m}^{3} / \mathrm{h}$ of $20^{\circ} \mathrm{C}$ water through the bioreactor jacket until the medium reaches $30^{\circ} \mathrm{C}$. The jacket has a heat-transfer area of $10 \mathrm{~m}^{2}$ and for this operation the average overall heat-transfer coefficient $U$ for cooling is $2000 \mathrm{~kJ} /\left(\mathrm{h} \cdot \mathrm{m}^{2} \cdot \mathrm{~K}\right)$. The heat-resistant bacterial spores in the medium can be characterized by an Arrhenius coefficient $\left(k_{d 0}\right)$ of $5.7 \times 10^{39} \mathrm{~h}^{-1}$ and an activation energy ( $E_{d}$ ) of $2.834 \times 10^{5} \mathrm{~kJ} / \mathrm{kmol}$ [Refs. 9, 10]. The thermal death constant $\left(k_{d}\right)$ at $122^{\circ} \mathrm{C}$ is $197.6 / \mathrm{h}$. The heat capacity and density of the medium are $4.187 \mathrm{~kJ} / \mathrm{kg} \cdot \mathrm{K}$ and $1000 \mathrm{~kg} / \mathrm{m}^{3}$, respectively. Estimate the required holding time.

## Calculation Procedure

1. Determine the del factor that pertains to this sterilization operation. The del factor, $\nabla$, is the natural logarithm of the ratio of $n_{0}$, the original number of bacteria present, to $n$, the number allowed to remain. Thus,

$$
\begin{equation*}
\nabla=\ln \left(n_{0} / n\right)=\ln \left\{\left[\left(10 \times 10^{12} \mathrm{~m}^{-3}\right)\left(20 \mathrm{~m}^{3}\right)\right] /\left[1 \times 10^{-3}\right]\right\}=39.8 \tag{17.1}
\end{equation*}
$$

## 2. Determine the time $t$ needed to heat the system from its initial temperature $T_{0}$ of $25^{\circ} \mathrm{C}$ to a temperature $T$ of $122^{\circ} \mathrm{C}$

$$
\begin{equation*}
T=T_{0}+\frac{H_{m s} t}{c\left(M+m_{\mathrm{s}} t\right)} \tag{17.2}
\end{equation*}
$$

where $c$ is heat capacity, $H_{m s}$ is the enthalpy of the saturated steam relative to that of the raw mixture, and $M$ and $m$ are the masses of medium and steam, respectively.

From the steam table, the enthalpies of saturated steam at 345 kPa and water at $25^{\circ} \mathrm{C}$ are 2731 and $105 \mathrm{~kJ} / \mathrm{kg}$ respectively. Therefore the enthalpy of saturated steam at 345 kPa relative to raw medium temperature $25^{\circ} \mathrm{C}$ is

$$
\begin{equation*}
H=2731-105=2626 \mathrm{~kJ} / \mathrm{kg} \tag{17.3}
\end{equation*}
$$

which can be used to calculate the time required to heat the medium from $25^{\circ} \mathrm{C}$ to $122.1^{\circ} \mathrm{C}$ :

$$
\begin{align*}
T & =T_{0}+\frac{(2626 \mathrm{~kJ} / \mathrm{kg})(2500 \mathrm{~kg} / \mathrm{h}) t}{(4.187 \mathrm{k} \cdot \mathrm{JK})\left[\left(20 \mathrm{~m}^{3}\right)\left(1000 \mathrm{~kg} / \mathrm{m}^{3}\right)+(2500 \mathrm{~kg} / \mathrm{h}) t\right]}  \tag{17.4}\\
& =T_{0}+\frac{78.4 t}{1+0.125 t} \tag{17.5}
\end{align*}
$$

Trial-and error solution of Eq. (17.5) when $T=122^{\circ} \mathrm{C}(395 \mathrm{~K})$ and $T_{0}=25^{\circ} \mathrm{C}(298 \mathrm{~K})$ yields a $t$ value of 1.46 h .
3. Determine the del factor for the heating step, $\nabla_{\text {heat }}$. The thermal death of microorganisms typically follows a first-order process,

$$
\begin{equation*}
\frac{d n_{v}}{d t}=-k n_{v}=-k_{0} e^{[-E / R T(t)]} n_{v} \tag{17.6}
\end{equation*}
$$

or

$$
\begin{equation*}
\nabla=\ln \frac{n_{0}}{n}=\int_{0}^{t} k_{d} d t=k_{d 0} \int_{0}^{t} e^{\left(-E_{d} / R T\right)} d t \tag{17.7}
\end{equation*}
$$

where $k_{d 0}$ and $E_{d}$ are Arrhenius coefficient and activation energy, respectively, $T$ is absolute temperature, and $t$ is elapsed time. Then,

$$
\begin{align*}
\nabla_{\text {heat }} & =5.7 \times 10^{39} \int_{0}^{1.46} \exp \left[\frac{-2.834 \times 10^{5}}{8.318}\left(298+\frac{78.4 t}{1+0.125 t}\right)^{-1}\right] d t  \tag{17.8}\\
& =14.8 \tag{17.9}
\end{align*}
$$

4. Determine the time needed to cool the mixture to $30^{\circ} \mathrm{C}(303 \mathrm{~K})$ and the del factor for that cooling step, $\nabla_{\text {cool }}$. During the cooling process, the change of temperature can be approximated by

$$
\begin{align*}
T & =T_{\mathrm{co}}+\left(T_{\mathrm{o}}-T_{\mathrm{co}}\right) \exp \left[\left(1-e^{\left(-u A / m_{\mathrm{c}} C\right)}\right) m_{\mathrm{c}} t / M\right]  \tag{17.10}\\
& =293+102 e^{(-0.674) t} \tag{17.11}
\end{align*}
$$

where $T_{c 0}$ is the temperature of the cooling medium, $U$ is the overall heat-transfer coefficient [ $2000 \mathrm{~kJ} /$ $\left.\left(\mathrm{h} \cdot \mathrm{m}^{2} \cdot \mathrm{~K}\right)\right], A$ is the heat-transfer area $\left(10 \mathrm{~m}^{2}\right)$, and $m_{\mathrm{c}}$ and $c$ refer to the mass and heat capacity of the $20^{\circ} \mathrm{C}$ coolant water. Then, solving for $t$ when the final temperature is 303 K yields a cooling time of 3.45 h . Accordingly,

$$
\begin{align*}
\nabla_{\text {cool }} & =5.7 \times 10^{39} \int_{0}^{3.45} \exp \left[-\frac{2.834 \times 10^{5}}{8.318[293+102 \exp (-0.674 t)]}\right] d t  \tag{17.12}\\
& =13.9
\end{align*}
$$

5. Find the del factor for the holding time, $\nabla_{\text {hold }}$, and, accordingly, the required holding time, $\boldsymbol{t}_{\text {hold }}$. The del factor for the holding time $\left(\nabla_{\text {hold }}\right)$ is

$$
\begin{align*}
\nabla_{\text {hold }} & =\nabla_{\text {total }}-\nabla_{\text {heat }}-\nabla_{\text {cool }}  \tag{17.13}\\
& =39.8-14.8-13.9  \tag{17.14}\\
& =11.1 \tag{17.15}
\end{align*}
$$

The thermal death constant $\left(k_{d}\right)$ is $197.6 \mathrm{~h}^{-1}$ (at $122^{\circ} \mathrm{C}$ ). Therefore

$$
\begin{align*}
t_{\mathrm{hold}}=\frac{\nabla_{\mathrm{hold}}}{k_{d}} & =\frac{11.1}{197.6}  \tag{17.16}\\
& =0.056 \mathrm{~h}=3.37 \mathrm{~min} \tag{17.17}
\end{align*}
$$

Related Calculations. The value of $k_{d}$, the specific death rate, depends not only on the type of species but also on the physiological form of the cells. The temperature dependence of $k_{d}$ can be assumed to follow the Arrhenius equation,

$$
\begin{equation*}
k_{d}=k_{d 0} e^{\left(-E_{d} / R T(t)\right)} \tag{17.18}
\end{equation*}
$$

where $E_{d}$ is activation energy, which can be obtained from the slope of the $k_{d}$ versus $1 / T$ plot.

### 17.3 DETERMINING THE REQUIRED SIZE FOR A STERILIZER

A continuous sterilizer with a direct steam injector and a flash cooler will be used to sterilize a medium continuously. The medium will flow through the sterilizer at a rate of $2 \mathrm{~m}^{3} / \mathrm{h}$. The typical bacterial count, $n_{v 0}$, for the medium is $5 \times 10^{12} \mathrm{~m}^{3}$; this must be lowered to such a level, $n_{v}$, that only one organism can survive during a month of continuous operation. The heat-resistant bacterial spores in the medium can be characterized by an Arrhenius coefficient, $k_{d 0}$, of $5.7 \times 10^{39} \mathrm{~h}^{-1}$ [Refs. 9, 10]. The activation energy, $E_{d}$, is $2.834 \times 10^{5} \mathrm{~kJ} / \mathrm{kmol}$. The sterilizer will be fabricated with a pipe having an inner diameter of 0.102 m . Steam at 600 kPa gage pressure is available to bring the sterilizer to an operating temperature of $125^{\circ} \mathrm{C}$. The physical properties of the medium at that temperature are heat capacity, $c_{p}$, of $4.187 \mathrm{~kJ} /(\mathrm{kg}) \cdot(\mathrm{K})$, density, ${ }_{\rho}$ of $1000 \mathrm{~kg} / \mathrm{m}^{3}$, and viscosity, $\mu$, of $4 \mathrm{~kg} /(\mathrm{m}) \cdot(\mathrm{h})$. How long should the sterilizer pipe be, if ideal plug flow is assumed?

## Calculation Procedure

1. Determine the relevant del factor (see Example 17.2). Use Eq. (17.1), in which $k_{d}$ is the death rate:

$$
\begin{equation*}
\nabla=\ln \frac{n_{v 0}}{n_{v}}=\int_{0}^{t} k_{d} d t=k_{d 0} \int_{0}^{t} e^{\left(-E_{d} / R T\right)} d t \tag{17.19}
\end{equation*}
$$

or,

$$
\begin{align*}
\nabla=\ln \frac{n_{v 0}}{n_{v}} & =\ln \left[\frac{\left(5 \times 10^{12} \mathrm{~m}^{-3}\right)\left(2 \mathrm{~m}^{3} / \mathrm{h}\right)(24 \mathrm{~h} / \text { day })(30 \text { days })}{1}\right] \\
& =36.51 \tag{17.20}
\end{align*}
$$

2. Determine the required holding time, $\tau_{\text {hold }}$. Since the temperature of the holding section is constant, Eq. (17.20) simplifies to

$$
\begin{equation*}
\nabla_{\text {heat }}=k_{d} \tau_{\text {hold }} \tag{17.21}
\end{equation*}
$$

From the given data, $k_{d}$ can be calculated by using the equation

$$
\begin{equation*}
k_{d}=k_{d 0} e^{\left(-E_{d} / R T\right)} \tag{17.22}
\end{equation*}
$$

to yield

$$
\begin{equation*}
k_{d}=378.6 \mathrm{~h}^{-1} \tag{17.23}
\end{equation*}
$$

Therefore,

$$
\begin{equation*}
\tau_{\text {hold }}=\frac{\nabla}{k_{d}}=\frac{36.51}{378.6}=0.10 \mathrm{~h} \tag{17.24}
\end{equation*}
$$

3. Determine the velocity of the medium through the sterilizer. The velocity of the medium, $u$, is the volumetric flowrate divided by the cross-sectional area of the sterilizer:

$$
u=\left[2 \mathrm{~m}^{3} / \mathrm{h}\right] /\left[(\pi / 4)(0.102 \mathrm{~m})^{2}\right]=245 \mathrm{~m} / \mathrm{h}
$$

4. Determine the required length of the sterilizer. The length, $L$, equals the required holding time multiplied by the velocity of the medium:

$$
L=u \tau_{\text {hold }}=(0.10 \mathrm{~h})(245 \mathrm{~m} / \mathrm{h})=24.5 \mathrm{~m}
$$

### 17.4 FINDING THE MASS TRANSFER COEFFICIENT FOR DISSOLVING OXYGEN IN WATER

Calculate the mass transfer coefficient, $k_{L}$, for dissolution of oxygen from the air into $25^{\circ} \mathrm{C}$ water at 1 atm in a mixing vessel equipped with a flat-blade disk turbine and sparger. At those conditions, the diffusivity of oxygen in water, $D_{A B}$, is $2.5 \times 10^{-9} \mathrm{~m}^{2} / \mathrm{s}$, the viscosity of water is $8.904 \times 10^{-4}$ $\mathrm{kg} /(\mathrm{m}-\mathrm{s})$, and the density of water is $997.08 \mathrm{~kg} / \mathrm{m}^{3}$. Use Calderbank and Moo-Young's correlations (see Ref. 14).

## Calculation Procedure

1. Determine the density of air, $\rho_{\text {air }}$, at $25^{\circ}$ C. Use the ideal gas law:

$$
\begin{aligned}
\rho_{\text {air }} & =(\text { pressure })(\text { molecular weight }) /(\text { gas constant })(\text { temperature }) \\
\rho_{\text {air }} & =\left(1.01325 \times 10^{5} \mathrm{~Pa}\right)(29 \mathrm{~kg} / \mathrm{kg}-\mathrm{mol}) /\left(8.314 \times 10^{3}\right)(298 \mathrm{~K}) \\
& =1.186 \mathrm{~kg} / \mathrm{m}^{3}
\end{aligned}
$$

2. Calculate the relevant Schmidt number, $\boldsymbol{N}_{S c}$. The relevant Schmidt number is the ratio of liquid viscosity to the product of liquid density and the diffusivity:

$$
N_{S c}=\left(8.904 \times 10^{-4}\right) /(997.08)\left(2.5 \times 10^{-9}\right)=357.2
$$

3. Determine $k_{L}$ for small bubbles. Use the correlation,

$$
\begin{equation*}
k_{L}=0.31 N_{S c}{ }^{-2 / 3}\left(\frac{\Delta \rho \mu_{c} g}{\rho_{c}^{2}}\right)^{1 / 3} \tag{17.25}
\end{equation*}
$$

in which the density difference is between that of the water and the air, the subscript c refers to the liquid, and $g$ is the acceleration of gravity. Then,

$$
\begin{align*}
k_{L} & =0.31(357.2)^{-2 / 3}\left[\frac{(997.08-1.186) 8.904 \times 10^{-4}(9.81)}{(997.08)^{2}}\right]^{1 / 3}  \tag{17.26}\\
& =1.27 \times 10^{-4} \mathrm{~m} / \mathrm{s} \tag{17.27}
\end{align*}
$$

4. Determine $\boldsymbol{k}_{L}$ for large bubbles. For large bubbles, substituting in the equation

$$
\begin{equation*}
k_{L}=0.42 N_{S c}^{-1 / 2}\left(\frac{\Delta \rho \mu_{c} g}{\rho_{c}^{2}}\right)^{1 / 3} \tag{17.28}
\end{equation*}
$$

gives

$$
\begin{align*}
k_{L} & =0.42(357.2)^{-1 / 2}\left[\frac{(997.08-1.186) 8.904 \times 10^{-4}(9.81)}{(997.08)^{2}}\right]^{1 / 3}  \tag{17.29}\\
& =4.58 \times 10^{-4} \mathrm{~m} / \mathrm{s} \tag{17.30}
\end{align*}
$$

Comment. Note that for small bubbles and large bubbles alike, the mass transfer coefficients are independent of both the mixer power consumption and the gas flowrate.

### 17.5 MAKING ESTIMATES FOR DIFFUSIVITY OF OXYGEN IN WATER, AND ASSESSING THE RESULTS

Estimate the diffusivity for oxygen in water, $D_{A B}$ (with oxygen as component A and water as component B), at $25^{\circ} \mathrm{C}$, using both the Wilke-Chang and the Othmer-Thakar correlations (see Refs. 7 and 5), and compare the findings with the experimental value of $2.5 \times 10^{-9} \mathrm{~m}^{2} / \mathrm{s}$. (which, itself, has a possible error of $\pm 20 \%$ ). Then, convert the experimental value to one corresponding to a temperature of $40^{\circ} \mathrm{C}$. The molecular volume of oxygen, $V_{b A}$, is $0.0256 \mathrm{~m}^{3} / \mathrm{kmol}$; the association factor, $\xi$, for water is 2.26 ; the viscosity of water at $25^{\circ} \mathrm{C}$ is $8.904 \times 10^{-4} \mathrm{~kg} /(\mathrm{m}-\mathrm{s})$; the viscosity of water at $40^{\circ} \mathrm{C}$ is $6.529 \times 10^{-4} \mathrm{~kg} /(\mathrm{m}-\mathrm{s})$.

## Calculation Procedure

1. Estimate $\boldsymbol{D}_{A B}$ via the Wilke-Chang correlation. The Wilke-Chang correlation is as follows:

$$
\begin{equation*}
D_{A B}^{\circ}=\frac{1.173 \times 10^{-16}\left(\xi M_{B}\right)^{0.5} T}{\mu V_{b A}^{0.6}} \tag{17.31}
\end{equation*}
$$

with $M_{B}$ representing molecular weight of water.
Then,

$$
\begin{align*}
D_{A B}^{\circ} & =\frac{1.173 \times 10^{-16}[2.26(18)]^{0.5} 298}{8.904 \times 10^{-4}(0.0256)^{0.6}}  \tag{17.32}\\
& =2.25 \times 10^{-9} \mathrm{~m} / \mathrm{s} \tag{17.33}
\end{align*}
$$

2. Estimate $D_{A B}$ via the Othmer-Thakar correlation. The Othmer-Thakar correlation is as follows:

$$
\begin{equation*}
D_{A B}^{\circ}=\frac{1.112 \times 10^{-13}}{\mu^{1.1} V_{b A}^{0.6}} \tag{17.34}
\end{equation*}
$$

Then,

$$
\begin{align*}
D_{A B}^{\circ} & =\frac{1.112 \times 10^{-13}}{\left(8.904 \times 10^{-4}\right)^{1.1}(0.0256)^{0.6}}  \tag{17.35}\\
& =2.27 \times 10^{-9} \mathrm{~m}^{2} / \mathrm{s} \tag{17.36}
\end{align*}
$$

3. Assess the errors between these estimated values and the experimental one. If we define the error between these predictions and the experimental value as

$$
\begin{equation*}
\% \text { error }=\frac{\left(D_{A B}^{\circ}\right)_{\text {predicted }}-\left(D_{A B}^{\circ}\right)_{\text {Experimental }}}{\left(D_{A B}^{\circ}\right)_{\text {Experimental }}} \times 100 \tag{17.37}
\end{equation*}
$$

the resulting errors are $-10 \%$ and $-9.2 \%$, respectively. Since the experimental result itself comes with an accuracy of $\pm 20 \%$, both estimates are satisfactory.
4. Convert the estimated value to one that corresponds to $\mathbf{4 0}$. $\boldsymbol{C}$. The Wilke-Chang correlation (see step 1) suggests that ( $D_{A B}^{\circ} \mu / T$ ) is constant for a given liquid system. We may use that assumption
to estimate the diffusivity at $40^{\circ} \mathrm{C}$ :

$$
\begin{aligned}
D_{A B}^{\circ} \text { at } 40^{\circ} \mathrm{C} & =\left(D_{A B}^{\circ} \text { at } 25^{\circ} \mathrm{C}\right)(\text { ratio of viscosities }) \text { (ratio of absolute temperatures) } \\
& =\left[2.5 \times 10^{-9}\right]\left[\left(8.904 \times 10^{-4}\right) /\left(6.529 \times 10^{-4}\right)\right][313 / 298] \\
& =3.58 \times 10^{-9} \mathrm{~m}^{2} / \mathrm{s}
\end{aligned}
$$

Alternatively, the Othmer-Thakar correlation (see step 2) suggests that $D_{A B}^{\circ} \mu^{1.1}$ is constant. Under this assumption,

$$
\begin{aligned}
D_{A B}^{\circ} \text { at } 40^{\circ} \mathrm{C} & =\left(D_{A B}^{\circ} \text { at } 25^{\circ} \mathrm{C}\right)(\text { ratio of viscosities })^{1.1} \\
& =\left[2.5 \times 10^{-9}\right]\left[\left(8.904 \times 10^{-4}\right) /\left(6.529 \times 10^{-4}\right)\right]^{1.1} \\
& =3.52 \times 10^{-9} \mathrm{~m}^{2} / \mathrm{s}
\end{aligned}
$$

### 17.6 CALCULATING PARAMETERS FOR SPARGED BIOCHEMICAL VESSELS

A dished head tank of diameter $D_{T}=1.22 \mathrm{~m}$ is filled with water to an operating level equal to the tank diameter. The tank is equipped with four equally spaced baffles whose width is one-tenth of the tank diameter. The tank is agitated with a 0.36 -m-diameter, flat, six-blade disk turbine. The impeller rotational speed is $2.8 \mathrm{rev} / \mathrm{s}$. The sparging air enters through an open-ended tube situated below the impeller, and its volumetric flow, $Q$, is $0.00416 \mathrm{~m}^{3} / \mathrm{s}$ at $25^{\circ} \mathrm{C}$. Calculate the following: the impeller power requirement, $P_{m}$; gas holdup (the volume fraction of gas phase in the dispersion), $H$; and Sauter mean diameter of the dispersed bubbles. The viscosity of the water, $\mu$, is $8.904 \times 10^{-4} \mathrm{~kg} /(\mathrm{m}-\mathrm{s})$, the density, $\rho$, is $997.08 \mathrm{~kg} / \mathrm{m}^{3}$, and, therefore, the kinematic viscosity, $v$, is $8.93 \times 10^{-7} \mathrm{~m}^{2} / \mathrm{s}$. The interfacial tension for the air-water interface, $\sigma$, is $0.07197 \mathrm{~kg} / \mathrm{s}^{2}$. Assume that the air bubbles are in the range of $2-5 \mathrm{~mm}$ diameter.

## Calculation Procedure

1. Calculate the impeller Reynolds number. The formula for impeller Reynolds number is

$$
N_{\mathrm{Re}}=\frac{\rho N D_{I}^{2}}{\mu}
$$

where $N$ is impeller rotational speed and $D_{i}$ is impeller diameter (for more information on impeller Reynolds number, see Chapter 12).

Therefore,

$$
N_{\mathrm{Re}}=(997.08)(2.8)(0.36)^{2} / 8.904 \times 10^{-4}=406,357
$$

2. Calculate $P_{m o}$, the impeller power that would be required if there were no gas sparging. Rearrange the formula for turbulent power number, $N_{P}$ (see Chapter 12) so as to solve for impeller power:

$$
P_{m o}=\left(N_{P}\right) \rho N^{3} D^{5}
$$

Since the impeller Reynolds number is over 10,000 , the impeller power number is constant at 6 . Therefore, $P_{m o}=(6)(997.08)(2.8)^{3}(0.36)^{5}=794 \mathrm{~W}$.
3. Calculate $\boldsymbol{P}_{\boldsymbol{m}}$, the power required in the gas-sparged system. $P_{m}$ is calculated from the following equation:

$$
\log _{10} \frac{P_{m}}{P_{m o}}=192\left(\frac{D_{I}}{D_{T}}\right)^{4.38}\left(\frac{D_{I}^{2} N}{v}\right)^{0.115}\left(\frac{D_{I} N^{2}}{g}\right)^{1.96\left(\frac{D_{I}}{D_{T}}\right)}\left(\frac{Q}{N D_{I}^{3}}\right)
$$

where $g$ is the acceleration due to gravity. Therefore,

$$
\log _{10} \frac{P_{m}}{794}=192\left(\frac{0.36}{1.22}\right)^{4.38}\left\{\frac{\left(0.36^{2}\right)(2.8)}{8.93 \times 10^{-7}}\right\}^{0.115}\left(\frac{(0.36)\left(2.8^{2}\right)}{9.81}\right)^{1.96\left(\frac{0.36}{1.26)}\right.}\left(\frac{0.00416}{(2.8)\left(0.36^{3}\right)}\right)
$$

Therefore, $P_{m}=687 \mathrm{~W}$.
4. Calculate $\boldsymbol{v}$, the volume of the gas-liquid system. This is simply the volume of the fluid system:

$$
v=\pi(1.22)^{2}(1.22) / 4=1.43 \mathrm{~m}^{3}
$$

5. Calculate $\boldsymbol{V}_{s}$, the superficial velocity of the sparged gas. Use the formula, $V_{s}=4 Q / \pi\left(D_{T}\right)^{2}$. Thus,

$$
V_{s}=4(0.00416) / 3.1416(1.22)^{2}=0.00356 \mathrm{~m} / \mathrm{s}
$$

6. Calculate H, the gas holdup. Use the equation

$$
H=\left(\frac{V_{s} H}{V_{t}}\right)^{1 / 2}+2.16 \times 10^{-4}\left[\frac{\left(P_{m} / v\right)^{0.4} \rho_{c}^{0.2}}{\sigma^{0.6}}\right]\left(\frac{V_{s}}{V_{t}}\right)^{1 / 2}
$$

where $V_{t}$, the terminal gas-bubble velocity during free rise is $0.265 \mathrm{~m} / \mathrm{s}$ when the bubble size is in the range of $2-5 \mathrm{~mm}$ diameter. (For high superficial gas velocities $\left(V_{s}>0.02 \mathrm{~m} / \mathrm{s}\right.$ ), replace $P_{m}$ and $V_{t}$ with effective power input $P_{e}$ and $\left(V_{t}+V_{s}\right)$, respectively [see Ref. 8].)
Then,

$$
\begin{aligned}
H & =\left(\frac{0.00356 H}{0.265}\right)^{1 / 2}+2.16 \times 10^{-4}\left[\frac{(687 / 1.43)^{0.4}(997.08)^{0.2}}{0.07197^{0.6}}\right]\left(\frac{0.00356}{0.265}\right)^{1 / 2} \\
& =0.023
\end{aligned}
$$

7. Calculate the Sauter mean diameter, $\boldsymbol{D}_{32}$. The Sauter mean diameter is the diameter of a hypothetical droplet in which the ratio of droplet volume to droplet surface equals that of the entire dispersion. Use the formula

$$
D_{32}=4.15\left[\frac{\sigma^{0.6}}{\left(P_{m} / v\right)^{0.4} \rho_{c}^{0.2}}\right] H^{0.5}+9.0 \times 10^{-4}
$$

This gives

$$
\begin{aligned}
D_{32} & =4.15\left[\frac{0.07197^{0.6}}{(687 / 1.43)^{0.4} 997.08^{0.2}}\right](0.023)^{0.5}+9.0 \times 10^{-4} \\
& =0.00366 \mathrm{~m} \\
& =3.66 \mathrm{~mm}
\end{aligned}
$$

Related Calculations. For calculation of the liquid-phase mass transfer coefficient, $k_{L}$, the following formula can be used [Ref. 14], where $N_{S c}$ is the Schmidt number and subscript $c$ refers to the liquid phase:
For bubbles less than 2.5 mm in diameter,

$$
k_{L}=0.31 N_{S c}^{-2 / 3}\left(\frac{\Delta \rho \mu_{c} g}{\rho_{c}^{2}}\right)^{1 / 3}
$$

For bubbles larger than 2.5 mm in diameter,

$$
k_{L}=0.42 N_{S c}^{-1 / 2}\left(\frac{\Delta \rho \mu_{c} g}{\rho_{c}^{2}}\right)^{1 / 3}
$$

### 17.7 SIZING A FILTER FOR MICROFILTRATION OF A PROTEIN SOLUTION

We wish to concentrate and achieve a solvent switch for a solution by batch crossflow microfiltration. The flux, $j_{v}$, for the ceramic microfiltration membrane is $10 \mathrm{gal} /\left(\mathrm{h}-\mathrm{ft}^{2}\right)$. The initial solution volume is 1800 gal ; the final volume is 360 gal . The amount of protein present is 18.0 kg , and the molecular weight is $1,213.43 \mathrm{~g} / \mathrm{mole}$. The pressure drop is 30 psi (essentially 2 atm ) and the operating temperature is 277 K . Calculate the area, $A$, required to complete the filtration in 2 h .

## Calculation Procedure

1. Set out the equation that governs the time needed for microfiltration. The equation is as follows, with $L_{p}$ representing solvent permeability and $n_{1}$ the number of moles of solute present:

$$
\begin{equation*}
t=\left[\frac{1}{A L_{p} \Delta p}\right]\left\{\left(V_{0}-V\right)+\left(\frac{R T n_{1}}{\Delta p}\right) \ln \left(\frac{V_{0}-\frac{R T n_{1}}{\Delta p}}{V-\frac{R T n_{1}}{\Delta p}}\right)\right\} \tag{17.38}
\end{equation*}
$$

2. Simplify the equation in Step 1 by inserting known numerical values. The term,

$$
\begin{equation*}
\frac{R T n_{1}}{\Delta P}=\frac{\left[0.082 \mathrm{~L}-\mathrm{atm} /(\mathrm{gmole}-\mathrm{K}](277 \mathrm{~K})\left(\frac{18 \times 10^{3} \mathrm{~g}}{1213.43 \mathrm{~g} / \mathrm{gmole}}\right)\right.}{2 \mathrm{~atm}}=168.33 \mathrm{~L} \tag{17.39}
\end{equation*}
$$

And from Eq. (17.38), the term,

$$
\begin{equation*}
\prod=\left\{\left(V_{0}-V\right)+\left(\frac{R T n_{1}}{\Delta p}\right) \ln \left(\frac{V_{0}-\frac{R T n_{1}}{\Delta p}}{V-\frac{R T n_{1}}{\Delta p}}\right)\right\} \tag{17.40}
\end{equation*}
$$

can be calculated as

$$
\begin{align*}
\prod= & \{(1800 \mathrm{gal} \times 3.78 \mathrm{~L} / \mathrm{gal}-360 \mathrm{gal} \times 3.78 \mathrm{~L} / \mathrm{gal}) \\
& \left.+168.33 \mathrm{~L} \ln \left(\frac{1800 \mathrm{gal} \times 3.78 \mathrm{~L} / \mathrm{gal}-168.33 \mathrm{~L}}{360 \mathrm{gal} \times 3.78 \mathrm{~L} / \mathrm{gal}-168.33 \mathrm{~L}}\right)\right\}  \tag{17.41}\\
= & 1,516.41 \mathrm{gal} \tag{17.42}
\end{align*}
$$

Therefore, Eq. (17.38) reduces to

$$
\begin{equation*}
t=\left[\frac{1}{A L_{p} \Delta p}\right](1,516.41 \mathrm{gal}) \tag{17.43}
\end{equation*}
$$

## 3. Set out, then rearrange the equation for flowrate, $d V / d t$, through the filter

$$
\begin{equation*}
\frac{d V}{d t}=-A j_{v}=-A L_{p} \Delta p\left(1-\frac{R T c_{1}}{\Delta p}\right) \tag{17.44}
\end{equation*}
$$

But,

$$
\begin{equation*}
n_{1}=c_{1} V \tag{17.45}
\end{equation*}
$$

or

$$
\begin{equation*}
c_{1}=\frac{n_{1}}{V}=\frac{\frac{18 \times 10^{3} \mathrm{~g}}{1213.43 \mathrm{~g} / \mathrm{gmole}}}{1800 \mathrm{gal} \times 3.78 \mathrm{~L} / \mathrm{gal}}=0.002 \mathrm{gmole} / \mathrm{L} \tag{17.46}
\end{equation*}
$$

Substituting gives

$$
\begin{equation*}
\frac{R T c_{1}}{\Delta P}=\frac{[0.082 \mathrm{~L}-\mathrm{atm} /(\mathrm{gmole}-\mathrm{K})]\left(277^{\circ} \mathrm{K}\right)(0.002 \mathrm{gmole} / \mathrm{L})}{2 \mathrm{~atm}}=0.02 \tag{17.47}
\end{equation*}
$$

## 4. Rearrange Eq. (17.38) and solve it for the required area

$$
\begin{equation*}
A=\frac{\Pi}{L_{p} \Delta p t} \tag{17.48}
\end{equation*}
$$

Therefore from Eqs. (17.44) and (17.47) we have

$$
\begin{equation*}
j_{v}=L_{p} \Delta p(0.98) \tag{17.49}
\end{equation*}
$$

Then Eq. (17.48) reduces to

$$
\begin{align*}
A & =\frac{\prod(0.98)}{j_{v} t}  \tag{17.50}\\
& =\frac{1516.49 \mathrm{gal}(0.98)}{(2 \mathrm{~h}) \times\left(10 \mathrm{gal} /\left(\mathrm{h}-\mathrm{ft}^{2}\right)\right)} \tag{17.51}
\end{align*}
$$

And therefore,

$$
A=74.31 \mathrm{ft}^{2}
$$

is the area required to cross flow 1800 gal to 360 gal in 2 h .
Related Calculations. The same calculational approach can be used for nanofiltration.
In either case, if the membrane completely rejects the solute and the concentration polarization is negligible, then the concentration across the boundary layer is constant and small. Equation (17.38) consequently reduces to

$$
\begin{equation*}
t=\left[\frac{1}{A L_{p} \Delta p}\right]\left(V_{0}-V\right) \tag{17.52}
\end{equation*}
$$

or

$$
\begin{equation*}
t=\left[\frac{1}{A L_{p} \Delta p}\right](1800 \mathrm{gal}-360 \mathrm{gal}) \tag{17.53}
\end{equation*}
$$

or

$$
\begin{equation*}
t=\left[\frac{1}{A L_{p} \Delta p}\right](1440 \mathrm{gal}) \tag{17.54}
\end{equation*}
$$

And because $R T c_{l} / \Delta P$ becomes small and negligible, and because $n_{1}=c_{1} V$, then

$$
\begin{equation*}
\frac{d V}{d t}=-A j_{v}=-A L_{p} \Delta p\left(1-\frac{R T c_{l}}{\Delta p}\right) \tag{17.55}
\end{equation*}
$$

reduces to

$$
\begin{equation*}
j_{v} \cong L_{p} \Delta p \tag{17.56}
\end{equation*}
$$

Then modify Eq. (17.54) to

$$
\begin{equation*}
A=\frac{1440 \mathrm{gal}}{L_{p} \Delta p t} \tag{17.57}
\end{equation*}
$$

or

$$
\begin{equation*}
A=\frac{1440 \mathrm{gal}}{j_{v} t} \tag{17.58}
\end{equation*}
$$

or

$$
\begin{equation*}
A=\frac{(1440 \mathrm{gal})}{(2 \mathrm{~h}) \times\left(10 \mathrm{gal} /\left(\mathrm{h}-\mathrm{ft}^{2}\right)\right)} \tag{17.59}
\end{equation*}
$$

And therefore,

$$
A=72 \mathrm{ft}^{2}
$$

is the area required to cross flow 1800 gal to 360 gal in 2 h , when the concentration polarization is negligible.

The percent additional membrane area required because of concentration polarization is

$$
\Delta A \%=\frac{74.31 \mathrm{ft}^{2}-72 \mathrm{ft}^{2}}{74.31 \mathrm{ft}^{2}} \frac{1}{100}=3.12 \%
$$

### 17.8 ESTIMATING THE CAPACITY OF A WESTFALIA SEPARATOR TO REMOVE BACTERIA FROM BROTH

Estimate the throughput capacity of a Westfalia clarifier Type CSA 8 to separate $E$. coli bacteria from a fermentation broth. The specifications of the separator are as follows:

Bowl speed:

$$
\text { Number of disks: } \quad z=72
$$

$$
\begin{aligned}
& n=9200 \mathrm{~L} / \mathrm{min}, \text { i.e., } \omega=963 \mathrm{~s}^{-1} \\
& z=72 \\
& \varphi=55^{\circ} \\
& r_{1}=0.081 \mathrm{~m} \\
& r_{2}=0.036 \mathrm{~m}
\end{aligned}
$$

Disk angle:
External radius of disk:
Internal radius of disk:
The characteristics of the $E$-coli are as follows:
Smallest E-coli bacteria to be separated:

$$
\begin{aligned}
& d_{\text {limit }}=0.8 \mu \mathrm{~m}=0.8 \times 10^{-6} \mathrm{~m} \\
& \rho_{1}=1.05 \mathrm{~g} / \mathrm{cm}^{3}=1050 \mathrm{~kg} / \mathrm{m}^{3} \\
& \rho_{2}=1.02 \mathrm{~g} / \mathrm{cm}^{3}=1020 \mathrm{~kg} / \mathrm{m}^{3} \\
& \Delta \rho=0.03 \mathrm{~g} / \mathrm{cm}^{3}=30 \mathrm{~kg} / \mathrm{m}^{3} \\
& \eta=1.02 \times 10^{-3} \mathrm{~kg} / \mathrm{m}-\mathrm{s} \\
& g=9.81 \mathrm{~m} / \mathrm{s}^{2}
\end{aligned}
$$

Solids density:
Density of nutrient:
Density difference:
Dynamic viscosity:
Acceleration due to gravity:

## Calculation Procedure

## 1. Apply the following equation to arrive at the capacity $Q$

$$
\begin{equation*}
Q=\left(\frac{d_{\text {limit }}^{2} \Delta \rho}{18 \eta}\right) g\left(\frac{2 \pi}{3 g}\right)\left(\omega^{2} z \tan \varphi\right)\left(r_{1}^{3}-r_{2}^{3}\right) \tag{17.60}
\end{equation*}
$$

Substituting the data in Eq. (17.60) we have

$$
\begin{align*}
Q= & {\left[\frac{\left(0.8 \times 10^{-6} \mathrm{~m}\right)^{2}\left(30 \mathrm{~kg} / \mathrm{m}^{3}\right)}{18\left(1.02 \times 10^{-3} \mathrm{~kg} / \mathrm{m}-\mathrm{s}\right)}\right] g\left(\frac{2 \pi}{3 g}\right) } \\
& \times\left(963 \mathrm{~s}^{-1}\right)(72)\left(\tan 55^{\circ}\right)\left[(0.081 \mathrm{~m})^{3}-(0.036 \mathrm{~m})^{3}\right]  \tag{17.61}\\
& =1.01 \times 10^{-4} \mathrm{~m}^{3} / \mathrm{s}=365 \mathrm{~L} / \mathrm{h} \tag{17.62}
\end{align*}
$$

Related Calculations. In biotechnology separations such as this, data such as those for the density difference, viscosity, and cell size distribution are typically not known with certainty, so the calculation here can be regarded as providing only an approximate value; for more precision, experimental means must be used. E. coli suspensions with cell sizes between 0.8 and $1.8 \mu \mathrm{~m}$ have in practice been separated, with efficiencies of over $98 \%$, at rates of 200 to $400 \mathrm{~L} / \mathrm{h}$. This suggests that the approximation made here is a good one.

Equation (17.60) combines the formula for Stokes settling velocity, $v_{S}$, and that for the equivalent clarification area, $\Sigma_{T}$, also known as the comparison coefficient: $Q=\left(v_{S}\right)\left(\Sigma_{T}\right)$. The $v_{S}$ term is
calculated from the properties of the process material:

$$
v_{s}=\frac{d_{\text {limit }}^{2} \Delta \rho}{18 \eta} g
$$

The $\Sigma_{T}$ term, by contrast, is made up of design data for the disk-type bowl:

$$
\Sigma_{T}=\frac{2 \pi}{3 g} \omega^{2} z \tan \varphi\left(r_{1}^{3}-r_{2}^{3}\right)
$$

It corresponds to the amount of surface that would be required in a sedimentation vessel to achieve the same results as in a centrifugal separator (such as the Westfaila). It can be used for comparing the capacities of separators of different size of design. Specifically, the capacities $Q_{1}$ and $Q_{2}$ of two separator are related as follows:

$$
\frac{Q_{1}}{\Sigma_{T 1}}=\frac{Q_{2}}{\Sigma_{T 2}}
$$

or

$$
Q_{1}=\frac{Q_{2}}{\Sigma_{T 2}} \cdot \Sigma_{T 1}
$$

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## SECTION 18

# COST ENGINEERING 

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### 18.1 PLANT CAPITAL COST ESTIMATION VIA SCALING FACTOR 18.3 <br> 18.2 CAPITAL AND ANNUAL COST ESCALATION 18.4 <br> 18.3 UNIT OPERATION TOTAL CAPITAL INVESTMENT 18.6 <br> 18.4 PROCESS ANNUAL COSTS 18.10 <br> 18.5 NET PRESENT WORTH (NPW) ANALYSIS 18.11

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18.6 INTERNAL RATE OF RETURN (IRR)
    ANALYSIS 18.13
18.7 EQUIVALENT UNIFORM
    ANNUAL REVENUE (EUAR)
    ANALYSIS 18.15
18.8 EVALUATING CAPITAL INVESTMENT
    ALTERNATIVES 18.17
REFERENCES 18.18
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Before examining the problems for this chapter, we need to present some basic cost engineering concepts. First, there are two general cost categories: total capital investment (TCI) and total annual cost (TAC). Also referred to as the capital cost or first cost, the $T C I$ of a plant, process, operation, or similar activity includes all costs required to purchase the necessary equipment; the costs of the materials and labor needed to install that equipment (the direct installation costs); the costs for site preparation and buildings; and the costs for engineering, contractor fees, contingencies, and other indirect installation costs. The TCI also includes costs for land, working capital, and off-site facilities.

The equations that follow show how the various elements of the total capital investment are related.

$$
\begin{equation*}
T C I=\text { total depreciable investment }+ \text { total nondepreciable investment } \tag{18.1}
\end{equation*}
$$

$$
\begin{align*}
\text { Total depreciable investment }= & \text { total direct cost }+ \text { total indirect cost } \\
& + \text { off-sites facilities cost } \tag{18.2}
\end{align*}
$$

where total direct cost $=$ costs of equipment, direct installation, site preparation and buildings

$$
\begin{equation*}
\text { Total nondepreciable investment }=\text { costs of land and working capital } \tag{18.3}
\end{equation*}
$$

The total direct cost (TDC) includes both the direct installation costs and the costs of site preparation and buildings. Further, the sum of the total direct cost and total indirect cost (or direct installation costs) is termed the "battery limits" cost. Finally, the battery limits cost plus the cost of off-site facilities (e.g., a railroad spur) comprise the total depreciable investment. Put simply, this is the portion of the $T C I$ for which the firm is permitted to take a depreciation deduction on its corporate income tax return. The other portion of the TCI, namely, land and working capital, may not be depreciated. Hence, this portion is called the total nondepreciable investment.

The TAC consists of direct annual costs (DAC) and indirect annual costs (IAC). Also termed the "operating and maintenance" (O\&M) cost, the DAC are those costs that tend to be proportional or partially proportional to the production rate, stream flowrate, or some other measure of activity. These include costs for raw materials, utilities (e.g., electricity, steam, or natural gas), labor, maintenance, royalties, and waste treatment and disposal. Conversely, the IAC are those costs whose values are generally independent of the activity level and that, in fact, would be incurred even if the process were not operating. The IAC include administrative and laboratory charges, property taxes, and insurance. (With some cost calculation methods, the indirect annual cost also includes the capital recovery cost [CRC]; however, this is not true in general. See the subsequent discussion on the equivalent-uniform-annual-revenue method.) Those interested in a more detailed discussion of cost engineering terminology should refer to Basic Cost Engineering [Ref. 1], Estimating Costs of Air Pollution Control [Ref. 2], or other introductory works.

If a process is to be profitable, the total annual cost must be offset by the revenue $(R)$ the process generates. Moreover, if the revenue exceeds the TAC, income taxes will be owed. Finally, if income taxes are a consideration, so will be the depreciation of the process equipment. (Depreciation, an income tax book entry, should not be confused with the capital recovery cost; see later discussion on the EUAR method.) Space does not permit a thorough discussion of either income taxes or depreciation, as the rules governing the calculation of both are quite complex. For our purposes, the following equation, which encompasses all of these variables, will suffice:

$$
\begin{equation*}
N C F_{k}=(1-t)\left(R_{k}-T A C_{k}\right)+t D e p_{k} \tag{18.4}
\end{equation*}
$$

where $t=$ combined state and federal marginal income tax rate
$D e p_{k}=$ depreciation deduction taken in year $k$ of the project
$N C F_{k}=$ net cash flow in year $k$ of the project
$T A C_{k}=$ total annual cost in year $k$
$R_{k}=$ revenue in year $k$
As Eq. (18.4) suggests, the revenue, TAC, and depreciation might be different for each year in the project's life. For instance, during the first years of a project, the depreciation allowance could be higher than in later years, especially if certain depreciation computation methods (such as doubledeclining balance) are used. Similarly, the revenue in the earlier years could be lower as the "bugs" are removed from the process and the product market share is achieved. In any event, the net cash flow (large/small, positive/negative) is the quantity that ties all of these variables together.

Typically, firms have a limited amount of funds to invest in new projects. How do they decide which of several competing projects to finance? These decisions are made via one or more "measures of merit." The three most commonly used measures are: (1) net present worth (NPW), (2) internal rate of return (IRR), and (3) equivalent uniform annual revenue (EUAR). Inextricably tied to each of these measures is the annual interest rate, $i$, or "opportunity cost." A succinct definition of the opportunity cost is: "A dollar today is worth more than the prospect of a dollar tomorrow."

In the present worth (or discounted cash flow) method, each annual net cash flow for a project is "discounted" to the beginning of the project (year zero), in order to express all cash flows on the same basis. This discounting is done via the following equation:

$$
\begin{equation*}
\text { Discounted } N C F_{k}=N C F_{k} /(1+i)_{k} \tag{18.5}
\end{equation*}
$$

where $1 /(1+i)_{k}=$ the discount factor
$i=$ annual after-tax discount (interest) rate
The sum of these discounted NCFs over the life of the project is the project's net present worth. The project with the highest positive net present worth would be the one selected. The discount rate used in Eq. (18.5) is the firm's marginal acceptable rate of return (MARR) for anticipated projects or its "hurdle rate." Note that the discount rate is expressed on an after-tax basis to be consistent with the $N C F$. Also, when comparing projects via the present worth method, all projects must have equal
lives. Finally, by convention, $T C I$ is incurred when the project comes on-line (in year zero). Hence, the $N C F$ for year zero is equal to minus $T C I$, because, for that year, the revenue is zero and there are no other costs.

The internal rate of return method is a special case of the present worth method. With the $I R R$, the net present worth of each project first is arbitrarily set equal to zero, with the discount rate kept as an independent variable. Then, each $N P W$ equation is solved (via an iterative procedure) for the unique discount rate/internal rate of return that yields an $N P W$ of zero. The project with the highest positive $I R R$ would be the one selected.

The third method, $E U A R$, is easy to use and to understand. It also allows the comparison of projects with unequal lives. However, it is cumbersome to use when the $N C F$ s vary from year to year. But in special cases where the annual cash flow is constant, use of the EUAR method is recommended.

The $E U A R$ is calculated according to the following equation:

$$
\begin{equation*}
E U A R=N C F-C R C \tag{18.6}
\end{equation*}
$$

where $E U A R=$ equivalent uniform annual revenue
$N C F=$ net cash flow
$C R C=$ capital recovery cost
In this equation, note that the $C R C$ is given a negative sign, because it is a negative cash flow item. The $C R C$, in turn, is the product of the $T C I$ and the capital recovery factor, or

$$
\begin{equation*}
\left.C R C=T C I\left\{i(1+i)^{n} /(1+i)^{n}-1\right)\right\} \tag{18.7}
\end{equation*}
$$

where $i=$ discount (hurdle) rate
$n=$ project life (years)
The term in braces is the capital recovery factor (CRF).
In essence, the $C R C$ converts the $T C I$ (a one-time cost) to a series of equal annual payments over the life of the project.

### 18.1 PLANT CAPITAL COST ESTIMATION VIA SCALING FACTOR

Given that the total capital investment (TCI) of a 50,000-ton/year polypropylene unit is $\$ 60,000,000$ (in 2002 dollars), find the $T C I$ required for a 75,000 -ton/year polypropylene unit via the scaling factor method.

## Calculation Procedure

1. Apply the appropriate power-function formula. In the scaling factor method, the $T C I$ is estimated via the following formula (a power function):

$$
\begin{equation*}
T C I_{2}=T C I_{1}\left(C_{2} / C_{1}\right)^{E} \tag{18.8}
\end{equation*}
$$

where $T C I_{1}$ and $T C I_{2}=$ total capital investment of existing and planned unit, respectively, in dollars

$$
T C I_{1}=\$ 60,000,000
$$

$C_{1}, C_{2}=$ capacity of existing and planned unit, respectively, in tons/year
$C_{1}=50,000$ and $C_{2}=75,000$
$E=$ scaling exponent $=0.70[$ Ref. 3]

Thus

$$
T C I_{2}=60,000(75,000 / 50,000)^{0.70}=\$ 80,000,000 \text { (rounded) }
$$

Related Calculations. The scaling factor method is an appropriate procedure for estimating the TCI only under the following conditions:

1. The existing and planned units are identical (or nearly so), in terms of processing steps, end products, major equipment items used, and other respects.
2. The desired estimate falls within the category of "order-of-magnitude/screening/scoping" cost estimates (i.e., those estimates with a presumed accuracy less precise than $\pm 30 \%$ ).
3. The capacity of the planned unit falls within the capacity range for which the scaling exponent is valid. Rarely is the power function relationship between $T C I$ and capacity a smooth curve over the entire capacity range. Typically, the scaling exponent increases in value with increasing capacity. However, as the scaling exponent approaches unity, it becomes less costly to build two units, each with half the capacity of the large plant, than to construct a single, large-capacity plant.
4. The costs of both the existing and planned units are expressed in dollars of the same period. In this example, the TCIs are in 2002 dollars. If the costs are not of the same vintage, the cost of the existing plant (which is likely older) will have to be adjusted to the same year dollars as that of the planned unit. However, unless the cost vintages are much different (e.g., five years or more), adjustments for escalation would be "fine tuning," compared to the relative inaccuracy of these scaling factor estimates. (See Problem 18.2 for more on cost escalation.)

### 18.2 CAPITAL AND ANNUAL COST ESCALATION

The TCI of a 2500 -ton/day oxygen plant constructed in 1998 was $\$ 78,700,000$. The direct annual ("O\&M") costs for this facility (also in 1998 dollars) were as follows:

| Natural gas: | $\$ 3,450,000$ |
| :--- | ---: |
| Electricity: | $1,650,000$ |
| Labor (w/overhead) | $1,640,000$ |
| Maintenance: | $2,360,000$ |
| Total O\&M cost: | $\$ 9,100,000$ |

Find the total capital investment (capital) and O\&M costs in 2001 dollars.

## Procedure

1. Scale up the capital cost, using an index. To adjust (escalate) these costs from 1998 to 2001, published generic escalation indices must be used, as no single index has been formulated specifically for oxygen plants. One index will be used to escalate the capital cost, while others will be employed to adjust the various O\&M costs. To escalate the capital cost, the Chemical Engineering Plant Cost Index (CEPCI) will be used. Designed specifically for chemical process industry facilities, the CEPCI is updated and published monthly in Chemical Engineering magazine [Ref. 4].

The escalated capital cost is calculated via the following formula:
TCI in 2001 dollars $=$ [TCI in 1998 dollars][(CEPCI for 2001)/(CEPCI for 1998)]
where CEPCI is the annual index for the year in question and the ratio of the CEPCIs is the escalation factor.

Values of the CEPCI are

$$
\begin{aligned}
& \text { CEPCI }(1998)=389.5 \\
& \text { CEPCI }(2001)=394.3
\end{aligned}
$$

Substituting these index values and the given $T C I$ into this formula, we obtain

$$
T C I \text { in } 2001 \text { dollars }=78,700,000(394.3 / 389.5)=\$ 79,669,859, \text { or } \$ 79,700,000(\text { rounded })
$$

2. Scale up the individual O\&M costs using indexes. Each of the O\&M costs is escalated via the same formula, but by using a different index. The index to use for each cost is a Producer Price Index (PPI), compiled and published by the U.S. Department of Labor's Bureau of Labor Statistics [Ref. 5]. The PPI index numbers, names, and average 1998 and 2001 values used are as follows:

| O\&M cost | PPI number | PPI name | 1998 <br> avg. | 2001 <br> avg. | Escalation <br> factor |
| :--- | :--- | :--- | :---: | :---: | :---: |
| Natural gas | wpu05310105 | Fuels \& related products/natural gas | 106.3 | 217.8 | 2.0489 |
| Electricity |  |  |  |  |  |
| wpu0543 | Fuels \& related products/indus. <br> electric power | 130.0 | 141.1 | 1.0854 |  |
| Labor | eeu32280006 | Chemicals \& allied products/hourly <br> earnings | 17.09 | 18.61 | 1.0889 |

Because the maintenance cost typically is calculated as a percentage of the TCI, the CEPCI can also be used for its escalation:

$$
\begin{aligned}
\text { Maintenance in } 2001 \text { dollars } & =(\text { maintenance in } 1998 \text { dollars })(394.3 / 389.5) \\
& =\$ 2,389,083
\end{aligned}
$$

Applying the escalation factors tabulated here to the 1998 costs, we obtain the following escalated O\&M costs (in 2001 dollars):

Natural gas: $\quad \$ 7,068,705$
Electricity: $1,790,910$
Labor: 1,785,796
The total O\&M cost in 2001 dollars is the sum of the individual escalated costs, or $\$ 13,034,500$ (rounded).

## Related Calculations

1. Although it is easy to escalate capital and annual costs, escalation over periods longer than $5-10$ years is not recommended, as it tends to introduce additional inaccuracy to the estimates. For longer periods, rather than escalate the costs via an index, the cost estimator should obtain current cost quotes from equipment vendors and other sources (such as utilities).
2. Selecting the "right" escalation index is often difficult, as different published indices can appear to be applicable. For instance, when escalating the capital cost of a refinery hydrosulfurization unit, should one use the CEPCI, the Nelson-Farrar Refinery Index, or a combination of the two indexes? The decision often rests as much on engineering judgment as it does on hard data.
3. In this problem, note that escalating the capital cost from 1998 to 2001 dollars only adds another $\$ 1$ million (about a $1 \%$ increase), whereas the escalated O\&M cost is over $40 \%$ higher than the 1998 cost. Most of this increase is due to the doubling in natural gas prices over this three-year period. By
contrast, the electricity and labor costs only increased by about $9 \%$. Nevertheless, as this problem shows, it would be most inadvisable to use a capital cost index to escalate $O \& M$ costs, and vice versa.

### 18.3 UNIT OPERATION TOTAL CAPITAL INVESTMENT

A packed gas-absorber column is installed in a sulfuric acid plant to control sulfur dioxide $\left(\mathrm{SO}_{2}\right)$ emissions. The absorber unit consists of the column, packing, ductwork, fan, and solvent feed pump. Pertinent input data are as follows:

- Stream specifications:

Inlet waste gas flow rate, actual cubic feet per minute (acfm): 12,500
Inlet waste gas temperature, ${ }^{\circ} \mathrm{F}: 100$
Inlet waste gas pressure, atmospheres: 1.00
Inlet waste gas $\mathrm{SO}_{2}$ concentration, mole fraction: 0.001871
$\mathrm{SO}_{2}$ removal efficiency, fractional: 0.990
Solvent: aqueous ammonia $\left(\mathrm{NH}_{4} \mathrm{OH}\right)$
Inlet $\mathrm{SO}_{2}$ concentration in solvent: 0

- Packing:

Packing type: 2-in. ceramic Raschig rings, costing \$20/ft ${ }^{3}$ in 1991
Surface-area-to-volume ratio, $\mathrm{ft}^{2} / \mathrm{ft}^{3}: 28$

- Column:

Material of construction: fiber-reinforced plastic (FRP)
Gas flowrate, lb-mol/h: 1835
Solvent flowrate, lb-mol/h: 31.86
Outlet solvent pollutant concentration, mole fraction: 0.0964
Outlet gas pollutant concentration, mole fraction: $1.87447 \times 10^{-5}$
Slope of equilibrium line: 0.001037396
Absorption factor: 16.77
Column cross-sectional area, $A_{c}, \mathrm{ft}^{2}: 30.93$
Column diameter, $D_{c}, \mathrm{ft}^{2}: 6.275$
Number of transfer units: 4.831
Height of a transfer unit, ft : 2.377
Packing depth, ft: 11.483
Column total height, $\mathrm{ft}: 25.29$
Column surface area, $\mathrm{ft}^{2}$ : 560.4
Packing volume, $\mathrm{ft}^{3}$ : 355.2

- Ductwork:

Material of construction: FRP
Gas velocity, ft/min: 2000
Diameter, in: 38.20
Length, in feet of equivalent straight duct: 150

- Fan, motor, and motor starter:

Fan design: backward-curved centrifugal
Material of construction: FRP
Wheel diameter, in: 45

- Pump, motor, and motor starter:

Pump design: single-stage centrifugal
Material of construction: cast iron/bronze fitted with stainless steel mechanical seal
Power, hp: 0.5
Find the total capital investment (TCI) of the gas absorber unit in 2001 dollars.

## Calculation Procedure

1. Estimate the cost of the column and packing. The solution to the problem begins with calculating the cost of each of the major equipment items (MEIs) comprising the gas absorber unit. The MEIs consist of the column and packing, ductwork, fan, and pump. We start with the cost of the column and packing. The sizing and costing procedure for the column and packing as presented here closely follows that in the U.S. Environmental Protection Agency (EPA) report, EPA Air Pollution Control Cost Manual [Ref. 6].

The cost of the column is a function of its surface area, which is calculated from the column diameter $\left(D_{c}\right)$ and height $\left(H_{c}\right)$ via the following formula:

$$
\begin{align*}
S\left(\mathrm{ft}^{2}\right) & =\pi D_{c}\left(H_{c}+D_{c} / 2\right) \\
& =\pi(6.275)(25.29+6.275 / 2) \\
& =560.4 \mathrm{ft}^{2} \tag{18.9}
\end{align*}
$$

Based on FRP fabrication, the column equipment cost $\left(C_{c}\right)$ in 1991 dollars is

$$
C_{c}=161 S=\$ 90,224
$$

The packing cost, $C_{p}$, is a function of the packing volume, $V_{p}$, which is in turn a product of the packing depth, $H_{p}$, and column cross-sectional area, $A_{c}$ :

$$
\begin{equation*}
V_{p}\left(\mathrm{ft}^{3}\right)=H_{p} A_{c}=(11.483)(30.93)=355.2 \mathrm{ft}^{3} \tag{18.10}
\end{equation*}
$$

The cost of this packing (Raschig rings) is $\$ 20 / \mathrm{ft}^{3}$ in 1991 dollars. The packing cost is the product of the unit cost and the packing volume, or $\$ 7104$.

The column-plus-packing equipment cost is, therefore, $\$ 97,328$ in 1991 dollars.
However, this cost in 1991 dollars has to be escalated to 2001 dollars. As shown in Problem 18.2, the escalated cost is the product of the base cost and the escalation factor. The costs of gas absorbers can be escalated via one of the Vatavuk Air Pollution Control Cost Indexes (VAPCCIs). Updated quarterly since 1994 and published in Chemical Engineering, the VAPCCIs have been developed for gas absorbers and eight other types of air pollution control devices. The annual indices for gas absorbers for the years 1994 and 2001 are 100.8 and 114.4, respectively. In addition, the EPA study documenting the development of the VAPCCIs showed that gas absorber prices increased by 5.06\% from 1991 to 1994 [Ref. 7]. Combining this increase with the VAPCCI data, we get

$$
\text { Escalation factor }=1.0506(114.4 / 100.8)=1.192
$$

The escalated cost of the column and packing is the product of this factor and the cost in 1991 dollars,
or $(1.192)(97,378)$, or

$$
\text { Escalated cost }=\$ 116,075 \text { in } 2001 \text { dollars }
$$

2. Estimate the cost of the ductwork. In calculating the ductwork cost, we use the equivalent straight duct run (see the list earlier in this section) that is long enough to cover the cost of the fittings (elbows, tees, etc.). Based on this equivalent length, the duct diameter ( $D_{d}$ ), and a duct cost equation obtained from an EPA report [Ref. 8], the following relationship can be used:

$$
\begin{equation*}
\text { Unit duct cost }(\$ / \mathrm{ft}, \text { in } 1993 \text { dollars })=11.8 e^{\left(0.0542 D_{d}\right)} \tag{18.11}
\end{equation*}
$$

where $e$ is the base of natural logarithms. Substituting the duct diameter into this equation, we get

$$
\begin{aligned}
\text { Unit duct cost } & =11.8 e^{[(0.0542)(38.20)]} \\
& =\$ 93.55 / \mathrm{ft}
\end{aligned}
$$

Lastly, multiply this unit cost by the equivalent straight duct length:

$$
\text { Duct cost in } 1993 \text { dollars }=(93.55)(150)=\$ 14,033
$$

Escalate this cost to 2001 dollars via the Producer Price Index for plastic pipe (pcu3084\#1). The annual index values for 1993 and 2001 are 98.2 and 101.0, respectively. Then

$$
\text { Escalated duct cost }=\$ 14,033(101.0 / 98.2)=\$ 14,433 \text { in } 2001 \text { dollars }
$$

3. Estimate the cost of the fan package. The costs of a fan, motor, and motor starter (fan package) in 1988 dollars are combined in the following equation from Ref. 9:

$$
\begin{equation*}
\text { Fan package cost }=42.3 D_{f}^{1.20} \tag{18.12}
\end{equation*}
$$

where $D_{f}$ is the fan wheel diameter in inches ( 45 in ). Substituting the wheel diameter gives

$$
\text { Fan package cost in } 1988 \text { dollars }=42.3(45)^{1.20}=\$ 4076
$$

To escalate this cost to 2001 dollars, use the Producer Price Index for centrifugal fans and blowers (pcu3564\#3). Index values for 1988 and 2001 are 106.8 and 151.1, respectively.

Therefore,
Fan package cost in 2001 dollars $=\$ 4076(151.1 / 106.8)=\$ 5767$
4. Estimate the cost of the pump package. The cost of a pump package (pump, motor, and motor starter) in 1988 dollars is provided by the following relationship:

$$
\begin{equation*}
\text { Pump package cost }=538(H P)^{0.438} \tag{18.13}
\end{equation*}
$$

where $H P=$ pump horsepower $=0.5$
Thus,

$$
\text { Pump package cost in } 1988 \text { dollars }=538(0.5)^{0.438}=\$ 397
$$

To escalate this cost to 2001 dollars, use the Producer Price Index for industrial pumps (pcu3561\#1). Annual values for 1988 and 2001 are 112.3 and 171.1, in turn.

Thus, the
Pump package cost in 2001 dollars $=\$ 397(171.1 / 112.3)=\$ 605$
5. Estimate the total equipment cost of the absorber unit in 2001 dollars. The total gas absorber unit equipment cost (TEC) is the sum of the individual equipment costs:

$$
\begin{aligned}
T E C & =\$ 116,075+14,433+5767+605 \\
& =\$ 136,880
\end{aligned}
$$

6. Estimate the purchased equipment cost. The total equipment $\operatorname{cost}(T E C)$ is the foundation of the total capital investment, which is computed from this equipment cost by adding fixed percentages or "factors" of it. Therefore, this category of total capital investment is known as a "factored estimate" or "study estimate." Factored or study estimates represent a step above scaling factor estimates (see Problem 18.1), in that they require more effort to make but are more accurate (nominally $\pm 30$ percent). Unlike scaling factor estimates, for which the only required process input is the plant capacity, study estimates require a number of process-specific inputs, including a process flow sheet, preliminary energy and material balances, specifications for the major equipment items, preliminary ducting and piping layouts, and similar data.

As already indicated, the gas absorber sizing and equipment cost-estimating procedure used here closely follows that in the EPA Air Pollution Control Cost Manual [Ref. 6]. Accordingly, this manual's methodology for estimating the capital cost will also be followed. In that methodology, the purchased equipment cost (PEC) first is factored from the TEC. Then, the various direct and indirect installation costs are factored from the $P E C$. Finally, the $T C I$ is calculated by adding the $P E C$ to the direct and indirect installation costs. The same reasoning can be applied to $T C I$ estimates that do not involve air-pollution-control facilities.

According to the EPA Manual procedure, the PEC is made up of three elements in addition to the total equipment cost: (1) freight cost, (2) sales taxes, and (3) instrumentation cost. The percentages the EPA Manual assigns to these costs are $5 \%, 3 \%$, and $10 \%$ of the total equipment cost, respectively. For this problem, the costs are, accordingly, as follows:

| Total equipment: | $\$ 136,880$ |
| :--- | ---: |
| Freight: | 6,844 |
| Sales tax: | 4,106 |
| Instrumentation: | 13,688 |
| PEC: | $\$ 161,518$ |

7. Estimate the direct and indirect installation costs. As previously explained, the various installation costs are factored from the PEC. The EPA Manual factors, which apply to a gas absorber installed under "typical conditions," along with the costs factored from the PEC here, are as follows:

| Direct installation cost | Cost factor $(\times$ PEC $)$ | Calculated cost |
| :--- | :---: | ---: |
| Foundations and supports | 0.12 | $\$ 19,382$ |
| Handling and erection | 0.40 | 64,607 |
| Electrical | 0.01 | 1615 |
| Piping | 0.30 | 48,455 |
| Insulation | 0.01 | 1615 |
| Painting | 0.01 | 1615 |
|  | $\underline{2}$ | $\$ 137,289$ |


| Indirect installation cost | Cost factor $(\times$ PEC $)$ | Calculated cost |
| :--- | :---: | :---: |
| Engineering | 0.10 | $\$ 16,152$ |
| Construction and field expense | 0.10 | 16,152 |
| Contractor fees | 0.10 | 16,152 |
| Start-up | 0.01 | 1615 |
| Performance test | 0.01 | 1615 |
| Contingencies | 0.03 | 4846 |
| Subtotal, indirect installation | $\underline{0.35}$ | $\$ 56,532$ |

8. Estimate the total capital investment. The total capital investment is the sum of the PEC and the direct and indirect installation costs: $\$ 161,518+137,289+56,532=\$ 355,339$, or $\$ 355,300$ (rounded).

### 18.4 PROCESS ANNUAL COSTS

A 70,000 ton/year, $\$ 22,000,000$ plant was started up in 2001 . Since then, it has been operating at capacity for an average of $7200 \mathrm{~h} /$ year. It is staffed by 25 full-time production workers ( $\$ 32 / \mathrm{h}$ ), two maintenance workers ( $@ \$ 35 / \mathrm{h}$ ), and four shift supervisors ( $@ \$ 39 / \mathrm{h}$ ). All labor rates include payroll and plant overhead. The process consumes 530 kilowatts of electricity ( $@ \$ 0.045 / \mathrm{kWh}$ ), $50,000 \mathrm{gal} / \mathrm{h}$ of water (@\$0.15/thousand gal), and 8.75 tons/h of feedstock (@\$0.78/lb). Maintenance materials are estimated as equivalent to maintenance labor. Royalties amount to $\$ 4.20$ per ton of product. The property taxes, insurance, and administrative charges total $5.2 \%$ of the total capital investment. Find the direct and indirect annual costs for the plant.

## Calculation Procedure

1. Determine the direct annual costs. The direct annual costs equal the sum of the costs of production and maintenance labor, maintenance materials, supervisory labor, electricity, water, feedstock, and royalties. Thus:

Production labor: $(25$ workers $/ \mathrm{h})(7200 \mathrm{~h} /$ year $)(\$ 32 / \mathrm{h})=\$ 5,760,000$
Maintenance labor: $(2$ workers $/ \mathrm{h})(7200 \mathrm{~h} /$ year $)(\$ 35 / \mathrm{h})=\$ 504,000$
Maintenance materials $=$ maintenance labor $=\$ 504,000$
Supervisory labor: (4 supervisors/h) $(7200 \mathrm{~h} /$ year $)(\$ 39 / \mathrm{h})=\$ 1,123,200$
Electricity: $(530 \mathrm{~kW})(7200 \mathrm{~h} /$ year $)(\$ 0.045 / \mathrm{kWh})=\$ 171,720$
Water: $(50$ thousand gal/h $)(7200 \mathrm{~h} /$ year $)(\$ 0.15 /$ thousand gal $)=\$ 54,000$
Feedstock: $(8.75$ tons $/ \mathrm{h})(7200 \mathrm{~h} /$ year $)(\$ 0.078 / \mathrm{lb})(2000 \mathrm{lb} /$ ton $)=\$ 9,828,000$
Royalties: $(70,000$ tons/year) $(\$ 4.20 /$ ton $)=\$ 294,000$

The total direct annual cost is the sum of these, or $\$ 18,238,920$.
2. Determine the indirect annual costs. The indirect annual costs, consisting of property taxes, insurance, and administrative charges are given in the problem statement as $5.2 \%$ of the total capital investment. Thus,

$$
\text { Indirect annual costs }=(0.052)(\$ 22,000,000)=\$ 1,144,000
$$

3. Determine the total annual costs. From steps 1 and 2 , the sum is $\$ 18,238,920+1,144,000$, or \$19,382,920.

### 18.5 NET PRESENT WORTH (NPW) ANALYSIS

A firm is evaluating two competing projects. The first is a new ("grass roots") inorganic chemicals plant, while the second is the expansion of a textile fibers facility. The process engineers have estimated the projected annual revenue, total capital investment, and total annual cost (without capital recovery) for each project, as follows:

|  | Cost (2002 dollars) |  |
| :--- | :---: | :---: |
| Cost category | Inorganic chemicals plant | Textile fibers plant expansion |
| Revenue (projected) | $\$ 33,700,000$ | $\$ 30,900,000$ |
| Total capital investment | $52,500,000$ | $57,300,000$ |
| Total annual cost | $25,100,000$ | $21,500,000$ |

Both the new and expanded plants would have an estimated life of 20 years. The firm's hurdle rate (marginal acceptable rate of return) is $12.5 \%$ (before tax), and its marginal state and federal corporate income tax rate is $52 \%$. Assuming straight-line depreciation (with zero salvage) and that $100 \%$ of the investment is depreciable, calculate the net present worth of each project.

## Calculation Procedure

1. Find the annual depreciation for each project. Based on straight-line depreciation, the annual depreciations for the two projects would be simply their total capital investments divided by 20 years. Thus,

Annual depreciation for inorganic chemical plant: $\$ 52,500,000 / 20=\$ 2,625,000$.
Annual depreciation for textile fibers plant: $\$ 57,300,000 / 20=\$ 2,865,000$.
2. Calculate the after-tax discount or hurdle rate. The after-tax discount rate, which applies to each of the two proposals, equals the before-tax rate multiplied by 1 minus the tax rate. Thus, the after-tax hurdle rate, $i^{*}$, equals $12.5 \%(1-0.52)=6.0 \%$.
3. Calculate the annual undiscounted net cash flows (NCFs) for the inorganic chemicals plant. For the inorganic chemicals plant, for the beginning of the project (year zero), the net cash flow will be negative, as the only cash flow item will be the total capital investment. That is, $N C F$ (year zero) $=-\$ 52,500,000$. However, for each of the following years (year 1 through year 20, the end of the
project) the $N C F$ will be calculated by Eq. (18.4) from the introduction to this chapter:

$$
\begin{aligned}
N C F(\text { year } 1,2, \ldots, 20) & =(R-T A C)(1-t)+t D e p \\
& =(33,700,000-25,100,000)(1-0.52)+0.52(2,625,000) \\
& =\$ 5,493,000
\end{aligned}
$$

4. Calculate the net present worth (NPW) for the inorganic chemicals plant. Step 3 determined undiscounted $N C F$ s. To determine the net present worth, $N P W$, it is necessary to determine the discounted $N C F$ for each year in the project life and then their sum. The discounted $N C F$ for year $k$ is the product of the discount factor $\left(1 /\left[1+i^{*}\right] k\right)$ and the undiscounted NCF. The discounted NCFs for the various years, and their sum the $N P W$, are as follows:

| Year | Discount factor (rounded) | $N C F$ (discounted) |
| :---: | :---: | :---: |
| 0 | - | $-52,500,000$ |
| 1 | 0.9434 | $5,182,075$ |
| 2 | 0.8900 | $4,888,750$ |
| 3 | 0.8396 | $4,612,029$ |
| 4 | 0.7921 | $4,350,970$ |
| 5 | 0.7473 | $4,104,689$ |
| 6 | 0.7050 | $3,872,348$ |
| 7 | 0.6651 | $3,653,159$ |
| 8 | 0.6274 | $3,446,376$ |
| 9 | 0.5919 | $3,251,298$ |
| 10 | 0.5584 | $3,067,263$ |
| 11 | 0.5268 | $2,893,644$ |
| 12 | 0.4970 | $2,729,853$ |
| 13 | 0.4688 | $2,575,333$ |
| 14 | 0.4423 | $2,429,559$ |
| 15 | 0.4173 | $2,292,037$ |
| 16 | 0.3936 | $2,162,299$ |
| 17 | 0.3714 | $2,039,905$ |
| 18 | 0.3503 | $1,924,438$ |
| 19 | 0.3305 | $1,815,508$ |
| 20 | 0.3118 | $1,712,743$ |
|  |  |  |

5. Calculate the annual undiscounted net cash flows (NCFs) for the textile fibers plant. Follow the procedure of step 3, but apply it to the data for the textile fibers plant. Thus,

$$
N C F \text { for year zero }=-T C I=-\$ 57,300,000
$$

Undiscounted $N C F$ for years $1,2, \ldots, 20=(30,900,000-21,500,000)(1-0.52)$

$$
+0.52(2,865,000)=\$ 6,001,800
$$

6. Calculate the net present worth (NPW) for the textile fibers plant. Follow the procedure of step 4, but apply it to the data for the textile fibers plant. The discounted NCFs for the various years
for the textile fibers plant, and their sum the $N P W$, are as follows:

| Year | Discount factor (rounded) | $N C F$ (discounted) |
| :---: | :---: | :---: |
| 0 | - | $-57,300,000$ |
| 1 | 0.9434 | $5,662,075$ |
| 2 | 0.8900 | $5,341,581$ |
| 3 | 0.8396 | $5,039,227$ |
| 4 | 0.7921 | $4,753,988$ |
| 5 | 0.7473 | $4,484,894$ |
| 6 | 0.7050 | $4,231,032$ |
| 7 | 0.6651 | $3,991,540$ |
| 8 | 0.6274 | $3,765,604$ |
| 9 | 0.5919 | $3,552,456$ |
| 10 | 0.5584 | $3,351,374$ |
| 11 | 0.5268 | $3,161,673$ |
| 12 | 0.4970 | $2,982,711$ |
| 13 | 0.4688 | $2,813,878$ |
| 14 | 0.4423 | $2,654,602$ |
| 15 | 0.4173 | $2,504,341$ |
| 16 | 0.3936 | $2,362,586$ |
| 17 | 0.3714 | $2,228,855$ |
| 18 | 0.3503 | $2,102,693$ |
| 19 | 0.3305 | $1,983,673$ |
| 20 | 0.3118 | $1,871,390$ |
|  |  |  |

7. Select the more attractive project. Because the projected net present worth of the textile fibers plant expansion project is higher than that of the inorganic chemicals plant, the firm's funds would be better spent on it.

Related Calculations. Under the conditions stated here, the preferred project would be the textile fibers plant expansion. However, this might not have been the case if we had assumed a different hurdle rate, plant life, revenues, or total annual costs.

Another key assumption is that the revenues and total annual costs are constant over the life of the project. That is, they are expressed in constant (2002) dollars. Neither the costs nor the revenues have been adjusted for inflation.

By accounting convention, depreciation is never adjusted for inflation, even if the other costs and revenues are so adjusted. Depreciation is assumed to be constant in this constant-dollar analysis as well. Technically, this assumption is incorrect, as the depreciation cash flows should have been adjusted. However, to minimize the example's complexity, this adjustment was not been made. Another simplification is the assumption of straight-line depreciation. Current U.S. tax laws are more generous, in that they allow for larger depreciation deductions in the earlier years of the project than later. In such cases, the depreciation deduction would vary from year to year.

### 18.6 INTERNAL RATE OF RETURN (IRR) ANALYSIS

Given the data for the inorganic chemicals plant and the textile fibers plant expansion in the problem statement for Example 18.5, use the internal rate of return method to determine which project the firm should fund.

## Calculation Procedure

1. Take into account how this approach differs from that for NPW analysis. The project lives, TCIs, TACs, depreciation, undiscounted net cash flows, plant lives, and tax rate are the same as those given for Example 18.5, on $N P W$ analysis. However, in this present example, the hurdle (discount) rate is not an input. In Example 18.5, the hurdle rate was an input and, based on this rate, the net present worth was calculated for each project. In this example, by contrast, the net present worth is arbitrarily set to zero and the unique discount rate that produces a $N P W$ of zero is solved for. This discount rate is the internal rate of return $(I R R)$. The project with the higher internal rate of return is selected as the one to be funded.

Because the $N P W$ is the sum of a geometric series, the $I R R$ cannot be solved for algebraically. Instead, it is necessary to use an iterative procedure: Guess a value for the $I R R$, determine the sum of the discounted cash flows that result from your guessed $I R R$, and repeat the procedure until it leads to a sum that is virtually zero.
2. Find, by iteration, the IRR for the inorganic chemicals plant. Iterations not shown here lead ultimately to an $I R R$ of $8.3643 \%$ after-tax, which implies $17.4255 \%$ pre-tax (see Example 18.5, step 2). The employment of 8.3643 as after-tax hurdle rate to find the discounted net case flows for the inorganic chemicals plant leads to the following results:

| Year | Discount factor (rounded) | $N C F$ (discounted) |
| :---: | :---: | :---: |
| 0 | - | $-\$ 52,500,000$ |
| 1 | 0.9228 | $5,069,014$ |
| 2 | 0.8516 | $4,677,755$ |
| 3 | 0.7859 | $4,316,695$ |
| 4 | 0.7252 | $3,983,504$ |
| 5 | 0.6692 | $3,676,031$ |
| 6 | 0.6176 | $3,392,291$ |
| 7 | 0.5699 | $3,130,452$ |
| 8 | 0.5259 | $2,888,823$ |
| 9 | 0.4853 | $2,665,845$ |
| 10 | 0.4479 | $2,460,078$ |
| 11 | 0.4133 | $2,270,193$ |
| 12 | 0.3814 | $2,094,965$ |
| 13 | 0.3520 | $1,933,262$ |
| 14 | 0.3248 | $1,784,040$ |
| 15 | 0.2997 | $1,646,336$ |
| 16 | 0.2766 | $1,519,261$ |
| 17 | 0.2552 | $1,401,994$ |
| 18 | 0.2355 | $1,293,779$ |
| 19 | 0.2174 | $1,193,917$ |
| 20 | 0.2006 | $1,101,763$ |
|  |  | $-\$ 1$ |

3. Find, by iteration, the IRR for the textile fibers plant expansion. Repeat step 2 with respect to the expansion of the textile fibers plant. This iteration leads to an after-tax $I R R$ of $8.3792 \%$, or
$17.4568 \%$ pre-tax. The computation and summing of the discounted NCFs with a discount rate of $8.3792 \%$ leads to the following results:

| Year | Discount factor (rounded) | $N C F$ (discounted) |
| :---: | :---: | :---: |
| 0 | - | $-\$ 57,300,000$ |
| 1 | 0.9227 | $5,537,776$ |
| 2 | 0.8513 | $5,109,628$ |
| 3 | 0.7855 | $4,714,581$ |
| 4 | 0.7248 | $4,350,077$ |
| 5 | 0.6688 | $4,013,755$ |
| 6 | 0.6171 | $3,703,435$ |
| 7 | 0.5693 | $3,417,107$ |
| 8 | 0.5253 | $3,152,916$ |
| 9 | 0.4847 | $2,909,151$ |
| 10 | 0.4472 | $2,684,233$ |
| 11 | 0.4127 | $2,476,704$ |
| 12 | 0.3808 | $2,285,220$ |
| 13 | 0.3513 | $2,108,540$ |
| 14 | 0.3242 | $1,945,520$ |
| 15 | 0.2991 | $1,795,104$ |
| 16 | 0.2760 | $1,656,317$ |
| 17 | 0.2546 | $1,528,260$ |
| 18 | 0.2349 | $1,410,104$ |
| 19 | 0.2168 | $1,301,083$ |
| 20 | 0.2000 | $1,200,491$ |
|  |  |  |
|  | $N P W:$ | $\$ 2$ |

4. Select the more attractive project. Based on these results, we conclude that the textile fibers plant expansion would be the preferred project, as its after-tax $\operatorname{IRR}$ (about $8.38 \%$ ) is slightly higher than the after-tax $I R R$ for the inorganic chemicals plant (about $8.36 \%$ ).

Related Calculations. The difference between the two internal rates of returns is so small that, on a purely economic basis, the projects are virtually indistinguishable. By contrast, the difference in the projects' net present worths (see Example 18.5) is large enough to make the textile fibers expansion the clear choice for funding. As with the net present worth method, the internal rate of return procedure cannot be used unless the lifetimes of the competing projects are equal.

### 18.7 EQUIVALENT UNIFORM ANNUAL REVENUE (EUAR) ANALYSIS

Given the data for the inorganic chemicals plant and the textile fibers plant expansion provided in the problem statement of Example 18.5, employ equivalent uniform annual revenue (EUAR) analysis to determine which project the firm should fund.

## Calculation Procedure

1. Calculate the capital recovery factor. In this method, each of the undiscounted net cash flows $(N C F \mathrm{~s})$ for years 1 to 20 is algebraically added to the capital recovery cost $(C R C)$ to obtain the equivalent uniform annual revenue $(E U A R)$. The $C R C$ is the product of the total capital investment,
$T C I$, and the capital recovery factor, CRF, which is defined and calculated by Eq. (18.7) of the introduction. The project with the higher $E U A R$ will be the one to fund. The pertinent input data are as follows:

|  | Revenue/cost (2002 dollars) |  |
| :--- | :---: | :---: |
| Revenue/cost category | Inorganic chemicals plant | Textile fibers plant expansion |
| Revenue (projected) | $\$ 33,700,000$ | $\$ 30,900,000$ |
| Total capital investment | $52,500,000$ | $57,300,000$ |
| Total annual cost | $25,100,000$ | $21,500,000$ |
| Net cash flow (undiscounted) | $5,493,000$ | $6,001,800$ |

From Eq. (18.7) of the introduction, using the after-tax hurdle rate as calculated in Example 18.5, step 2, we obtain

$$
C R F=i(1+i)^{n} /(1+i)^{n}-1=0.06(1.06)^{20} / 1.06^{20}-1=0.08718
$$

2. Calculate the capital recovery cost for the inorganic chemicals plant

$$
C R C=(T C I)(C R F)=(52,500,000)(0.08718)=\$ 4,576,950
$$

## 3. Calculate the equivalent uniform annual revenue for the inorganic chemicals plant

Equivalent uniform annual revenue $=N C F-C R C=5,493,000-4,576,950=\$ 916,050$

## 4. Calculate the capital recovery cost for the textile fibers plant expansion

$$
C R C=(T C I)(C R F)=(57,300,000)(0.08718)=\$ 4,995,414
$$

## 5. Calculate the equivalent uniform annual revenue for the inorganic chemicals plant

Equivalent uniform annual revenue $=N C F-C R C=6,001,800-4,995,414=\$ 1,006,386$
6. Determine the more attractive process. Based on the $E U A R$ measure, the textile fibers plant expansion would be the clear choice to fund, because its $E U A R$ of $\$ 1,006,386$ is larger than the $\$ 916,050$ EUAR of the inorganic chemicals plant.

Related Calculations. The EUAR for the textile fibers plant expansion is $9.86 \%$ higher than that of the inorganic chemicals plant. The textile fibers plant $N P W$ is also $9.86 \%$ higher than the inorganic chemicals plant $N P W$ (see Example 18.5). This is not a coincidence. In fact, the EUAR and $N P W$ methods will always yield the same results and can be shown to be mathematically equivalent.

Even so, the EUAR method is best suited to those situations where (as in this case) the undiscounted net cash flows are constant. However, when they are not constant, each NCF must be discounted back to year zero, summed, and annualized by multiplying it by the CRF. Finally, this annualized NCF must be added to the capital recovery cost. By the time the analyst has done all of this, he or she could just as well have calculated the net present worths or internal rates of return of the competing projects.

### 18.8 EVALUATING CAPITAL INVESTMENT ALTERNATIVES

A portland cement plant ball mill emits particulate matter (PM) emissions that must be controlled to meet state air pollution regulations. Three PM control devices, each of which can control these emissions to the same level, are being evaluated: (1) a high-energy wet scrubber (scrubber), (2) an electrostatic precipitator (ESP), and (3) a fabric filter (baghouse). Unlike the wet scrubber, the ESP and the baghouse each recover salable cement dust, and, accordingly, revenue can be attributed to those two options. Two scenarios are visualized, with after-tax hurdle rates of $6 \%$ and $18 \%$, respectively. The economic specifications for the three devices are as follows:

| Parameter <br> (all revenues and costs in 2002 dollars) | Control device |  |  |
| :--- | :---: | :---: | :---: |
|  | Scrubber | ESP | Baghouse |
| Life (years) | 10 | 20 | 15 |
| Marginal tax rate | 0.52 | 0.52 | 0.52 |
| Hurdle rate (after tax) |  |  |  |
| - Scenario "A" | 0.06 | 0.06 | 0.06 |
| - Scenario "B" | 0.18 | 0.18 | 0.18 |
| Revenue | 0 | $\$ 290,000$ | $\$ 290,000$ |
| Total capital investment | $\$ 5,300,000$ | $\$ 9,750,000$ | $\$ 7,870,000$ |
| Total annual cost | $2,770,000$ | $1,840,000$ | $2,345,000$ |
| Salvage value | 0 | 0 | 0 |
| Depreciation (straight line) | 530,000 | 487,500 | 524,667 |

For each of the two scenarios, determine the most economical control device to control the dust from the ball mill.

## Calculation Procedure

1. Select the most appropriate evaluation method. Note that the control devices have different economic lives. Thus, neither the net present worth nor the internal rate of return method can be used, as both require that all options have the same economic life. However, the equivalent uniform annual revenue method can be used, as this restriction does not apply to it.
2. Determine the EUAR for each option, assuming a $\mathbf{6 \%}$ hurdle rate. Following the procedure of Example 18.7, calculate for each option the undiscounted net cash flow, the capital recovery factor, the capital recovery cost, and the EUAR. The results are as follows:

| Cost/cost factor (2002 dollars) | Control device |  |  |
| :---: | :---: | :---: | :---: |
|  | Scrubber | ESP | Baghouse |
| NCF | -\$1,054,000 | -\$490,500 | -\$713,573 |
| CRF (rounded) | 0.1359 | 0.0872 | 0.1030 |
| CRC | 720,100 | 850,049 | 810,317 |
| EUAR | -\$1,774,100 | -\$1,340,540 | -\$1,523,890 |

Under this scenario, the most economical control device is the ESP, as its EUAR is the largest (i.e., least negative) of the three. (Put another way, it has the lowest equivalent uniform annual cost.)
3. Determine the EUAR for each option, assuming an $\mathbf{1 8 \%}$ hurdle rate. Repeat Step 2, but with the $18 \%$ hurdle rate. In this case, the results are as follows:

|  | Control device |  |  |
| :--- | ---: | ---: | ---: |
| Cost/cost factor <br> $(2002$ dollars) | Scrubber | ESP | Baghouse |
| NCF | $-\$ 1,054,000$ | $-\$ 490,500$ | $-\$ 713,573$ |
| $C R F$ (rounded) | 0.2225 | 0.1868 | 0.1964 |
| $C R C$ | $1,179,328$ | $1,821,495$ | $1,545,690$ |
| $E U A R$ | $-\$ 2,233,328$ | $-\$ 2,311,995$ | $-\$ 2,259,263$ |

Under this scenario, the most economical control device is the wet scrubber, as it has the least negative EUAR.

Related Calculations. Clearly, the EUAR and the selection of the most economical control device depend on the hurdle rate, even when the other inputs are held constant. Moreover, a given firm's hurdle rate can vary according to general economic conditions, the expected risk associated with a project, and other factors. Thus, the control device selection in this hypothetical situation or in any similar, real-world situation could also be affected by these factors.

In this problem, the analysis is done on an after-tax basis. However, the analysis could just as well be performed on a before-tax basis, using a pre-tax hurdle rate. If so, the depreciation term would be zero and the net cash flow equation would simplify to

$$
N C F=\text { revenue }-T A C
$$

and the EUAR expression would reduce to

$$
E U A R=\text { revenue }-T A C-C R C
$$

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# OTHER CHEMICAL ENGINEERING CALCULATIONS* 

\author{
19.1 STEAM MOLLIER DIAGRAM AND STEAM-TABLE USE 19.1 <br> 19.2 INTERPOLATION OF STEAM-TABLE VALUES 19.4 <br> 19.3 CONSTANT-PRESSURE STEAM PROCESS 19.6 <br> 19.4 CONSTANT-VOLUME STEAM PROCESS 19.8 <br> 19.5 CONSTANT-TEMPERATURE STEAM PROCESS 19.10 <br> 19.6 CONSTANT-ENTROPY STEAM PROCESS 19.11 <br> 19.7 IRREVERSIBLE ADIABATIC EXPANSION OF STEAM 19.13 <br> ```
19.8 IRREVERSIBLE ADIABATIC STEAM COMPRESSION 19.14

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}
19.12 WATER-SOFTENER SELECTION AND ANALYSIS 19.20
19.13 COMPLETE DEIONIZATION OF WATER 19.22
19.14 COOLING-POND SIZE FOR A KNOWN HEAT LOAD 19.24
19.15 PROCESS TEMPERATURE-CONTROL ANALYSIS 19.26
19.16 CONTROL-VALVE SELECTION FOR PROCESS CONTROL 19.27
19.17 CONTROL-VALVE
CHARACTERISTICS AND RANGEABILITY 19.29
19.18 CAVITATION, SUBCRITICAL, AND CRITICAL-FLOW CONSIDERATIONS IN CONTROLLER SELECTION 19.30
19.19 INDIRECT DRYING OF SOLIDS 19.34
19.20 VACUUM DRYING OF SOLIDS 19.36
19.21 ESTIMATING THERMODYNAMIC AND TRANSPORT PROPERTIES OF WATER 19.37
19.22 ASSESSING THE ADEQUACY OF VESSEL-LIFTING EARS 19.39

\subsection*{19.1 STEAM MOLLIER DIAGRAM AND STEAM-TABLE USE}
(1) Determine from the Mollier diagram for steam: (a) the enthalpy of 100 pisa ( 689.5 kPa ) saturated steam; (b) the enthalpy of \(10 \mathrm{psia}(68.9 \mathrm{kPa})\) steam containing \(40 \%\) moisture; \((c)\) the enthalpy of \(100 \mathrm{psia}(689.5 \mathrm{kPa})\) steam at \(600^{\circ} \mathrm{F}\left(315.6^{\circ} \mathrm{C}\right)\). (2) Determine from the steam tables: (a) the enthalpy, specific volume, and entropy of steam at \(145.3 \mathrm{psig}(1001.8 \mathrm{kPag}) ;(b)\) the enthalpy and specific volume of superheated steam at \(1100 \mathrm{psia}(7584.2 \mathrm{kPa})\) and \(600^{\circ} \mathrm{F}\left(315.6^{\circ} \mathrm{C}\right) ;(c)\) the enthalpy and specific volume of high-pressure steam at \(7500 \mathrm{psia}(51,710.7 \mathrm{kPa})\) and \(1200^{\circ} \mathrm{F}\left(648.9^{\circ} \mathrm{C}\right) ;(d)\) the enthalpy, specific volume, and entropy of \(10-\mathrm{psia}(68.9-\mathrm{kPa})\) steam containing \(40 \%\) moisture.
*Unless otherwise indicated, the material in this section is taken from T. G. Hicks, Standard Handbook of Engineering Calculations, McGraw-Hill.


FIGURE 19.1 Simplified Mollier diagram for steam. (Note: \(1 \mathrm{psia}=6.895 \mathrm{kPa}\).)

\section*{Procedure}

\section*{1. Use the pressure and saturation (or moisture) lines to find enthalpy}
a. Enter the Mollier diagram by finding the \(100-\mathrm{psia}(689.5-\mathrm{kPa}\) ) pressure line (Fig. 19.1). In the Mollier diagram for steam, the pressure lines slope upward to the right from the lower left-hand corner. For saturated steam, the enthalpy is read at the intersection of the pressure line with the saturation curve \(\operatorname{cef}\) (Fig. 19.1).

Thus, project along the \(100-\mathrm{psia}(689.5-\mathrm{kPa})\) pressure curve until it intersects the saturation curve, point \(g\). From here project horizontally to the left-hand scale and read the enthalpy of \(100-\mathrm{psia}(689.5-\mathrm{kPa})\) saturated steam as \(1187 \mathrm{Btu} / \mathrm{lb}(2761.0 \mathrm{~kJ} / \mathrm{kg})\). (The Mollier diagram in Fig. 19.1 has fewer grid divisions than large-scale diagrams to permit easier location of the major elements of the diagram.)
b. On a Mollier diagram, the enthalpy of wet steam is found at the intersection of the saturation pressure line with the percent moisture curve corresponding to the amount of moisture in the
steam. In a Mollier diagram for steam, the moisture curves slope down-ward to the right from the saturated liquid line \(c d\) (Fig. 19.1).

To find the enthalpy of \(10-\mathrm{psia}(68.9-\mathrm{kPa})\) steam containing \(40 \%\) moisture, project along the \(10-\mathrm{psia}(68.9-\mathrm{kPa})\) saturation pressure line until the \(40 \%\) moisture curve is intersected. From here project horizontally to the left-hand scale and read the enthalpy of \(10-\mathrm{psia}(68.9-\mathrm{kPa})\) wet steam containing \(40 \%\) moisture as \(750 \mathrm{Btu} / \mathrm{lb}(1744.5 \mathrm{~kJ} / \mathrm{kg})\).

\section*{2. Find the steam properties from the steam tables}
a. Steam tables normally list absolute pressures or temperature in degrees Fahrenheit as one of their arguments. Therefore, when the steam pressure is given in terms of a gage reading, it must be converted to an absolute pressure before the table can be entered. To convert gage pressure to absolute pressure, add 14.7 to the gage pressure, or \(p_{a}=p_{g}+14.7\). In this instance, \(p_{a}=\) \(145.3+14.7=160.0 \mathrm{psia}(1103.2 \mathrm{kPa})\). Once the absolute pressure is known, enter the saturation pressure table of the steam table at this value and project horizontally to the desired values. For \(160-\mathrm{psia}(1103.2-\mathrm{kPa})\) steam, using the ASME or Keenan and Keyes, Thermodynamic Properties of Steam, the enthalpy of evaporation \(h_{f g}=859.2 \mathrm{Btu} / \mathrm{lb}(1998.5 \mathrm{~kJ} / \mathrm{kg})\); enthalpy of saturated vapor \(h_{g}=1195.1 \mathrm{Btu} / \mathrm{lb}(2779.8 \mathrm{~kJ} / \mathrm{kg})\), read from the respective columns of the steam tables. The specific volume \(v_{g}\) of the saturated vapor of \(160-\mathrm{psia}(1103.2-\mathrm{kPa})\) steam is, from the tables, \(2.834 \mathrm{ft}^{3} / \mathrm{lb}\left(0.18 \mathrm{~m}^{3} / \mathrm{kg}\right)\), and the entropy \(s_{g}\) is \(1.5640 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)\left[6.55 \mathrm{~kJ} /(\mathrm{kg})\left({ }^{\circ} \mathrm{C}\right)\right]\).
b. Every steam table contains a separate tabulation of properties of superheated steam. To enter the superheated steam table, two arguments are needed-the absolute pressure and the temperature of the steam in degrees Fahrenheit. To determine the properties of \(1100-\mathrm{psia}(7584.5-\mathrm{kPa})\) steam at \(600^{\circ} \mathrm{F}\left(315.6^{\circ} \mathrm{C}\right)\), enter the superheated steam table at the given absolute pressure and project horizontally from this absolute pressure ( 1100 psia or 7584.5 kPa ) to the column corresponding to the superheated temperature \(\left(600^{\circ} \mathrm{F}\right.\) or \(\left.315.6^{\circ} \mathrm{C}\right)\) to read the enthalpy of the superheated vapor as \(h=1236.7 \mathrm{Btu} / \mathrm{lb}(2876.6 \mathrm{~kJ} / \mathrm{kg})\) and the specific volume of the superheated vapor \(v=0.4532 \mathrm{ft}^{3} / \mathrm{lb}\left(0.03 \mathrm{~m}^{3} / \mathrm{kg}\right)\).
c. For high-pressure steam use the ASME Steam Table, entering it in the same manner as the superheated steam table. Thus, for \(7500-\mathrm{psia}(51,712.5 \mathrm{kPa})\) steam at \(1200^{\circ} \mathrm{F}\left(648.9^{\circ} \mathrm{C}\right)\), the enthalpy of the superheated vapor is \(1474.9 \mathrm{Btu} / \mathrm{lb}(3430.6 \mathrm{~kJ} / \mathrm{kg})\), and the specific volume of the superheated vapor is \(0.1060 \mathrm{ft}^{3} / \mathrm{lb}\left(0.0066 \mathrm{~m}^{3} / \mathrm{kg}\right)\).
d. To determine the enthalpy, specific volume, and the entropy of wet steam having \(y\) percent moisture by using steam tables instead of the Mollier diagram, apply these relations: \(h=h_{g}-y h_{f g} / 100\); \(v=v_{g}-y v_{f g} / 100\); and \(s=s_{g}-y s_{f g} / 100\), where \(y\) is percent moisture expressed as a whole number. For \(10-\mathrm{psia}(68.9-\mathrm{kPa})\) steam containing \(40 \%\) moisture, obtain the needed values \(h_{g}, h_{f g}\), \(v_{g}, v_{f g}, s_{g}\), and \(s_{f g}\) from the saturation-pressure steam table and substitute in the preceding relations. Thus,
\[
\begin{aligned}
& h=1143.3-\frac{40(982.1)}{100}=750.5 \mathrm{Btu} / \mathrm{lb}(1745.7 \mathrm{~kJ} / \mathrm{kg}) \\
& v=38.42-\frac{40(38.40)}{100}=23.06 \mathrm{ft}^{3} / \mathrm{lb}\left(1.44 \mathrm{~m}^{3} / \mathrm{kg}\right) \\
& s=1.7876-\frac{40(1.5041)}{100}=1.1860 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)\left[4.97 \mathrm{~kJ} /(\mathrm{kg})\left({ }^{\circ} \mathrm{C}\right)\right]
\end{aligned}
\]

Note that in Keenan and Keyes, Thermodynamic Properties of Steam, \(v_{f g}\) is not tabulated. Therefore, this value must be obtained by subtraction of the tabulated values, or \(v_{f g}=v_{g}-v_{f}\). The value \(v_{f g}\) thus obtained is used in the relation for the volume of the wet steam. For \(10-\mathrm{psia}\) \((68.9-\mathrm{kPa})\) steam containing \(40 \%\) moisture \(v_{g}=38.42 \mathrm{ft}^{3} / \mathrm{lb}\left(2.398 \mathrm{~m}^{3} / \mathrm{kg}\right)\), and \(v_{f}=0.017 \mathrm{ft}^{3} / \mathrm{lb}\) \(\left(0.0011 \mathrm{~m}^{3} / \mathrm{kg}\right)\). Then, \(v_{f g}=38.42-0.017=38.403 \mathrm{ft}^{3} / \mathrm{lb}\left(1.773 \mathrm{~m}^{3} / \mathrm{kg}\right)\).

In some instances, the quality of steam may be given instead of its moisture content in percent. The quality of steam is the percent vapor in the mixture. In the preceding calculation, the quality of the steam is \(60 \%\) because \(40 \%\) is moisture. Thus, quality \(=1-m\), where \(m\) is percent moisture, expressed as a decimal.

\subsection*{19.2 INTERPOLATION OF STEAM-TABLE VALUES}
(1) Determine the enthalpy, specific volume, entropy, and temperature of saturated steam at 151 psia \((1041.1 \mathrm{kPa})\). (2) Determine the enthalpy, specific volume, entropy, and pressure of saturated steam at \(261^{\circ} \mathrm{F}\left(127.2^{\circ} \mathrm{C}\right)\). (3) Determine the pressure of steam at \(1000^{\circ} \mathrm{F}\left(537.8^{\circ} \mathrm{C}\right)\) if its specific volume is \(2.6150 \mathrm{ft}^{3} / \mathrm{lb}\left(0.16 \mathrm{~m}^{3} / \mathrm{kg}\right)\). (4) Determine the enthalpy, specific volume, and entropy of \(300-\mathrm{psia}\) \((2068.5-\mathrm{kPa})\) steam at \(567.22^{\circ} \mathrm{F}\left(297.3^{\circ} \mathrm{C}\right)\).

\section*{Calculation Procedure}
1. Use the saturation-pressure steam table. Study of the saturation-pressure table shows that there is no pressure value listed for \(151 \mathrm{psia}(1041.1 \mathrm{kPa})\). Therefore, it will be necessary to interpolate between the next higher and next lower tabulated pressure values. In this instance, these values are 152 and 150 psia ( 1048.0 and 1034.3 kPa ), respectively. The pressure for which properties are being found ( 151 psia or 1041.1 kPa ) is called the "intermediate pressure." At 152 psia (1048.0 \(\mathrm{kPa}), h_{g}=1194.3 \mathrm{Btu} / \mathrm{lb}(2777.5 \mathrm{~kJ} / \mathrm{kg}) ; v_{g}=2.977 \mathrm{ft}^{3} / \mathrm{lb}\left(0.19 \mathrm{~m}^{3} / \mathrm{kg}\right) ; s_{g}=1.5683 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)\) \(\left[6.57 \mathrm{~kJ} /(\mathrm{kg})\left({ }^{\circ} \mathrm{C}\right)\right]\); and \(t=359.46^{\circ} \mathrm{F}\left(181.9^{\circ} \mathrm{C}\right)\). At \(150 \mathrm{psia}(1034.3 \mathrm{kPa}), h_{g}=1194.1 \mathrm{Btu} / \mathrm{lb}(2777.5\) \(\mathrm{kJ} / \mathrm{kg}) ; v_{g}=3.015 \mathrm{ft}^{3} / \mathrm{lb}\left(0.19 \mathrm{~m}^{3} / \mathrm{kg}\right) ; s_{g}=1.5694 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)\left[6.57 \mathrm{~kJ} /(\mathrm{kg})\left({ }^{\circ} \mathrm{C}\right)\right]\); and \(t=358.42^{\circ} \mathrm{F}\) ( \(181.3^{\circ} \mathrm{C}\) ).

For the enthalpy, note that as the pressure increases, so does \(h_{g}\). Therefore, the enthalpy at 151 psia ( 1041.1 kPa ) (the intermediate pressure) will equal the enthalpy at 150 psia ( 1034.3 kPa ) (the lower pressure used in the interpolation) plus the proportional change (difference between the intermediate pressure and the lower pressure) for a \(1-\mathrm{psi}(6.9-\mathrm{kPa})\) pressure increase. Or, at any higher pressure, \(h_{g i}=h_{g l}+\left[\left(p_{i}-p_{l}\right) /\left(p_{h}-p_{l}\right)\right]\left(h_{h}-h_{l}\right)\), where \(h_{g i}\) is enthalpy at the intermediate pressure, \(h_{g l}\) is enthalpy at the lower pressure used in the interpolation; \(h_{h}\) is enthalpy at the higher pressure used in the interpolation, \(p_{i}\) is intermediate pressure, and \(p_{h}\) and \(p_{l}\) are higher and lower pressures used in the interpolation. Thus, using the enthalpy values obtained from the steam table for 150 and 152 psia (1034.3 and 1048.0 kPa\(), h_{g i}=1194.1+[(151-150) /(152-150)](1194.3-1194.1)=1194.2 \mathrm{Btu} / \mathrm{lb}\) \((2777.7 \mathrm{~kJ} / \mathrm{kg})\) at \(151 \mathrm{psia}(1041.1 \mathrm{kPa})\) saturated.

Next, study the steam table to determine the direction of change of specific volume between the lower and higher pressures. This study shows that the specific volume decreases as the pressure increases. Therefore, the specific volume at \(151 \mathrm{psia}(1041.1 \mathrm{kPa}\) ) (the intermediate pressure) will equal the specific volume at \(150 \mathrm{psia}(1034.3 \mathrm{kPa})\) (the lower pressure used in the interpolation) minus the proportional change (difference between the intermediate pressure and the lower interpolating pressure) for a 1-psi (6.9-kPa) pressure incease. Or, at any pressure, \(v_{g i}=v_{g l}-\left[\left(p_{i}-p_{l}\right) /\left(p_{h}-\right.\right.\) \(\left.\left.p_{l}\right)\right]\left(v_{l}-v_{h}\right)\), where the subscripts are the same as above and \(v\) is specific volume at the respective pressure. With the volume values obtained from steam tables for 150 and \(152 \mathrm{psia}(1034.3\) and 1048.0 kPa ), \(v_{g i}=3.015-[(151-150) /(152-150)](3.015-2.977)=2.996 \mathrm{ft}^{3} / \mathrm{lb}\left(0.19 \mathrm{~m}^{3} / \mathrm{kg}\right)\) at 151 psia \((1041.1 \mathrm{kPa})\) saturated.

Study of the steam table for the direction of entropy change shows that entropy, like specific volume, decreases as the pressure increases. Therefore, the entropy at \(151 \mathrm{psia}(1041.1 \mathrm{kPa})\) (the intermediate pressure) will equal the entropy at 150 psia ( 1034.3 kPa ) (the lower pressure used in the interpolation) minus the proportional change (difference between the intermediate pressure and the lower interpolating pressure) for a \(1-\mathrm{psi}(6.9-\mathrm{kPa})\) pressure increase. Or, at any higher pressure, \(s_{g i}=s_{g l}-\left[\left(p_{i}-p_{l}\right) /\left(p_{h}-p_{l}\right)\right]\left(s_{l}-s_{h}\right)=1.5164-[(151-150) /(152-150)](1.5694-\) \(1.5683)=1.56885 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)\left[6.6 \mathrm{~kJ} /(\mathrm{kg})\left({ }^{\circ} \mathrm{C}\right)\right]\) at \(151 \mathrm{psia}(1041.1 \mathrm{kPa})\) saturated.

Study of the steam table for the direction of temperature change shows that the saturation temperature, like enthalpy, increases as the pressure increases. Therefore, the temperature at 151 psia \((1041.1 \mathrm{kPa})\) (the intermediate pressure) will equal the temperature at \(150 \mathrm{psia}(1034.3 \mathrm{kPa})\) (the lower pressure used in the interpolation) plus the proportional change (difference between the intermediate pressure and the lower interpolating pressure) for a \(1-\mathrm{psi}(6.9-\mathrm{kPa})\) increase. Or, at any higher pressure, \(t_{g i}=t_{g l}+\left[\left(p_{i}-p_{l}\right) /\left(p_{h}-p_{l}\right)\right]\left(t_{h}-t_{l}\right)=358.42+[(151-150) /(152-\) \(150)](359.46-358.42)=358.94^{\circ} \mathrm{F}\left(181.6^{\circ} \mathrm{C}\right)\) at \(151 \mathrm{psia}(1041.1 \mathrm{kPa})\) saturated.
2. Use the saturation-temperature steam table. Study of the saturation-temperature table shows that there is no temperature value listed for \(261^{\circ} \mathrm{F}\left(127.2^{\circ} \mathrm{C}\right)\). Therefore, it will be necessary to interpolate between the next higher and next lower tabulated temperature values. In this instance, these values are 262 and \(260^{\circ} \mathrm{F}\left(127.8\right.\) and \(126.7^{\circ} \mathrm{C}\) ), respectively. The temperature for which properties are being found \(\left(261^{\circ} \mathrm{F}\right.\) or \(\left.127.2^{\circ} \mathrm{C}\right)\) is called the "intermediate temperature."

At \(262^{\circ} \mathrm{F}\left(127.8^{\circ} \mathrm{C}\right), h_{g}=1168.0 \mathrm{Btu} / \mathrm{lb}(2716.8 \mathrm{~kJ} / \mathrm{kg}) ; v_{g}=11.396 \mathrm{ft}^{3} / \mathrm{lb}\left(0.71 \mathrm{~m}^{3} / \mathrm{kg}\right) ; s_{g}=\) \(1.6833 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)\left[7.05 \mathrm{~kJ} /(\mathrm{kg})\left({ }^{\circ} \mathrm{C}\right)\right]\); and \(p_{g}=36.646 \mathrm{psia}(252.7 \mathrm{kPa})\). At \(260^{\circ} \mathrm{F}\left(126.7^{\circ} \mathrm{C}\right)\), \(h_{g}=1167.3 \mathrm{Btu} / \mathrm{lb}(2715.1 \mathrm{~kJ} / \mathrm{kg}) ; v_{g}=11.763 \mathrm{ft}^{3} / \mathrm{lb}\left(0.73 \mathrm{~m}^{3} / \mathrm{kg}\right) ; s_{g}=1.6860 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)\) \(\left[7.06 \mathrm{~kJ} /(\mathrm{kg})\left({ }^{\circ} \mathrm{C}\right)\right]\); and \(p_{g}=35.429 \mathrm{psia}(244.3 \mathrm{kPa})\).

For enthalpy, note that as the temperature increases, so does \(h_{g}\). Therefore, the enthalpy at \(261^{\circ} \mathrm{F}\) \(\left(127.2^{\circ} \mathrm{C}\right)\) (the intermediate temperature) will equal the enthalpy at \(260^{\circ} \mathrm{F}\left(126.7^{\circ} \mathrm{C}\right)\) (the lower temperature used in the interpolation) plus the proportional change (difference between the intermediate temperature and the lower temperature) for a \(1^{\circ} \mathrm{F}\left(0.6^{\circ} \mathrm{C}\right)\) temperature increase. Or, at any higher temperature, \(h_{g i}=h_{g l}+\left[\left(t_{i}-t_{l}\right) /\left(t_{h}-t_{l}\right)\right]\left(h_{h}-h_{l}\right)\), where \(h_{g l}\) is enthalpy at the lower temperature used in the interpolation, \(h_{h}\) is enthalpy at the higher temperature used in the interpolation, \(t_{i}\) is intermediate temperature, and \(t_{h}\) and \(t_{l}\) are higher and lower temperatures used in the interpolation. Thus, using the enthalpy values obtained from the steam table for 260 and \(262^{\circ} \mathrm{F}\left(126.7\right.\) and \(\left.127.8^{\circ} \mathrm{C}\right), h_{g i}=\) \(1167.3+[(261-260) /(262-260)](1168.0-1167.3)=1167.65 \mathrm{Btu} / \mathrm{lb}(2716.0 \mathrm{~kJ} / \mathrm{kg})\) at \(261^{\circ} \mathrm{F}\) \(\left(127.2^{\circ} \mathrm{C}\right)\) saturated.

Next, study the steam table to determine the direction of change of specific volume between the lower and higher temperatures. This study shows that the specific volume decreases as the pressure increases. Therefore, the specific volume at \(261^{\circ} \mathrm{F}\left(127.2^{\circ} \mathrm{C}\right)\) (the intermediate temperature) will equal the specific volume at \(260^{\circ} \mathrm{F}\left(126.7^{\circ} \mathrm{C}\right)\) (the lower temperature used in the interpolation) minus the proportional change (difference between the intermediate temperature and the lower interpolating temperature) for a \(1^{\circ} \mathrm{F}\left(0.6^{\circ} \mathrm{C}\right)\) temperature increase. Or, at any higher temperature, \(v_{g i}=v_{g l}-\left[\left(t_{i}-t_{l}\right) /\left(t_{h}-t_{l}\right)\right]\left(v_{l}-v_{h}\right)=11.763-[(261-260) /(262-260)](11.763-\) \(11.396)=11.5795 \mathrm{ft}^{3} / \mathrm{lb}\left(0.7 \mathrm{~m}^{3} / \mathrm{kg}\right)\) at \(261^{\circ} \mathrm{F}\left(127.2^{\circ} \mathrm{C}\right)\) saturated.

Study of the steam table for the direction of entropy change shows that entropy, like specific volume, decreases as the temperature increases. Therefore, the entropy at \(261^{\circ} \mathrm{F}\left(127.2^{\circ} \mathrm{C}\right)\) (the intermediate temperature) will equal the entropy at \(260^{\circ} \mathrm{F}\left(126.7^{\circ} \mathrm{C}\right)\) (the lower temperature used in the interpolation) minus the proportional change (difference between the intermediate temperature and the lower temperature) for a \(1^{\circ} \mathrm{F}\left(0.6^{\circ} \mathrm{C}\right)\) temperature increase. Or, at any higher temperature, \(s_{g i}=s_{g l}-\left[\left(t_{i}-t_{l}\right) /\left(t_{h}-t_{l}\right)\right]\left(s_{l}-s_{h}\right)=1.6860-[(261-260) /(262-260)](1.6860-1.6833)=\) 1.68465 Btu/(lb) \(\left({ }^{\circ} \mathrm{F}\right)\left[7.1 \mathrm{~kJ} /(\mathrm{kg})\left({ }^{\circ} \mathrm{C}\right)\right]\) at \(261^{\circ} \mathrm{F}\left(127.2^{\circ} \mathrm{C}\right)\).

Study of the steam table for the direction of pressure change shows that the saturation pressure, like enthalpy, increases as the temperature increases. Therefore, the pressure at \(261^{\circ} \mathrm{F}\left(127.2^{\circ} \mathrm{C}\right)\) (the intermediate temperature) will equal the pressure at \(260^{\circ} \mathrm{F}\left(126.7^{\circ} \mathrm{C}\right)\) (the lower temperature used in the interpolation) plus the proportional change (difference between the intermediate temperature and the lower interpolating temperature) for a \(1^{\circ} \mathrm{F}\left(0.6^{\circ} \mathrm{C}\right)\) temperature increase. Or, at any higher temperature, \(p_{g i}=p_{g l}+\left[\left(t_{i}-t_{l}\right) /\left(t_{h}-t_{l}\right)\right]\left(p_{h}-p_{l}\right)=35.429+[(261-260) /(262-\) \(260)](36.646-35.429)=36.0375 \mathrm{psia}(248.5 \mathrm{kPa})\) at \(261^{\circ} \mathrm{F}\left(127.2^{\circ} \mathrm{C}\right)\) saturated.
3. Use the superheated-steam table. Choose the superheated-steam table for steam at \(1000^{\circ} \mathrm{F}\) \(\left(537.9^{\circ} \mathrm{C}\right)\) and \(2.6150 \mathrm{ft}^{3} / \mathrm{lb}\left(0.16 \mathrm{~m}^{3} / \mathrm{kg}\right)\) because the highest temperature at which saturated steam can exist is \(705.4^{\circ} \mathrm{F}\left(374.1^{\circ} \mathrm{C}\right)\). This is also the highest temperature tabulated in some saturatedtemperature tables. Therefore, the steam is superheated when at a temperature of \(1000^{\circ} \mathrm{F}\left(537.9^{\circ} \mathrm{C}\right)\).

Look down the \(1000^{\circ} \mathrm{F}\left(537.9^{\circ} \mathrm{C}\right)\) columns in the superheat table until a specific-volume value of 2.6150 is found. This occurs between \(325 \mathrm{psia}(2240.9 \mathrm{kPa}, v=2.636\) or 0.16 ) and 330 psia ( \(2275.4 \mathrm{kPa}, v=2.596\) or 0.16 ). Since there is no volume value exactly equal to 2.6150 tabulated, it will be necessary to interpolate. List the values from the steam table thus: \(p=325 \mathrm{psia}(2240.9 \mathrm{kPa})\); \(t=1000^{\circ} \mathrm{F}\left(537.9^{\circ} \mathrm{C}\right) ; v=2.636 \mathrm{ft}^{3} / \mathrm{lb}\left(0.16 \mathrm{~m}^{3} / \mathrm{kg}\right)\); and \(p=330 \mathrm{psia}(2275.4 \mathrm{kPa}) ; t=1000^{\circ} \mathrm{F}\) \(\left(537.9^{\circ} \mathrm{C}\right) ; v=2.596 \mathrm{ft}^{3} / \mathrm{lb}\left(0.16 \mathrm{~m}^{3} / \mathrm{kg}\right)\).

Note that as the pressure rises, at constant temperature, the volume decreases. Therefore, the intermediate (or unknown) pressure is found by subtracting from the higher interpolating pressure ( 330 psia or 2275.4 kPa in this instance) the product of the proportional change in the specific volume and the difference in the pressures used for the interpolation, or, \(p_{g i}=p_{h}-\left[\left(v_{i}-v_{h}\right) /\left(v_{l}-v_{h}\right)\right]\left(p_{h}-p_{l}\right)\), where the subscripts \(h, l\), and \(i\) refer to the high, low, and intermediate (or unknown) pressures, respectively. In this instance, \(p_{g i}=330-[(2.615-2.596) /(2.636-2.596)](330-325)=327.62\) psia \((2258.9 \mathrm{kPa})\) at \(1000^{\circ} \mathrm{F}\left(537.9^{\circ} \mathrm{C}\right)\) and a specific volume of \(2.6150 \mathrm{ft}^{3} / \mathrm{lb}\left(0.16 \mathrm{~m}^{3} / \mathrm{kg}\right)\).
4. Use the superheated-steam table. When given a steam pressure and temperature, determine, before performing any interpolation, the state of the steam. Do this by entering the saturation-pressure table at the given pressure and noting the saturation temperature. If the given temperature exceeds the saturation temperature, the steam is superheated. In this instance, the saturation-pressure table shows that at \(300 \mathrm{psia}(2068.5 \mathrm{kPa})\), the saturation temperature is \(417.33^{\circ} \mathrm{F}\left(214.1^{\circ} \mathrm{C}\right)\). Since the given temperature of the steam is \(567.22^{\circ} \mathrm{F}\left(297.3^{\circ} \mathrm{C}\right)\), the steam is superheated because its actual temperature is greater than the saturation temperature.

Enter the superheated-steam table at \(300 \mathrm{psia}(2068.5 \mathrm{kPa})\) and find the next temperature lower than \(567.22^{\circ} \mathrm{F}\left(297.3^{\circ} \mathrm{C}\right)\); this is \(560^{\circ} \mathrm{F}\left(293.3^{\circ} \mathrm{C}\right)\). Also find the next higher temperature; this is \(580^{\circ} \mathrm{F}\) \(\left(304.4^{\circ} \mathrm{C}\right)\). Tabulate the enthalpy, specific volume, and entropy for each of these temperatures thus: \(t=560^{\circ} \mathrm{F}\left(293.3^{\circ} \mathrm{C}\right) ; h=1292.5 \mathrm{Btu} / \mathrm{lb}(3006.4 \mathrm{~kJ} / \mathrm{kg}) ; v=1.9128 \mathrm{ft}^{3} / \mathrm{lb}\left(0.12 \mathrm{~m}^{3} / \mathrm{kg}\right) ; s=1.6054\) \(\mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)\left[6.72 \mathrm{~kJ} /(\mathrm{kg})\left({ }^{\circ} \mathrm{C}\right)\right]\); and \(t=580^{\circ} \mathrm{F}\left(304.4^{\circ} \mathrm{C}\right) ; h=1303.7 \mathrm{Btu} / \mathrm{lb}(3032.4 \mathrm{~kJ} / \mathrm{kg}) ; v=\) \(1.9594 \mathrm{ft}^{3} / \mathrm{lb}\left(0.12 \mathrm{~m}^{3} / \mathrm{kg}\right) ; s=1.6163 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)\left[6.77 \mathrm{~kJ} /(\mathrm{kg})\left({ }^{\circ} \mathrm{C}\right)\right]\).

Use the same procedures for each property-enthalpy, specific volume, and entropy-as given in step 2, but change the sign between the lower volume and entropy and the proportional factor (temperature in this instance), because for superheated steam, the volume and entropy increase as the steam temperature increases. Thus,
\[
\begin{aligned}
h_{g i} & =1292.5+\frac{567.22-560}{580-560}(1303.7-1292.5)=1269.6 \mathrm{Btu} / \mathrm{lb}(3015.9 \mathrm{~kJ} / \mathrm{kg}) \\
v_{g i} & =1.9128+\frac{567.22-560}{580-560}(1.9594-1.9128)=1.9296 \mathrm{ft}^{3} / \mathrm{lb}\left(0.12 \mathrm{~m}^{3} / \mathrm{kg}\right) \\
s_{g i} & =1.6054+\frac{567.22-560}{580-560}(1.6163-1.6054) \\
& =1.6093 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)\left[6.7 \mathrm{~kJ} /(\mathrm{kg})\left({ }^{\circ} \mathrm{C}\right)\right]
\end{aligned}
\]

Note: Also observe the direction of change of a property before interpolating. Use a plus or minus sign between the higher interpolating value and the proportional change depending on whether the tabulated value increases \((+)\) or decreases \((-)\).

\subsection*{19.3 CONSTANT-PRESSURE STEAM PROCESS}

Three pounds of wet steam containing \(15 \%\) moisture and initially at a pressure of 400 psia \((2758.0 \mathrm{kPa})\) expands at constant pressure \((P=C)\) to \(600^{\circ} \mathrm{F}\left(315.6^{\circ} \mathrm{C}\right)\). Determine the initial temperature \(T_{1}\), enthalpy \(H_{1}\), internal energy \(E_{1}\), volume \(V_{1}\), entropy \(S_{1}\), final enthalpy \(H_{2}\), final internal energy


FIGURE 19.2 Constant-pressure process (Example 19.3).
\(E_{2}\), final volume \(V_{2}\), final entropy \(S_{2}\), heat added to the steam \(Q_{1}\), work output \(W_{2}\), change in internal energy \(\Delta E\), change in specific volume \(\Delta V\), and change in entropy \(\Delta S\).

\section*{Calculation Procedure}
1. Determine the initial steam temperature from the steam tables. Enter the saturation-pressure table at \(400 \mathrm{psia}(2758.0 \mathrm{kPa})\) and read the saturation temperature as \(444.59^{\circ} \mathrm{F}\left(229.2^{\circ} \mathrm{C}\right)\).
2. Correct the saturation values for the moisture of the steam in the initial state. Sketch the process on a pressure-volume \((P-V)\), Mollier \((H-S)\), or temperature-entropy \((T-S)\) diagram, Fig. 19.2. In state \(1, y=\) moisture content \(=15 \%\). Using the appropriate values from the saturation-pressure steam table for \(400 \mathrm{psia}(2758.0 \mathrm{kPa})\), correct them for a moisture content of \(15 \%\) :
\[
\begin{aligned}
& H_{1}=h_{g}-y h_{f g}=1204.5-0.15(780.5)=1087.4 \mathrm{Btu} / \mathrm{lb}(2529.3 \mathrm{~kJ} / \mathrm{kg}) \\
& E_{1}=u_{g}-y u_{f g}=1118.5-0.15(695.9)=1015.1 \mathrm{Btu} / \mathrm{lb}(2361.1 \mathrm{~kJ} / \mathrm{kg}) \\
& V_{1}=v_{g}-y v_{f g}=1.1613-0.15(1.1420)=0.990 \mathrm{ft}^{3} / \mathrm{lb}\left(0.06 \mathrm{~m}^{3} / \mathrm{kg}\right) \\
& S_{1}=s_{g}-y s_{f g}=1.4844-0.15(0.8630)=1.2945 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)\left[5.4 \mathrm{~kJ} /(\mathrm{kg})\left({ }^{\circ} \mathrm{C}\right)\right]
\end{aligned}
\]
3. Determine the steam properties in the final state. Since this is a constant-pressure process, the pressure in state 2 is \(400 \mathrm{psia}(2758.0 \mathrm{kPa})\), the same as state 1 . The final temperature is given as \(600^{\circ} \mathrm{F}\left(315.6^{\circ} \mathrm{C}\right)\). This is greater than the saturation temperature of \(444.59^{\circ} \mathrm{F}\left(229.2^{\circ} \mathrm{C}\right)\). Hence, the steam is superheated when in state 2 . Use the superheated-steam tables, entering at 400 psia ( 2758.8 \(\mathrm{kPa})\) and \(600^{\circ} \mathrm{F}\left(315.6^{\circ} \mathrm{C}\right)\). At this condition, \(H_{2}=1306.9 \mathrm{Btu} / \mathrm{lb}(3039.8 \mathrm{~kJ} / \mathrm{kg})\), and \(V_{2}=1.477\) \(\mathrm{ft}^{3} / \mathrm{lb}\left(0.09 \mathrm{~m}^{3} / \mathrm{kg}\right)\). Then, \(E_{2}=h_{2 g}-P_{2} V_{2} / J=1306.9-400(144)(1.477) / 778=1197.5 \mathrm{Btu} / \mathrm{lb}\) \((2785.4 \mathrm{~kJ} / \mathrm{kg})\). In this equation, the constant 144 converts psia to psfa , and \(J\) is the mechanical equivalent of heat and equals \(778 \mathrm{ft} \cdot \mathrm{lb} / \mathrm{Btu}(1 \mathrm{~N} \cdot \mathrm{~m} / \mathrm{J})\). From the steam tables, \(S_{2}=1.5894 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)\) \(\left[6.7 \mathrm{~kJ} /(\mathrm{kg})\left({ }^{\circ} \mathrm{C}\right)\right]\).
4. Compute the process inputs, outputs, and changes. \(W_{2}=\left(P_{1} / J\right)\left(V_{2}-V_{1}\right) m=\) \([400(144) / 778](1.4770-0.9900)(3)=108.1 \mathrm{Btu}(114.1 \mathrm{~kJ})\). In this equation, \(m\) is the weight of steam used in the process, which is \(3 \mathrm{lb}(1.4 \mathrm{~kg})\). Then,
\[
\begin{aligned}
& Q_{1}=\left(H_{2}-H_{1}\right) m=(1306.9-1087.4)(3)=658.5 \mathrm{Btu}(694.4 \mathrm{~kJ}) \\
& \Delta E=\left(E_{2}-E_{1}\right) m=(1197.5-1014.1)(3)=550.2 \mathrm{Btu}(580.2 \mathrm{~kJ}) \\
& \Delta V=\left(V_{2}-V_{1}\right) m=(1.4770-0.9900)(3)=1.461 \mathrm{ft}^{3}\left(0.041 \mathrm{~m}^{3}\right) \\
& \Delta S=\left(S_{2}-S_{1}\right) m=(1.5894-1.2945)(3)=0.8847 \mathrm{Btu} /{ }^{\circ} \mathrm{F}\left(1.680 \mathrm{~kJ} /{ }^{\circ} \mathrm{C}\right)
\end{aligned}
\]
5. Check the computations. The work output \(W_{2}\) should equal the change in internal energy plus the heat input, or \(W_{2}=E_{1}-E_{2}+Q_{1}=-550.2+658.5=108.3 \mathrm{Btu}(114.3 \mathrm{~kJ})\). This value very nearly equals the computed value of \(W_{2}=108.1 \mathrm{Btu}(114.1 \mathrm{~kJ})\), and is close enough for all normal engineering computations. The difference can be traced to calculator input errors. In computing the work output, the internal-energy change has a negative sign because there is a decrease in \(E\) during the process.

Related Calculations. Use this procedure for all constant-pressure steam processes.

\subsection*{19.4 CONSTANT-VOLUME STEAM PROCESS}

Five pounds \((2.3 \mathrm{~kg})\) of wet steam initially at \(120 \mathrm{psia}(827.4 \mathrm{kPa})\) with \(30 \%\) moisture is heated at constant volume \((V=C)\) to a final temperature of \(1000^{\circ} \mathrm{F}\left(537.8^{\circ} \mathrm{C}\right)\). Determine the initial temperature \(T_{1}\), enthalpy \(H_{1}\), internal energy \(E_{1}\), volume \(V_{1}\), final pressure \(P_{2}\), final enthalpy \(H_{2}\), final internal energy \(E_{2}\), final volume \(V_{2}\), heat added \(Q_{1}\), work output \(W\), change in internal energy \(\Delta E\), change in volume \(\Delta V\), and change in entropy \(\Delta S\).

\section*{Calculation Procedure}
1. Determine the initial steam temperature from the steam tables. Enter the saturation-pressure table at \(120 \mathrm{psia}(827.4 \mathrm{kPa})\), the initial pressure, and read the saturation temperature: \(T_{1}=341.25^{\circ} \mathrm{F}\) (171.8 \(\left.{ }^{\circ} \mathrm{C}\right)\).
2. Correct the saturation values for the moisture in the steam in the initial state. Sketch the process on \(P-V, H-S\), or \(T-S\) diagrams (Fig. 19.3). Using the appropriate values from the saturationpressure table for \(120 \mathrm{psia}(827.4 \mathrm{kPa})\), correct them for a moisture content of \(30 \%\) :
\[
\begin{aligned}
& H_{1}=h_{g}-y h_{f g}=1190.4-0.3(877.9)=927.0 \mathrm{Btu} / \mathrm{lb}(2156.2 \mathrm{~kJ} / \mathrm{kg}) \\
& E_{1}=u_{g}-y u_{f g}=1107.6-0.3(795.6)=868.9 \mathrm{Btu} / \mathrm{bb}(2021.1 \mathrm{~kJ} / \mathrm{kg}) \\
& V_{1}=v_{g}-y v_{f g}=3.7280-0.3(3.7101)=2.6150 \mathrm{ft} / \mathrm{lb}\left(0.16 \mathrm{~m}^{3} / \mathrm{kg}\right) \\
& S_{1}=s_{g}-y S_{f g}=1.5878-0.3(1.0962)=1.2589 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)\left[5.3 \mathrm{~kJ} /(\mathrm{kg})\left({ }^{\circ} \mathrm{C}\right)\right]
\end{aligned}
\]


FIGURE 19.3 Constant-volume process (Example 19.4).
3. Determine the steam volume in the final state. \(\quad T_{2}=1000^{\circ} \mathrm{F}\left(537.8^{\circ} \mathrm{C}\right)\), given. Since this is a constant-volume process, \(V_{2}=V_{1}=2.6150 \mathrm{ft}^{3} / \mathrm{lb}\left(0.16 \mathrm{~m}^{3} / \mathrm{kg}\right)\). The total volume of the vapor equals the product of the specific volume and the number of pounds of vapor used in the process, or total volume equals \(2.6150(5)=13.075 \mathrm{ft}^{3}\left(0.37 \mathrm{~m}^{3}\right)\).
4. Determine the final steam pressure. The final steam temperature \(\left(1000^{\circ} \mathrm{F}\right.\) or \(\left.537.8^{\circ} \mathrm{C}\right)\) and the final steam volume ( \(2.6150 \mathrm{ft}^{3} / \mathrm{lb}\) or \(0.16 \mathrm{~m}^{3} / \mathrm{kg}\) ) are known. To determine the final steam pressure, find in the steam tables the state corresponding to the preceding temperature and specific volume. Since a temperature of \(1000^{\circ} \mathrm{F}\left(537.8^{\circ} \mathrm{C}\right)\) is higher than any saturation temperature \(\left(705.4^{\circ} \mathrm{F}\right.\) or \(374.1^{\circ} \mathrm{C}\) is the highest saturation temperature for saturated steam), the steam in state 2 must be superheated. Therefore, the superheated-steam tables must be used to determine \(P_{2}\).

Enter the \(1000^{\circ} \mathrm{F}\left(537.8^{\circ} \mathrm{C}\right)\) column in the steam table and look for a superheated-vapor specific volume of \(2.6150 \mathrm{ft}^{3} / \mathrm{lb}\left(0.16 \mathrm{~m}^{3} / \mathrm{kg}\right)\). At a pressure of \(325 \mathrm{psia}(2240.9 \mathrm{kPa}), v=2.636 \mathrm{ft}^{3} / \mathrm{lb}\) \(\left(0.16 \mathrm{~m}^{3} / \mathrm{kg}\right) ; h=1542.5 \mathrm{Btu} / \mathrm{lb}(3587.9 \mathrm{~kJ} / \mathrm{kg}) ;\) and \(s=1.7863 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)\left[7.48 \mathrm{~kJ} /(\mathrm{kg})\left({ }^{\circ} \mathrm{C}\right)\right]\); and at a pressure of \(330 \mathrm{psia}(2275.4 \mathrm{kPa}), v=2.596 \mathrm{ft}^{3} / \mathrm{lb}\left(0.16 \mathrm{~m}^{3} / \mathrm{kg}\right) ; h=1524.4 \mathrm{Btu} / \mathrm{lb}\) ( \(3545.8 \mathrm{~kJ} / \mathrm{kg}\) ); and \(s=1.7845 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)\left[7.47 \mathrm{~kJ} /(\mathrm{kg})\left({ }^{\circ} \mathrm{C}\right)\right]\). Thus, 2.6150 lies between 325 and 330 psia ( 2240.9 and 2275.4 kPa ). To determine the pressure corresponding to the final volume, it is necessary to interpolate between the specific-volume values, or \(P_{2}=330-[(2.615-\) \(2.596) /(2.636-2.596)](330-325)=327.62 \mathrm{psia}(2258.9 \mathrm{kPa})\). In this equation, the volume values correspond to the upper ( 330 psia or 2275.4 kPa ), lower ( 325 psia or 2240.9 kPa ), and unknown pressures.
5. Determine the final enthalpy, entropy, and internal energy. The final enthalpy can be interpolated in the same manner, using the enthalpy at each volume instead of the pressure. Thus \(H_{2}=\) \(1524.5-[(2.615-2.596) /(2.636-2.596)](1524.5-1524.4)=1524.45 \mathrm{Btu} / \mathrm{lb}(3545.8 \mathrm{~kJ} / \mathrm{kg})\). Since the difference in enthalpy between the two pressures is only \(0.1 \mathrm{Btu} / \mathrm{lb}(0.23 \mathrm{~kJ} / \mathrm{kg})\) \((=1524.5-1524.4)\), the enthalpy at 327.62 psia could have been assumed equal to the enthalpy at the lower pressure ( 325 psia or 2240.9 kPa ), or \(1524.4 \mathrm{Btu} / \mathrm{lb}(3545.8 \mathrm{~kJ} / \mathrm{kg}\) ), and the error would have been only \(0.05 \mathrm{Btu} / \mathrm{lb}(0.12 \mathrm{~kJ} / \mathrm{kg})\), which is negligible. However, where the enthalpy values vary by more than \(1.0 \mathrm{Btu} / \mathrm{lb}(2.3 \mathrm{~kJ} / \mathrm{kg})\), interpolate as shown if accurate results are desired.

Find \(S_{2}\) by interpolating between pressures, or
\[
\begin{aligned}
S_{2} & =1.7863-\frac{327.62-325}{330-325}(1.7863-1.7845) \\
& =1.7854 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)\left[7.5 \mathrm{~kJ} /(\mathrm{kg})\left({ }^{\circ} \mathrm{C}\right)\right] \\
E_{2} & =H_{2}-P_{2} V_{2} / J=1524.4-\frac{327.62(144)(2.615)}{778} \\
& =1365.9 \mathrm{Btu} / \mathrm{lb}(3177.1 \mathrm{~kJ} / \mathrm{kg})
\end{aligned}
\]
6. Compute the changes resulting from the process. \(\quad Q_{1}=\left(E_{2}-E_{1}\right) m=(1365.9-868.9)\) \(\times(5)=2485\) Btu \((2621.8 \mathrm{~kJ}) ; \Delta S=\left(S_{2}-S_{1}\right) m=(1.7854-1.2589)(5)=2.6325 \mathrm{Btu} /{ }^{\circ} \mathrm{F}(5.0\) \(\mathrm{kJ} /{ }^{\circ} \mathrm{C}\) ).

By definition, \(W=0 ; \Delta V=0 ; \Delta E=Q_{1}\). Note that the curvatures of the constant-volume line on the \(T-S\) chart (Fig. 19.3) are different from the constant-pressure line (Fig. 19.2). Adding heat \(Q_{1}\) to a constant-volume process affects only the internal energy. The total entropy change must take into account the total steam mass \(m=5 \mathrm{lb}(2.3 \mathrm{~kg})\).

Related Calculations. Use this general procedure for all constant-volume steam processes.

\subsection*{19.5 CONSTANT-TEMPERATURE STEAM PROCESS}

Six pounds ( 2.7 kg ) of wet steam initially at \(1200 \mathrm{psia}(8274.0 \mathrm{kPa}\) ) and \(50 \%\) moisture expands at constant temperature \((T=C)\) to \(300 \mathrm{psia}(2068.5 \mathrm{kPa})\). Determine the initial temperature \(T_{1}\), enthalpy \(H_{1}\), internal energy \(E_{1}\), specific volume \(V_{1}\), entropy \(S_{1}\), final temperature \(T_{2}\), final enthalpy \(H_{2}\), final internal energy \(E_{2}\), final volume \(V_{2}\), final entropy \(S_{2}\), heat added \(Q_{1}\), work output \(W_{2}\), change in internal energy \(\Delta E\), change in volume \(\Delta V\), and change in entropy \(\Delta S\).

\section*{Calculation Procedure}
1. Determine the initial steam temperature from the steam tables. Enter the saturation-pressure table at \(1200 \mathrm{psia}(8274.0 \mathrm{kPa})\), and read the saturation temperature: \(T_{1}=567.22^{\circ} \mathrm{F}\left(297.3^{\circ} \mathrm{C}\right)\).
2. Correct the saturation values for the moisture in the steam in the initial state. Sketch the process on \(P-V, H-S\), or \(T-S\) diagrams (Fig. 19.4). Using the appropriate values from the saturationpressure table for \(1200 \mathrm{psia}(8274.0 \mathrm{kPa})\), correct them for the moisture content of \(50 \%\).
\[
\begin{aligned}
& H_{1}=h_{g}-y_{1} h_{f g}=1183.4-0.5(611.7)=877.5 \mathrm{Btu} / \mathrm{lb}(2041.1 \mathrm{~kJ} / \mathrm{kg}) \\
& E_{1}=u_{g}-y_{1} u_{f g}=1103.0-0.5(536.3)=834.8 \mathrm{Btu} / \mathrm{lb}(1941.7 \mathrm{~kJ} / \mathrm{kg}) \\
& V_{1}=v_{g}-y_{1} v_{f g}=0.3619-0.5(0.3396)=0.1921 \mathrm{ft}^{3} / \mathrm{lb}\left(0.012 \mathrm{~m}^{3} / \mathrm{kg}\right) \\
& S_{1}=s_{g}-y_{1} s_{f g}=1.3667-0.5(0.5956)=1.0689 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)\left[4.5 \mathrm{~kJ} /(\mathrm{kg})\left({ }^{\circ} \mathrm{C}\right)\right]
\end{aligned}
\]
3. Determine the steam properties in the final state. Since this is a constant-temperature process, \(T_{2}=T_{1}=567.22^{\circ} \mathrm{F}\left(297.3^{\circ} \mathrm{C}\right) ; P_{2}=300 \mathrm{psia}(2068.5 \mathrm{kPa})\), given. The saturation temperature of \(300 \mathrm{psia}(2068.5 \mathrm{kPa})\) is \(417.33^{\circ} \mathrm{F}\left(214.1^{\circ} \mathrm{C}\right)\). Therefore, the steam is superheated in the final state because \(567.22^{\circ} \mathrm{F}\left(297.3^{\circ} \mathrm{C}\right)>417.33^{\circ} \mathrm{F}\left(214.1^{\circ} \mathrm{C}\right)\), the saturation temperature.

To determine the final enthalpy, entropy, and specific volume, it is necessary to interpolate between the known final temperature and the nearest tabulated temperatures greater and less than the final temperature. Or, at \(T=560^{\circ} \mathrm{F}\left(293.3^{\circ} \mathrm{C}\right), v=1.9128 \mathrm{ft}^{3} / \mathrm{lb}\left(0.12 \mathrm{~m}^{3} / \mathrm{kg}\right) ; h=1292.5 \mathrm{Btu} / \mathrm{lb}(3006.4\) \(\mathrm{kJ} / \mathrm{kg})\); and \(s=1.6054 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)\left[6.72 \mathrm{~kJ} /(\mathrm{kg})\left({ }^{\circ} \mathrm{C}\right)\right]\). At \(T=580^{\circ} \mathrm{F}\left(304.4{ }^{\circ} \mathrm{C}\right), v=1.9594 \mathrm{ft}^{3} / \mathrm{lb}\) \(\left(0.12 \mathrm{~m}^{3} / \mathrm{kg}\right) ; h=1303.7 \mathrm{Btu} / \mathrm{lb}(3032.4 \mathrm{~kJ} / \mathrm{kg})\); and \(s=1.6163 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)\left(6.76 \mathrm{~kJ} /(\mathrm{kg})\left({ }^{\circ} \mathrm{C}\right)\right]\).


FIGURE 19.4 Constant-temperature process (Example 19.5).

Then,
\[
\begin{aligned}
H_{2} & =1292.5+\frac{567.22-560}{580-560}(1303.7-1292.5)=1296.5 \mathrm{Btu} / \mathrm{lb}(3015.7 \mathrm{~kJ} / \mathrm{kg}) \\
S_{2} & =1.6054+\frac{567.22-560}{580-560}(1.6163-1.6054) \\
& =1.6093 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)\left[6.7 \mathrm{~kJ} /(\mathrm{kg})\left({ }^{\circ} \mathrm{C}\right)\right] \\
V_{2} & =1.9128+\frac{567.22-560}{580-560}(1.9594-1.9128)=1.9296 \mathrm{ft}^{3} / \mathrm{lb}\left(0.12 \mathrm{~m}^{3} / \mathrm{kg}\right) \\
E_{2} & =H_{2}-P_{2} V_{2} / J=1296.5-300(144)(1.9296) / 778 \\
& =1109.3 \mathrm{Btu} / \mathrm{lb}(2580.2 \mathrm{~kJ} / \mathrm{kg})
\end{aligned}
\]
4. Compute the process changes. \(\quad Q_{1}=T\left(S_{2}-S_{1}\right) m\), where \(T_{1}\) is absolute initial temperature. Thus, \(Q_{1}=(567.22+460)(1.6093-1.0689)(6)=3330\) Btu \((3513.3 \mathrm{~kJ})\), or \(555 \mathrm{Btu} / \mathrm{lb}(1291 \mathrm{~kJ} /\) \(\mathrm{kg})\). Then,
\[
\begin{aligned}
\Delta E & =E_{2}-E_{1}=1109.3-834.8=274.5 \mathrm{Btu} / \mathrm{lb}(638.5 \mathrm{~kJ} / \mathrm{kg}) \\
\Delta H & =H_{2}-H_{1}=1296.5-877.5=419.0 \mathrm{Btu} / \mathrm{lb}(974.6 \mathrm{~kJ} / \mathrm{kg}) \\
W_{2} & =\left(Q_{1}-\Delta E\right) m=(555-274.5)(6)=1683 \mathrm{Btu}(1776 \mathrm{~kJ}) \\
\Delta S & =S_{2}-S_{1}=1.6093-1.0689=0.5404 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)\left[2.3 \mathrm{~kJ} /(\mathrm{kg})\left({ }^{\circ} \mathrm{C}\right)\right] \\
\Delta V & =V_{2}-V_{1}=1.9296-0.1921=1.7375 \mathrm{ft}^{3} / \mathrm{lb}\left(0.11 \mathrm{~m}^{3} / \mathrm{kg}\right)
\end{aligned}
\]

Related Calculations. Use this procedure for any constant-temperature steam process.

\subsection*{19.6 CONSTANT-ENTROPY STEAM PROCESS}

Ten pounds ( 4.5 kg ) of steam expands under two conditions-nonflow and steady flow-at constant entropy \((S=C)\) from an initial pressure of \(2000 \mathrm{psia}(13,790.0 \mathrm{kPa})\) and a temperature of \(800^{\circ} \mathrm{F}\) \(\left(426.7^{\circ} \mathrm{C}\right)\) to a final pressure of \(2 \mathrm{psia}(13.8 \mathrm{kPa})\). In the steady-flow process, assume that the initial kinetic energy \(E_{k 1}\) equals the final kinetic energy \(E_{k 2}\). Determine the initial enthalpy \(H_{1}\), initial internal energy \(E_{1}\), initial volume \(V_{1}\), initial entropy \(S_{1}\), final temperature \(T_{2}\), percent moisture \(y\), final enthalpy \(H_{2}\), final internal energy \(E_{2}\), final volume \(V_{2}\), final entropy \(S_{2}\), change in internal energy \(\Delta E\), change in enthalpy \(\Delta H\), change in entropy \(\Delta S\), change in volume \(\Delta V\), heat added \(Q_{1}\), and work output \(W_{2}\).

\section*{Calculation Procedure}
1. Determine the initial enthalpy, volume, and entropy from the steam tables. Enter the superheated-vapor table at \(2000 \mathrm{psia}(13,790.0 \mathrm{kPa})\) and \(800^{\circ} \mathrm{F}\left(427.6^{\circ} \mathrm{C}\right)\) and read \(H_{1}=1335.5 \mathrm{Btu} / \mathrm{lb}\) \((3106.4 \mathrm{~kJ} / \mathrm{kg}) ; V_{1}=0.3074 \mathrm{ft}^{3} / \mathrm{lb}\left(0.019 \mathrm{~m}^{3} / \mathrm{kg}\right)\); and \(S_{1}=1.4576 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)\left[6.1 \mathrm{~kJ} /(\mathrm{kg})\left({ }^{\circ} \mathrm{C}\right)\right]\).

\section*{2. Compute the initial energy}
\[
E_{1}=H_{1}-\frac{P_{1} V_{1}}{J}=1335.5-\frac{2000(144)(0.3074)}{778}=1221.6 \mathrm{Btu} / \mathrm{lb}(2841.1 \mathrm{~kJ} / \mathrm{kg})
\]


FIGURE 19.5 Constant-entropy process (Example 19.6).
3. Determine the vapor properties on the final state. Sketch the process on \(P-V, H-S\), or \(T-S\) diagrams (Fig. 19.5). Note that the expanded steam is wet in the final state because the 2-psia ( \(13.8-\mathrm{kPa}\) ) pressure line is under the saturation curve on the \(H-S\) and \(T-S\) diagrams. Therefore, the vapor properties in the final state must be corrected for the moisture content. Read, from the saturation-pressure steam table, the liquid and vapor properties at \(2 \mathrm{psia}(13.8 \mathrm{kPa})\). Tabulate these properties thus: \(s_{f}=0.1749 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)\left[0.73 \mathrm{~kJ} /(\mathrm{kg})\left({ }^{\circ} \mathrm{C}\right)\right] ; s_{f g}=1.7451 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)\) \(\left[7.31 \mathrm{~kJ} /(\mathrm{kg})\left({ }^{\circ} \mathrm{C}\right)\right] ; s_{g}=1.9200 \mathrm{Btu} /(\mathrm{lbb})\left({ }^{\circ} \mathrm{F}\right)\left[8.04 \mathrm{~kJ} /(\mathrm{kg})\left({ }^{\circ} \mathrm{C}\right)\right] ; h_{f}=93.99 \mathrm{Btu} / \mathrm{lb}(218.6 \mathrm{~kJ} / \mathrm{kg})\); \(h_{f g}=1.022 .2 \mathrm{Btu} / \mathrm{lb}(2377.6 \mathrm{~kJ} / \mathrm{kg}) ; h_{g}=1.116 .3 \mathrm{Btu} / \mathrm{lb}(2596.5 \mathrm{~kJ} / \mathrm{kg}) ; u_{f}=93.98 \mathrm{Btu} / \mathrm{lb}(218.6\) \(\mathrm{kJ} / \mathrm{kg}) ; u_{f g}=957.9 \mathrm{Btu} / \mathrm{lb}(2228.1 \mathrm{~kJ} / \mathrm{kg}) ; u_{g}=1051.9 \mathrm{Btu} / \mathrm{lb}(2446.7 \mathrm{~kJ} / \mathrm{kg}) ; v_{f}=0.016 \mathrm{ft}^{3} / \mathrm{lb}\) \(\left(0.00010 \mathrm{~m}^{3} / \mathrm{kg}\right) ; v_{f g}=173.71 \mathrm{ft}^{3} / \mathrm{lb}\left(10.8 \mathrm{~m}^{3} / \mathrm{kg}\right) ; v_{g}=173.73 \mathrm{ft}^{3} / \mathrm{lb}\left(10.8 \mathrm{~m}^{3} / \mathrm{kg}\right)\).

Since this is a constant-entropy process, \(S_{2}=S_{1}=s_{g}-y_{2} s_{f g}\). Solve for \(y_{2}\), the percent moisture in the final state. Thus, \(y_{2}=\left(s_{g}-S_{1}\right) / s_{f g}=(1.9200-1.4576) / 1.7451=0.265\), or 26.5 percent. Then,
\[
\begin{aligned}
& H_{2}=h_{g}-y_{2} h_{f g}=1116.2-0.265(1022.2)=845.3 \mathrm{Btu} / \mathrm{lb}(1966.2 \mathrm{~kJ} / \mathrm{kg}) \\
& E_{2}=u_{g}-y_{2} u_{f g}=1051.9-0.265(957.9)=798.0 \mathrm{Btu} / \mathrm{lb}(1856.1 \mathrm{~kJ} / \mathrm{kg}) \\
& V_{2}=v_{g}-y_{2} v_{f g}=173.73-0.265(173.71)=127.7 \mathrm{ft}^{3} / \mathrm{lb}\left(8.0 \mathrm{~m}^{3} / \mathrm{kg}\right)
\end{aligned}
\]
4. Compute the changes resulting from the process. The total change in properties is for 10 lb \((4.5 \mathrm{~kg})\) of steam, the quantity used in this process. Thus,
\[
\begin{aligned}
\Delta E & =\left(E_{1}-E_{2}\right) m=(1221.6-798.0)(10)=4236 \mathrm{Btu}(4469.2 \mathrm{~kJ}) \\
\Delta H & =\left(H_{1}-H_{2}\right) m=(1335.5-845.3)(10)=4902 \mathrm{Btu}(5171.9 \mathrm{~kJ}) \\
\Delta S & =\left(S_{1}-S_{2}\right) m=(1.4576-1.4576)(10)=0 \mathrm{Btu} /{ }^{\circ} \mathrm{F}\left(0 \mathrm{~kJ} /{ }^{\circ} \mathrm{C}\right) \\
\Delta V & =\left(V_{1}-V_{2}\right) m=(0.3074-127.7)(10)=-1274 \mathrm{ft}^{3}\left(-36.1 \mathrm{~m}^{3}\right)
\end{aligned}
\]
\(Q_{1}=0\) Btu. (By definition, there is no transfer of heat in a constant-entropy process.) Nonflow \(W_{2}=\Delta E=4236\) Btu ( 4469.2 kJ ). Steady flow \(W_{2}=\Delta H=4902\) Btu ( 5171.9 kJ ). Note: In a constant-entropy process, the nonflow work depends on the change in internal energy. The steadyflow work depends on the change in enthalpy and is larger than the nonflow work by the amount of the change in the flow work.


FIGURE 19.6 Irreversible adiabatic process (Example 19.7).

\subsection*{19.7 IRREVERSIBLE ADIABATIC EXPANSION OF STEAM}

Ten pounds ( 4.5 kg ) of steam undergoes a steady-flow expansion from an initial pressure of 2000 psia \((13,790.0 \mathrm{kPa})\) and a temperature \(800^{\circ} \mathrm{F}\left(426.7^{\circ} \mathrm{C}\right)\) to a final pressure of \(2 \mathrm{psia}(13.9 \mathrm{kPa})\) at an expansion efficiency of 75 percent. In this steady flow, assume there is no kinetic-energy change. Determine \(\Delta E, \Delta H, \Delta S, \Delta V, Q\), and \(W_{2}\).

\section*{Calculation Procedure}
1. Determine the initial vapor properties from the steam tables. Enter the superheated-vapor tables at \(2000 \mathrm{psia}(13,790.0 \mathrm{kPa})\) and \(800^{\circ} \mathrm{F}\left(426.7^{\circ} \mathrm{C}\right)\) and read \(H_{1}=1335.5 \mathrm{Btu} / \mathrm{lb}(3106.4 \mathrm{~kJ} / \mathrm{kg})\); \(V_{1}=0.3074 \mathrm{ft}^{3} / \mathrm{lb}\left(0.019 \mathrm{~m}^{3} / \mathrm{kg}\right) ; E_{1}=1221.6 \mathrm{Btu} / \mathrm{lb}(2840.7 \mathrm{~kJ} / \mathrm{kg}) ;\) and \(S_{1}=1.4576 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)\) \(\left[6.1 \mathrm{~kJ} /(\mathrm{kg})\left({ }^{\circ} \mathrm{C}\right)\right]\).
2. Determine the vapor properties in the final state. Sketch the process on \(P-V, H-S\), or \(T-S\) diagrams (Fig. 19.6). Note that the expanded steam is wet in the final state because the 2-psia (13.9-kPa) pressure line is under the saturation curve on the \(H-S\) and \(T-S\) diagrams. Therefore, the vapor properties in the final state must be corrected for the moisture content. However, the actual final enthalpy cannot be determined until after the expansion efficiency \(\left(H_{1}-H_{2}\right) /\left(H_{1}-H_{2 s}\right)\) is evaluated.

To determine the final enthalpy \(H_{2}\), another enthalpy \(H_{2 s}\) must first be computed by assuming a constant-entropy expansion to \(2 \mathrm{psia}(13.8 \mathrm{kPa})\) and a temperature of \(126.08^{\circ} \mathrm{F}\left(52.3^{\circ} \mathrm{C}\right)\). Enthalpy \(H_{2 s}\) will then be that corresponding to a constant-entropy expansion into the wet region and the percent moisture will be that corresponding to the final state. This percentage is determined by finding the ratio of \(s_{g}-S_{1}\) to \(s_{f g}\), or \(y_{2 s}=\left(s_{g}-S_{1}\right) / s_{f g}=(1.9200-1.4576) / 1.7451=0.265\), where \(s_{g}\) and \(s_{f g}\) are entropies at \(2 \mathrm{psia}(13.8 \mathrm{kPa})\). Then, \(H_{2 s}=h_{g}-y_{2 s} h_{f g}=1116.2-0.265(1022.2)=845.3\) \(\mathrm{Btu} / \mathrm{lb}(1966.2 \mathrm{~kJ} / \mathrm{kg})\). In this relation, \(h_{g}\) and \(h_{f g}\) are enthalpies at \(2 \mathrm{psia}(13.8 \mathrm{kPa})\).

The expansion efficiency, given as 0.75 , then is \(\left(H_{1}-H_{2}\right) /\left(H_{1}-H_{2 s}\right)=\) actual work/ideal work \(=0.75=1335.5-H_{2} /(1335.5-845.3)\). Solve for \(H_{2}=967.9 \mathrm{Btu} / \mathrm{lb}(2251.3 \mathrm{~kJ} / \mathrm{kg})\).

Next, read from the saturation-pressure steam table the liquid and vapor properties at 2 psia \((13.8 \mathrm{kPa})\). Tabulate these properties thus: \(h_{f}=93.99 \mathrm{Btu} / \mathrm{lb}(218.6 \mathrm{~kJ} / \mathrm{kg}) ; h_{f g}=1022.2 \mathrm{Btu} / \mathrm{lb}\) \((2377.6 \mathrm{~kJ} / \mathrm{kg}) ; h_{g}=1116.2 \mathrm{Btu} / \mathrm{lb}(2596.3 \mathrm{~kJ} / \mathrm{kg}) ; s_{f}=0.1749 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)\left[0.73 \mathrm{~kJ} /(\mathrm{kg})\left({ }^{\circ} \mathrm{C}\right)\right]\); \(s_{f g}=1.7451 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)\left[7.31 \mathrm{~kJ} /(\mathrm{kg})\left({ }^{\circ} \mathrm{C}\right)\right] ; s_{g}=1.9200 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)\left[8.04 \mathrm{~kJ} /(\mathrm{kg})\left({ }^{\circ} \mathrm{C}\right)\right] ; u_{f}=\) 93.98 Btu/lb (218.60 kJ/kg); \(u_{f g}=957.9 \mathrm{Btu} / \mathrm{lb}(2228.1 \mathrm{~kJ} / \mathrm{kg}) ; u_{g}=1051.9 \mathrm{Btu} / \mathrm{lb}(2446.7 \mathrm{~kJ} / \mathrm{kg})\); \(v_{f}=0.016 \mathrm{ft}^{3} / \mathrm{lb}\left(0.0010 \mathrm{~m}^{3} / \mathrm{kg}\right) ; v_{f g}=173.71 \mathrm{ft}^{3} / \mathrm{lb}\left(10.84 \mathrm{~m}^{3} / \mathrm{kg}\right) ;\) and \(v_{g}=173.73 \mathrm{ft}^{3} / \mathrm{lb}\) \(\left(10.85 \mathrm{~m}^{3} / \mathrm{kg}\right)\).

Since the actual final enthalpy \(H_{2}\) is different from \(H_{2 s}\), the final actual moisture \(y_{2}\) must be computed using \(H_{2}\). Thus, \(y_{2}=\left(h_{g}-H_{2}\right) / h_{f g}=(1116.2-967.9) / 1022.2=0.1451\). Then,
\[
\begin{aligned}
E_{2} & =u_{g}-y_{2} u_{f g}=1051.9-0.1451(957.9)=912.9 \mathrm{Btu} / \mathrm{lb}(2123.4 \mathrm{~kJ} / \mathrm{kg}) \\
V_{2} & =v_{g}-y_{2} v_{f g}=173.73-0.1451(173.71)=148.5 \mathrm{ft}^{3} / \mathrm{lb}\left(9.3 \mathrm{~m}^{3} / \mathrm{kg}\right) \\
S_{2} & =s_{g}-y_{2} s_{f g}=1.9200-0.1451(1.7451) \\
& =1.6668 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)\left[7.0 \mathrm{~kJ} /(\mathrm{kg})\left({ }^{\circ} \mathrm{C}\right)\right]
\end{aligned}
\]
3. Compute the changes resulting from the process. The total change in properties is for 10 lb \((4.5 \mathrm{~kg})\) of steam, the quantity used in this process. Thus,
\[
\begin{aligned}
\Delta E & =\left(E_{1}-E_{2}\right) m=(1221.6-912.9)(10)=3087 \mathrm{Btu}(3257.0 \mathrm{~kJ}) \\
\Delta H & =\left(H_{1}-H_{2}\right) m=(1335.5-967.9)(10)=3676 \mathrm{Btu}(3878.4 \mathrm{~kJ}) \\
\Delta S & =\left(S_{2}-S_{1}\right) m=(1.6668-1.4576)(10)=2.092 \mathrm{Btu} /{ }^{\circ} \mathrm{F}\left(4.0 \mathrm{~kJ} /{ }^{\circ} \mathrm{C}\right) \\
\Delta V & =\left(V_{2}-V_{1}\right) m=(148.5-0.3074)(10)=1482 \mathrm{ft}^{3}\left(42.0 \mathrm{~m}^{3}\right)
\end{aligned}
\]
\(Q=0\). By definition, \(W_{2}=\Delta H=3676 \mathrm{Btu}(3878.4 \mathrm{~kJ})\) for the steady-flow process.

\subsection*{19.8 IRREVERSIBLE ADIABATIC STEAM COMPRESSION}

Two pounds \((0.9 \mathrm{~kg})\) of saturated steam at \(120 \mathrm{psia}(827.4 \mathrm{kPa})\) with 80 percent quality undergoes nonflow adiabatic compression to a final pressure of \(1700 \mathrm{psia}(11,721.5 \mathrm{kPa})\) at 75 percent compression efficiency. Determine the final steam temperature \(T_{2}\), change in internal energy \(\Delta E\), change in entropy \(\Delta S\), work input \(W\), and heat input \(Q\).

\section*{Calculation Procedure}
1. Determine the vapor properties in the initial state. From the saturation-pressure steam tables, \(T_{1}=341.25^{\circ} \mathrm{F}\left(171.8^{\circ} \mathrm{C}\right)\) at a pressure of \(120 \mathrm{psia}(827.4 \mathrm{kPa})\) saturated. With \(x_{1}=0.8, E_{1}=\) \(u_{f}+x_{1} u_{f g}=312.05+0.8(795.6)=948.5 \mathrm{Btu} / \mathrm{lb}(2206.5 \mathrm{~kJ} / \mathrm{kg})\), using internal-energy values from the steam tables. The initial entropy \(S_{1}\) equals


FIGURE 19.7 Irreversible adiabatic compression process (Example 19.8). \(s_{f}+x_{1} s_{f g}=0.4916+0.8(1.0962)=1.3686\) \(\mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)\left[5.73 \mathrm{~kJ} /(\mathrm{kg})\left({ }^{\circ} \mathrm{C}\right)\right]\).
2. Determine the vapor properties in the final state. Sketch a \(T\)-S diagram of the process (Fig. 19.7). Assume a constant-entropy compression from the initial to the final state. Then, \(S_{2 s}=S_{1}=\) \(1.3686 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)\left[5.7 \mathrm{~kJ} /(\mathrm{kg})\left({ }^{\circ} \mathrm{C}\right)\right]\).

The final pressure, \(1700 \mathrm{psia}(11,721.5 \mathrm{kPa})\), is known, as is the final entropy, 1.3686 Btu/(lb) \(\left({ }^{\circ} \mathrm{F}\right)\left[5.7 \mathrm{~kJ} /(\mathrm{kg})\left({ }^{\circ} \mathrm{C}\right)\right]\), with constant-entropy expansion. The \(T\)-S diagram (Fig. 19.7) shows that the steam is superheated in the final state. Enter the superheated steam table at 1700 psia \((11,721.5 \mathrm{kPa})\), project across to an entropy of 1.3686 , and read the final steam temperature
as \(650^{\circ} \mathrm{F}\left(343.3^{\circ} \mathrm{C}\right)\). (In most cases, the final entropy would not exactly equal a tabulated value and it would be necessary to interpolate between tabulated entropy values to determine the intermediate pressure value.)

From the same table, at \(1700 \mathrm{psia}(11,721.5 \mathrm{kPa})\) and \(650^{\circ} \mathrm{F}\left(343.3^{\circ} \mathrm{C}\right), H_{2 s}=1214.4 \mathrm{Btu} / \mathrm{lb}\) \((2827.4 \mathrm{~kJ} / \mathrm{kg})\), and \(V_{2 s}=0.2755 \mathrm{ft}^{3} / \mathrm{lb}\left(0.017 \mathrm{~m}^{3} / \mathrm{lb}\right)\). Then, \(E_{2 s}=H_{2 s}-P_{2} V_{2 s} / J=1214.4-\) \(1700(144)(0.2755) / 788=1127.8 \mathrm{Btu} / \mathrm{lb}(2623.3 \mathrm{~kJ} / \mathrm{kg})\). Since \(E_{1}\) and \(E_{2 s}\) are known, the ideal work \(W\) can be computed. Thus, \(W=E_{2 s}-E_{1}=1127.8-948.5=179.3 \mathrm{Btu} / \mathrm{lb}(417.1 \mathrm{~kJ} / \mathrm{kg})\).
3. Compute the vapor properties of the actual compression. Since the compression efficiency is known, the actual final internal energy can be found from compression efficiency \(=\) ideal \(\mathrm{W} /\) actual \(W=\left(E_{2 s}-E_{1}\right) /\left(E_{2}-E_{1}\right)\), or \(0.75=1127.8-948.5 /\left(E_{2}-948.5\right)\), and \(E_{2}=1187.6\) Btu \(/ \mathrm{lb}(2762.4 \mathrm{~kJ} / \mathrm{kg})\). Then, \(E=\left(E_{2}-E_{1}\right) m=(1187.6-948.5)(2)=478.2 \mathrm{Btu}(504.5 \mathrm{~kJ})\) for 2 lb \((0.9 \mathrm{~kg})\) of steam. The actual work input \(W\) equals \(\Delta E=478.2 \mathrm{Btu}(504.5 \mathrm{~kJ})\). By definition, \(Q=0\).

Finally, the actual final temperature and entropy must be computed. The final actual internal energy \(E_{2}=1187.6 \mathrm{Btu} / \mathrm{lb}(2762.4 \mathrm{~kJ} / \mathrm{kg})\) is known. Also, the \(T-S\) diagram (Fig. 19.7) shows that the steam is superheated. However, the superheated-steam tables do not list the internal energy of the steam. Therefore, it is necessary to assume a final temperature for the steam and then compute its internal energy. The computed value is compared with the known internal energy and the next assumption is adjusted as necessary. Therefore, assume a final temperature of \(720^{\circ} \mathrm{F}\left(382.2^{\circ} \mathrm{C}\right)\). This assumption is higher than the ideal final temperature of \(650^{\circ} \mathrm{F}\left(343.3^{\circ} \mathrm{C}\right)\) because the \(T-S\) diagram (Fig. 19.7) shows that the actual final temperature is higher than the ideal final temperature. Using values from the superheated-steam table for \(1700 \mathrm{psia}(11,721.5 \mathrm{kPa})\) and \(720^{\circ} \mathrm{F}\left(382.2^{\circ} \mathrm{C}\right)\),
\[
E=H-\frac{P V}{J}=1288.4-\frac{1700(144)(0.3283)}{778}=1185.1 \mathrm{Btu} / \mathrm{lb}(2756.5 \mathrm{~kJ} / \mathrm{kg})
\]

This value is less than the actual internal energy of \(1187.6 \mathrm{Btu} / \mathrm{lb}(2762.4 \mathrm{~kJ} / \mathrm{kg})\). Therefore, the actual temperature must be higher than \(720^{\circ} \mathrm{F}\left(382.2^{\circ} \mathrm{C}\right)\), since the internal energy increases with temperature. To obtain a higher value for the internal energy to permit interpolation between the lower, actual, and higher values, assume a higher final temperature - in this case the next temperature listed in the steam table, or \(740^{\circ} \mathrm{F}\left(393.3^{\circ} \mathrm{C}\right)\). Then, for \(1700 \mathrm{psia}(11,721.5 \mathrm{kPa})\) and \(740^{\circ} \mathrm{F}\left(393.3^{\circ} \mathrm{C}\right)\),
\[
E=1305.8-\frac{1700(144)(0.3410)}{778}=1198.5 \mathrm{Btu} / \mathrm{lb}(2757.7 \mathrm{~kJ} / \mathrm{kg})
\]

This value is greater than the actual internal energy of \(1187.6 \mathrm{Btu} / \mathrm{lb}(2762.4 \mathrm{~kJ} / \mathrm{kg})\). Therefore, the actual final temperature of the steam lies somewhere between 720 and \(740^{\circ} \mathrm{F}\left(382.2\right.\) and \(\left.393.3^{\circ} \mathrm{C}\right)\). Interpolate between the known internal energies to determine the final steam temperature and final entropy. Thus,
\[
\begin{aligned}
T_{2} & =720+\frac{1187.6-1185.1}{1198.5-1185.1}(740-720)=723.7^{\circ} \mathrm{F}\left(384.3^{\circ} \mathrm{C}\right) \\
S_{2} & =1.4333+\frac{1187.6-1185.1}{1198.5-1185.1}(1.4480-1.4333) \\
& =1.4360 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)\left[6.0 \mathrm{~kJ} /(\mathrm{kg})\left({ }^{\circ} \mathrm{C}\right)\right] \\
\Delta S & =\left(S_{2}-S_{1}\right) m=(1.4360-1.3686)(2)=0.1348 \mathrm{Btu} /{ }^{\circ} \mathrm{F}\left(0.26 \mathrm{~kJ} /{ }^{\circ} \mathrm{C}\right)
\end{aligned}
\]

Note that the final actual steam temperature is \(73.7^{\circ} \mathrm{F}\left(40.9^{\circ} \mathrm{C}\right)\) higher than that \(\left(650^{\circ} \mathrm{F}\right.\) or \(\left.343.3^{\circ} \mathrm{C}\right)\) for the ideal compression.

Related Calculations. Use this procedure for any irreversible adiabatic steam process.

\subsection*{19.9 THROTTLING PROCESSES FOR STEAM AND WATER}

A throttling process begins at \(500 \mathrm{psia}(3447.5 \mathrm{kPa})\) and ends at \(14.7 \mathrm{psia}(101.4 \mathrm{kPa})\) with (1) steam at \(500 \mathrm{psia}(3447.5 \mathrm{kPa})\) and \(500^{\circ} \mathrm{F}\left(260.0^{\circ} \mathrm{C}\right)\), (2) steam at \(500 \mathrm{psia}(3447.5 \mathrm{kPa})\) and \(4 \%\) moisture, (3) steam at \(500 \mathrm{psia}(3447.5 \mathrm{kPa})\) and \(50 \%\) moisture, and (4) saturated water at \(500 \mathrm{psia}(3447.5 \mathrm{kPa})\). Determine the final enthalpy \(H_{2}\), temperature \(T_{2}\), and moisture content \(y_{2}\) for each process.

\section*{Calculation Procedure}
1. Compute the final-state conditions of the superheated steam. From the superheated-steam table for \(500 \mathrm{psia}(3447.5 \mathrm{kPa})\) and \(500^{\circ} \mathrm{F}\left(260.0^{\circ} \mathrm{C}\right), H_{1}=1231.3 \mathrm{Btu} / \mathrm{lb}(2864.0 \mathrm{~kJ} / \mathrm{kg})\). By definition of a throttling process, \(H_{1}=H_{2}=1231.3 \mathrm{Btu} / \mathrm{lb}\)


FIGURE 19.8 Throttling process for steam (Example 19.9). ( \(2864.0 \mathrm{~kJ} / \mathrm{kg}\) ). Sketch the \(T-S\) diagram for a throttling process (Fig. 19.8).

To determine the final temperature, enter the superheated-steam table at 14.7 psia (101.4 kPa ), the final pressure, and project across to an enthalpy value equal to or less than the known enthalpy, \(1231.3 \mathrm{Btu} / \mathrm{lb}(2864.0 \mathrm{~kJ} / \mathrm{kg})\). [The superheated steam table is used because the \(T\)-S diagram (Fig. 19.8) shows that the steam is superheated in the final state.] At 14.7 psia (101.4 kPa ) there is no tabulated enthalpy value that exactly equals \(1231.3 \mathrm{Btu} / \mathrm{lb}(2864.0 \mathrm{~kJ} / \mathrm{kg})\). The next lower value is \(1230 \mathrm{Btu} / \mathrm{lb}(2861.0 \mathrm{~kJ} / \mathrm{kg})\) at \(T=380^{\circ} \mathrm{F}\left(193.3^{\circ} \mathrm{C}\right)\). The next higher value at \(14.7 \mathrm{psia}(101.4 \mathrm{kPa})\) is \(1239.9 \mathrm{Btu} / \mathrm{lb}(2884.0\) \(\mathrm{kJ} / \mathrm{kg})\) at \(T=400^{\circ} \mathrm{F}\left(204.4^{\circ} \mathrm{C}\right)\). Interpolate between these enthalpy values to find the final
steam temperature. Thus,
\[
T_{2}=380+\frac{1231.3-1230.5}{1239.9-1230.5}(400-380)=381.7^{\circ} \mathrm{F}\left(194.3^{\circ} \mathrm{C}\right)
\]

The steam does not contain any moisture in the final state because it is superheated.
2. Compute the final-state conditions of the slightly wet steam. Determine the enthalpy of 500psia \((3447.5-\mathrm{kPa})\) saturated steam from the saturation-pressure steam table: \(h_{g}=1204.4 \mathrm{Btu} / \mathrm{lb}\) \((2801.4 \mathrm{~kJ} / \mathrm{kg})\), and \(h_{f g}=755.0 \mathrm{Btu} / \mathrm{lb}(1756.1 \mathrm{~kJ} / \mathrm{kg})\). Correct the enthalpy for moisture: \(H_{1}=\) \(h_{g}-y_{1} h_{f g}=1204.4-0.04(755.0)=1174.2 \mathrm{Btu} / \mathrm{lb}(2731.2 \mathrm{~kJ} / \mathrm{kg})\). Then, by definition, \(H_{2}=\) \(H_{1}=1174.2 \mathrm{Btu} / \mathrm{lb}\).

Determine the final condition of the throttled steam (wet, saturated, or superheated) by studying the \(T-S\) diagram. If a diagram was not drawn, enter the saturation-pressure steam table at 14.7 psia \((101.4 \mathrm{kPa})\), the final pressure, and check the tabulated \(h_{g}\). If the tabulated \(h_{g}\) is less than \(H_{1}\), the throttled steam is superheated. If the tabulated \(h_{g}\) is greater than \(H_{1}\), the throttled steam is saturated. Examination of the saturation-pressure steam table shows that the throttled steam is superheated because \(H_{1}>h_{g}\).

Next, enter the superheated-steam table to find an enthalpy value \(H_{1}\) at \(14.7 \mathrm{psia}(101.4 \mathrm{kPa})\). There is no value equal to \(1174.2 \mathrm{Btu} / \mathrm{lb}(2731.2 \mathrm{~kJ} / \mathrm{kg})\). The next lower value is \(1173.8 \mathrm{Btu} / \mathrm{lb}\) \((2730.3 \mathrm{~kJ} / \mathrm{kg})\) at \(T=260^{\circ} \mathrm{F}\left(126.7^{\circ} \mathrm{C}\right)\). The next higher value at \(14.7 \mathrm{psia}(101.4 \mathrm{kPa})\) is 1183.3 \(\mathrm{Btu} / \mathrm{lb}(2752.4 \mathrm{~kJ} / \mathrm{kg})\) at \(T=280^{\circ} \mathrm{F}\left(137.8^{\circ} \mathrm{C}\right)\). Interpolate between these enthalpy values to find the
final steam temperature. Thus,
\[
T_{2}=260+\frac{1174.2-1173.8}{1183.3-1173.8}(280-260)=260.8^{\circ} \mathrm{F}\left(127.1^{\circ} \mathrm{C}\right)
\]

This is higher than the temperature of saturated steam at \(14.7 \mathrm{psia}(101.4 \mathrm{kPa})-212^{\circ} \mathrm{F}\left(100^{\circ} \mathrm{C}\right)-\) giving further proof that the throttled steam is superheated. The throttled steam therefore does not contain any moisture.
3. Compute the final-state conditions of the very wet steam. Determine the enthalpy of 500-psia \((3447.5-\mathrm{kPa})\) saturated steam from the saturation-pressure steam table. Thus, \(h_{g}=1204.4 \mathrm{Btu} / \mathrm{lb}\) ( \(2801.4 \mathrm{~kJ} / \mathrm{kg}\) ), and \(h_{f g}=755.0 \mathrm{Btu} / \mathrm{lb}\) ( \(1756.1 \mathrm{~kJ} / \mathrm{kg}\) ). Correct the enthalpy for moisture: \(H_{1}=\) \(H_{2}=h_{g}-y_{1} h_{f g}=1204.4-0.5(755.0)=826.9 \mathrm{Btu} / \mathrm{lb}(1923.4 \mathrm{~kJ} / \mathrm{kg})\). Then, by definition, \(H_{2}=\) \(H_{1}=826.9 \mathrm{Btu} / \mathrm{lb}(1923.4 \mathrm{~kJ} / \mathrm{kg})\).

Compare the final enthalpy, that is, \(H_{2}=826.9 \mathrm{Btu} / \mathrm{lb}(1923.4 \mathrm{~kJ} / \mathrm{kg})\), with the enthalpy of saturated steam at \(14.7 \mathrm{psia}(101.4 \mathrm{kPa})\), that is, \(1150.4 \mathrm{Btu} / \mathrm{lb}(2675.8 \mathrm{~kJ} / \mathrm{kg})\). Since the final enthalpy is less than the enthalpy of saturated steam at the same pressure, the throttled steam is wet. Since \(H_{1}=h_{g}-y_{2} h_{f g}, y_{2}=\left(h_{g}-H_{1}\right) / h_{f g}\). With a final pressure of 14.7 psia, use \(h_{g}\) and \(h_{f g}\) values at this pressure. Thus,
\[
y_{2}=\frac{1150.4-826.9}{970.3}=0.3335=33.35 \text { percent }
\]

The final temperature \(T_{2}\) of the steam is the same as the saturation temperature at the final pressure of \(14.7 \mathrm{psia}(101.4 \mathrm{kPa})\), or \(T_{2}=212^{\circ} \mathrm{F}\left(100^{\circ} \mathrm{C}\right)\).
4. Compute the final-state conditions of saturated water. Determine the enthalpy of 500-psia ( \(3447.5-\mathrm{kPa}\) ) saturated water from the saturation-pressure steam table at \(500 \mathrm{psia}(3447.5 \mathrm{kPa}\) ); \(H_{1}=h_{f}=449.4 \mathrm{Btu} / \mathrm{lb}(1045.3 \mathrm{~kJ} / \mathrm{kg})=H_{2}\), by definition. The \(T-S\) diagram (Fig. 19.8) shows that the throttled water contains some steam vapor. Or, comparing the final enthalpy of \(449.4 \mathrm{Btu} / \mathrm{lb}\) \((1045.3 \mathrm{~kJ} / \mathrm{kg})\) with the enthalpy of saturated liquid, \(180.07 \mathrm{Btu} / \mathrm{lb}(418.8 \mathrm{~kJ} / \mathrm{kg})\), at the final pressure, \(14.7 \mathrm{psia}(101.4 \mathrm{kPa})\), shows that the liquid contains some vapor in the final state because its enthalpy is greater.

Since \(H_{1}=H_{2}=H_{g}-y_{2} h_{f g}, y_{2}=\left(h_{g}-H_{1}\right) / h_{f g}\). Using enthalpies at 14.7 psia ( 101.4 kPa ) of \(h_{g}=1150.4 \mathrm{Btu} / \mathrm{lb}(2675.8 \mathrm{~kJ} / \mathrm{kg})\) and \(h_{f g}=970.3 \mathrm{Btu} / \mathrm{lb}(2256.9 \mathrm{~kJ} / \mathrm{kg})\) from the saturationpressure steam table, \(y_{2}=(1150.4-449.4) / 970.3=0.723\).

The final temperature of the steam is the same as the saturation temperature at the final pressure of \(14.7 \mathrm{psia}(101.4 \mathrm{kPa})\), or \(T_{2}=212^{\circ} \mathrm{F}\left(100^{\circ} \mathrm{C}\right)\).

Note: Calculation 2 shows that when starting with slightly wet steam, it can be throttled (expanded) through a large enough pressure range to produce superheated steam. This procedure is often used in a throttling calorimeter to determine the initial quality of the steam in a pipe. When very wet steam is throttled (calculation 3), the net effect may be to produce drier steam at a lower pressure. Throttling saturated water (calculation 4) can produce partial or complete flashing of the water to steam. All these processes find many applications in power-generation and process-steam plants.

\subsection*{19.10 USE OF A HUMIDITY CHART*}

The temperature and dew point of the air entering a certain dryer are 130 and \(60^{\circ} \mathrm{F}\) ( 328 and 289 K ), respectively. Using a humidity chart (Fig. 19.9), find the following properties of the air: its humidity, its percentage humidity, its adiabatic-saturation temperature, its humidity at adiabatic saturation, its humid heat, and its humid volume.

\footnotetext{
*Adapted from McCabe and Smith—Unit Operations of Chemical Engineering, 3d ed., McGraw-Hill, Inc.
}


FIGURE 19.9 Humidity chart (air-water at 1 atm ). (From McCabe and Smith—Unit Operations of Chemical Engineering.)

\section*{Calculation Procedure}
1. Find the humidity. In Fig. 19.9, the humidity is the ordinate (along the right side of the graph) of the point on the saturation line (the 100 percent humidity line) that corresponds to the dew point, the latter being read from the abscissa along the bottom. In the present case, the humidity is found to be 0.011 lb water per pound of dry air ( 0.011 kg water per kilogram of dry air).
2. Find the percentage humidity. Find the dry-bulb temperature, that is, \(130^{\circ} \mathrm{F}\), along the abscissa, erect a perpendicular to intersect the \(0.011-\mathrm{lb}\) humidity line (at point \(A\) in Fig. 19.9), and find the percentage-humidity line (interpolating a line if necessary) that passes through that intersection. In this case, the 10 percent line passes through, so the percentage humidity is 10 percent.
3. Find the adiabatic-saturation temperature. Find the adiabatic-cooling line (these are the straight lines having negative slope) that passes through point \(A\), interpolating a line if necessary, and read the abscissa of the point (point \(B\) ) where this line intersects the 100 percent humidity line. This abscissa is the adiabatic-saturation temperature. In the present case, it is \(80^{\circ} \mathrm{F}(300 \mathrm{~K})\).
4. Find the humidity at adiabatic saturation. The humidity at adiabatic saturation is the ordinate, along the right side of the graph, of point \(B\). Its value is 0.022 lb water per pound of dry air \((0.022 \mathrm{~kg}\) water per kilogram of dry air).
5. Find the humid heat. Find the intersection (point \(C\) ) of the \(0.011-\mathrm{lb}\)-humidity line with the humid-heat-versus-humidity line, and read the humid heat as the abscissa of point C along the top of the graph. This abscissa is \(0.245 \mathrm{Btu} /\left({ }^{\circ} \mathrm{F}\right)(\mathrm{lb}\) dry air) [or \(1024 \mathrm{~J} /(\mathrm{K})(\mathrm{kg}\) dry air)].
6. Find the humid volume. Erect a perpendicular through the abscissa (along the bottom of the graph) that corresponds to \(130^{\circ} \mathrm{F}\), the dry bulb temperature. Label the intersection of this perpendicular with the saturated-volume-versus-temperature line as point \(D\), and the intersection of the perpendicular with the specific-volume-dry-air-versus-temperature line as point \(E\). Then, along line \(E D\), find point \(F\) by moving upward from point \(E\) by a distance equal to
\[
\overline{E D}[(\text { percentage humidity }) / 100]
\]
or, in the present case \((\overline{E D})(10 / 100)\), where \(\overline{E D}\) is the length of line segment \(\overline{E D}\). The humid volume is the ordinate of point \(F\) as read along the left side of the graph. In this case, the humid volume is \(15.1 \mathrm{ft}^{3} / \mathrm{lb}\) dry air \(\left(0.943 \mathrm{~m}^{3} / \mathrm{kg}\right.\) dry air).

Related Calculations. Do not confuse percentage humidity with relative humidity. "Relative humidity" is the ratio of the partial pressure of the water vapor to the vapor pressure of water at the temperature of the air, this ratio usually being expressed as a percent. "Percentage humidity" is the ratio of the actual humidity to the saturation humidity that corresponds to the gas temperature, which is also usually expressed as a percent. At all humidities other than 0 or 100 percent, the percentage humidity is less than the relative humidity.

\subsection*{19.11 BLOWDOWN AND MAKEUP REQUIREMENTS} FOR COOLING TOWERS*

A cooling tower handles \(1000 \mathrm{gal} / \mathrm{min}\left(0.063 \mathrm{~m}^{3} / \mathrm{s}\right)\) of circulating water that is cooled from 110 to \(80^{\circ} \mathrm{F}\) ( 316 to 300 K ). How much blowdown and makeup are required if the concentration of dissolved solids is allowed to reach three times the concentration in the makeup?

\section*{Calculation Procedure}
1. Set out material-balance equations for the cooling tower. When the system is at equilibrium, the makeup must equal the losses, so, by definition,
\[
\begin{equation*}
M=E+B+W \tag{19.1}
\end{equation*}
\]
where \(M\) is makeup, \(E\) is evaporation loss, \(B\) is blowdown, and \(W\) is windage loss, all being expressed as percent of circulation.

Since the evaporation water will be essentially free of dissolved solids, all solids introduced with the makeup water must be removed by the blowdown plus windage loss, or
\[
M p_{m}=(B+W) p_{c}
\]
where \(p_{m}\) is concentration of solids in the makeup and \(p_{c}\) is concentration of solids in the circulating water, both in parts per million.

For cooling towers, the concentration in the recirculating water is arbitrarily defined as "cycles of concentration" \(C\), namely, \(C=\) (concentration in cooling water)/(concentration in makeup water).

\footnotetext{
*Adapted from Chemical Engineering, June 21, 1976.
}

Thus,
\[
\begin{equation*}
M=\frac{(B+W) p_{c}}{p_{m}}=(B+W) C \tag{19.2}
\end{equation*}
\]
2. Make appropriate assumptions about windage and evaporation losses and set out and solve an equation for blowdown. Windage losses will be about 1.0 to 5.0 percent for spray ponds, 0.3 to 1.0 percent for atmospheric cooling towers, and 0.1 to 0.3 percent for forced-draft cooling towers; for the forced-draft towers in this example, 0.1 percent can be assumed. As for evaporation losses, they are 0.85 to 1.25 percent of the circulation for each 10-degree drop in Fahrenheit temperature across the tower; it is usually safe to assume 1.0 percent, so \(E=\Delta T / 10\), where \(\Delta T\) is the temperature drop across the tower. Therefore, in the present case,
\[
\begin{equation*}
M=\frac{\Delta T}{10}+B+0.1 \tag{19.3}
\end{equation*}
\]

Combining Eqs. (19.2) and (19.3) gives
\[
B=\frac{\Delta T}{10(C-1)}
\]

In the present case, then \(B=(110-80) /[10(3-1)]=1.5\) percent. Thus the blowdown requirement is 1.5 percent of \(1000 \mathrm{gal} / \mathrm{min}\), or \(15 \mathrm{gal} / \mathrm{min}\left(9.45 \times 10^{-4} \mathrm{~m}^{3} / \mathrm{s}\right)\).
3. Find the makeup requirement. From Eq. (19.1), \(M=(110-80) / 10+1.5+0.1=4.6\) percent, or \(46 \mathrm{gal} / \mathrm{min}\left(2.9 \times 10^{-3} \mathrm{~m}^{3} / \mathrm{s}\right)\).

\subsection*{19.12 WATER-SOFTENER SELECTION AND ANALYSIS*}

Select a water softener that will treat \(100 \mathrm{gal} / \mathrm{min}\left(22.7 \mathrm{~m}^{3} / \mathrm{h}\right)\) of water at \(60^{\circ} \mathrm{F}(289 \mathrm{~K})\) that has the following dissolved components (with concentrations in parts per million as \(\mathrm{CaCO}_{3}\) ): calcium, 300; sodium, 100; magnesium, 100; and total cations, 500 . The unit must produce water with no more than 2 ppm hardness and must operate for 8 h between regenerations. Manufacturer's data on the watersoftening resin to be used include the following: (1) a regeneration level of 4 lb NaCl per cubic foot ( \(64 \mathrm{~kg} / \mathrm{m}^{3}\) ) will result in 2 ppm hardness leakage and a capacity of \(16 \mathrm{kgr} / \mathrm{ft}^{3}\left(36 \mathrm{~kg} / \mathrm{m}^{3}\right)\), assuming standard cocurrent operation; (2) pressure drop per linear foot of bed (per 0.305 m of bed) for \(60^{\circ} \mathrm{F}\) water at a linear velocity equivalent to \(7.1 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{2}\right)\left[17.3 \mathrm{~m}^{3} /(\mathrm{h})\left(\mathrm{m}^{2}\right)\right]\) is \(0.6 \mathrm{lb} / \mathrm{in}^{2}(4.14 \mathrm{kPa})\); (3) a flow rate of \(6.4 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{2}\right)\left[15.6 \mathrm{~m}^{3} /(\mathrm{h})\left(\mathrm{m}^{2}\right)\right]\) will bring about a bed expansion of 60 percent; and (4) rinse requirements are 25 to \(50 \mathrm{gal} / \mathrm{ft}^{3}\left(3.34\right.\) to \(\left.6.68 \mathrm{~m}^{3} / \mathrm{m}^{3}\right)\). Determine the resin volume needed, the pressure drop, the backwash requirement, the regenerant requirement, and the required volume of rinse water.

\section*{Procedure}
1. Determine the amount of water to be treated per cycle and the amount of hardness to be removed. Softening of water requires use of a cation-exchange resin operated in sodium form to exchange divalent hardness cations for sodium regenerated with aqueous sodium chloride solution. Total amount of water to be treated is \((100 \mathrm{gal} / \mathrm{min})(60 \mathrm{~min} / \mathrm{h})(8 \mathrm{~h} /\) cycle \()=48,000 \mathrm{gal} / \mathrm{cycle}\left(182 \mathrm{~m}^{3} /\right.\) cycle).

\footnotetext{
* Courtesy of Rohm \& Haas Co.
}

In determining the quantity of hardness to be removed, neglect the 2 ppm allowable hardness in the effluent (this is a conservative simplification) and assume complete hardness removal. Since the influence hardness is expressed as parts per million (equivalents as \(\mathrm{CaCO}_{3}\) ), it is necessary to convert to units consistent with resin manufacturers' capacity data, usually expressed as kilograins (as \(\mathrm{CaCO}_{3}\) ) per cubic foot of resin. A total of 400 ppm hardness (calcium plus magnesium) is to be removed. Convert this to kilograins as \(\mathrm{CaCO}_{3}\). Thus, \(\left(400 \mathrm{ppm}\right.\) as \(\left.\mathrm{CaCO}_{3}\right)(48,000 \mathrm{gal} / \mathrm{cycle}) /(1000 \mathrm{gr} /\) \(\mathrm{kgr})(17.1 \mathrm{ppm}\) per grain per gallon \()=1120 \mathrm{kgr}(73 \mathrm{~kg})\) as \(\mathrm{CaCO}_{3}\) per cycle.
2. Establish regeneration level and resin capacity. An optimal level of regeneration exists for each softening application. This relates level of regeneration (pounds of regenerant per cubic foot of softening resin), leakage (ions not exchanged and thus appearing in the effluent), and operating capacity. In the present case, the desired information is given (based on information from the resin manufacturer) in the statement of the example: The optimal regeneration level is 4 lb NaCl per cubic foot ( 64 kg NaCl per cubic meter).
3. Determine volume of softening resin needed. The hardness load per cycle is 1120 kgr , from step 1 , and the resin capacity is given as \(16 \mathrm{kgr} / \mathrm{ft}^{3}\). So the amount of resin needed is \(1120 \mathrm{kgr} /\) \(\left(16 \mathrm{kgr} / \mathrm{ft}^{3}\right)=70 \mathrm{ft}^{3}\left(1.98 \mathrm{~m}^{3}\right)\).

However, if water production must be continuous, two softening units must be obtained, so that one can be regenerated while the other is in service. The alternative is to supply storage facilities for several hours' production of water at \(100 \mathrm{gal} / \mathrm{min}\).
4. Determine column dimensions, pressure drop, and backwash requirements. In conventional water softening, an acceptable space velocity is usually between 1 and \(5 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{3}\right)\) [8 and 40 \(\left.\mathrm{m}^{3} /(\mathrm{h})\left(\mathrm{m}^{3}\right)\right]\). In the present case, space velocity is \((100 \mathrm{gal} / \mathrm{min}) / 70 \mathrm{ft}^{3}=1.43 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{3}\right)\), which is within the normal range and thus is acceptable.

Normal linear velocity in a softening unit is equivalent to the range 4 to \(10 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{2}\right)\) [9.75 to \(24.4 \mathrm{~m}^{3} /(\mathrm{h})\left(\mathrm{m}^{2}\right)\) ]. If the velocity is too high, the pressure drop is excessive; too low a velocity can cause poor distribution of flow through the unit. As for bed depth, it should normally be 3 to 6 ft ( 0.9 to 1.8 m ).

Given these norms, determination of column dimensions is usually done by trial and error. Thus assume a bed depth of \(5 \mathrm{ft}(1.5 \mathrm{~m})\). Then, cross-sectional area will be \(70 \mathrm{ft}^{3} / 5 \mathrm{ft}=14 \mathrm{ft}^{2}\), and linear velocity will be equivalent to \((100 \mathrm{gal} / \mathrm{min}) / 14 \mathrm{ft}^{2}=7.1 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{2}\right)\), which is acceptable because it falls in the normal range.

The column diameter is \((\operatorname{area} \times 4 / \pi)^{1 / 2}=(14 \times 4 / \pi)^{1 / 2}=4.2 \mathrm{ft}(1.28 \mathrm{~m})\). In establishing the column height, allow adequate head space, or freeboard, to permit backwashing. A good allowance is 100 percent of the bed height. Thus the column height is twice the bed height, or \(10 \mathrm{ft}(3.05 \mathrm{~m})\).

The pressure drop per foot of bed depth is given in the statement of the example as \(0.6 \mathrm{lb} / \mathrm{in}^{2}\). Thus total pressure drop for the resin bed is \(\left[0.6 \mathrm{lb} /\left(\mathrm{in}^{2}\right)(\mathrm{ft})\right](5 \mathrm{ft})=3.0 \mathrm{lb} / \mathrm{in}^{2}(21 \mathrm{kPa})\). This excludes the pressure drop due to the liquid distributors and collectors in the column, as well as that due to auxiliary fittings and valves.

Backwashing is necessary to keep the bed in a hydraulically classified condition, to minimize pressure drop, and to remove resin fines and suspended solids that have been filtered out of the influent water. Normal practice is to backwash at the end of each run for about 15 min , so as to obtain about 50 to 75 percent bed expansion. The flow rate required to achieve this expansion is obtained from the manufacturers' data. As noted in the statement of the example, an appropriate flow rate in this case is \(6.4 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{2}\right)\). The total backwash rate is thus \(\left[6.4 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{2}\right)\right]\left(14 \mathrm{ft}^{2}\right)=90 \mathrm{gal} / \mathrm{min}\). The total water requirement, then, is \((90 \mathrm{gal} / \mathrm{min})(15 \mathrm{~min})=1350 \mathrm{gal}\left(5.11 \mathrm{~m}^{3}\right)\).
5. Determine regenerant requirement and flow rate. The sodium chloride regeneration level necessary to hold leakage to 2 ppm is 4 lb NaCl per cubic foot, as noted in step 2 . The salt ( \(100 \%\) basis) requirement, then, is \(\left(4 \mathrm{lb} / \mathrm{ft}^{3}\right)\left(70 \mathrm{ft}^{3}\right)=280 \mathrm{lb} \mathrm{NaCl}\) per cycle. Now salt is typically administered as a \(10 \%\) solution at a rate of \(1 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{3}\right)\). The density of such a solution is \(8.94 \mathrm{lb} / \mathrm{gal}\). Thus the volumetric requirement is \((280 \mathrm{lb} \mathrm{NaCl}\) per cycle) \() /(0.10 \mathrm{lb} \mathrm{NaCl}\) per pound solution) \((8.94 \mathrm{lb}\) solution
per gallon), or about 310 gallons per cycle. This should be fed at a flow rate of \(\left[1 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{3}\right)\right]\) \(\left(70 \mathrm{ft}^{3}\right)=70 \mathrm{gal} / \mathrm{min}\left(15.9 \mathrm{~m}^{3} / \mathrm{h}\right)\).
6. Determine required volume of rinse water. The resin bed must be rinsed with water following regeneration with salt. Rinse-water requirements are obtained from manufacturers' literature; in the present case, they are 25 to \(50 \mathrm{gal} / \mathrm{ft}^{3}\). At \(35 \mathrm{gal} / \mathrm{ft}^{3}\), the total rinse required is \(\left(35 \mathrm{gal} / \mathrm{ft}^{3}\right)\left(70 \mathrm{ft}^{3}\right)=2450\) gallons per cycle. Normal practice is to rinse at \(1 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{3}\right)\) (in this case, \(70 \mathrm{gal} / \mathrm{min}\), or \(15.9 \mathrm{~m}^{3} / \mathrm{h}\) ) for the first 10 to 15 min and then at \(2 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{3}\right)\left(\mathrm{here}, 140 \mathrm{gal} / \mathrm{min}\right.\), or \(\left.31.8 \mathrm{~m}^{3} / \mathrm{h}\right)\) for the remainder.

Related Calculations. This example assumes standard cocurrent operation of the column with downflow feed and downflow regeneration. Countercurrent operation is a special case that is best handled by a manufacturer of ion-exchange equipment.

\subsection*{19.13 COMPLETE DEIONIZATION OF WATER*}

Select a deionization system to treat \(250 \mathrm{gal} / \mathrm{min}\left(56.8 \mathrm{~m}^{3} / \mathrm{h}\right)\) of water at \(60^{\circ} \mathrm{F}(289 \mathrm{~K})\) that has the following dissolved components (concentrations in parts per million as \(\mathrm{CaCO}_{3}\) equivalent): calcium, 75 ; sodium, 50 ; magnesium, 25 ; chloride, 30 ; sulfate, 80 ; bicarbonate, 40 ; and silica, 10 (as \(\mathrm{SiO}_{2}\) ). Maximum tolerable sodium leakage is 2 ppm ; silica leakage is to be under 0.05 ppm . Service-cycle length must be at least 12 h . The system is to use sodium hydroxide (available at \(120^{\circ} \mathrm{F}\) ) and sulfuric acid for regeneration.

Manufacturers' data on the resins to be used include the following: For the cation-exchange resin: (1) a regeneration level of \(6 \mathrm{lb} \mathrm{H}_{2} \mathrm{SO}_{4}\) per cubic foot ( \(96 \mathrm{~kg} \mathrm{H}_{2} \mathrm{SO}_{4}\) per cubic meter) will result in a sodium leakage of 2.0 ppm and an operating capacity of \(15.6 \mathrm{kgr} / \mathrm{ft}^{3}\left(35 \mathrm{~kg} / \mathrm{m}^{3}\right)\); (2) pressure drop per foot (per 0.305 m ) of bed depth for \(60^{\circ} \mathrm{F}\) water at a linear velocity equivalent to \(8.6 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{2}\right)\) \(\left[21 \mathrm{~m}^{3} /(\mathrm{h})\left(\mathrm{m}^{2}\right)\right]\) is \(0.75 \mathrm{lb} / \mathrm{in}^{2}(5.2 \mathrm{kPa})\); (3) a flow rate of \(6.4 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{2}\right)\left[15.6 \mathrm{~m}^{3} /(\mathrm{h})\left(\mathrm{m}^{2}\right)\right]\) will bring about a bed expansion of 60 percent; and (4) rinse requirements are 25 to \(50 \mathrm{gal} / \mathrm{ft}^{3}\) ( 3.34 to \(6.68 \mathrm{~m}^{3} / \mathrm{m}^{3}\) ) using deionized rinse water. For the anion-exchange resin: (1) a regeneration level of 4 lb NaOH per cubic foot ( 64 kg NaOH per cubic meter) will result in a silica leakage of 0.05 ppm and an operating capacity of \(15.3 \mathrm{kgr} / \mathrm{ft}^{3}\) ( \(35 \mathrm{~kg} / \mathrm{m}^{3}\) ); (2) pressure drop per foot (per 0.305 m ) of bed depth for \(60^{\circ} \mathrm{F}\) water at a linear velocity equivalent to \(8.5 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{2}\right)\left[20.8 \mathrm{~m}^{3} /(\mathrm{h})\left(\mathrm{m}^{2}\right)\right]\) is \(0.85 \mathrm{lb} / \mathrm{in}^{2}\) ( 5.9 kPa ); (3) a flow rate of \(2.6 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{2}\right)\left[6.34 \mathrm{~m}^{3} /(\mathrm{h})\left(\mathrm{m}^{2}\right)\right]\) will bring about a bed expansion of 60 percent; and (4) rinse requirements are 40 to \(90 \mathrm{gal} / \mathrm{ft}^{3}\) ( 5.34 to \(12.0 \mathrm{~m}^{3} / \mathrm{m}^{3}\) ) using deionized water. Determine the resin volumes, the pressure drops, the backwash, regenerant and rinse-water requirements, and overall operating conditions.

\section*{Procedure}
1. Decide on the ion-exchange system to be used. Deionization requires replacement of all cations by the hydrogen ion, accomplished by use of a cation-exchange resin in the hydrogen form, as well as replacement of all anions by the hydroxide ion, accomplished by use of an anion exchanger in the hydroxide form. Since complete removal of all anions, including carbon dioxide and silica, is required, it will be necessary to use a strongly basic anion exchanger, regenerated with sodium hydroxide. The simplest system, a strongly acidic cation exchanger followed by a strongly basic anion exchanger, will be employed here. More elaborate and, in some cases, more efficient systems involving use of degassing equipment, stratified beds of strong- and weak-electrolyte resins, or mixed-bed units are beyond the scope of this handbook.

\footnotetext{
* Courtesy of Rohm \& Haas Co.
}

\section*{2. Specify the cation-exchange column}
a. Determine quantity of water to be treated per cycle and quantity of cations to be removed. The amount of water is \((250 \mathrm{gal} / \mathrm{min})(60 \mathrm{~min} / \mathrm{h})(12 \mathrm{~h} /\) cycle \()=180,000 \mathrm{gal}\left(681 \mathrm{~m}^{3}\right)\). To determine the cation load, neglect the 2 ppm of sodium leakage and assume complete removal of all cations. Since the influence cation load is expressed as parts per million (equivalents as \(\mathrm{CaCO}_{3}\) ), it is necessary to convert to units consistent with resin manufacturers' capacity data, usually expressed as kilograins (as \(\mathrm{CaCO}_{3}\) ) per cubic foot of resin. Total cation load in this cast is \(75+50+25 \mathrm{ppm}\). Converting, \((150 \mathrm{ppm})(180,000 \mathrm{gal} / \mathrm{cycle}) /(1000 \mathrm{gr} / \mathrm{kgr})(17.1 \mathrm{ppm}\) per grain per gallon \()=1580 \mathrm{kgr}(102 \mathrm{~kg})\) as \(\mathrm{CaCO}_{3}\) per cycle.
b. Establish regeneration level and resin capacity. Using manufacturers' data will determine the least amount of regenerant that will produce water of acceptable quality. In the present case, the desired information is given in the statement of the example: The optimal regeneration level is 6 lb \(\mathrm{H}_{2} \mathrm{SO}_{4}\) per cubic foot ( \(96 \mathrm{~kg} \mathrm{H}_{2} \mathrm{SO}_{4}\) per cubic meter). Note: Care must be taken in regenerating cation-exchange resins with sulfuric acid to avoid precipitation of calcium sulfate.
c. Determine the volume of cation-exchange resin needed. The cation load per cycle is 1580 kgr , from step 2a, and the resin capacity is given as \(15.6 \mathrm{kgr} / \mathrm{ft}^{3}\). So the amount of resin needed is 1580 \(\mathrm{kgr} /\left(15.6 \mathrm{kgr} / \mathrm{ft}^{3}\right)=101 \mathrm{ft}^{3}\left(2.86 \mathrm{~m}^{3}\right)\). However, if water production must be continuous, two units are needed, so that one can be regenerated while the other is in service. The alternative is to provide storage for several hours of production of water at \(250 \mathrm{gal} / \mathrm{min}\).
d. Determine column dimensions, pressure drop, and backwash requirement. In conventional water treatment, an acceptable space velocity is usually between 1 and \(5 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{3}\right)\) [8 and \(\left.40 \mathrm{~m}^{3} /(\mathrm{h})\left(\mathrm{m}^{3}\right)\right]\). In the present case, space velocity is \((250 \mathrm{gal} / \mathrm{min}) / 101 \mathrm{ft}^{3}=2.5 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{3}\right)\), which is thus acceptable.

Normal linear velocity is equivalent to the range 4 to \(10 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{2}\right)\left[9.75\right.\) to \(\left.24.4 \mathrm{~m}^{3} /(\mathrm{h})\left(\mathrm{m}^{2}\right)\right]\). Given this norm, determination of column dimensions is usually trial-and-error. Thus, assume a bed depth of \(3.5 \mathrm{ft}(1.07 \mathrm{~m})\). Then the cross-sectional area will be \(101 \mathrm{ft}^{3} / 3.5 \mathrm{ft}=28.9 \mathrm{ft}^{2}\), and linear velocity will be equivalent to \((250 \mathrm{gal} / \mathrm{min}) / 28.9 \mathrm{ft}^{2}=8.6 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{2}\right)\), which is acceptable.

If either space velocity or linear velocity had been considerably greater than the normal ranges, it would have been necessary to assign more resin.

The column diameter is \((\operatorname{area} \times 4 / \pi)^{1 / 2}=(28.9 \times 4 / \pi)^{1 / 2}=6.1 \mathrm{ft}(1.86 \mathrm{~m})\). In establishing the column height, allow adequate head space, or freeboard, to permit backwashing. A good allowance is 100 percent of the bed height. Thus the column height is twice the bed height, or 7 ft ( 2.13 m ).

The pressure drop per foot of bed depth is given in the statement of the example as \(0.75 \mathrm{lb} / \mathrm{in}^{2}\). Thus total pressure drop for the cation-resin bed is \(\left[0.75 \mathrm{lb} /\left(\mathrm{in}^{2}\right)(\mathrm{ft})\right](3.5 \mathrm{ft})=2.6 \mathrm{lb} / \mathrm{in}^{2}(17.9 \mathrm{kPa})\). This excludes the pressure drop due to valves, fittings, or liquid distributors or collectors.

Backwashing is necessary to keep the bed in a hydraulically classified condition, to minimize pressure drop and provide for proper flow distribution, as well as to remove resin fines and suspended solids that have filtered out of the water. Normal practice is to backwash at the end of each run to achieve 50 to 75 percent bed expansion. The flow rate required for this expansion is given in the statement of the example as \(6.4 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{2}\right)\). The total backwash rate is, thus, \(\left[6.4 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{2}\right)\right]\left(28.9 \mathrm{ft}^{2}\right)=185 \mathrm{gal} / \mathrm{min}\left(42 \mathrm{~m}^{3} / \mathrm{h}\right)\).
e. Determine regenerant requirement and flow rate. The sulfuric acid regeneration level to hold sodium leakage to 2 ppm is \(6 \mathrm{lb} / \mathrm{ft}^{3}\), as noted earlier. The total acid requirement, then, is ( \(6 \mathrm{lb} / \mathrm{ft}^{3}\) ) \(\left(101 \mathrm{ft}^{3}\right)=606 \mathrm{lb}(275 \mathrm{~kg})\) per cycle.

A typical technique to avoid precipitation of calcium sulfate is to administer half the regenerant as a \(2 \%\) solution and then the rest at \(4 \%\). Thus, in this case, the first step would require \((1 / 2 \times 606 \mathrm{lb}\) \(\left.\mathrm{H}_{2} \mathrm{SO}_{4}\right) /\left(8.43 \mathrm{lb}\right.\) solution per gallon)( \(0.02 \mathrm{lb}_{2} \mathrm{SO}_{4}\) per pound solution), or about 1800 gal \(\left(6.8 \mathrm{~m}^{3}\right)\) of \(2 \%\) acid solution. The second stage requires \((1 / 2 \times 606) /[8.54(0.04)]\), or about 890 gal \(\left(3.37 \mathrm{~m}^{3}\right)\) of \(4 \%\) acid solution. (The 8.43 and \(8.54 \mathrm{lb} / \mathrm{gal}\) are densities of the acid solutions.) Each stage should be fed at a rate of 1 to \(1.5 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{3}\right)\), or in this case about 100 to \(150 \mathrm{gal} / \mathrm{min}(23\) to \(34 \mathrm{~m}^{3} / \mathrm{h}\) ).
f. Determine the required volume of rinse water. The column must be rinsed with water after regeneration. Rinse-water requirements, as noted earlier, are 25 to \(50 \mathrm{gal} / \mathrm{ft}^{3}\). In the present case, for \(101 \mathrm{ft}^{3}\), the requirement is about 2500 to \(5000 \mathrm{gal}\left(9.5\right.\) to \(\left.19 \mathrm{~m}^{3}\right)\). The first portion should be administered at \(1 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{3}\right)\left[8 \mathrm{~m}^{3} /(\mathrm{h})\left(\mathrm{m}^{3}\right)\right]\), and the rest at \(1.5 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{3}\right)\left[12 \mathrm{~m}^{3} /\right.\) (h) \(\left.\left(\mathrm{m}^{3}\right)\right]\).

\section*{3. Specify the anion-exchange column}
a. Determine quantity of water to be treated and quantity of anions to be removed. The amount of water, from step 2 a , is \(180,000 \mathrm{gal}\). Total anion load is \(30+80+40 \mathrm{ppm}\). Converting, ( 150 ppm ) \(\times(180,000 \mathrm{gal} / \mathrm{cycle}) /(1000 \mathrm{gr} / \mathrm{kgr})(17.1 \mathrm{ppm}\) per grain per gallon \()=1580 \mathrm{kgr}(102 \mathrm{~kg})\) as \(\mathrm{CaCO}_{3}\) per cycle.
b. Establish regeneration level and resin capacity. As given in the statement of the problem, the optimal regeneration level is 4 lb NaOH per cubic foot ( 4 kg NaOH per cubic meter), associated with an operating capacity of \(15.3 \mathrm{kgr} / \mathrm{ft}^{3}\).
c. Determine the volume of anion-exchange resin needed. The anion load per cycle is 1580 kgr , from step \(3 a\), and the resin capacity is \(15.3 \mathrm{kgr} / \mathrm{ft}^{3}\). So the amount of resin needed is \(1580 / 15.3=103 \mathrm{ft}^{3}\) \(\left(2.91 \mathrm{~m}^{3}\right)\). However, if water production must be continuous, it is necessary to either install a second anion-exchange column in parallel, so that one can be regenerated while the other is in service, or else provide for water storage.
d. Determine column dimensions, pressure drop, and backwash requirement. Space velocity is (250 \(\mathrm{gal} / \mathrm{min}) / 103 \mathrm{ft}^{3}=2.4 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{3}\right)\), which falls within the acceptable range (see step \(2 d\) ). As in step \(2 d\), assume a bed depth of \(3.5 \mathrm{ft}(1.07 \mathrm{~m})\). Then the cross-sectional area of the bed will be \(103 / 3.5=29.4 \mathrm{ft}^{2}\), and linear velocity will be equivalent to \((250 \mathrm{gal} / \mathrm{min}) / 29.4 \mathrm{ft}^{2}=8.5 \mathrm{gal} /\) \((\mathrm{min})\left(\mathrm{ft}^{2}\right)\), which is also acceptable.
The column diameter is \((\operatorname{area} \times 4 / \pi)^{1 / 2}=(29.4 \times 4 / \pi)^{1 / 2}=6.12 \mathrm{ft}(1.86 \mathrm{~m})\). Allowing 100 percent head space for backwashing, the column height is twice the bed height, or \(7 \mathrm{ft}(2.13 \mathrm{~m})\).
The pressure drop per foot of bed depth is given in the statement of the example as \(0.85 \mathrm{lb} / \mathrm{in}^{2}\). Thus total pressure drop for the anion-exchange bed is \((0.85)(3.5)=3 \mathrm{lb} / \mathrm{in}^{2}(20.7 \mathrm{kPa})\). This excludes the pressure drop due to valves, fittings, or liquid distributors or collectors.

As for the backwash requirement, as discussed in step \(2 d\), the flow rate required is [ \(2.6 \mathrm{gal} /\) \(\left.(\mathrm{min})\left(\mathrm{ft}^{2}\right)\right]\left(29.4 \mathrm{ft}^{2}\right)=76 \mathrm{gal} / \mathrm{min}\left(17.3 \mathrm{~m}^{3} / \mathrm{h}\right)\).
e. Determine the regenerant requirement and flow rate. The sodium hydroxide regeneration level is 4 lb NaOH per cubic foot, as noted earlier. Total hydroxide requirement, then, is \(\left(4 \mathrm{lb} / \mathrm{ft}^{3}\right)\left(103 \mathrm{ft}^{3}\right)\) \(=412 \mathrm{lb}(187 \mathrm{~kg}) \mathrm{NaOH}\) per cycle. Regenerant concentration is typically \(4 \% \mathrm{NaOH}\) solution having a density of \(8.68 \mathrm{lb} / \mathrm{gal}\). Total regenerant-solution requirement, then, is ( 412 lb NaOH per cycle)/( 0.04 lb NaOH per pound of solution)( 8.68 lb solution per gallon), or 1190 gal per cycle \(\left(4.5 \mathrm{~m}^{3}\right.\) per cycle). This should be applied at about \(0.5 \mathrm{gal} /(\mathrm{min})\left(\mathrm{ft}^{3}\right)\left[4 \mathrm{~m}^{3} /(\mathrm{h})\left(\mathrm{m}^{3}\right)\right]\).
f. Determine the required volume of rinse water. Rinse-water requirements, as noted earlier, are 40 to \(90 \mathrm{gal} / \mathrm{ft}^{3}\). In the present case, for \(103 \mathrm{ft}^{3}\), the requirement is about 4000 to \(9000 \mathrm{gal}\left(15.1\right.\) to \(\left.34.1 \mathrm{~m}^{3}\right)\). The first bed volume (i.e., first \(103 \mathrm{ft}^{3} \times 7.48 \mathrm{gal} / \mathrm{ft}^{3}\), or 750 gal ) should be applied at about \(50 \mathrm{gal} /\) \(\min \left(11.4 \mathrm{~m}^{3} / \mathrm{h}\right)\), and the remainder should be applied at about \(150 \mathrm{gal} / \mathrm{min}\left(34.1 \mathrm{~m}^{3} / \mathrm{h}\right)\).

\subsection*{19.14 COOLING-POND SIZE FOR A KNOWN HEAT LOAD}

How many spray nozzles and what surface area is needed to cool \(10,000 \mathrm{gal} / \mathrm{min}(630.8 \mathrm{~L} / \mathrm{s})\) of water from 120 to \(90^{\circ} \mathrm{F}\left(48.9\right.\) to \(\left.32.2^{\circ} \mathrm{C}\right)\) in a spray-type cooling pond if the average wet-bulb temperature is \(60^{\circ} \mathrm{F}\left(15.6^{\circ} \mathrm{C}\right)\) ? What would the approximate dimensions of the cooling pond be? Determine the total pumping head if the static head is \(10 \mathrm{ft}(29.9 \mathrm{kPa})\), the pipe friction is 35 ft of water \((104.6 \mathrm{kPa})\), and the nozzle pressure is \(8 \mathrm{lb} / \mathrm{in}^{2}(55.2 \mathrm{kPa})\).

\section*{Calculation Procedure}
1. Compute the number of nozzles required. Assume a water flow of \(50 \mathrm{gal} / \mathrm{min}(3.2 \mathrm{~L} / \mathrm{s})\) per nozzle; this is a typical flow rate for usual cooling-pond nozzles. Then, the number of nozzles required equals \(10,000 \mathrm{gal} /(\mathrm{min}) /(50 \mathrm{gal} / \mathrm{min}\) per nozzle \()=200\) nozzles. If six nozzles are used in each spray group in a series of crossed arms, with each arm containing one or more nozzles, then 200 nozzles divided by 6 nozzles per spray group means that \(331 / 3\) spray groups will be needed. Since a partial spray group is seldom used, 34 spray groups would be chosen.
2. Determine the surface area required. Usual design practice is to provide \(1 \mathrm{ft}^{2}\left(0.09 \mathrm{~m}^{2}\right)\) of pond area per 250 lb ( 113.4 kg ) of water cooled for water quantities exceeding \(1000 \mathrm{gal} / \mathrm{min}(63.1 \mathrm{~L} / \mathrm{s})\). Thus, in this pond, the weight of water cooled equals \((10,000 \mathrm{gal} / \mathrm{min})(8.33 \mathrm{lb} / \mathrm{gal})(60 \mathrm{~min} / \mathrm{h})=\) \(4,998,000\), say, \(5,000,000 \mathrm{lb} / \mathrm{h}\left(630.0 \mathrm{~kg} / \mathrm{s}\right.\) ). Then, the area required, using \(1 \mathrm{ft}^{2}\) of pond area per 250 lb of water ( \(0.82 \mathrm{~m}^{2}\) per 1000 kg ) cooled, is \(5,000,000 / 250=20,000 \mathrm{ft}^{2}\left(1858.0 \mathrm{~m}^{2}\right)\).

As a cross-check, use another commonly accepted area value: \(125 \mathrm{Btu} /\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)[2555.2 \mathrm{~kJ} /\) \(\left.\left(\mathrm{m}^{2}\right)\left({ }^{\circ} \mathrm{C}\right)\right]\), based on the temperature difference between the air wet-bulb temperature and the warm entering-water temperature. This is the equivalent of \((120-60)(125)=7500 \mathrm{Btu} / \mathrm{ft}^{2}(85,174\) \(\left.\mathrm{kJ} / \mathrm{m}^{2}\right)\) in this spray pond, because the air wet-bulb temperature is \(60^{\circ} \mathrm{F}\left(15.6^{\circ} \mathrm{C}\right)\) and the warmwater temperature is \(120^{\circ} \mathrm{F}\left(48.9^{\circ} \mathrm{C}\right)\). The heat removed from the water is (pounds per hour of water)(temperature decrease, in \(\left.{ }^{\circ} \mathrm{F}\right)(\) specific heat of water) \(=(5,000,000)(120-90)(1.0)=\) \(150,000,000 \mathrm{Btu} / \mathrm{h}(43,960.7 \mathrm{~kW})\). Then, area required equals (heat removed, in Btu/h)/(heat removal, in \(\left.B t u / \mathrm{ft}^{2}\right)=150,000,000 / 7,500=20,000 \mathrm{ft}^{2}\left(1858.0 \mathrm{~m}^{2}\right)\). This checks the previously obtained area value.
3. Determine the spray-pond dimensions. Spray groups on the same header or pipe main are usually arranged on about \(12-\mathrm{ft}(3.7-\mathrm{m})\) centers with the headers or pipe mains spaced on about \(25-\mathrm{ft}\) ( \(7.6-\mathrm{m}\) ) centers (Fig. 14.10). Assume that 34 spray groups are used, instead of the required \(331 / 3\), to provide an equal number of groups in two headers and a small extra capacity.

Sketch the spray pond and headers (Fig. 19.10). This shows that the length of each header will be about \(204 \mathrm{ft}(62.2 \mathrm{~m})\), because there are seventeen \(12-\mathrm{ft}(3.7-\mathrm{m})\) spaces between spray groups in each header. Allowing \(3 \mathrm{ft}(0.9 \mathrm{~m})\) at each end of a header for fittings and cleanouts gives an overall header length of \(210 \mathrm{ft}(64.0 \mathrm{~m})\). The distance between headers is \(25 \mathrm{ft}(7.6 \mathrm{~m})\). Allow \(25 \mathrm{ft}(7.6 \mathrm{~m})\) between the outer sprays and the edge of the pond. This gives an overall width of \(85 \mathrm{ft}(25.9 \mathrm{~m})\) for the pond, assuming the width of each arm in a spray group is \(10 \mathrm{ft}(3.0 \mathrm{~m})\). The overall length will


FIGURE 19.10 Spray-pond nozzle and piping layou(Example 19.14).
then be \(210+25+25=260 \mathrm{ft}(79.2 \mathrm{~m})\). A cold well for the pump suction and suitable valving for control of the incoming water must be provided, as shown in Fig. 19.10. The water depth in the pond should be 2 to \(3 \mathrm{ft}(0.6\) to 0.9 m\()\).
4. Compute the total pumping head. The total head, expressed in feet of water, equals static head + friction head + required nozzle head \(=10+35+8(0.434)=48.5 \mathrm{ft}\) of water \((145.0 \mathrm{kPa})\). A pump having a total head of at least 50 ft of water \((15.2 \mathrm{~m})\) would be chosen for this spray pond. If future expansion of the pond is anticipated, compute the probable total head required at a future date and choose a pump to deliver that head. Until the pond is expanded, the pump would operate with a throttled discharge. Normal nozzle inlet pressures range from about 6 to \(10 \mathrm{lb} / \mathrm{in}^{2}(41.4\) to 69.0 kPa ). Higher pressures should not be used, because there will be excessive spray loss and rapid wear of the nozzles.

Related Calculations. Unsprayed cooling ponds cool 4 to \(6 \mathrm{lb}(1.8\) to 2.7 kg\()\) of water from 100 to \(70^{\circ} \mathrm{F}\) per square foot ( 598.0 to \(418.6^{\circ} \mathrm{C} / \mathrm{m}^{2}\) ) of water surface. An alternative design rule is to assume that the pond will dissipate \(3.5 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left[19.9 \mathrm{~J} /\left(\mathrm{m}^{2}\right)\left({ }^{\circ} \mathrm{C}\right)(\mathrm{s})\right]\) of water surface per degree difference between the wet-bulb temperature of the air and the entering warm water.

\subsection*{19.15 PROCESS TEMPERATURE-CONTROL ANALYSIS}

A water storage tank (Fig. 19.11) contains \(500 \mathrm{lb}(226.8 \mathrm{~kg})\) of water at \(150^{\circ} \mathrm{F}\left(65.6^{\circ} \mathrm{C}\right)\) when full. Water is supplied to the tank at \(50^{\circ} \mathrm{F}\left(10.0^{\circ} \mathrm{C}\right)\) and is withdrawn at the rate of \(25 \mathrm{lb} / \mathrm{min}(0.19 \mathrm{~kg} / \mathrm{s})\). Determine the process time constant and the zero-frequency process gain if the thermal sensing pipe contains \(15 \mathrm{lb}(6.8 \mathrm{~kg})\) of water between the tank and thermal bulb and the maximum steam flow to the tank is \(8 \mathrm{lb} / \min (0.060 \mathrm{~kg} / \mathrm{s})\). The steam flow to the tank is controlled by a standard linear regulating valve whose flow range is 0 to \(10 \mathrm{lb} / \mathrm{min}(0\) to \(0.076 \mathrm{~kg} / \mathrm{s})\) when the valve operator pressure changes from 5 to \(30 \mathrm{lb} / \mathrm{in}^{2}(34.5\) to 206.9 kPa ).


FIGURE 19.11 Temperature control of a simple process (Example 19.15).

\section*{Calculation Procedure}
1. Compute the distance-velocity lag. The time in minutes needed for the thermal element to detect a change in temperature in the storage tank is the "distance-velocity lag," which is also called the "transportation lag" or "dead time." For this process, the distance-velocity lag \(d\) is the ratio of the quantity of water in the pipe between the tank and the thermal bulb, that is, \(15 \mathrm{lb}(6.8 \mathrm{~kg})\), and the rate of flow of water out of the tank, that is, \(25 \mathrm{lb} / \mathrm{min}(0.114 \mathrm{~kg} / \mathrm{s})\), or \(d=15 / 25=0.667 \mathrm{~min}\).
2. Compute the energy input to the tank. This is a "transient control process"-i.e., the conditions in the process are undergoing constant change instead of remaining fixed, as in steady-state conditions. For transient process conditions, the heat balance is \(H_{\text {in }}=H_{\text {out }}+H_{\text {stor }}\), where \(H_{\text {in }}\) is heat input, in \(\mathrm{Btu} / \mathrm{min} ; H_{\text {out }}\) is heat output, in Btu/min; \(H_{\text {stor }}\) is heat stored, in Btu/min.

The heat input to this process is the enthalpy of vaporization \(h_{f g}\), in \(\mathrm{Btu} /(\mathrm{lb})(\mathrm{min})\), of the steam supplied to the process. Since the regulating valve is linear, its sensitivity \(s\) is the (flow-rate change, in \(\mathrm{lb} / \mathrm{min}) /\left(\right.\) pressure change, in \(\left.\mathrm{lb} / \mathrm{in}^{2}\right)\). Or, using the known valve characteristics, \(s=(10-0) /(30-\) \(5)=0.4 \mathrm{lb} /(\mathrm{min})(\mathrm{psi})[0.00044 \mathrm{~kg} /(\mathrm{kPa})(\mathrm{s})]\).

With a change in steam pressure of \(p \mathrm{lb} / \mathrm{in}^{2}\left(p^{\prime} \mathrm{kPa}\right)\) in the valve operator, the change in the rate of energy supply to the process is \(H_{\mathrm{in}}=0.4 \mathrm{lb} /(\mathrm{min})(\mathrm{psi}) \times p \times h_{f g}\). Taking \(h_{f g}\) as \(938 \mathrm{Btu} / \mathrm{lb}(2181 \mathrm{~kJ} /\) \(\mathrm{kg}), H_{\text {in }}=375 p \mathrm{Btu} / \min \left(6.6 p^{\prime} \mathrm{kW}\right)\).
3. Compute the energy output from the system. The energy output \(H_{\text {out }}\) equals pounds per minute of liquid outflow times liquid specific heat, Btu/(lb) \(\left({ }^{\circ} \mathrm{F}\right), \times\left(T_{a}-150^{\circ} \mathrm{F}\right)\), where \(T_{a}\) is tank temperature, in \({ }^{\circ} \mathrm{F}\), at any time. When the system is in a state of equilibrium, the temperature of the liquid in the tank is the same as that leaving the tank or, in this instance, \(150^{\circ} \mathrm{F}\left(65.6^{\circ} \mathrm{C}\right)\). But when steam is supplied to the tank under equilibrium conditions, the liquid temperature will rise to \(150+T_{r}\), where \(T_{r}\) is temperature rise, in \({ }^{\circ} \mathrm{F}\left(T_{r}^{\prime}\right.\) in \(\left.{ }^{\circ} \mathrm{C}\right)\), produced by introducing steam into the water. Thus, the preceding equation becomes \(H_{\text {out }}=25 \mathrm{lb} / \mathrm{min} \times 1.0 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right) \times T_{r}=25 T_{r} \mathrm{Btu} / \mathrm{min}\) ( \(0.44 T_{r}^{\prime} \mathrm{kW}\) ).
4. Compute the energy stored in the system. With rapid mixing of the steam and water, \(H_{\text {stor }}=\) liquid storage, in pounds, times liquid specific heat, in \(\mathrm{Btu}(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)\), times \(T_{r} q=500 \times 1.0 \times T_{r} q\), where \(q\) is derivative of the tank outlet temperature with respect to time.
5. Determine the time constant and process gain. Write the process heat balance, substituting the computed values in \(H_{\mathrm{in}}=H_{\mathrm{out}}+H_{\mathrm{stor}}\), or \(375 p=25 T_{r}+500 T_{r} q\). Solving, \(T_{r} / p=375 /(25+\) \(500 q)=15 /(1+20 q)\).

The denominator of this linear first-order differential equation gives the process system time constant of 20 min in the expression \(1+20 q\). Likewise, the numerator gives the zero-frequency process gain of \(15^{\circ} \mathrm{F} /(\mathrm{lb})\left(\mathrm{in}^{2}\right)\).

Related Calculations. This general procedure is valid for any liquid using any gaseous heating medium for temperature control with a single linear lag. Likewise, this general procedure is also valid for temperature control with a double linear lag and pressure control with a single linear lag.

\subsection*{19.16 CONTROL-VALVE SELECTION FOR PROCESS CONTROL}

Select a steam control valve for a heat exchanger requiring a flow of \(1500 \mathrm{lb} / \mathrm{h}(0.19 \mathrm{~kg} / \mathrm{s})\) of saturated steam at \(80 \mathrm{psig}(551.6 \mathrm{kPag})\) at full load and \(300 \mathrm{lb} / \mathrm{h}(0.038 \mathrm{~kg} / \mathrm{s})\) at \(40 \mathrm{psig}(275.8 \mathrm{kPag})\) at minimum load. Steam at \(100 \mathrm{psig}(689.5 \mathrm{kPag})\) is available for heating.

\section*{Calculation Procedure}
1. Compute the valve flow coefficient. The valve flow coefficient \(C_{v}\) is a function of the maximum steam flow rate through the valve and the pressure drop that occurs at this flow rate. When choosing a control valve for a process control system, the usual procedure is to assume a maximum flow rate for the valve based on a considered judgment of the overload the system may carry. Usual overloads do not exceed 25 percent of the maximum rated capacity of the system. Using this overload range as a guide, assume that the valve must handle a 20 percent overload, or \(0.20(1500)=300 \mathrm{lb} / \mathrm{h}(0.038 \mathrm{~kg} / \mathrm{s})\). Hence, the rated capacity of this valve should be \(1500+300=1800 \mathrm{lb} / \mathrm{h}(0.23 \mathrm{~kg} / \mathrm{s})\).

The pressure drop across a steam control valve is a function of the valve design, size, and flow rate. The most accurate pressure-drop estimate that is usually available is that given in the valve manufacturer's engineering data for a specific valve size, type, and steam flow rate. Without such data, assume a pressure drop of 5 to 15 percent across the valve as a first approximation. This means that the pressure loss across this valve, assuming a 10 percent drop at the maximum steam flow rate, would be \(0.10 \times 80=8 \mathrm{psig}(55.2 \mathrm{kPag})\).

With these data available, compute the valve flow coefficient from \(C_{v}=W K / 3\left(\Delta p P_{2}\right)^{0.5}\), where \(W\) is steam flow rate, in \(\mathrm{lb} / \mathrm{h}, K\) equals \(1+\left(0.0007 \times{ }^{\circ} \mathrm{F}\right.\) superheat of the steam \(), p\) is pressure drop across the valve at the maximum steam flow rate, in \(\mathrm{lb} / \mathrm{in}^{2}\), and \(P_{2}\) is control-valve outlet pressure at maximum steam flow rate, in psia. Since the steam is saturated, it is not superheated, and \(K=1\). Then, \(C_{v}=1500 / 3(8 \times 94.7)^{0.5}=18.1\).
2. Compute the low-load steam flow rate. Use the relation \(W=3\left(C_{v} \Delta p P_{2}\right)^{0.5} / K\), where all the symbols are as before. Thus, with a \(40-\mathrm{psig}(275.5-\mathrm{kPag})\) low-load heater inlet pressure, the valve pressure drop is \(80-40=40 \mathrm{psig}(275.8 \mathrm{kPag})\). The flow rate through the valve is then \(W=3(18.1 \times 40 \times 54.7)^{0.5} / 1=598 \mathrm{lb} / \mathrm{h}(0.75 \mathrm{~kg} / \mathrm{s})\).

Since the heater requires \(300 \mathrm{lb} / \mathrm{h}(0.038 \mathrm{~kg} / \mathrm{s})\) of steam at the minimum load, the valve is suitable. Had the flow rate of the valve been insufficient for the minimum flow rate, a different pressure drop, i.e., a larger valve, would have to be assumed and the calculation repeated until a flow rate of at least \(300 \mathrm{lb} / \mathrm{h}(0.038 \mathrm{~kg} / \mathrm{s})\) was obtained.

Related Calculations. The flow coefficient \(C_{v}\) of the usual 1-in-diameter \((2.5-\mathrm{cm})\) double-seated control valve is 10 . For any other size valve, the approximate \(C_{v}\) valve can be found from the product \(10 \times d^{2}\), where \(d\) is nominal body diameter of the control valve, in inches. Thus, for a 2-in-diameter


FIGURE 19.12 Flow-lift characteristics for control valves. (Taylor Instrument Process Control Division of Sybron Corporation.)
(5.1-cm) valve, \(C_{v}=10 \times 2^{2}=40\). Using this relation and solving for \(d\), the nominal diameter of the valve analyzed in steps 1 and 2 is \(d=\left(C_{v} / 10\right)^{0.5}=(18.1 / 10)^{0.5}=1.35\) in ( 3.4 cm ); use a \(1.5-\mathrm{in}(3.8-\mathrm{cm})\) valve because the next smaller standard control valve size, 1.25 in \((3.2 \mathrm{~cm})\), is too small. Standard double-seated control-valve sizes are: \(3 / 4,1,1 \frac{1}{4}, 1 \frac{1}{2}, 2,2 \frac{1}{2}, 3,4,6,8,10\), and 12 in . Figure 19.12 shows typical flow-lift characteristics of popular types of control valves.

To size control valves for liquids, use a similar procedure and the relation \(C_{v}=V(G / \Delta p)\), where \(V\) is flow rate through the valve, in gal \(/ \mathrm{min}, \Delta p\) is pressure drop across the valve at maximum flow rate, in \(\mathrm{lb} / \mathrm{in}^{2}\), and \(G\) is specific gravity of the liquid. When a liquid has a specific gravity of 100 SSU or less, the effect of viscosity on the control action is negligible.

To size control valves for gases, use the relation \(C_{v}=Q\left(G T_{a}\right)^{0.5} /\left[1360\left(\Delta p P_{2}\right)^{0.5}\right]\), where \(Q\) is gas flow rate, in \(\mathrm{ft}^{3} / \mathrm{h}\) at \(14.7 \mathrm{psia}(101.4 \mathrm{kPa})\) and \(60^{\circ} \mathrm{F}\left(15.6^{\circ} \mathrm{C}\right), T_{a}\) is temperature of the flowing gas, in \({ }^{\circ} \mathrm{F}\) abs \(=460+\mathrm{F}\); other symbols as before. When the valve outlet pressure \(P_{2}\) is less than \(0.5 P_{1}\), where \(P_{1}\) is valve inlet pressure, in psia, use the value of \(P_{1} / 2\) in place of \(\left(\Delta p P_{2}\right)^{0.5}\) in the denominator of the relation.

To size control valves for vapors other than steam, use the relation \(C_{v}=W\left(v_{2} / \Delta p\right)^{0.5} / 63.4\), where \(W\) is vapor flow rate, in \(\mathrm{lb} / \mathrm{h}, v_{2}\) is specific volume of the vapor at the outlet pressure \(P_{2}\), in \(\mathrm{ft}^{3} / \mathrm{lb}\);


FIGURE 19.13 Pressure-drop correction factor for water in the liquid state. (International Engineering Associates.) other symbols as before. When \(P_{2}\) is less than \(0.5 P_{1}\), use the value of \(P_{1} / 2\) in place of \(\Delta p\) and use the corresponding value of \(v_{2}\) at \(P_{1} / 2\).

When the control valve handles a flashing mixture of water and steam, compute \(C_{v}\) using the relation for liquids given earlier after determining which pressure drop to use in the equation. Use the actual pressure drop or the allowable pressure drop, whichever is smaller. Find the allowable pressure drop by taking the product of the supply pressure, in psia, and the correction factor \(R\), where \(R\) is obtained from Fig. 19.13. For a further discussion of controlvalve sizing, see Considine-Process Instruments and Controls Handbook, McGraw-Hill, and G. F. Brockett and C. F. King-"Sizing Control Valves Handling Flashing Liquids," Texas A \& M Symposium.

\subsection*{19.17 CONTROL-VALVE CHARACTERISTICS AND RANGEABILITY}

A flow control valve will be installed in a process system in which the flow may vary from 100 to 20 percent while the pressure drop in the system rises from 5 to 80 percent. What is the required rangeability of the control valve? What type of control-valve characteristic should be used? Show how the effective characteristic is related to the pressure drop the valve should handle.

\section*{Calculation Procedure}
1. Compute the required valve rangeability. Use the relation \(R=\left(Q_{1} / Q_{2}\right)\left(\Delta P_{2} / \Delta P_{1}\right)^{0.5}\), where \(R\) is valve rangeability, \(Q_{1}\) is valve initial flow, in percent of total flow, \(Q_{2}\) is valve final flow, in percent of total flow, \(P_{1}\) is initial pressure drop across the valve, in percent of total pressure drop, and \(P_{2}\) is percent final pressure drop across the valve. Substituting, \(R=(100 / 20)(80 / 5)^{0.5}=20\).
2. Select the type of valve characteristic to use. Table 19.1 lists the typical characteristics of various control valves. Study of Table 19.1 shows that an equal-percentage valve must be used if a rangeability of 20 is required. Such a valve has equal stem movements for equal-percentage changes

TABLE 19.1 Control-Valve Characteristics
\begin{tabular}{lcc}
\hline \multicolumn{1}{c}{ Valve type } & Typical flow rangeability & \multicolumn{1}{c}{ Stem movement } \\
\hline Linear & \(12-1\) & \begin{tabular}{c} 
Equal stem movement for equal \\
flow change \\
Equal stem movement for equal-percentage \\
flow change* \\
Equal percentage
\end{tabular}\(\quad 30-1\) to \(50-1\)
\end{tabular} \begin{tabular}{c} 
Same as linear up to on-off range \\
On-off \\
of travel; on-off thereafter for first 25 percent
\end{tabular}
*At constant pressure drop.


FIGURE 19.14 (a) Inherent flow characteristics of valves at constant pressure drop; \((b)\) effective characteristics of a linear valve; (c) effective characteristics of a \(50: 1\) equal-percentage valve.
in flow at a constant pressure drop based on the flow occurring just before the change is made.* The equal-percentage valve finds use where large rangeability is desired and where equal-percentage characteristics are necessary to match the process characteristics.
3. Show how the valve effective characteristic is related to pressure drop. Figure 19.14 shows the inherent and effective characteristics of typical linear, equal-percentage, and on-off control valves. The inherent characteristic is the theoretical performance of the valve.* If a valve is to operate at a constant load without changes in the flow rate, the characteristic of the valve is not important, since only one operating point of the valve is used.

Figure \(19.14 b\) and \(c\) give definite criteria for the amount of pressure drop the control valve should handle in the system. This pressure drop is not an arbitrary value, such as \(5 \mathrm{lb} / \mathrm{in}^{2}\), but rather a percent of the total dynamic drop. The control valve should take at least 33 percent of the total dynamic system pressure drop if an equal-percentage valve is used and is to retain its inherent characteristics. A linear valve should not take less than a 50 percent pressure drop if its linear properties are desired.

There is an economic compromise in the selection of every control valve. Where possible, the valve pressure drop should be as high as needed to give good control. If experience or an economic study dictates that the requirement of additional horsepower to provide the needed pressure is not worth the investment in additional pumping or compressor capacity, the valve should take less pressure drop with the resulting poorer control.

\subsection*{19.18 CAVITATION, SUBCRITICAL, AND CRITICAL-FLOW CONSIDERATIONS IN CONTROLLER SELECTION}

Using the sizing formulas of the Fluid Controls Institute, Inc., size control valves for the cavitation, subcritical, and critical flow situations described below. Show how accurate the FCI formulas are.

\footnotetext{
*E. Ross Forman-"Fundamentals of Process Control," Chemical Engineering, June 21, 1965.
}

Cavitation: Select a control valve for a situation where cavitation may occur. The fluid is steam condensate; inlet pressure \(P_{1}\) is \(167 \mathrm{psia}(1151.5 \mathrm{kPa}) ; \Delta P\) is \(105 \mathrm{lb} / \mathrm{in}^{2}(724.0 \mathrm{kPa})\); inlet temperature \(T_{1}\) is \(180^{\circ} \mathrm{F}\left(82.2^{\circ} \mathrm{C}\right)\); vapor pressure \(P_{v}\) is \(7.5 \mathrm{psia}(51.7 \mathrm{kPa})\).

Subcritical gas flow: Determine the valve capacity required at these conditions; fluid is air; flow \(Q_{g}\) is \(160,000 \mathrm{std} \mathrm{ft}^{3} / \mathrm{h}\left(1.3 \mathrm{std} \mathrm{m}^{3} / \mathrm{s}\right)\); inlet pressure \(P_{1}\) is \(275 \mathrm{psia}(1896 \mathrm{kPa}) ; \Delta P\) is \(90 \mathrm{lb} / \mathrm{in}^{2}\) ( 620.4 kPa ); gas temperature \(T_{1}\) is \(60^{\circ} \mathrm{F}\left(15.6^{\circ} \mathrm{C}\right)\).

Critical vapor flow: A heavy-duty angle valve is suggested for a steam pressure-reducing application. Determine the capacity required and compare an alternate valve type. The fluid is saturated steam; flow \(W\) is \(78,000 \mathrm{lb} / \mathrm{h}(9.8 \mathrm{~kg} / \mathrm{s})\); inlet pressure \(P_{1}\) is \(1260 \mathrm{psia}(8688 \mathrm{kPa})\); and outlet pressure \(P_{2}\) is \(300 \mathrm{psia}(2068.5 \mathrm{kPa})\).

\section*{Calculation Procedure}
1. Choose the valve type and determine its critical-flow factor for the cavitation situation. If otherwise suitable (i.e., with respect to size, materials, and space considerations), a butterfly control valve is acceptable on a steam-condensate application. Find, from Table 19.2, the value of the critical flow factor \(C_{f}=0.68\) for a butterfly valve with \(60^{\circ}\) operation.
2. Compute the maximum allowable pressure differential for the valve. Use the relation \(\Delta P_{m}=\) \(C_{f}^{2}\left(P_{1}-P_{v}\right)\), where \(\Delta P_{m}\) is maximum allowable pressure differential, in \(\mathrm{lb} / \mathrm{in}^{2}, P_{1}\) is inlet pressure, in psia, and \(P_{v}\) is vapor pressure, in psia. Substituting, \(\Delta P_{m}=(0.68)^{2}(167-7.5)=74 \mathrm{lb} / \mathrm{in}^{2}\) \((510.2 \mathrm{kPa})\). Since the actual pressure drop, \(105 \mathrm{lb} / \mathrm{in}^{2}(724.0 \mathrm{kPa})\), exceeds the allowable drop, \(74 \mathrm{lb} / \mathrm{in}^{2}(510.2 \mathrm{kPa})\), cavitation will occur.
3. Select another valve and repeat the cavitation calculation. For a single-port top-guided valve with flow to open plug, find \(C_{f}=0.90\) from Table 19.2. Then \(\Delta P_{m}=(0.90)^{2}(167-7.5)=129 \mathrm{lb} /\) \(\mathrm{in}^{2}\) ( 889.5 kPa ).

In the case of the single-port top-guided valve, the allowable pressure drop, \(129 \mathrm{lb} / \mathrm{in}^{2}(889.5 \mathrm{kPa})\), exceeds the actual pressure drop, \(105 \mathrm{lb} / \mathrm{in}^{2}(724.0 \mathrm{kPa})\), by a comfortable margin. This valve is a better selection because cavitation will be avoided. A doubleport valve might also be used, but the single-port valve offers lower seat leakage. However, the double-port valve offers the possibility of a more economical actuator, especially in larger valve sizes. This concludes the steps for choosing the valve where cavitation conditions apply.
4. Apply the FCI formula for subcritical flow. The FCI formula for subcritical gas flow is \(C_{v}=\) \(Q_{g} /\left[1360(\Delta P / G T)^{0.5}\right]\left[\left(P_{1}+P_{2}\right) / 2\right]^{0.5}\), where \(C_{v}\) is valve flow coefficient, \(Q_{g}\) is gas flow, in std \(\mathrm{ft}^{3} / \mathrm{h}, \Delta P\) is pressure differential, in \(\mathrm{lb} / \mathrm{in}^{2}, G\) is specific gravity of gas at \(14.7 \mathrm{psia}(101.4 \mathrm{kPa})\) and \(60^{\circ} \mathrm{F}\) \(\left(15.6^{\circ} \mathrm{C}\right)\), and \(T\) is absolute temperature of the gas, in \(R\); other symbols as given earlier. Substituting, \(C_{v}=160,000 /\left[1360(90 / 520)^{0.5}\right][(275+185) / 2]^{0.5}=18.6\).
5. Compute \(\boldsymbol{C}_{\boldsymbol{v}}\) using the unified gas-sizingformula. For greater accuracy, many engineers use the unified gas-sizing formula. Assuming a single-port top-guided valve installed open to flow, Table 19.2 shows \(C_{f}=0.90\). Then, \(Y=\left(1.63 / C_{f}\right)\left(\Delta P / P_{1}\right)^{0.5}\), where \(Y\) is defined by the equation and the other symbols are as given earlier. Substituting, \(Y=(1.63 / 0.90)(90 / 275)^{0.5}=1.04\). Figure 19.15 shows the flow correlation established from actual test data for many valve configurations at a maximum valve opening and relates \(Y\) and the fraction of the critical flow rate.

Find from Fig. 19.16 the value of \(Y-0.148 Y^{3}=0.87\). Compute \(C_{v}=Q_{g}(G T)^{0.5} /\left[834 C_{f}\right.\) \(\left.\times\left(Y-0.148 Y^{3}\right)\right]\), where all the symbols are as given earlier. Or, \(C_{v}=160,000(520)^{0.5} /[834(0.90)\) \((275)(0.87)]=20.4\). This value represents an error of approximately 10 percent in the use of the FCI formula.
6. Determine \(\boldsymbol{C}_{\boldsymbol{f}}\) for critical vapor flow. Assuming reduced valve trim for a heavy-duty angle valve, \(C_{f}=0.55\) from Table 16.2.



FIGURE 19.15 Flow correlation established from actual data for many valve configurations at maximum valve opening.


FIGURE 19.16 Correction-factor values.
7. Compute the critical pressure drop in the valve. Use \(\Delta P_{c}=0.5\left(C_{f}\right)^{2} P_{1}\), where \(P_{c}\) is critical pressure drop, in in \({ }^{2}\); other symbols are as given earlier. Substituting, \(\Delta P_{c}=0.5(0.55)^{2}(1260)=\) \(191 \mathrm{lb} / \mathrm{in}^{2}(1316.9 \mathrm{kPa})\).
8. Determine the value of \(\boldsymbol{C}_{v}\). Use the relation \(C_{v}=W /\left[1.83 C_{f} P_{1}\right]\), where the symbols are as given earlier. Substituting, \(C_{v}=78,000 /[1.83(0.55)(1260)]=61.5\). A lower \(C_{v}\) could be attained by using the valve flow to open, but a more economical choice is a single-port top-guided valve installed open to flow.

For a single-port top-guided valve flow to open, \(C_{f}=0.90\) from Table 19.2. Hence, \(C_{v}=\) \(78,000 /[1.83(0.90)(1260)]=37.6\).

A lower capacity is required at critical flow for a valve with less pressure recovery. Although this may not lead to a smaller body size because of velocity and stability considerations, the choice of a more economical body type and a smaller actuator requirement is attractive. The heavy-duty angle valve finds its application generally on flashing-hydrocarbon liquid service with a coking tendency.

This Calculation Procedure is the work of Henry W. Boger, Engineering Technical Group Manager, Worthington Controls Co.

\subsection*{19.19 INDIRECT DRYING OF SOLIDS}

An indirect dryer consisting of a heating section, a constant-rate-drying section, and a falling-ratedrying section in series is to lower the water content of \(1000 \mathrm{lb} / \mathrm{h}(454 \mathrm{~kg} / \mathrm{h})\) of feed from 20 to 5 percent. The feed temperature is \(60^{\circ} \mathrm{F}(289 \mathrm{~K})\), and the product leaves the dryer at \(260^{\circ} \mathrm{F}(400 \mathrm{~K})\). The specific heat of the solid is \(0.4 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)[1.67 \mathrm{~kJ} /(\mathrm{kg})(\mathrm{K})]\); that of water is \(1.0 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right)\) \([4.19 \mathrm{~kJ} /(\mathrm{kg})(\mathrm{K})]\). The heating medium is \(338^{\circ} \mathrm{F}(443 \mathrm{~K})\) steam. The heat-transfer rates in the heating, constant-rate-drying and falling-rate-drying sections are 25,40 , and \(15 \mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\), respectively. The surface loading in the three sections is 100,80 , and 60 percent, respectively. Thermal data for the moisture and solids are as follows:

Evaporation enthalpy:
Water enthalpy at \(212^{\circ} \mathrm{F}\) :
Water-vapor enthalpy, averaged over 212 to \(260^{\circ} \mathrm{F}\)
Solids temperature during constant-rate drying
Product moisture at start of falling-rate drying
```

970.3 Btu/lb (2257 kJ/kg)
180.2 Btu/lb (419 kJ/kg)
1159.0 Btu/lb (2696 kJ/kg)
212}\mp@subsup{}{}{\circ}\textrm{F}(373\textrm{K}
1 0 percent

```

Determine the heat load for each section of the dryer, as well as the area required for each.

\section*{Calculation Procedure}
1. Calculate the flow rate of dry solids \(\boldsymbol{W}_{S}\). As the feed moisture is 20 percent and the total flow rate is \(1000 \mathrm{lb} / \mathrm{h}, W_{s}=1000(1-0.20)=800 \mathrm{lb} / \mathrm{h}(363 \mathrm{~kg} / \mathrm{h})\).
2. Determine the product flow rate \(\boldsymbol{W}_{\boldsymbol{P}}\). Since \(W_{S}\) is \(800 \mathrm{lb} / \mathrm{h}\) and the product moisture is 5 percent, \(W_{P}=800 /(1-0.05)=842.1 \mathrm{lb} / \mathrm{h}(382 \mathrm{~kg} / \mathrm{h})\).
3. Calculate the total amount of liquid to be removed. Because the feed rate is \(1000 \mathrm{lb} / \mathrm{h}\) and the product rate \(842.1 \mathrm{lb} / \mathrm{h}\), the liquid removed (i.e., evaporated) is \(1000-842.1=157.9 \mathrm{lb} / \mathrm{h}\) ( \(71.7 \mathrm{~kg} / \mathrm{h}\) ).
4. Determine the amount of moisture in the in-process material as it passes from the constantrate section into the falling-rate section. As the moisture content at this point is 10 percent and the dry-solids rate is \(800 \mathrm{lb} / \mathrm{h}\), the flow rate for the in-process material at this point is \(800 /\) \((1-0.10) \mathrm{lb} / \mathrm{h}\). The moisture in the material is, then, \([800 /(1-0.10)][0.10]\), or \(88.9 \mathrm{lb} / \mathrm{h}(40.4 \mathrm{~kg} / \mathrm{h})\).
5. Calculate the moisture leaving in the final product. The product rate is \(842.1 \mathrm{lb} / \mathrm{h}\) and its moisture content 5 percent, so the moisture leaving in the final product is \((842.1)(0.05)\), or \(42.1 \mathrm{lb} / \mathrm{h}\) (19.1 kg/h).
6. Determine the moisture removed in the falling-rate zone. Because the moisture entering this zone is \(88.9 \mathrm{lb} / \mathrm{h}\) and the amount leaving in the product is \(42.1 \mathrm{lb} / \mathrm{h}\), the amount removed from the in-process material in this zone is \(88.9-42.1\), or \(46.8 \mathrm{lb} / \mathrm{h}(21.2 \mathrm{~kg} / \mathrm{h})\).
7. Find the amount of moisture removed in the constant-rate zone. The total removed in the dryer is \(157.9 \mathrm{lb} / \mathrm{h}\) and the amount removed in the falling-rate zone is \(46.8 \mathrm{lb} / \mathrm{h}\), so the amount removed in the constant-rate zone is \(157.9-46.8\), or \(111.1 \mathrm{lb} / \mathrm{h}(50.4 \mathrm{~kg} / \mathrm{h})\).
8. Calculate \(\boldsymbol{Q}_{H S}\), the heat load for the solid in the heating zone. Now, \(Q_{H S}=W_{S} C_{S} \Delta T\), where \(W_{S}\) is the solid flow rate, \(C_{S}\) the specific heat of the solid, and \(\Delta T\) the temperature rise for the solid in this zone. Thus, \(Q_{H S}=(800)(0.4)(212-60)=48,640 \mathrm{Btu} / \mathrm{h}(14.25 \mathrm{~kW})\).
9. Calculate \(Q_{H L}\), the heat load for the liquid in this zone. Use the same procedure as in step 8, but with the liquid flow rate and specific heat. Thus, \(Q_{H L}=[(0.20)(1000)][1.0][212-60]=30,400\) Btu/h ( 8.91 kW ).
10. Find \(Q_{H}\), the total heat load for this zone. It is the sum of the solid and liquid heat loads: \(Q_{H}=48,640+30,400=79,040 \mathrm{Btu} / \mathrm{h}(23.16 \mathrm{~kW})\).
11. Determine \(Q_{C}\), the heat load in the constant-rate-drying zone. The heat in this zone serves solely for evaporation, with no sensible heating. The amount of water evaporated in this zone was found in step 7. Then, \(Q_{C}=(970.3)(111.1)=107,800 \mathrm{Btu} / \mathrm{h}(31.58 \mathrm{~kW})\).
12. Calculate \(Q_{F S}\), the heat load for the solid in the falling-rate zone. As in step \(8, Q_{F S}=\) \((800)(0.4)(260-212)=15,360 \mathrm{Btu} / \mathrm{h}(4.5 \mathrm{~kW})\).
13. Find \(Q_{F E}\), the heat load for evaporation in the falling-rate zone. The amount of water removed in this zone was found in step 6 . For the heat load per pound of evaporated water, use the difference in enthalpy between that for water at \(212^{\circ} \mathrm{F}\) and the averaged value for water vapor between 212 and \(260^{\circ} \mathrm{F}\), as stated at the beginning of the problem. Thus, \(Q_{F E}=(46.8)(1159-180.2)=\) 45,808 Btu/h (13.4 kW).
14. Calculate \(Q_{F L}\), the heat load for unevaporated liquid in the falling-rate zone. This is the liquid that remains as moisture in the final product. The amount was calculated in step 5. In the falling-rate zone, it becomes heated from 212 to \(260^{\circ} \mathrm{F}\). As in step \(8, Q_{F L}=(42.1)(1.0)(260-212)=2021 \mathrm{Btu} / \mathrm{h}\) (592 W).
15. Calculate \(Q_{F}\), the total heat load in the falling-rate zone. Sum the quantities calculated in the previous three steps. Thus, \(Q_{F}=15,360+45,808+2021=63,189 \mathrm{Btu} / \mathrm{h}(18.51 \mathrm{~kW})\).
16. Calculate \(\Delta T_{m H}\), the log-mean temperature difference in the heating zone. Let \(T_{i}\) and \(T_{o}\) be the heating-medium (i.e., steam) temperature at the zone inlet and outlet, respectively, and \(t_{i}\) and \(t_{o}\) correspondingly be the temperature of the in-process material at the zone inlet and outlet. Then
\[
\begin{aligned}
\Delta T_{m H} & =\left[\left(T_{i}-t_{o}\right)-\left(T_{o}-t_{i}\right)\right] / \ln \left[\left(T_{i}-t_{o}\right) /\left(T_{o}-t_{i}\right)\right] \\
& =[(338-212)-(338-60)] / \ln [(338-212) /(338-60)]=192.1 \text { Fahrenheit degrees } .
\end{aligned}
\]
17. Determine \(A_{H}\), the surface area required in the heating zone. Use the equation \(A=\) \(Q / U \Delta T L\), where \(A\) is the required surface area, \(Q\) the heat load (from step 10), \(U\) the overall heat-transfer coefficient, \(\Delta T\) the \(\log\) mean temperature difference, and \(L\) the surface loading. Thus, \(A=79,040 /(25)(192.1)(1.0)=16.46 \mathrm{ft}^{2}\left(1.53 \mathrm{~m}^{2}\right)\).
18. Calculate \(A_{C}\), the surface area required in the constant-rate-drying zone. In this case, the temperature difference between the \(338^{\circ} \mathrm{F}\) steam and the \(212^{\circ} \mathrm{F}\) in-process material is constant. Thus, via the equation from step \(17, A=107,800 /(40)(338-212)(0.8)=26.74 \mathrm{ft}^{2}\left(2.49 \mathrm{~m}^{2}\right)\).
19. Calculate \(\Delta T_{m F}\), the log-mean temperature difference in the falling-rate zone. As in step 16, \(\Delta T_{m F}=[(338-260)-(338-212)] / \ln [(338-260) /(338-212)]=100.1\) Fahrenheit degrees.
20. Calculate \(A_{F}\), the surface area required for the falling-rate zone. As in step \(18, A=\) \(63,189 /(15)(100.1)(0.6)=70.14 \mathrm{ft}^{2}\left(6.52 \mathrm{~m}^{2}\right)\).
21. Determine the total surface area required for the dryer. From steps 17, 18, and 20, the total is \(16.46+26.74+70.14=113.3 \mathrm{ft}^{2}\left(10.54 \mathrm{~m}^{2}\right)\).
22. Find the total heat load. From steps 10,11 , and 15 , the total is \(79,040+107,800+63,189=\) 250,029 Btu/h ( 73.3 kW ).

Related Calculations. This example is adapted from Process Drying Practice by Cook and DuMont, published in 1991 by McGraw-Hill. More details are available in that source. Similar calculation for direct dryers is far more complex, involving the psychrometric relations of moist air. Trial-and-error loops are required, and manual calculation is not only time-consuming but also error-prone. A sequence of equations suitable for setting into a computer program can be found in the aforementioned Cook and DuMont.

\subsection*{19.20 VACUUM DRYING OF SOLIDS}

A material having a wet bulk density of \(40 \mathrm{lb} / \mathrm{ft}^{3}\left(640 \mathrm{~kg} / \mathrm{m}^{3}\right)\) and containing \(30 \%\) water is to be fully dried in a rotary vacuum batch dryer. The dryer is \(5 \mathrm{ft}(1.5 \mathrm{~m})\) in diameter and \(20 \mathrm{ft}(6.1 \mathrm{~m})\) long, and has a working volume of \(196 \mathrm{ft}^{3}\left(5.5 \mathrm{~m}^{3}\right)\) and a wetted surface of \(206 \mathrm{ft}^{2}\left(19.1 \mathrm{~m}^{2}\right)\). The maximum product temperature is \(125^{\circ} \mathrm{F}(325 \mathrm{~K})\). Cooling water at \(85^{\circ} \mathrm{F}(302 \mathrm{~K})\) is available to condense the water vapor removed, in a shell-and-tube surface condenser. The condenser is to maintain a vacuum of 85 torr, at which level the vapors will condense at \(115^{\circ} \mathrm{F}(319 \mathrm{~K})\). Pilot studies indicate that the dryer will dry the material at an effective rate of \(1.0 \mathrm{lb} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left[4.9 \mathrm{~kg} /(\mathrm{h})\left(\mathrm{m}^{2}\right)\right]\) and a peak rate of \(2.0 \mathrm{lb} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left[9.8 \mathrm{~kg} /(\mathrm{h})\left(\mathrm{m}^{2}\right)\right]\). On average, how many pounds per hour of dry product can it produce? How much condenser surface is required?

\section*{Calculation Procedure}
1. Determine the charge that the dryer can handle. Multiply the working volume of the dryer by the wet bulk density of the feed. Thus, \(\left(196 \mathrm{ft}^{3}\right)\left(40 \mathrm{lb} / \mathrm{ft}^{3}\right)=7840 \mathrm{lb}(3559 \mathrm{~kg})\).
2. Determine the rate at which the dryer can remove vapor. Multiply the wetted surface by the effective drying rate. Thus, \(\left(206 \mathrm{ft}^{2}\right)\left[1.0 \mathrm{lb} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\right]=206 \mathrm{lb} / \mathrm{h}(93.5 \mathrm{~kg} / \mathrm{h})\).
3. Determine the amount of water to be removed per batch. Multiply the amount of material charged by its water content. Thus, \((0.30)(7840 \mathrm{lb})=2352 \mathrm{lb}(1068 \mathrm{~kg})\) of water.
4. Calculate the drying time per batch. Divide the water to be removed by the rate at which the dryer can remove it. Thus, \(2352 \mathrm{lb} /(206 \mathrm{lb} / \mathrm{h})=11.4 \mathrm{~h}\).
5. Determine the amount of dry product produced per batch. Subtract the amount of water removed (see step 3) from the amount of material charged (step 1). Thus, \(7840 \mathrm{lb}-2352 \mathrm{lb}=5488 \mathrm{lb}\) \((2492 \mathrm{~kg}\) ) dry product.
6. Determine the average production rate in pounds per hour. Divide the amount of dry product per batch by the drying time per batch. Thus, \(5488 \mathrm{lb} / 11.4 \mathrm{~h}=481 \mathrm{lb} / \mathrm{h}(218 \mathrm{~kg} / \mathrm{h})\).
7. Determine the amount of water removed under peak drying conditions. Multiply the wetted surface area by the peak drying rate. Thus, \(\left(206 \mathrm{ft}^{2}\right)\left[2.0 \mathrm{lb} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\right]=412 \mathrm{lb} / \mathrm{h}(187 \mathrm{~kg} / \mathrm{h})\).
8. Determine the required condenser surface. Enter the graph in Fig. 19.17 with \(412 \mathrm{lb} / \mathrm{h}\) peak water removal as abscissa and system operating pressure of 75 torr as the parameter. From the ordinate, read \(190 \mathrm{ft}^{2}\left(17.7 \mathrm{~m}^{2}\right)\) as the required condenser surface.

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How to use:
1. Determine vapor rate in \(\mathrm{lb} / \mathrm{h}\)
2. Select line indicating operating pressure of system
3. Read left from point where vapor rate and system pressure line meet to select proper condenser size


FIGURE 19.17 Shell-and-tube condenser surface as a function of vapor rate and system operating pressure (cooling water at \(85^{\circ} \mathrm{F}\) ). (From Chemical Engineering, January 17, 1977, copyright 1977 by McGraw-Hill, Inc., New York. Reprinted by special permission.)

Related Calculations. Figure 19.17 is valid for condensers of shell-and-tube design, employing cooling water at \(85^{\circ} \mathrm{F}\). This example is adapted from "Vacuum Dryers," Chem. Eng., January 17, 1977.

\subsection*{19.21 ESTIMATING THERMODYNAMIC AND TRANSPORT PROPERTIES OF WATER}

Estimate the following properties of liquid water at \(80^{\circ} \mathrm{F}\) : (1) vapor pressure, (2) density, (3) latent heat of vaporization, (4) viscosity, (5) thermal conductivity. Also, estimate the following properties for saturated water vapor at \(200^{\circ} \mathrm{F}\) : (6) density, (7) specific heat, (8) viscosity, (9) thermal conductivity. And calculate the boiling point of water at 30 psia .

\section*{Calculation Procedure}

For each of the estimates, the procedure consists of using correlation equations that have been derived by regression analysis of the properties of saturated steam, as discussed in more detail under "Related Calculations." The temperatures are to be entered into the equations in degrees Fahrenheit and the pressure (for the boiling-point example) in pounds per square inch absolute. The results are likewise in English units, as indicated below. These correlations are valid only over the range 32 to \(440^{\circ} \mathrm{F}\).
1. Estimate the vapor pressure. The equation is
\[
P=\exp \left[10.9955-9.6866 \ln T+1.9779(\ln T)^{2}-0.085738(\ln T)^{3}\right]
\]

Thus, \(P=\exp \left[10.9955-9.6866(\ln 80)+1.9779(\ln 80)^{2}-0.085738(\ln 80)^{3}\right]=0.504\) psia.
2. Estimate the liquid density. The equation is
\[
\rho_{L}=62.7538-3.5347 \times 10^{-3} T-4.8193 \times 10^{-5} T^{2}
\]

Thus, \(\rho_{L}=62.7538-3.5347 \times 10^{-3}(80)-4.8193 \times 10^{-5}(80)^{2}=62.16 \mathrm{lb} / \mathrm{ft}^{3}\).
3. Estimate the latent heat of vaporization. The equation is
\[
\Delta H_{\text {vap }}=1087.54-0.43110 T-5.5440 \times 10^{-4} T^{2}
\]

Thus, \(\Delta H_{\text {vap }}=1087.54-0.43110(80)-5.5440 \times 10^{-4}(80)^{2}=1049.5 \mathrm{Btu} / \mathrm{lb}\).
4. Estimate the liquid viscosity. The equation is
\[
\mu_{L}=-0.23535+208.65 / T-2074.8 / T^{2}
\]

Thus, \(\mu_{L}=-0.23535+208.65 / 80-2074.8 /(80)^{2}=2.05 \mathrm{lb} /(\mathrm{h})(\mathrm{ft})\).
5. Estimate the liquid thermal conductivity. The equation is
\[
k_{L}=0.31171+6.2278 \times 10^{-4} T-1.1159 \times 10^{-6} T^{2}
\]

Thus, \(k_{L}=0.31171+6.2278 \times 10^{-4}(80)-1.1159 \times 10^{-6}(80)^{2}=0.369 \mathrm{Btu} /(\mathrm{h})(\mathrm{ft})\left({ }^{\circ} \mathrm{F}\right)\).
6. Estimate the vapor density. The equation is
\[
\rho_{V}=\exp \left(-9.3239+4.1055 \times 10^{-2} T-7.1159 \times 10^{-5} T^{2}+5.7039 \times 10^{-8} T^{3}\right)
\]

Thus, \(\rho_{V}=\exp \left[-9.3239+4.1055 \times 10^{-2}(200)-7.1159 \times 10^{-5}(200)^{2}\right.\)
\[
\begin{aligned}
& \left.+5.7039 \times 10^{-8}(200)^{3}\right] \\
= & 0.0301 \mathrm{lb} / \mathrm{ft}^{3}
\end{aligned}
\]
7. Estimate the specific heat of the vapor. The equation is
\[
\begin{aligned}
& C_{p}=0.43827+1.3348 \times 10^{-4} T-5.9590 \times 10^{-7} T^{2}+4.6614 \times 10^{-9} T^{3} \\
& \text { Thus, } \begin{aligned}
C_{p} & =0.43827+1.3348 \times 10^{-4}(200)-5.9590 \times 10^{-7}(200)^{2}+4.6614 \times 10^{-9}(200)^{3} \\
& =0.478 \mathrm{Btu} /(\mathrm{lb})\left({ }^{\circ} \mathrm{F}\right) .
\end{aligned}
\end{aligned}
\]
8. Estimate the vapor viscosity. The equation is
\[
\mu_{V}=0.017493+5.7455 \times 10^{-5} T-1.3717 \times 10^{-8} T^{2}
\]

Thus, \(\mu_{V}=0.017493+5.7455 \times 10^{-5}(200)-1.3717 \times 10^{-8}(200)^{2}=0.028435 \mathrm{lb} /(\mathrm{h})(\mathrm{ft})\).
9. Estimate the thermal conductivity of the vapor. The equation is
\[
k_{V}=0.0097982+2.2503 \times 10^{-5} T-3.3841 \times 10^{-8} T^{2}+1.3153 \times 10^{-10} T^{3}
\]

Thus, \(k_{V}=0.0097982+2.2503 \times 10^{-5}(200)-3.3814 \times 10^{-8}(200)^{2}\)
\[
+1.3153 \times 10^{-10}(200)^{3}=0.01400 \mathrm{Btu} /(\mathrm{h})(\mathrm{ft})\left({ }^{\circ} \mathrm{F}\right)
\]
10. Estimate the boiling point. The equation is
\[
\begin{aligned}
T_{B} & =\exp \left[4.6215+0.34977 \ln P-0.03727(\ln P)^{2}+0.0034492(\ln P)^{3}\right] \\
\text { Thus, } T_{B} & =\exp \left[4.6215+0.34977(\ln 30)-0.03727(\ln 30)^{2}+0.0034492(\ln 30)^{3}\right]=248.6^{\circ} \mathrm{F} .
\end{aligned}
\]

Related Calculations. These equations are presented in Dickey, D.S.,* Practical Formulas Calculate Water Properties, Parts 1 and 2, Chem. Eng., Sept. 1991, pp. 207, 208 and November 1991, pp. 235, 236. That author developed the equations via regression analysis of the properties of saturated steam as presented in Perry's Chemical Engineers' Handbook, 6th ed., McGraw-Hill. The maximum error (compared to tabulated values) and sample standard deviation of the correlations are as follows:
\begin{tabular}{lcc}
\hline \multicolumn{1}{c}{ Property correlation } & Maximum error, \% & Sample standard deviation \\
\hline Vapor pressure & 3.64 & 1.84 \\
Liquid density & 0.26 & 0.10 \\
Latent heat & 0.63 & 0.19 \\
Liquid viscosity & 20.23 & 6.13 \\
Liquid thermal conductivity & 0.43 & 0.20 \\
Vapor density & 7.81 & 1.99 \\
Vapor specific heat & 0.49 & 0.13 \\
Vapor viscosity & 0.37 & 0.19 \\
Vapor thermal conductivity & 1.09 & 0.29 \\
Boiling point & 2.66 & 1.43 \\
\hline
\end{tabular}

The original reference also includes correlations for liquid and vapor specific volume, liquid thermal expansion coefficient, liquid and vapor enthalpy, liquid specific heat, and liquid and vapor Prandtl numbers.

\subsection*{19.22 ASSESSING THE ADEQUACY OF VESSEL-LIFTING EARS}

A horizontal process vessel with an outside diameter of 1400 mm , wall thickness of 6 mm , length of 2500 mm , and total weight of 950 kg , including its nozzles and saddles, is to be lifted by means of two longitudinal lifting ears of 6-mm thickness, \(t\), with dimensions as shown in Fig. 19.18. Other relevant data are as follows: yield stress for ears and vessel shell is \(250 \mathrm{~N} / \mathrm{mm}^{2}\); Young's modulus, \(E\), is \(192,000 \mathrm{~N} / \mathrm{mm}^{2}\); Poisson's ratio, \(v\), is 0.30 ; the radius, \(r_{\mathrm{s}}\), of the shackle pins is 19 mm ; the cables attached to the ears make an angle of 30 deg with the vertical; the plant management requires a safety margin of 2 for hoisting operations; the basic design stress, \(f\), is taken as two-thirds of the yield stress, that is, \((2 / 3)(250)\), or \(166.7 \mathrm{~N} / \mathrm{mm}^{2}\); the moment load, \(M\), of each lifting ear on the cylindrical shell equals \(164,500 \mathrm{~N}-\mathrm{mm}\). Are these lifting ears strong enough?

\section*{Calculation Procedure}

For strength assessment of lifting ears, three stresses are critical:
- the Hertzian contact stress, or, the surface stress due to the load transfer from the hoist line's shackle pin into the eye of the lifting ear;
- the stress arising in the smallest cross-sectional areas next to the eye; and
- the local load stresses in the vessel wall adjacent to the ear.

\footnotetext{
* Dickey is the author of Sec. 12 on liquid agitation in this present handbook.
}


FIGURE 19.18 A horizontal process vessel. Diagrams are not to scale. Dimensions are in millimeters.

Acceptability criteria with respect to each of these three stresses are shown (at the points where needed to solve the problem) in steps 2,3 , and 5 to follow.
1. Determine the force to which the eye in each lifting ear is subjected. Since there are two ears and the angle between the cables and the vertical is 30 deg, each eye is subjected to a force, \(F\), of \((9500 / 2) /[\cos (30 \mathrm{deg})]\), or 5485 N .
2. Calculate the Hertzian contact stress, \(\sigma\), and assess its acceptability by comparing it with the yield stress. This stress can be found from the following formula:
\[
\sigma=\sqrt{\frac{E(F / t)}{2 \pi\left(1-v^{2}\right) r_{\mathrm{e}} r_{\mathrm{s}} /\left(r_{\mathrm{e}}-r_{\mathrm{s}}\right)}}
\]
where \(r_{\mathrm{e}}\) is the radius of the lifting ear eye ( 20 mm ) and the other terms are as previously defined. To accommodate the safety factor of 2 , calculate this stress using a value of (2)(5485), or \(10,970 \mathrm{~N}\), for \(F\). Thus,
\[
\sigma=\left\{[192,000(10,970 / 6)] /\left[2 \pi\left(1-0.30^{2}\right)(20)(19) /(20-19)\right]\right\}^{1 / 2}=402 \mathrm{~N} / \mathrm{mm}^{2}
\]

With respect to Hertzian contact stress, it is recommended that in the absence of actual data, \(\sigma\) should be no greater than twice the yield stress of the ear material. Since the yield stress is given as \(250 \mathrm{~N} / \mathrm{mm}^{2}\), that criterion is satisfied in this example.
3. Determine the normal and bending stresses, \(\sigma_{m e m}\) and \(\sigma_{b e n d}\), in the minimum cross-sectional areas near the eye, and assess the acceptability of the results. The normal (or membrane) stress is calculated by the formula
\[
\sigma_{\mathrm{mem}}=F /(2 w t)
\]
where \(w\), the width of area adjacent to the eye, equals \(0.5 L-r_{\mathrm{e}}, L\) being the ear length \((100 \mathrm{~mm}\) in this case).

Thus, again using \(10,970 \mathrm{~N}\), for \(F\),
\[
\sigma_{\text {mem }}=10,970 /\{2[(0.5)(100)-20][6]\}=30.5 \mathrm{~N} / \mathrm{mm}^{2}
\]

The bending stress is calculated by the formula
\[
\begin{aligned}
\sigma_{\text {bend }} & =1.5\left[\left(r_{\mathrm{e}}+0.5 \mathrm{w}\right) /\left(w^{2} t\right)\right][F] \\
& =1.5\left\{[20+(0.5)(30)] /\left[30^{2}\right][6]\right\}\{10,970\}=106.7 \mathrm{~N} / \mathrm{mm}^{2}
\end{aligned}
\]

The acceptable limits for these two stresses are as follows:
\[
\begin{aligned}
\sigma_{\mathrm{mem}} & \leq f \\
\sigma_{\mathrm{mem}}+\sigma_{\mathrm{bend}} & \leq 1.5 f
\end{aligned}
\]

From the problem statement, \(f\) equals \(166.7 \mathrm{~N} / \mathrm{mm}^{2}\). So, the calculated stresses are acceptable with respect to the smallest cross-sectional area near the eye of the lifting ear.
4. Calculate the line thrust load and the line moment load. The line thrust load equals \(P / L\), where \(P\) is the radial thrust force with respect to the cylindrical vessel ( \(9500 \mathrm{~N} / 2\), or 4750 N ) and \(L\) is the length of the ear. Thus, \(P / L\) equals \(4750 / 100=47.5 \mathrm{~N} / \mathrm{mm}\).

The line moment load equals \(6 M / L^{2}\); in this case, (6) \((164,500) /(100)^{2}=98.7 \mathrm{~N} / \mathrm{mm}\).
5. Calculate the stress intensities for thrust and moment in the vessel wall, and assess their acceptabilities. For both calculations, the formula is
\[
\sigma=\operatorname{SCF}\left[(R T)^{0.5} / T^{2}\right][\text { line load }]
\]

The value of SCF depends on whether the ear is mounted longitudinally (as in this case) or circumferentially and on whether the load is a thrust load or a moment load. For thrust loads on longitudinal ears,
\[
S C F=1.55(R / T)^{0.38}(L / R+0.125)
\]
where \(R\) is the vessel radius ( \(1400 / 2\), or 700 mm , in this case).
Thus
\[
S C F(\text { thrust load, longitudinal ears })=1.55[700 / 6]^{0.38}[(100 / 700)+0.125]=2.53
\]

Therefore,
\[
\sigma(\text { thrust load, longitudinal ears })=2.53\left\{[(700)(6)]^{0.5} /[6]^{2}\right\}\{47.5\}=216 \mathrm{~N} / \mathrm{mm}^{2}
\]

For moment loads with longitudinal ears,
\[
S C F=0.23(R / T)^{0.62}(L / R)=(0.23)(700 / 6)^{0.62}(100 / 700)=0.628
\]

Therefore,
\[
\sigma(\text { moment load, longitudinal ears })=0.628\left\{[(700)(6)]^{0.5} /[6]^{2}\right\}\{98.7\}=112 \mathrm{~N} / \mathrm{mm}^{2}
\]

Note that both of these SCF equations are only applicable within the ranges of \(40<(R / T)<250\) together with \(0.04<(L / R)<0.6\) and that they apply only to cylindrical shells.

The acceptable limit with respect to local load stresses is
\[
\sigma_{\text {thrust }}+\sigma_{\text {moment }} \leq 2 f
\]

In this example, \(217+112\) is indeed less than \(2 \times 166.7\), so the ears are acceptable as regards local load stresses.

In summary, the ears meet all three criteria stated at the beginning of the problem, and they are thus acceptable.

Related Calculations. The expression for calculating the Hertzian contact stress can be simplifies to
\[
0.418 \sqrt{\frac{E(F / t)}{r_{\mathrm{e}} r_{\mathrm{s}} /\left(r_{\mathrm{e}}-r_{\mathrm{s}}\right)}}
\]
if the assumption is made that the Poisson stress equals 0.30 , its typical value.
For thrust loads and moment loads or circumferential (instead of longitudinal) ears, the SCF equations (within the same validity ranges as shown in step 5) are respectively as follows:
\[
\begin{aligned}
S C F \text { (thrust load, circumferential ears) } & =1.50(R / T)^{0.38}(L / R+0.3) \\
S C F \text { (moment load, circumferential ears) } & =0.18(R / T)^{0.74}(L / R)
\end{aligned}
\]

This example is adapted, with permission, from Chemical Engineering, June 1996, pp. 120ff.```


[^0]:    Note: Superscript ${ }^{\text {exp }}$ means experimental.
    *Values determined graphically by extrapolation.

[^1]:    * This correlation was developed by Fuller, Schettler, and Giddings [31].

[^2]:    *Example 2.8 is adapted from Smith, Chemical Process Design, McGraw-Hill; Examples 2.9, 2.10, and 2.11 are taken from T.G. Hicks, Standard Handbook of Engineering Calculations, McGraw-Hill.

[^3]:    *Example 4.10, Calculating Reaction Conversions, Selectivities, and Yields, is from Smith, Chemical Process Design, McGraw-Hill.

[^4]:    *Example 6.10 is from Chemical Engineering magazine. All the other examples are from T. G. Hicks, Standard Handbook of Engineering Calculations, McGraw-Hill.

[^5]:    * At atmospheric pressure.
    Note: $U=\mathrm{Btu} /(\mathrm{h})\left(\mathrm{ft}^{2}\right)\left({ }^{\circ} \mathrm{F}\right)\left[\mathrm{W} /\left(\mathrm{m}^{2}\right)\left({ }^{\circ} \mathrm{C}\right)\right]$, Under many conditions, either higher or lower values may be realized.

[^6]:    *For copper, multiply table data by 2.0 . For brass, multiply table data by 1.6.
    ${ }^{\dagger}$ Mean temperature difference, ${ }^{\circ} \mathrm{F}$ or ${ }^{\circ} \mathrm{C}$, equals temperature of steam minus average liquid temperature. Heat-transfer data for calculating this table obtained from and used by permission of the American Radiator \& Standard Sanitary Corp.

[^7]:    *Value diameter measured in inches (millimeters).
    Source: Clark-Reliance Corporation.

[^8]:    *Based on bypass operation until the booster pump is put into operation. Larger system factors apply if rough pumping flow must pass through the idling mechanical booster. Any time needed for operating valves and getting the mechanical booster pump up to speed must also be added.

    Source: From Van Atta—Vacuum Science and Engineering, McGraw-Hill.

[^9]:    Source: Link-Belt Div. of FMC Corp.

[^10]:    *Example 7.43, Heat Exchanger Networking, has been adapted from Smith, Chemical Process Design, McGraw-Hill.

[^11]:    1. McAdams-Heat Transmission, 3d ed., McGraw-Hill.
    2. Krieth—Principles of Heat Transfer, 3d ed., Intext Educational Publishers.
    3. Kern-Process Heat Transfer, McGraw-Hill.
    4. Holman-Heat Transfer, 2d ed., McGraw-Hill.
    5. Collier-Convective Boiling and Condensation, McGraw-Hill.
    6. Rohsenow and Hartnett (eds.)—Handbook of Heat Transfer, McGraw-Hill.
    7. Chapman-Heat Transfer, 3d ed., McMillan.
[^12]:    * Portions of the remarks under "Related calculations" at the conclusions of Examples 8.1, 8.3, 8.4, and 8.7 were compiled and appended by the handbook editor.

[^13]:    Note: Flexiring and Flexipac are trademarks of Koch Engineering Co., Inc.

[^14]:    * Called ChemScale levels by Chemineer-Kenics.

[^15]:    * Standard speeds for common agitator drives are $230,190,155,125,100,84,68,56,45$, and $37 \mathrm{r} / \mathrm{min}$ based on actual speeds of nominal 1800 and $1200 \mathrm{r} / \mathrm{min}$ motors and standard gear reductions, which are a geometric progression of the $\sqrt{1.5}$ for enclosed, helical, and spiral bevel gearing (American Gear Manufacturers' Association Standard 420.04, December 1975, p. 29).

[^16]:    Downloaded from Digital Engineering Library @ McGraw-Hill (www.digitalengineeringlibrary.com) Copyright © 2004 The McGraw-Hill Companies. All rights reserved.
    Any use is subject to the Terms of Use as given at the website.

[^17]:    *Example 13.10 is adapted from an article in Chemical Engineering magazine.

[^18]:    * M. Hosseini, M.Sc. thesis, University of Manchester, 1977.

[^19]:    Note: $1.0 \mathrm{gal} / \mathrm{ft}^{2}=0.041 \mathrm{~m}^{3} / \mathrm{m}^{2} ; 1.0 \mathrm{lbm}$ solute $/ \mathrm{gal}=120.02 \mathrm{~kg}$ solute $/ \mathrm{m}^{3}$.

[^20]:    Note: $\mathrm{m}^{3} / \mathrm{s} \times 35.3147=\mathrm{ft}^{3} / \mathrm{s}$.
    $\mathrm{m}^{3} \times 35.3147=\mathrm{ft}^{3}$.
    $\mathrm{mg} / \mathrm{L}=\mathrm{g} / \mathrm{m}^{3}$.

