

Chapter 5 – Single Phase Systems

Lecture 14

5.1 Liquid and Solid Densities

Concept → incompressible

The most accurate way to determine the density of a mixture of liquids or a solution of a solid in a liquid is from experimental data. *Perry's Chemical Engineers' Handbook* provides data for mixtures and solutions of a number of substances on pp. 2-99 through 2-118 and lists additional sources of data on p. 2-99.

In the absence of data, the density $\bar{\rho}$ of a mixture of n liquids (A_1, A_2, \dots, A_n) can be estimated from the component mass fractions [x_i] and pure-component densities [ρ_i] in two ways. First, we might assume *volume additivity*—that is, if 2 mL of liquid A and 3 mL of liquid B are mixed, the resulting volume would be exactly 5 mL. Making this assumption and recognizing that component masses are always additive leads to the formula

$$\frac{1}{\bar{\rho}} = \sum_{i=1}^n \frac{x_i}{\rho_i} \quad (5.1-1)$$

Second, we might simply average the pure-component densities, weighting each one by the mass fraction of the component:

$$\bar{\rho} = \sum_{i=1}^n x_i \rho_i \quad (5.1-2)$$

(Equation 5.1-1 calculates the inverse of the mixture density, or the *specific volume* of the mixture, as the weighted average of the pure-component specific volumes.)

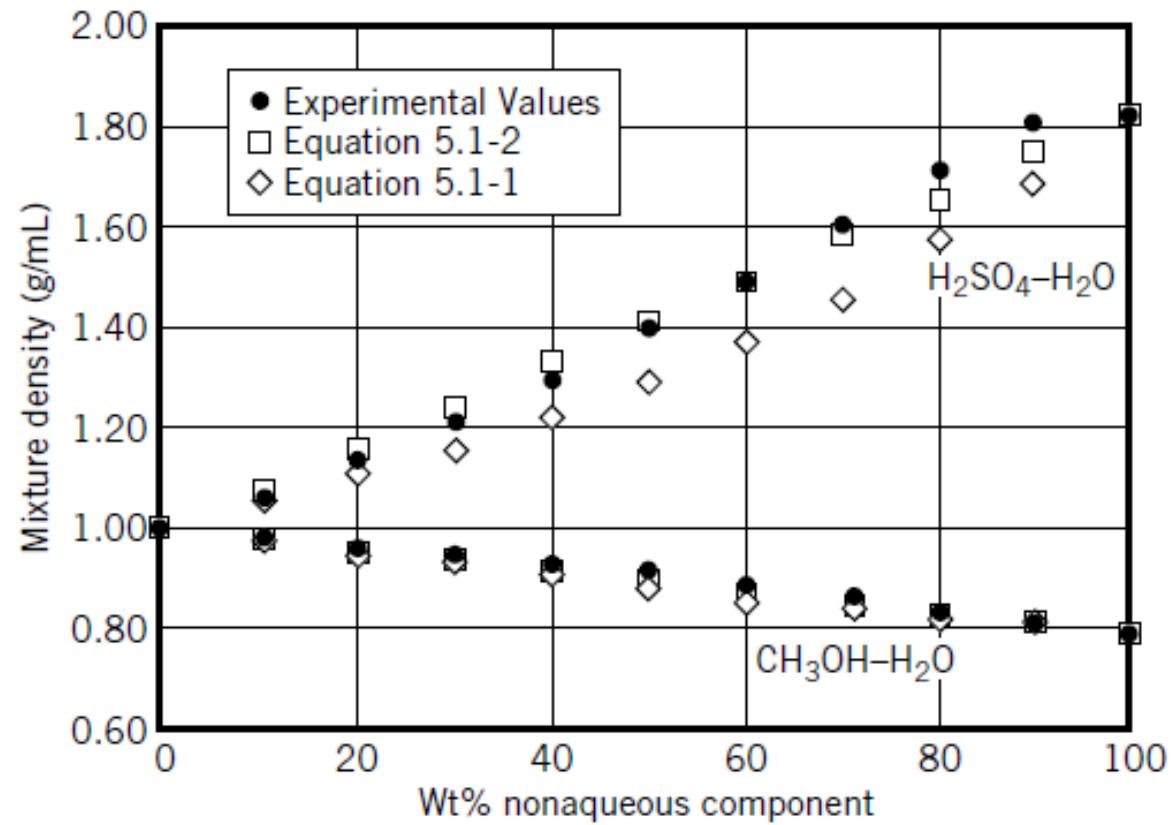


Figure 5.1-1 Experimental and estimated mixture densities. Experimental values from *Perry's Chemical Engineers' Handbook*, p. 2-107 for sulfuric acid–water and p. 2-111 for methanol–water, both at 20°C.

EXAMPLE 5.1-1

Determine the density in g/cm³ of a 50 wt% aqueous solution of H₂SO₄ at 20°C, both by (1) looking up a tabulated value and (2) assuming volume additivity of the solution components.

SOLUTION

- 1. Look It Up.** *Perry's Chemical Engineers' Handbook*, pp. 2-107 and 2-108, tabulates specific gravities of sulfuric acid solutions. From this table,

$$\rho(50\% \text{ H}_2\text{SO}_4, 20^\circ\text{C}) = 1.3951 \text{ g/cm}^3$$

- 2. Estimate It.** The pure-component densities are

$$\rho(\text{H}_2\text{O}, 20^\circ\text{C}) = 0.998 \text{ g/cm}^3 \text{ (*Handbook*, p. 2-91)}$$

$$\rho(\text{H}_2\text{SO}_4, 18^\circ\text{C}) = 1.834 \text{ g/cm}^3 \text{ (*Handbook*, p. 2-25)}$$

We will neglect the density change for H₂SO₄ between 18°C and 20°C, although *Perry's Chemical Engineers' Handbook*, p. 2-131, gives thermal expansion data for H₂SO₄ that could be used to make this minor correction. We then estimate from Equation 5.1-1:

$$1/\bar{\rho} = (0.500/0.998 + 0.500/1.834) \text{ cm}^3/\text{g} = 0.7736 \text{ cm}^3/\text{g}$$



$$\bar{\rho} = 1.29 \text{ g/cm}^3$$

The density estimated assuming volume additivity thus differs from the true density, given in part (1), by $[(1.29 - 1.3951)/1.3951] \times 100\% = -7.3\%$. Alternatively, we could estimate the density from Equation 5.1-2:

$$\bar{\rho} = (0.500 \times 0.998 + 0.500 \times 1.834) \frac{\text{g}}{\text{cm}^3} = 1.42 \text{ g/cm}^3$$

This leads to an estimation error of $[(1.42 - 1.3951)/1.3951] \times 100\% = 1.5\%$. Clearly, the accuracy of Equation 5.1-2 is better in this instance than that of Equation 5.1-1.

5.2 Ideal Gases

An **equation of state** relates the molar quantity and volume of a gas to temperature and pressure. The simplest and most widely used of these relationships is the **ideal gas equation of state** (the familiar $PV = nRT$), which, while approximate, is adequate for many engineering calculations involving gases at low pressures. However, some gases deviate from ideal behavior at nearly all conditions and all gases deviate substantially at certain conditions (notably at high pressures and/or low temperatures). In such cases it is necessary to use more complex equations of state for *PVT* calculations.

5.2a Ideal gas equation of state

$$PV = nRT \quad \text{or} \quad P\dot{V} = \dot{n}RT \quad (5.2-1)$$

where

P = *absolute pressure* of a gas

$V(\dot{V})$ = *volume (volumetric flow rate)* of the gas

$n(\dot{n})$ = *number of moles (molar flow rate)* of the gas

R = the *gas constant*, whose value depends on the units of P , V , n , and T

T = *absolute temperature* of the gas

The equation may also be written as

$$P\hat{V} = RT \quad (5.2-2)$$

where $\hat{V} = V/n$ (or $\dot{\hat{V}}/\dot{n}$) is the **specific molar volume** of the gas.

The ideal gas equation of state is an approximation. It works well under some conditions—generally speaking, at temperatures above about 0°C and pressures below about 1 atm—but at other conditions its use may lead to substantial errors. Here is a useful rule of thumb for when it is reasonable to assume ideal gas behavior. Let X_{ideal} be a quantity calculated using the ideal gas equation of state [$X = P$ (absolute), T (absolute), n or V] and ϵ be the error in the estimated value,

$$\epsilon = \frac{X_{\text{ideal}} - X_{\text{true}}}{X_{\text{true}}} \times 100\%$$

An error of no more than about 1% may be expected if the quantity RT/P (the *ideal specific molar volume*) satisfies the following criterion.³

$$|\epsilon| < 1\% \text{ if } \hat{V}_{\text{ideal}} = \frac{RT}{P} > 5 \text{ L/mol (80 ft}^3/\text{lb-mole)} \quad (\text{diatomic gases}) \quad (5.2-3a)$$

$$> 20 \text{ L/mol (320 ft}^3/\text{lb-mole)} \quad (\text{other gases}) \quad (5.2-3b)$$

EXAMPLE 5.2-1

The Ideal Gas Equation of State

One hundred grams of nitrogen is stored in a container at 23.0°C and 3.00 psig.

1. Assuming ideal gas behavior, calculate the container volume in liters.
2. Verify that the ideal gas equation of state is a good approximation for the given conditions.

SOLUTION

1. The ideal gas equation of state relates absolute temperature, absolute pressure, and the quantity of a gas in moles. We therefore first calculate

$$n = \frac{100.0 \text{ g}}{28.0 \text{ g/mol}} = 3.57 \text{ mol}$$

$$T = 296 \text{ K}$$

and (assuming $P_{\text{atm}} = 14.7 \text{ psia}$) $P = 17.7 \text{ psia}$. Then from the ideal gas equation of state

$$\begin{aligned} V(\text{liters}) &= \frac{nRT}{P} \\ &= \frac{(3.57 \text{ mol})(296 \text{ K})}{17.7 \text{ psia}} \left| \begin{array}{c|c} R(\text{liter}\cdot\text{psia}) & \\ \hline & (\text{mol}\cdot\text{K}) \end{array} \right. \end{aligned}$$

Unfortunately, the table of gas constants at the back of this book does not list the value of R with this particular set of units. In its absence, we use an available value and carry out the necessary additional unit conversions.

$$V = \frac{(3.57 \text{ mol})(296 \text{ K})}{17.7 \text{ psi}} \left| \begin{array}{c|c|c} 0.08206 \text{ liter}\cdot\text{atm} & 14.7 \text{ psi} & 72.0 \text{ liters} \\ \hline \text{mol}\cdot\text{K} & \text{atm} & \end{array} \right.$$

2. To check the assumption of ideal gas behavior for N_2 (a diatomic gas), we apply Criterion 5.3-a. Since we have already determined n and V_{ideal} , we can determine $\hat{V}_{\text{ideal}} = V_{\text{ideal}}/n$ rather than as RT/P . (Both calculations yield the same value, which you might want to verify for yourself.)

$$\hat{V}_{\text{ideal}} = \frac{V}{n} = \frac{72.0 \text{ L}}{3.57 \text{ mol}} = 20.2 \text{ L/mol} > 5 \text{ L/mol}$$

Since the calculated value of \hat{V}_{ideal} exceeds the criterion value of 5 L/mol, the ideal gas equation of state should yield an error of less than 1%.

5.2b Standard Temperature and Pressure

The standard conditions most commonly used are shown in Table 5.2-1. Standard temperature ($T_s = 0^\circ\text{C} \implies 273\text{ K}$) and standard pressure ($P_s = 1\text{ atm}$) are easy to remember. You should also commit to memory the following values of the standard specific molar volume:

$$\hat{V}_s = 22.4 \frac{\text{m}^3(\text{STP})}{\text{kmol}} \iff 22.4 \frac{\text{L}(\text{STP})}{\text{mol}} \iff 359 \frac{\text{ft}^3(\text{STP})}{\text{lb-mole}} \quad (5.2-6)$$

Table 5.2-1 Standard Conditions for Gases

System	T_s	P_s	V_s	n_s
SI	273 K	1 atm	0.022415 m ³	1 mol
CGS	273 K	1 atm	22.415 L	1 mol
American Engineering	492°R	1 atm	359.05 ft ³	1 lb-mole

EXAMPLE 5.2-2**Conversion from Standard Conditions**

Butane (C_4H_{10}) at 360°C and 3.00 atm absolute flows into a reactor at a rate of 1100 kg/h. Calculate the volumetric flow rate of this stream using conversion from standard conditions.

SOLUTION

As always, molar quantities and absolute temperature and pressure must be used.

$$\dot{n} = \frac{1100 \text{ kg/h}}{58.1 \text{ kg/kmol}} = 19.0 \text{ kmol/h}$$

$$T = 633 \text{ K}, \quad P = 3.00 \text{ atm}$$

From Equation 5.2-5

$$\frac{P\dot{V}}{P_s\hat{V}_s} = \dot{n}\frac{T}{T_s} \implies \dot{V} = \dot{n}\hat{V}_s \frac{T}{T_s} \frac{P_s}{P}$$



$$\dot{V} = \frac{19.0 \text{ kmol}}{\text{h}} \left| \begin{array}{c|c|c|c} 22.4 \text{ m}^3(\text{STP}) & 633 \text{ K} & 1.00 \text{ atm} \\ \hline \text{kmol} & 273 \text{ K} & 3.00 \text{ atm} \end{array} \right. = \boxed{329 \frac{\text{m}^3}{\text{h}}}$$

5.2c Ideal Gas Mixtures

Suppose n_A moles of substance A, n_B moles of B, n_C moles of C, and so on, are contained in a volume V at a temperature T and total pressure P . The **partial pressure** p_A and **pure-component volume** v_A of A in the mixture are defined as follows:

p_A : the pressure that would be exerted by n_A moles of A alone in the same total volume V at the same temperature T .

v_A : the volume that would be occupied by n_A moles of A alone at the total pressure P and temperature T of the mixture.

Suppose next that each of the individual mixture components and the mixture as a whole behave in an ideal manner. (This is the definition of an **ideal gas mixture**.) If there are n moles of all species in the volume V at pressure P and temperature T , then

$$PV = nRT$$

In addition, from the definition of partial pressure,

$$p_A V = n_A RT$$

Dividing the second equation by the first yields

$$\frac{p_A}{P} = \frac{n_A}{n} = y_A \quad (\text{the mole fraction of A in the gas})$$

or

$$\boxed{p_A = y_A P} \quad (5.2-7)$$

That is, *the partial pressure of a component in an ideal gas mixture is the mole fraction of that component times the total pressure.*⁴ Moreover, since $y_A + y_B + \dots = 1$,

$$p_A + p_B + \dots = (y_A + y_B + \dots)P = P \quad (5.2-8)$$

or, *the partial pressures of the components of an ideal gas mixture add up to the total pressure (Dalton's law).*

A similar series of calculations can be performed for pure-component volumes:

$$\begin{aligned} Pv_A &= n_A RT \\ &\downarrow \text{Divide by } PV = nRT \\ \frac{v_A}{V} &= \frac{n_A}{n} = y_A \end{aligned}$$

or

$$\boxed{v_A = y_A V} \quad (5.2-9)$$

and

$$v_A + v_B + \dots = V \quad (\text{Amagat's law})$$

EXAMPLE 5.2-5

Material Balances on an Evaporator-Compressor

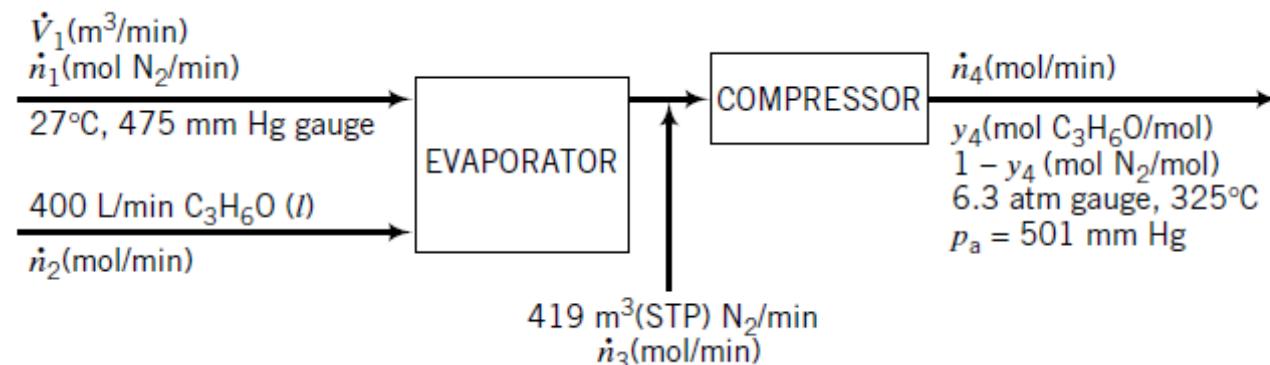
Liquid acetone (C_3H_6O) is fed at a rate of 400 L/min into a heated chamber, where it evaporates into a nitrogen stream. The gas leaving the heater is diluted by another nitrogen stream flowing at a measured rate of $419 \text{ m}^3(\text{STP})/\text{min}$. The combined gases are then compressed to a total pressure $P = 6.3 \text{ atm gauge}$ at a temperature of 325°C . The partial pressure of acetone in this stream is $p_a = 501 \text{ mm Hg}$. Atmospheric pressure is 763 mm Hg.

1. What is the molar composition of the stream leaving the compressor?
2. What is the volumetric flow rate of the nitrogen entering the evaporator if the temperature and pressure of this stream are 27°C and 475 mm Hg gauge?

SOLUTION

Basis: Given Feed Rates

Assume ideal gas behavior. Let $\dot{n}_1, \dot{n}_2, \dots$ (mol/min) be the molar flow rates of each stream.



You should be able to examine the flowchart and see exactly how the solution will proceed.

1. Calculate \dot{n}_2 (from the given volumetric flow rate and a tabulated density of liquid acetone), \dot{n}_3 (from the ideal gas equation of state), and y_4 ($= p_a/P$).
2. Calculate \dot{n}_4 (overall acetone balance), \dot{n}_1 (overall mass balance), and \dot{V}_1 (ideal gas equation of state).

Calculate Molar Flow Rate of Acetone

From Table B.1 in Appendix B, the density of liquid acetone is 0.791 g/cm³ (791 g/L), so that

$$\dot{n}_2 = \frac{400 \text{ L}}{\text{min}} \left| \begin{array}{c} 791 \text{ g} \\ \text{L} \end{array} \right| \frac{1 \text{ mol}}{58.08 \text{ g}} = 5450 \frac{\text{mol C}_3\text{H}_6\text{O}}{\text{min}}$$

Determine Mole Fractions from Partial Pressures

In the stream leaving the compressor,

$$\frac{p_a}{P} = y_4 \left(\frac{\text{mol C}_3\text{H}_6\text{O}}{\text{mol}} \right)$$

$$P = P_{\text{gauge}} + P_{\text{atm}} = \frac{6.3 \text{ atm}}{\left| \begin{array}{c} 760 \text{ mm Hg} \\ 1 \text{ atm} \end{array} \right|} + 763 \text{ mm Hg} = 5550 \text{ mm Hg}$$

so that

$$y_4 = \frac{501 \text{ mm Hg}}{5550 \text{ mm Hg}} = 0.0903 \frac{\text{mol C}_3\text{H}_6\text{O}}{\text{mol}}$$

$$1 - y_4 = 0.9097 \frac{\text{mol N}_2}{\text{mol}}$$

Calculate \dot{n}_3 from PVT Information

$$\dot{n}_3 = \frac{419 \text{ m}^3(\text{STP})}{\text{min}} \left| \frac{1 \text{ mol}}{0.0224 \text{ m}^3(\text{STP})} \right. = 18,700 \frac{\text{mol}}{\text{min}}$$

Overall Mole Balance on Acetone $\dot{n}_2 = \dot{n}_4 y_4$

$$\begin{array}{l} \downarrow \\ \dot{n}_2 = 5450 \text{ mol/min} \\ y_4 = 0.0903 \end{array}$$

$$\dot{n}_4 = 60,400 \text{ mol/min}$$

Overall Mole Balance $\dot{n}_1 + \dot{n}_2 + \dot{n}_3 = \dot{n}_4$

$$\begin{array}{l} \downarrow \\ \dot{n}_2 = 5450 \text{ mol/min} \\ \dot{n}_3 = 18,700 \text{ mol/min} \\ \dot{n}_4 = 60,400 \text{ mol/min} \end{array}$$

$$\dot{n}_1 = 36,200 \text{ mol/min}$$

$$\begin{array}{l} \downarrow \\ \text{Ideal gas equation of state} \\ T_1 = 27^\circ\text{C (300 K)} \\ P_1 = 475 \text{ mm Hg gauge (1238 mm Hg)} \end{array}$$

$$\dot{V}_1 = \dot{n}_1 \frac{V_s}{n_s} \frac{T_1}{T_s} \frac{P_s}{P_1}$$

$$= \frac{36,200 \text{ mol/min}}{1 \text{ mol}} \left| \frac{0.0224 \text{ m}^3}{1 \text{ mol}} \right| \left| \frac{300 \text{ K}}{273 \text{ K}} \right| \left| \frac{760 \text{ mm Hg}}{1238 \text{ mm Hg}} \right|$$



$$\dot{V}_1 = 550 \text{ m}^3 \text{ N}_2/\text{min}$$

Chapter 6 – Multiphase Systems

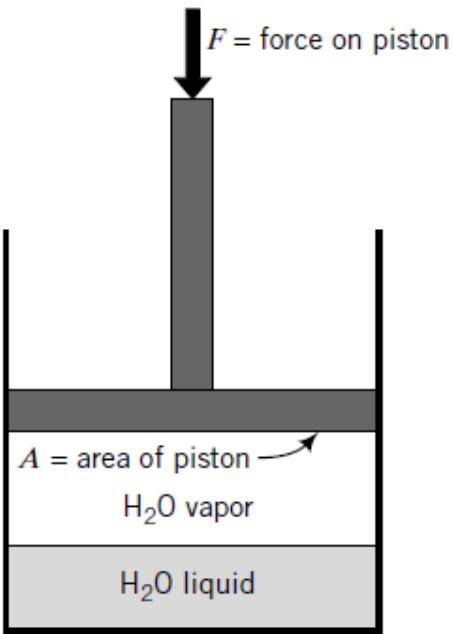
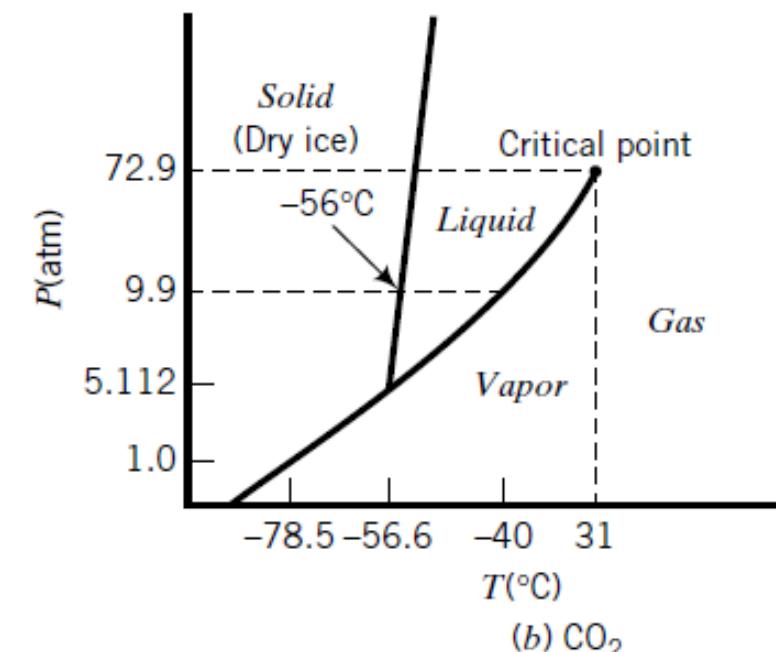
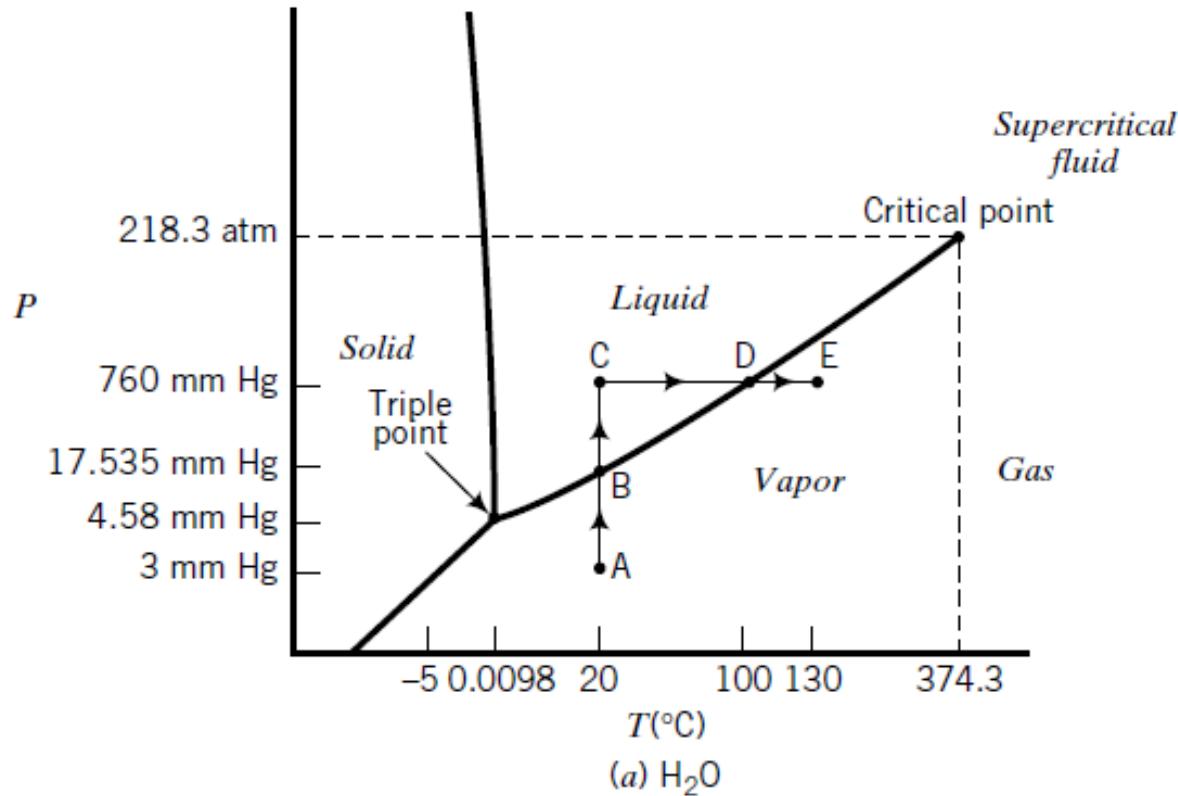
Lecture 15

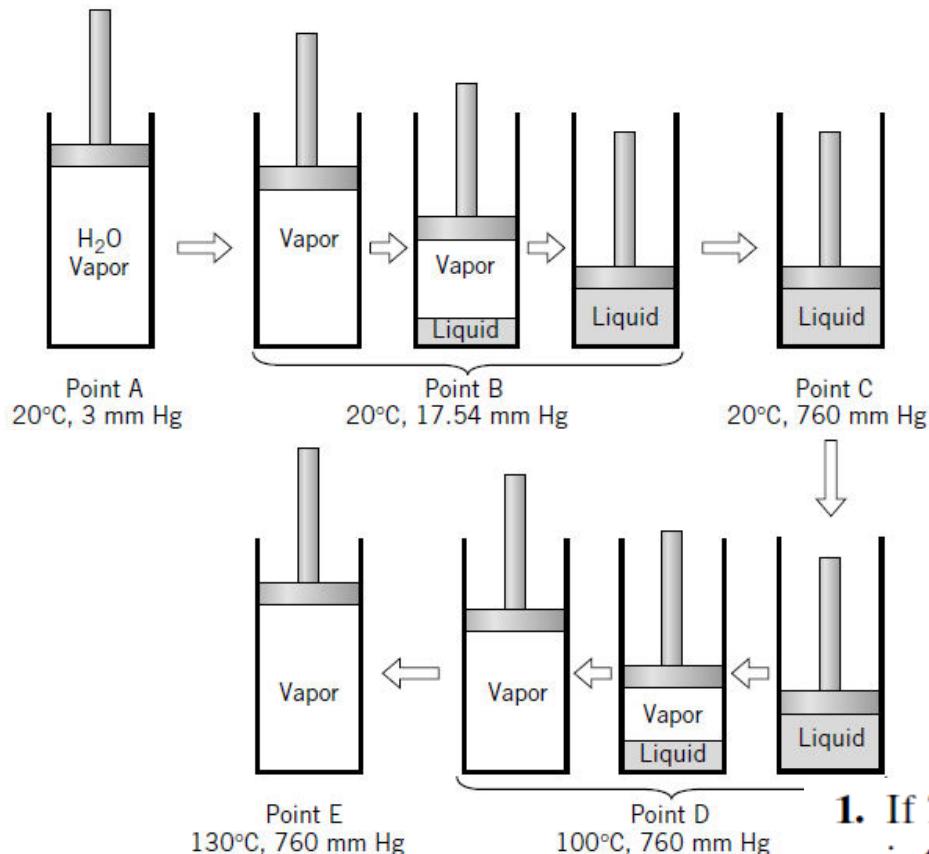
Phase change operations - separations, purifications etc...

- **Brewing a cup of coffee.** Hot liquid water and solid ground coffee beans are contacted. Soluble constituents of the beans are transferred from the solid phase to a liquid solution (coffee), and then the residual solids (grounds) are filtered from the solution. The operation of dissolving a component of a solid phase in a liquid solvent is referred to as **leaching**.
- **Removal of sulfur dioxide from a gas stream.** If a fuel that contains sulfur is burned, the product gas contains sulfur dioxide. If the gas is released directly into the atmosphere, the SO_2 combines with atmospheric oxygen to form sulfur trioxide. The SO_3 in turn combines with water vapor in the atmosphere to form sulfuric acid (H_2SO_4), which eventually precipitates as *acid rain*. To prevent this occurrence, the combustion product gas is contacted with a liquid solution in an **absorption** or **scrubbing** process. The SO_2 dissolves in the solvent and the clean gas that remains is released to the atmosphere.
- **Recovery of methanol from an aqueous solution.** After being used as a reactant or solvent, methanol (methyl alcohol) often leaves a process in an aqueous mixture (combined with water). Methanol has a higher *vapor pressure* than water, meaning that it has a greater tendency to vaporize when a mixture of the two species is heated. The separation process **distillation** exploits this difference by partially vaporizing a liquid mixture, yielding a vapor relatively rich in methanol and a residual liquid relatively rich in water. Subsequent partial condensations and vaporizations can be used to recover almost pure methanol. The recovered methanol can be recycled and reused, resulting in considerable savings in raw material costs.

6.1 Single-Component Phase Equilibrium

6.1a Phase Diagrams





- If T and P correspond to a point on the vapor–liquid equilibrium curve for a substance, P is the **vapor pressure** of the substance at temperature T , and T is the **boiling point** (more precisely, the **boiling point temperature**) of the substance at pressure P .
- The boiling point of a substance at $P = 1 \text{ atm}$ is the **normal boiling point** of that substance.
- If (T, P) falls on the solid–liquid equilibrium curve, then T is the **melting point** or **freezing point** at pressure P .
- If (T, P) falls on the solid–vapor equilibrium curve, then P is the vapor pressure of the solid at temperature T , and T is the **sublimation point** at pressure P .
- The point (T, P) at which solid, liquid, and vapor phases can all coexist is called the **triple point** of the substance.
- The vapor–liquid equilibrium curve terminates at the **critical temperature** and **critical pressure** (T_c and P_c). Above and to the right of the critical point, two separate phases never coexist.

6.1b Estimation of Vapor Pressures

The **volatility** of a species is the degree to which the species tends to transfer from the liquid (or solid) state to the vapor state. At a given temperature and pressure, a highly volatile substance is much more likely to be found as a vapor than is a substance with low volatility, which is more likely to be found in a condensed phase (liquid or solid).

Separation processes such as distillation are used to separate more volatile species from less volatile species by partially vaporizing liquid mixtures. The vapor product is relatively rich in the more volatile feed components and the residual liquid is rich in the components with lower volatility. *The vapor pressure of a species is a measure of its volatility:* the higher the vapor pressure at a given temperature, the greater the volatility of the species at that temperature. Engineers who design and analyze separation processes therefore need to know the vapor pressures of process species as functions of temperature.

A relationship between p^* , the vapor pressure of a pure substance, and T , the absolute temperature, is the **Clapeyron equation**

$$\frac{dp^*}{dT} = \frac{\Delta\hat{H}_v}{T(\hat{V}_g - \hat{V}_l)} \quad (6.1-1)$$

where T is *absolute* temperature; \hat{V}_g and \hat{V}_l are the specific molar volumes (volume/mole) of gas (vapor) and liquid, respectively; and $\Delta\hat{H}_v$ is the **latent heat of vaporization**, or the energy required to vaporize one mole of the liquid (to be defined more precisely in Chapter 8).

Unless the pressure is extremely high, the specific volume of the liquid is negligible relative to that of the vapor (i.e., $\hat{V}_g - \hat{V}_l \approx \hat{V}_g$). If we assume that this is the case, apply the ideal gas equation of state to the vapor (so that \hat{V}_g is replaced with RT/p^* in Equation 6.1-1) and rearrange the resulting equation with the aid of elementary calculus. We obtain

$$\frac{d(\ln p^*)}{d(1/T)} = -\frac{\Delta\hat{H}_v}{R} \quad (6.1-2)$$

Suppose now that the heat of vaporization of a substance is independent of temperature (or nearly so) in the temperature range over which vapor pressures are available. Equation 6.1-2 may then be integrated to yield the **Clausius–Clapeyron equation**

$$\ln p^* = -\frac{\Delta \hat{H}_v}{RT} + B \quad (6.1-3)$$

EXAMPLE 6.1-1

Vapor Pressure Estimation Using the Clausius–Clapeyron Equation

The vapor pressure of benzene is measured at two temperatures, with the following results:

$$T_1 = 7.6^\circ\text{C}, \quad p_1^* = 40 \text{ mm Hg}$$

$$T_2 = 15.4^\circ\text{C}, \quad p_2^* = 60 \text{ mm Hg}$$

Calculate the latent heat of vaporization and the parameter B in the Clausius–Clapeyron equation and then estimate p^* at 42.2°C using this equation.

SOLUTION

$p^*(\text{mm Hg})$	$T(\text{ }^\circ\text{C})$	$T(\text{K})$
40	7.6	280.8
60	15.4	288.6

The slope of the line through the two data points on a plot of $\ln p^*$ versus $1/T$ is

$$\begin{aligned}-\frac{\Delta \hat{H}_v}{R} &= \frac{\ln(p_2^*/p_1^*)}{[(1/T_2) - (1/T_1)]} = \frac{T_1 T_2 \ln(p_2^*/p_1^*)}{(T_1 - T_2)} \\ &= \frac{(280.8 \text{ K})(288.6 \text{ K}) \ln(60 \text{ mm Hg}/40 \text{ mm Hg})}{(280.8 - 288.6) \text{ K}} = -4213 \text{ K}\end{aligned}$$

The intercept B is obtained from Equation 6.1-3 as

$$\begin{aligned}B &= \ln p_1^* + \frac{\Delta \hat{H}_v}{RT_1} \\ &= \ln 40 + (4213/280.8) = 18.69\end{aligned}$$

The Clausius–Clapeyron equation is therefore

$$\boxed{\ln p^* = -\frac{4213 \text{ K}}{T(\text{K})} + 18.69} \quad p^* \text{ in mm Hg}$$

Check: $T = 15.4^\circ\text{C} \implies 288.6 \text{ K}$

$$\ln p^* = -\frac{4213}{288.6} + 18.69 = 4.093$$



$$p^* = \exp(4.093) = 60 \text{ mm Hg} \quad \checkmark$$

Finally, at $T = 42.2^\circ\text{C} = 315.4 \text{ K}$

$$\ln p^* = -\frac{4213}{315.4} + 18.69 = 5.334$$



$$p^* = \exp(5.334) = \boxed{207 \text{ mm Hg}}$$

Perry's Chemical Engineers' Handbook, p. 2-61, lists the vapor pressure of benzene at 42.2°C as 200 mm Hg, so that the use of the Clausius–Clapeyron equation results in an estimation error of approximately 3.5%.

The heat of vaporization of benzene $\hat{\Delta}H_v$ may be estimated from the slope of the Clausius–Clapeyron plot ($-\hat{\Delta}H_v/R$) as

$$\begin{aligned}\hat{\Delta}H_v &= (\hat{\Delta}H_v/R)(R) \\ &= \frac{4213 \text{ K}}{\text{mol}\cdot\text{K}} \left| \frac{8.314 \text{ J}}{\text{mol}\cdot\text{K}} \right| = \boxed{35,030 \text{ J/mol}}\end{aligned}$$

(The true value is approximately 31,000 J/mol.)

A relatively simple empirical equation that correlates vapor pressure–temperature data extremely well is the **Antoine equation**

$$\log_{10} p^* = A - \frac{B}{T + C} \quad (6.1-4)$$

Values of A , B , and C for several compounds are listed in Table B.4. Observe the units of p^* and T (mm Hg and °C for the constants in Table B.4) and the logarithm base (10 in the case of Equation 6.1-4 and Table B.4). Gathering parameters from multiple sources increases the need for care relative to the units used.

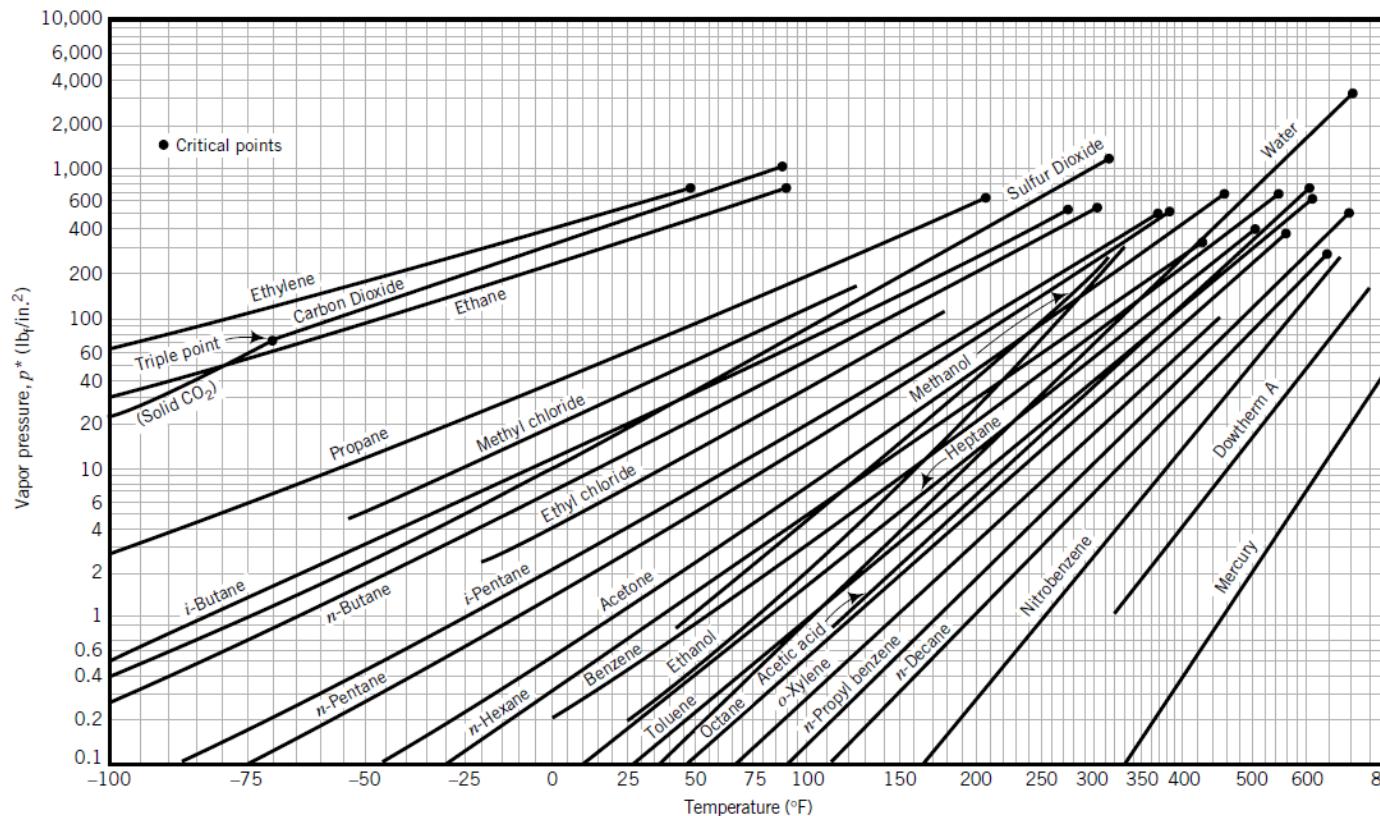
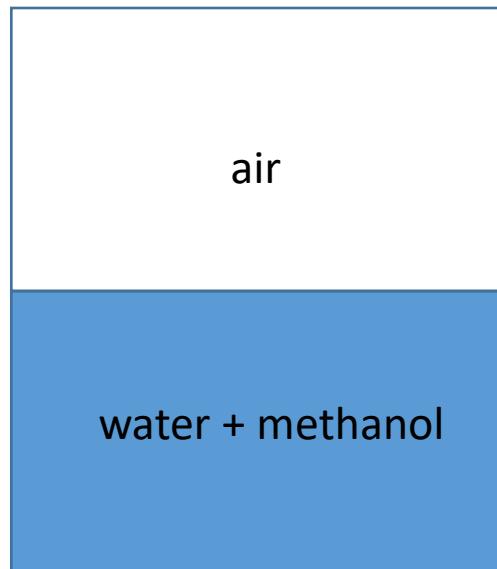


Figure 6.1-4 Cox chart vapor pressure plots. (From A. S. Foust et al., *Principles of Unit Operations*, Wiley, New York, 1960, p. 550.)

Lecture 16

6.2 The Gibbs Phase Rule



The variables that describe the condition of a process system fall into two categories: **extensive variables**, which depend on the size of the system, and **intensive variables**, which do not. Mass and volume are examples of extensive variables; intensive variables include temperature, pressure, density and specific volume, and mass and mole fractions of individual system components in each phase.

The number of intensive variables that can be specified independently for a system at equilibrium is called the **degrees of freedom** of the system. Let

$$\Pi = \text{number of phases in a system at equilibrium}$$

$$c = \text{number of chemical species}$$

$$DF = \text{degrees of freedom}$$

The relationship among DF , Π , and c is given by the **Gibbs phase rule**. If no reactions occur among the system components, the phase rule is

$$DF = 2 + c - \Pi$$

(6.2-1)

EXAMPLE 6.2-1**The Gibbs Phase Rule**

Determine the degrees of freedom for each of the following systems at equilibrium. Specify a feasible set of independent variables for each system.

1. Pure liquid water

One phase ($\Pi = 1$), one component ($c = 1$)



$$DF = 2 + 1 - 1 = 2$$

Two intensive variables must be specified to fix the state of the system, for example, T and P . Once these variables have been specified, other intensive variables such as density and viscosity may be determined.

2. A mixture of liquid, solid, and vapor water

Three phases ($\Pi = 3$), one component ($c = 1$)



$$DF = 2 + 1 - 3 = 0$$

No further information about the system may be specified and all intensive variables are fixed. Note from Figure 6.1-1a that three phases coexist at equilibrium at only one temperature and pressure.

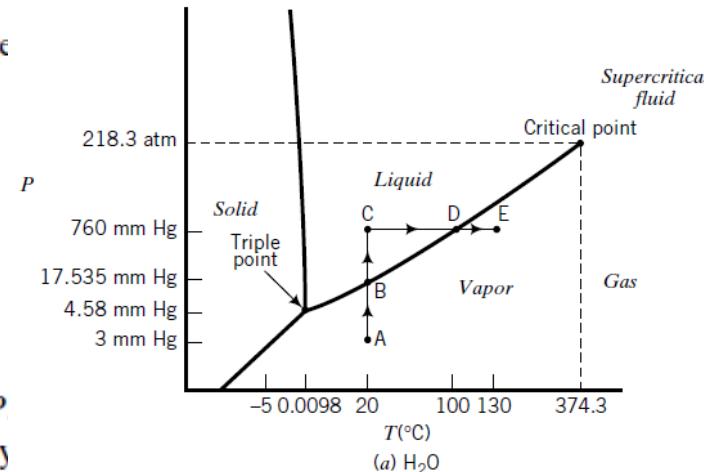
3. A vapor-liquid mixture of acetone and methyl ethyl ketone

Two phases ($\Pi = 2$), two components ($c = 2$)



$$DF = 2 + 2 - 2 = 2$$

Two variables must be specified to fix the state of the system. For example, setting T and P fixes the acetone and MEK mole fractions in both the vapor and liquid phases. Alternatively, T and the acetone mole fraction in the vapor may be specified, and P and the acetone mole fraction in the liquid are then fixed.



6.3 Gas-Liquid Systems: One Condensable Component

Systems containing several components, of which only one is capable of existing as a liquid at the process conditions, are common in industrial processes. Separation processes that involve such systems include **evaporation**, **drying**, and **humidification**—all of which involve transfer of liquid into the gas phase—and **condensation** and **dehumidification**, which involve transfer of the condensable species from the gas to the liquid phase.

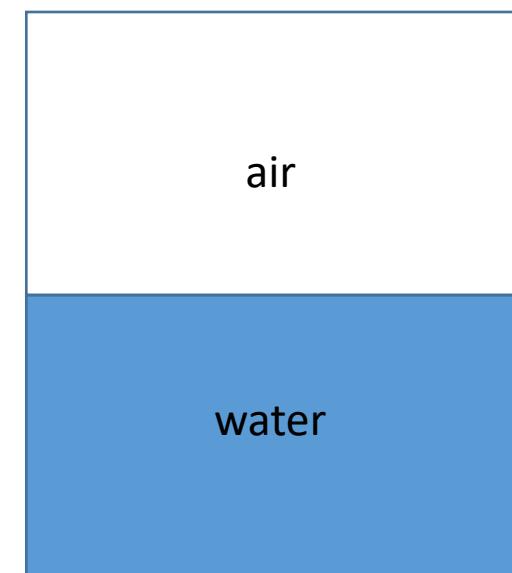
Suppose liquid water is introduced into a chamber that initially contains dry air and that the temperature and pressure in the system are kept constant at 75°C and 760 mm Hg. Initially the gas phase contains no water ($p_{\text{H}_2\text{O}} = 0$), and water molecules consequently begin to evaporate. The mole fraction of water in the gas phase, $y_{\text{H}_2\text{O}}$, increases, and hence so does the partial pressure of water, $p_{\text{H}_2\text{O}} = y_{\text{H}_2\text{O}}P$. Eventually, however, the amount of water in the gas phase is such that the rate at which water molecules enter the gas phase approaches zero, and thereafter no change occurs in the amount or composition of either phase. The gas phase is then said to be **saturated** with water—it contains all the water it can hold at the system temperature and pressure—and the water in the gas phase is referred to as a **saturated vapor**.

Let us apply the Gibbs phase rule to this equilibrium system. Since there are two phases and two components,

$$DF = 2 + c - \Pi = 2$$

It follows that only two out of the three intensive variables T , P , and $y_{\text{H}_2\text{O}}$ can be specified, and that some relationship must exist that uniquely determines the value of the third variable once the first two have been specified.³

A law that describes the behavior of gas-liquid systems over a wide range of conditions provides the desired relationship. *If a gas at temperature T and pressure P contains a saturated vapor whose mole fraction is y_i (mol vapor/mol total gas), and if this vapor is the only species that would condense if the temperature were slightly lowered, then the partial pressure of the vapor in the gas equals the pure-component vapor pressure $p_i^*(T)$ at the system temperature.*



Raoult's Law, Single Condensable Species: $p_i = y_i P = p_i^*(T)$ (6.3-1)

EXAMPLE 6.3-1***Composition of a Saturated Gas-Vapor System***

Air and liquid water are contained at equilibrium in a closed chamber at 75°C and 760 mm Hg. Calculate the molar composition of the gas phase.

Since the gas and liquid are in equilibrium, the air must be saturated with water vapor (if it were not, more water would evaporate), so that Raoult's law may be applied:

$$y_{\text{H}_2\text{O}} = p_{\text{H}_2\text{O}}^*(75^\circ\text{C})/P$$

From Table B.3 in Appendix B, $p_{\text{H}_2\text{O}}^*(75^\circ\text{C}) = 289 \text{ mm Hg}$. Consequently,

$$y_{\text{H}_2\text{O}} = \frac{289 \text{ mm Hg}}{760 \text{ mm Hg}} = \boxed{0.380 \frac{\text{mol H}_2\text{O}}{\text{mol}}}$$

$$y_{\text{dry air}} = 1 - y_{\text{H}_2\text{O}} = \boxed{0.620 \frac{\text{mol dry air}}{\text{mol}}}$$

Table B.3 Vapor Pressure of Water^a

p_v (mm Hg) versus T (°C)											
Example: The vapor pressure of liquid water at 4.3°C is 6.230 mm Hg											
T (°C)	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	
Ice	-14	1.361	1.348	1.336	1.324	1.312	1.300	1.288	1.276	1.264	1.253
	-13	1.490	1.477	1.464	1.450	1.437	1.424	1.411	1.399	1.386	1.373
	-12	1.632	1.617	1.602	1.588	1.574	1.559	1.546	1.532	1.518	1.504
	-11	1.785	1.769	1.753	1.737	1.722	1.707	1.691	1.676	1.661	1.646
	-10	1.950	1.934	1.916	1.899	1.883	1.866	1.849	1.833	1.817	1.800
	-9	2.131	2.122	2.093	2.075	2.057	2.039	2.021	2.003	1.985	1.968
	-8	2.326	2.306	2.285	2.266	2.246	2.226	2.207	2.187	2.168	2.149
	-7	2.537	2.515	2.493	2.472	2.450	2.429	2.408	2.387	2.367	2.346
	-6	2.765	2.742	2.718	2.695	2.672	2.649	2.626	2.603	2.581	2.559
	-5	3.013	2.987	2.962	2.937	2.912	2.887	2.862	2.838	2.813	2.790
	-4	3.280	3.252	3.225	3.198	3.171	3.144	3.117	3.091	3.065	3.039
	-3	3.568	3.539	3.509	3.480	3.451	3.422	3.393	3.364	3.336	3.308
	-2	3.880	3.848	3.816	3.785	3.753	3.722	3.691	3.660	3.630	3.599
	-1	4.217	4.182	4.147	4.113	4.079	4.045	4.012	3.979	3.946	3.913
	-0	4.579	4.542	4.504	4.467	4.431	4.395	4.359	4.323	4.287	4.252
Liquid water	0	4.579	4.613	4.647	4.681	4.715	4.750	4.785	4.820	4.855	4.890
	1	4.926	4.962	4.998	5.034	5.070	5.107	5.144	5.181	5.219	5.256
	2	5.294	5.332	5.370	5.408	5.447	5.486	5.525	5.565	5.605	5.645
	3	5.685	5.725	5.766	5.807	5.848	5.889	5.931	5.973	6.015	6.058
	4	6.101	6.144	6.187	6.230	6.274	6.318	6.363	6.408	6.453	6.498
	5	6.543	6.589	6.635	6.681	6.728	6.775	6.822	6.869	6.917	6.965
	6	7.013	7.062	7.111	7.160	7.209	7.259	7.309	7.360	7.411	7.462
	7	7.513	7.565	7.617	7.669	7.722	7.775	7.828	7.882	7.936	7.990
	8	8.045	8.100	8.155	8.211	8.267	8.323	8.380	8.437	8.494	8.551
	9	8.609	8.668	8.727	8.786	8.845	8.905	8.965	9.025	9.086	9.147
	10	9.209	9.271	9.333	9.395	9.458	9.521	9.585	9.649	9.714	9.779
	11	9.844	9.910	9.976	10.042	10.109	10.176	10.244	10.312	10.380	10.449
	12	10.518	10.588	10.658	10.728	10.799	10.870	10.941	11.013	11.085	11.158
	13	11.231	11.305	11.379	11.453	11.528	11.604	11.680	11.756	11.833	11.910
	14	11.987	12.065	12.144	12.223	12.302	12.382	12.462	12.543	12.624	12.706
	15	12.788	12.870	12.953	13.037	13.121	13.205	13.290	13.375	13.461	13.547
	16	13.634	13.721	13.809	13.898	13.987	14.076	14.166	14.256	14.347	14.438
	17	14.530	14.622	14.715	14.809	14.903	14.997	15.092	15.188	15.284	15.380
	18	15.477	15.575	15.673	15.772	15.871	15.971	16.771	16.171	16.272	16.374
	19	16.477	16.581	16.685	16.789	16.894	16.999	17.105	17.212	17.319	17.427
	20	17.535	17.644	17.753	17.863	17.974	18.085	18.197	18.309	18.422	18.536
	21	18.650	18.765	18.880	18.996	19.113	19.231	19.349	19.468	19.587	19.707
	22	19.827	19.948	20.070	20.193	20.316	20.440	20.565	20.690	20.815	20.941
	23	21.068	21.196	21.324	21.453	21.583	21.714	21.845	21.977	22.110	22.243
	24	22.377	22.512	22.648	22.785	22.922	23.060	23.198	23.337	23.476	23.616

T (°C)	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
25	23.756	23.897	24.039	24.182	24.326	24.471	24.617	24.764	24.912	25.060
26	25.209	25.359	25.509	25.660	25.812	25.964	26.117	26.271	26.426	26.582
27	26.739	26.897	27.055	27.214	27.374	27.535	27.696	27.858	28.021	28.185
28	28.349	28.514	28.680	28.847	29.015	29.184	29.354	29.525	29.697	29.870
29	30.043	30.217	30.392	30.568	30.745	30.923	31.102	31.281	31.461	31.642
30	31.824	32.007	32.191	32.376	32.561	32.747	32.934	33.122	33.312	33.503
31	33.695	33.888	34.082	34.276	34.471	34.667	34.864	35.062	35.261	35.462
32	35.663	35.865	36.068	36.272	36.477	36.683	36.891	37.099	37.308	37.518
33	37.729	37.942	38.155	38.369	38.584	38.801	39.018	39.237	39.457	39.677
34	39.898	40.121	40.344	40.569	40.796	41.023	41.251	41.480	41.710	41.942
35	42.175	42.409	42.644	42.880	43.117	43.355	43.595	43.836	44.078	44.320
36	44.563	44.808	45.054	45.301	45.549	45.799	46.050	46.302	46.556	46.811
37	47.067	47.324	47.582	47.841	48.102	48.364	48.627	48.891	49.157	49.424
38	49.692	49.961	50.231	50.502	50.774	51.048	51.323	51.600	51.879	52.160
39	52.442	52.725	53.009	53.294	53.580	53.867	54.156	54.446	54.737	55.030
40	55.324	55.61	55.91	56.21	56.51	56.81	57.11	57.41	57.72	58.03
41	58.34	58.65	58.96	59.27	59.58	59.90	60.22	60.54	60.86	61.18
42	61.50	61.82	62.14	62.47	62.80	63.13	63.46	63.79	64.12	64.46
43	64.80	65.14	65.48	65.82	66.16	66.51	66.86	67.21	67.56	67.91
44	68.26	68.61	68.97	69.33	69.69	70.05	70.41	70.77	71.14	71.51
45	71.88	72.25	72.62	72.99	73.36	73.74	74.12	74.50	74.88	75.26
46	75.65	76.04	76.43	76.82	77.21	77.60	78.00	78.40	78.80	79.20
47	79.60	80.00	80.41	80.82	81.23	81.64	82.05	82.46	82.87	83.29
48	83.71	84.13	84.56	84.99	85.42	85.85	86.28	86.71	87.14	87.58
49	88.02	88.46	88.90	89.34	89.79	90.24	90.69	91.14	91.59	92.05
T (°C)	0	1	2	3	4	5	6	7	8	9
50	92.51	97.20	102.09	107.20	112.51	118.04	123.80	129.82	136.08	142.60
60	149.38	156.43	163.77	171.38	179.31	187.54	196.09	204.96	214.17	223.73
70	233.7	243.9	254.6	265.7	277.2	289.1	301.4	314.1	327.3	341.0
80	355.1	369.7	384.9	400.6	416.8	433.6	450.9	468.7	487.1	506.1
T (°C)	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
90	525.76	527.76	529.77	531.78	533.80	535.82	537.86	539.90	541.95	544.00
91	546.05	548.11	550.18	552.26	554.35	556.44	558.53	560.64	562.75	564.87
92	566.99	569.12	571.26	573.40	575.55	577.71	579.87	582.04	584.22	586.41
93	588.60	590.80	593.00	595.21	597.43	599.66	601.89	604.13	606.38	608.64
94	610.90	613.17	615.44	617.72	620.01	622.31	624.61	626.92	629.24	631.57
95	633.90	636.24	638.59	640.94	643.30	645.67	648.05	650.43	652.82	655.22
96	657.62	660.03	662.45	664.88	667.31	669.75	672.20	674.66	677.12	679.69
97	682.07	684.55	687.04	689.54	692.05	694.57	697.10	699.63	702.17	704.71
98	707.27	709.83	712.40	714.98	717.56	720.15	722.75	725.36	727.98	730.61
99	733.24	735.88	738.53	741.18	743.85	746.52	749.20	751.89	754.58	757.29
100	760.00	762.72	765.45	768.19	770.93	773.68	776.44	779.22	782.00	784.78
101	787.57	790.37	793.18	796.00	798.82	801.66	804.50	807.35	810.21	

Several important points concerning the behavior of gas–liquid systems and several terms used to describe the state of such systems are summarized here.

1. A gas in equilibrium with a liquid must be saturated with the volatile components of that liquid.
2. The partial pressure of a vapor at equilibrium in a gas mixture containing a single condensable component cannot exceed the vapor pressure of the pure component at the system temperature. If $p_i = p_i^*$, the vapor is saturated; any attempt to increase p_i —either by adding more vapor to the gas phase or by increasing the total pressure at constant temperature—must instead lead to condensation.
3. A vapor present in a gas in less than its saturation amount is referred to as a **superheated vapor**. For such a vapor,

$$p_i = \boxed{y_i P < p_i^*(T)} \quad (6.3-2)$$

Since only a saturated vapor can condense (why?), to achieve condensation in a system containing a superheated vapor one or more of the variables of Equation 6.3-2 must be changed so that the inequality becomes the equality of Raoult's law. This can be done in several ways, such as by increasing the pressure at constant temperature (the left side increases, while the right side stays constant) or by decreasing the temperature at constant pressure (the left side remains constant, and the right side decreases).

4. If a gas containing a single superheated vapor is cooled at constant pressure, the temperature at which the vapor becomes saturated is referred to as the **dew point** of the gas. From Raoult's law (Equation 6.3-1),

$$p_i = \boxed{y_i P = p_i^*(T_{dp})} \quad (6.3-3)$$

The difference between the temperature and the dew point of a gas is called the **degrees of superheat** of the gas. If any two of the quantities y_i , P , and T_{dp} (or, equivalently, the temperature of the gas and the degrees of superheat) are known, the third quantity may be determined from Equation 6.3-3 and a table, graph, or equation relating p_i^* and T .

EXAMPLE 6.3-2

Material Balances Around a Condenser

A stream of air at 100°C and 5260 mm Hg contains 10.0% water by volume.

1. Calculate the dew point and degrees of superheat of the air.
2. Calculate the percentage of the vapor that condenses and the final composition of the gas phase if the air is cooled to 80°C at constant pressure.
3. Calculate the percentage condensation and the final gas-phase composition if, instead of being cooled, the air is compressed isothermally to 8500 mm Hg.
4. Suppose the process of part 2 is run, the product gas is analyzed, and the mole fraction of water differs considerably from the calculated value. What could be responsible for the disparity between calculated and measured values? (List several possibilities.)

SOLUTION

1. $p_{\text{H}_2\text{O}} = y_{\text{H}_2\text{O}} P = (0.100)(5260 \text{ mm Hg}) = 526 \text{ mm Hg}$
 $p_{\text{H}_2\text{O}}^*(100^\circ\text{C}) = 760 \text{ mm Hg} > p_{\text{H}_2\text{O}}$ \Rightarrow the vapor is superheated (see Inequality 6.3-2)

From Equation 6.3-3

$$p_{\text{H}_2\text{O}} = p_{\text{H}_2\text{O}}^*(T_{\text{dp}}) = 526 \text{ mm Hg}$$

\downarrow Table B.3

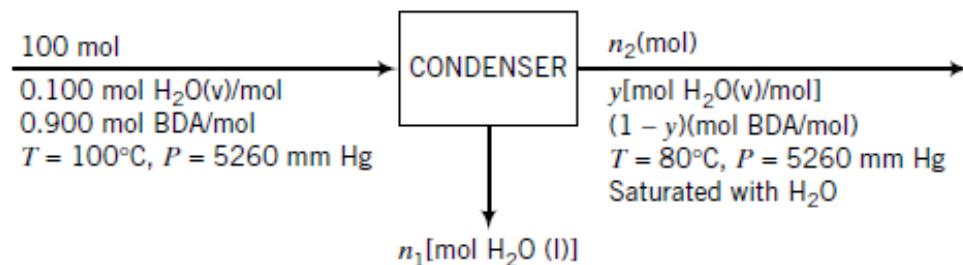
$$T_{\text{dp}} = 90^\circ\text{C}$$

and the air has $100^\circ\text{C} - 90^\circ\text{C} =$ 10°C of superheat

2. Since the air becomes saturated at 90°C, further cooling must lead to condensation. Since the products are liquid water in equilibrium with a gas phase, the water vapor in the gas must remain saturated.

On the following flowchart, the symbol BDA stands for **bone-dry air**, a term used to signify the water-free component of an air–water vapor mixture.

Basis: 100 mol Feed Gas



Let us first do the degree-of-freedom analysis. Three unknown variables appear on the chart— n_1 , n_2 , and y . Since only two species are involved in the process, we can only write two independent material balances, leaving us one equation short. If we fail to observe that the gas at the condenser outlet is saturated with water, solution of the problem would be impossible; however, the saturation condition supplies the needed third equation, Raoult's law.

The solution outline is as follows: apply Raoult's law at the outlet to determine y , the mole fraction of water in the outlet gas; then use a dry air balance to determine n_2 and a total mole balance or a water balance to determine the final unknown, n_1 .

Raoult's Law at Outlet $yP = p_{\text{H}_2\text{O}}^*(T)$



$$y = \frac{p_{\text{H}_2\text{O}}^*(80^\circ\text{C})}{P} = \frac{355 \text{ mm Hg}}{5260 \text{ mm Hg}} = \boxed{0.0675 \frac{\text{mol H}_2\text{O}}{\text{mol}}}$$

Balance on Dry Air

$$\frac{100 \text{ mol}}{\text{mol}} \left| \begin{array}{c} 0.900 \text{ mol BDA} \\ \hline \end{array} \right. = n_2(1 - y)$$

$$\downarrow y = 0.0675$$

$$n_2 = 96.5 \text{ mol}$$

Total Mole Balance

$$100 \text{ mol} = n_1 + n_2$$

$$\downarrow n_2 = 96.5 \text{ mol}$$

$$n_1 = 3.5 \text{ mol H}_2\text{O condensed}$$

Percentage Condensation

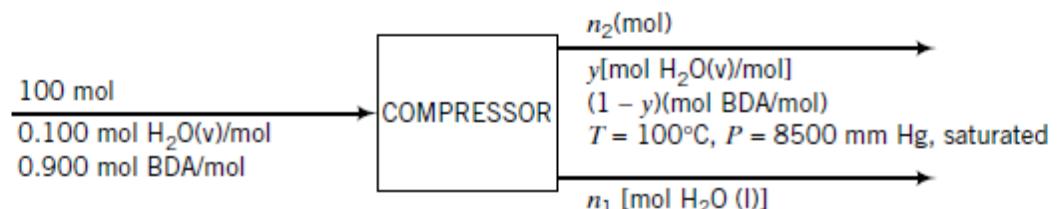
$$\frac{3.5 \text{ mol H}_2\text{O condensed}}{(0.100 \times 100) \text{ mol H}_2\text{O fed}} \times 100\% = \boxed{35\%}$$

3. Initially $y_{\text{H}_2\text{O}}P < p_{\text{H}_2\text{O}}^*(100^\circ\text{C})$. Saturation occurs when P is high enough for the inequality to become an equality, or

$$P_{\text{saturation}} = \frac{p_{\text{H}_2\text{O}}^*(100^\circ\text{C})}{y_{\text{H}_2\text{O}}} = \frac{760 \text{ mm}}{0.100} = 7600 \text{ mm Hg}$$

Any increase in P above 7600 mm Hg must cause condensation, so that the products from the compression to 8500 mm Hg must include a liquid stream.

Basis: 100 mol Feed Gas



Before going through the solution, try to outline it as was done following the flowchart of part 2.

Raoult's Law $y = \frac{p_{\text{H}_2\text{O}}^*(100^\circ\text{C})}{P} = \frac{760 \text{ mm Hg}}{8500 \text{ mm Hg}} = \boxed{0.0894 \frac{\text{mol H}_2\text{O}}{\text{mol}}}$

Balance on Dry Air $(100 \text{ mol})(0.900) = n_2(1 - y)$
 $\downarrow y = 0.0894$
 $n_2 = 98.8 \text{ mol}$

Total Mole Balance $100 \text{ mol} = n_1 + n_2$
 $\downarrow n_2 = 98.8 \text{ mol}$
 $n_1 = 1.2 \text{ mol H}_2\text{O condensed}$

Percentage Condensation $\frac{1.2 \text{ mol H}_2\text{O condensed}}{(0.100 \times 100) \text{ mol H}_2\text{O fed}} \times 100\% = \boxed{12\%}$

4. (a) Experimental error (you should be able to list many possibilities). (b) The condenser was not at steady state when the measurements were made, possibly because the system had not yet leveled out following startup or because water vapor was adsorbing on the walls of the condenser. (c) The emerging gas and liquid streams were not at equilibrium (e.g., condensation actually occurred at a temperature below 100°C and the product streams were separated and reheated before emerging). (d) Raoult's law does not apply (this is not a likely explanation for the air–water system at the given conditions).

Several quantities besides those introduced in the previous section are commonly used to describe the state and composition of a gas containing a single condensable vapor. *In the definitions to be given, the term “saturation” refers to any gas–vapor combination, while “humidity” refers specifically to an air–water system.*

Suppose a gas at temperature T and pressure P contains a vapor whose partial pressure is p_i and whose vapor pressure is $p_i^*(T)$.

$$\textbf{Relative Saturation (Relative Humidity)} \quad s_r(h_r) = \frac{p_i}{p_i^*(T)} \times 100\% \quad (6.3-4)$$

A relative humidity of 40%, for example, signifies that the partial pressure of water vapor equals $\frac{4}{10}$ of the vapor pressure of water at the system temperature.

Molal Saturation (Molal Humidity)

$$s_m(h_m) = \frac{p_i}{P - p_i} = \frac{\text{moles of vapor}}{\text{moles of vapor-free (dry) gas}} \quad (6.3-5)$$

(Can you prove the second equality?)

Absolute Saturation (Absolute Humidity)

$$s_a(h_a) = \frac{p_i M_i}{(P - p_i) M_{\text{dry}}} = \frac{\text{mass of vapor}}{\text{mass of dry gas}} \quad (6.3-6)$$

where M_i is the molecular weight of the vapor and M_{dry} is the average molecular weight of the dry (vapor-free) gas.

Percentage Saturation (Percentage Humidity)

$$s_p(h_p) = \frac{s_m}{s_m^*} \times 100\% = \frac{p_i / (P - p_i)}{p_i^* / (P - p_i^*)} \times 100\% \quad (6.3-7)$$

EXAMPLE 6.3-3

Humid air at 75°C, 1.1 bar, and 30% relative humidity is fed into a process unit at a rate of 1000 m³/h. Determine (1) the molar flow rates of water, dry air, and oxygen entering the process unit, (2) the molal humidity, absolute humidity, and percentage humidity of the air, and (3) the dew point.

1. $h_r(\%) = 100p_{\text{H}_2\text{O}}/p_{\text{H}_2\text{O}}^*(75^\circ\text{C})$

$$\begin{array}{l} \downarrow \\ h_r = 30\% \\ \downarrow \\ p_{\text{H}_2\text{O}}^*(75^\circ\text{C}) = 289 \text{ mm Hg (from Table B.3)} \end{array}$$

$$p_{\text{H}_2\text{O}} = (0.3)(289 \text{ mm Hg}) = 86.7 \text{ mm Hg}$$

$$\begin{array}{l} \downarrow \\ y_{\text{H}_2\text{O}} = p_{\text{H}_2\text{O}}/P \\ \downarrow \\ P = 1.1 \text{ bar} \implies 825 \text{ mm Hg} \end{array}$$

$$y_{\text{H}_2\text{O}} = (86.7 \text{ mm Hg})/(825 \text{ mm Hg}) = 0.105 \text{ mol H}_2\text{O/mol}$$

The molar flow rate of wet air is given by the ideal gas equation of state as

$$\dot{n} = P\dot{V}/RT = \frac{1000 \text{ m}^3}{\text{h}} \left| \begin{array}{c} 1.1 \text{ bar} \\ 348 \text{ K} \end{array} \right| \frac{\text{kmol}\cdot\text{K}}{0.0831 \text{ m}^3\cdot\text{bar}} = 38.0 \frac{\text{kmol}}{\text{h}}$$

Consequently,

$$\dot{n}_{\text{H}_2\text{O}} = \frac{38.0 \text{ kmol}}{\text{h}} \left| \begin{array}{c} 0.105 \text{ kmol H}_2\text{O} \\ \text{kmol} \end{array} \right| = \boxed{3.99 \frac{\text{kmol H}_2\text{O}}{\text{h}}}$$

$$\dot{n}_{\text{BDA}} = \frac{38.0 \text{ kmol}}{\text{h}} \left| \begin{array}{c} (1 - 0.105) \text{ kmol BDA} \\ \text{kmol} \end{array} \right| = \boxed{34.0 \frac{\text{kmol BDA}}{\text{h}}}$$

$$\dot{n}_{\text{O}_2} = \frac{34.0 \text{ kmol BDA}}{\text{h}} \left| \begin{array}{c} 0.21 \text{ kmol O}_2 \\ \text{kmol BDA} \end{array} \right| = \boxed{7.14 \frac{\text{kmol O}_2}{\text{h}}}$$

2.
$$h_m = \frac{p_{H_2O}}{P - p_{H_2O}} = \frac{86.7 \text{ mm Hg}}{(825 - 86.7) \text{ mm Hg}} = \boxed{0.117 \frac{\text{mol H}_2\text{O}}{\text{mol BDA}}}$$

The same result could have been obtained from the results of part 1 as $(3.99 \text{ kmol H}_2\text{O/h}) / (34.0 \text{ kmol BDA/h})$.

$$h_a = \frac{0.117 \text{ kmol H}_2\text{O}}{\text{kmol BDA}} \left| \frac{18.0 \text{ kg H}_2\text{O}}{\text{kmol H}_2\text{O}} \right| \frac{1 \text{ kmol BDA}}{29.0 \text{ kg BDA}} = \boxed{0.0726 \frac{\text{kg H}_2\text{O}}{\text{kg BDA}}}$$

$$h_m^* = \frac{p_{H_2O}^*}{P - p_{H_2O}^*} = \frac{289 \text{ mm Hg}}{(825 - 289) \text{ mm Hg}} = 0.539 \frac{\text{kmol H}_2\text{O}}{\text{kmol BDA}}$$

$$h_p = 100h_m/h_m^* = (100)(0.117)/(0.539) = \boxed{21.7\%}$$

3. $p_{H_2O} = 86.7 \text{ mm Hg} = p_{H_2O}^*(T_{dp})$

\downarrow Table B.3

$$\boxed{T_{dp} = 48.7^\circ\text{C}}$$

Lecture 17

6.4 Multicomponent Gas-Liquid Equilibrium

6.4a Vapor-Liquid Equilibrium Data

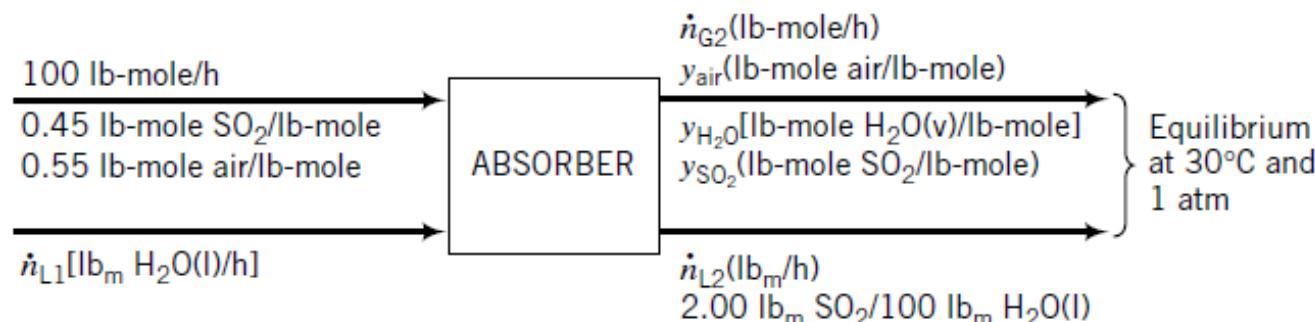
EXAMPLE 6.4-1

Absorption of SO_2

A gas stream consisting of 100 lb-mole/h of an SO_2 -air mixture containing 45 mole % SO_2 is contacted with liquid water in a continuous absorber at 30°C. The liquid leaving the absorber is analyzed and found to contain 2.00 g of SO_2 per 100 g of H_2O . Assuming that the gas and liquid streams leaving the absorber are in equilibrium at 30°C and 1 atm, calculate the fraction of the entering SO_2 absorbed in the water and the required water feed rate.

SOLUTION

Basis: Given Feed Rate of Gas



From Table 3-12 on p. 3-65 of the 6th Edition of *Perry's Chemical Engineers' Handbook*,⁴ the equilibrium partial pressures of H₂O and SO₂ over a solution of the indicated composition are

$$p_{\text{H}_2\text{O}} = 31.6 \text{ mm Hg}$$

$$p_{\text{SO}_2} = 176 \text{ mm Hg}$$

so that the composition of the exit gas stream is

$$y_{\text{H}_2\text{O}} = \frac{31.6 \text{ mm Hg}}{760 \text{ mm Hg}} = 0.0416 \frac{\text{lb-mole H}_2\text{O}}{\text{lb-mole}}$$

$$y_{\text{SO}_2} = \frac{176 \text{ mm Hg}}{760 \text{ mm Hg}} = 0.232 \frac{\text{lb-mole SO}_2}{\text{lb-mole}}$$

$$y_{\text{air}} = 1 - y_{\text{H}_2\text{O}} - y_{\text{SO}_2} = 0.727 \frac{\text{lb-mole air}}{\text{lb-mole}}$$

Three unknown process variables remain— \dot{n}_{L_1} , \dot{n}_{G_2} , and \dot{n}_{L_2} —and since a total of three independent balances can be written, the system is determinate.

Air Balance

$$(0.55 \times 100) \frac{\text{lb-mole air}}{\text{h}} = y_{\text{air}} \dot{n}_{G_2}$$

\Downarrow

$$y_{\text{air}} = 0.727 \text{ lb-mole air/lb-mole}$$

$$\dot{n}_{G_2} = 75.7 \text{ lb-mole/h}$$

To write the remaining two balances, it is necessary to determine the mass fractions of SO₂ and H₂O in the liquid effluent.

$$\frac{2.00 \text{ lb}_m \text{ SO}_2}{100 \text{ lb}_m \text{ H}_2\text{O}} \implies \frac{2.00 \text{ lb}_m \text{ SO}_2}{102 \text{ lb}_m \text{ total}} \implies x_{\text{SO}_2} = 0.0196 \text{ lb}_m \text{ SO}_2/\text{lb}_m$$

\Downarrow

$$x_{\text{SO}_2} + x_{\text{H}_2\text{O}} = 1$$

$$x_{\text{H}_2\text{O}} = 0.9804 \text{ lb}_m \text{ H}_2\text{O}/\text{lb}_m$$

SO₂ Balance

$$\frac{100 \text{ lb-mole}}{\text{h}} \left| \begin{array}{c} 0.45 \text{ lb-mole SO}_2 \\ \text{lb-mole} \end{array} \right. = \dot{n}_{G_2} y_{\text{SO}_2} + \frac{\dot{L}_2 (\text{lb}_m)}{(\text{h})} \left| \begin{array}{c} x_{\text{SO}_2} (\text{lb}_m \text{ SO}_2) \\ (\text{lb}_m) \end{array} \right. \left| \begin{array}{c} \text{lb-mole} \\ 64 \text{ lb}_m \text{ SO}_2 \end{array} \right.$$

\downarrow
 $\dot{n}_{G_2} = 75.7 \text{ lb-mole/h}$
 $y_{\text{SO}_2} = 0.232$
 $x_{\text{SO}_2} = 0.0196$
 $\dot{n}_{L_2} = 89,600 \text{ lb}_m/\text{h}$

H₂O Balance

$$\dot{n}_{L_1} (\text{lb}_m \text{ H}_2\text{O}/\text{h}) = \frac{\dot{n}_{G_2} (\text{lb-mole})}{(\text{h})} \left| \begin{array}{c} y_{\text{H}_2\text{O}} (\text{lb-mole H}_2\text{O}) \\ (\text{lb-mole}) \end{array} \right. \left| \begin{array}{c} 18 \text{ lb}_m \text{ H}_2\text{O} \\ \text{lb-mole} \end{array} \right. + \dot{n}_{L_2} x_{\text{H}_2\text{O}}$$

\downarrow
 $\dot{n}_{G_2} = 75.7 \text{ lb-mole/h}$
 $y_{\text{H}_2\text{O}} = 0.0416 \text{ lb-mole H}_2\text{O/lb-mole}$
 $\dot{n}_{L_2} = 89,600 \text{ lb}_m/\text{h}$
 $x_{\text{H}_2\text{O}} = 0.9804 \text{ lb}_m \text{ H}_2\text{O/lb}_m$

$\dot{n}_{L_1} = 87,900 \text{ lb}_m \text{ H}_2\text{O/h}$ (feed to absorber)

Fraction SO₂ Absorbed

$$\begin{aligned} \text{SO}_2 \text{ absorbed} &= \frac{89,600 \text{ lb}_m \text{ liquid effluent}}{\text{h}} \left| \begin{array}{c} 0.0196 \text{ lb}_m \text{ SO}_2 \\ \text{lb}_m \end{array} \right. \\ &= 1756 \frac{\text{lb}_m \text{ SO}_2 \text{ absorbed}}{\text{h}} \\ \text{SO}_2 \text{ fed} &= \frac{100 \text{ lb-mole}}{\text{h}} \left| \begin{array}{c} 0.45 \text{ lb-mole SO}_2 \\ \text{lb-mole} \end{array} \right. \left| \begin{array}{c} 64 \text{ lb}_m \text{ SO}_2 \\ \text{lb-mole SO}_2 \end{array} \right. = 2880 \frac{\text{lb}_m \text{ SO}_2 \text{ fed}}{\text{h}} \\ &\quad \downarrow \\ \frac{1756 \text{ lb}_m \text{ SO}_2 \text{ absorbed/h}}{2880 \text{ lb}_m \text{ SO}_2 \text{ fed/h}} &= \boxed{0.610 \frac{\text{lb}_m \text{ SO}_2 \text{ absorbed}}{\text{lb}_m \text{ SO}_2 \text{ fed}}} \end{aligned}$$

6.4b Raoult's Law and Henry's law

Relationships governing the distribution of a substance between gas and liquid phases are the subject matter of **phase-equilibrium thermodynamics** and, for the most part, fall beyond the scope of this text. However, we will cover several simple approximate relationships that provide reasonably accurate results over a wide range of conditions. Such relationships form the bases of more precise methods that must be used when system conditions require them.

Suppose A is a substance contained in a gas–liquid system in equilibrium at temperature T and pressure P . Two simple expressions—**Raoult's law** and **Henry's law**—provide relationships between p_A , the partial pressure of A in the gas phase, and x_A , the mole fraction of A in the liquid phase.

Raoult's Law:

$$p_A = y_A P = x_A p_A^*(T) \quad (6.4-1)$$

where p_A^* is the vapor pressure of pure liquid A at temperature T and y_A is the mole fraction of A in the gas phase.

Raoult's law is an approximation that is generally valid when x_A is close to 1—that is, when the liquid is almost pure A. It is also sometimes valid over the entire range of compositions for mixtures of similar substances, such as paraffinic hydrocarbons of similar molecular weights.

Note: When $x_A = 1$ —that is, when the liquid is pure A—Raoult's law reduces to the expression $p_A = p_A^*(T)$ given previously for systems with only one condensable component.

Henry's Law:

$$p_A = y_A P = x_A H_A(T) \quad (6.4-2)$$

where $H_A(T)$ is the **Henry's law constant** for A in a specific solvent.

Henry's law is generally valid for solutions in which x_A is close to 0 (dilute solutions of A) provided that A does not dissociate, ionize, or react in the liquid phase. The law is often ap-

EXAMPLE 6.4-2

Raoult's Law and Henry's Law

Use either Raoult's law or Henry's law to solve the following problems.

1. A gas containing 1.00 mole % ethane is in contact with water at 20.0°C and 20.0 atm. Estimate the mole fraction of dissolved ethane.
2. An equimolar liquid mixture of benzene (B) and toluene (T) is in equilibrium with its vapor at 30.0°C. What is the system pressure and the composition of the vapor?

SOLUTION

1. Hydrocarbons normally are relatively insoluble in water, so that the solution of ethane is probably extremely dilute. Let us therefore apply Henry's law. Page 2-126 of *Perry's Chemical Engineers' Handbook* (see footnote 1) gives the Henry's law constant for ethane in water at 20°C as 2.63×10^4 atm/mole fraction. From Equation 6.4-2

$$x_{\text{C}_2\text{H}_6} = \frac{y_{\text{C}_2\text{H}_6} P}{H_{\text{C}_2\text{H}_6}} = \frac{(0.0100)(20.0 \text{ atm})}{2.63 \times 10^4 \text{ atm/mole fraction}} = \boxed{7.60 \times 10^{-6} \frac{\text{mol C}_2\text{H}_6}{\text{mol}}}$$

2. Since benzene and toluene are structurally similar compounds, we may apply Raoult's law. From Table B.4,

$$\log_{10} p_B^* = 6.906 - \frac{1211}{T + 220.8} \xrightarrow{T = 30^\circ\text{C}} p_B^* = 119 \text{ mm Hg}$$

$$\log_{10} p_T^* = 6.9533 - \frac{1343.9}{T + 219.38} \xrightarrow{T = 30^\circ\text{C}} p_T^* = 36.7 \text{ mm Hg}$$

Using Equation 6.4-1,

$$p_B = x_B p_B^* = (0.500)(119 \text{ mm Hg}) = 59.5 \text{ mm Hg}$$

$$p_T = x_T p_T^* = (0.500)(36.7 \text{ mm Hg}) = 18.35 \text{ mm Hg}$$

$$P = p_B + p_T = \boxed{77.9 \text{ mm Hg}}$$

$$y_B = p_B / P = \boxed{0.764 \text{ mole benzene/mole}}$$

$$y_T = p_T / P = \boxed{0.236 \text{ mole toluene/mole}}$$

Table B.4 Antoine Equation Constants^a

$\log_{10} p^* = A - \frac{B}{T + C}$ p^* in mm Hg, T in °C					
Example: The vapor pressure of acetaldehyde at 25°C is determined as follows:					
$\log_{10} p_{\text{C}_2\text{H}_4\text{O}}^*(25^\circ\text{C}) = 8.00552 - \frac{1600.017}{25 + 291.809} = 2.9551$					
$\Rightarrow p_{\text{C}_2\text{H}_4\text{O}}^*(25^\circ\text{C}) = 10^{2.9551} = 902 \text{ mm Hg}$					
Compound	Formula	Range (°C)	A	B	C
Acetaldehyde	$\text{C}_2\text{H}_4\text{O}$	-0.2 to 34.4	8.00552	1600.017	291.809
Acetic acid	$\text{C}_2\text{H}_4\text{O}_2$	29.8 to 126.5	7.38782	1533.313	222.309
Acetic acid*	$\text{C}_2\text{H}_4\text{O}_2$	0 to 36	7.18807	1416.7	225
Acetic anhydride	$\text{C}_4\text{H}_6\text{O}_3$	62.8 to 139.4	7.14948	1444.718	199.817
Acetone	$\text{C}_3\text{H}_6\text{O}$	-12.9 to 55.3	7.11714	1210.595	229.664
Acrylic acid	$\text{C}_3\text{H}_4\text{O}_2$	20.0 to 70.0	5.65204	648.629	154.683
Ammonia*	NH_3	-83 to 60	7.55466	1002.711	247.885
Aniline	$\text{C}_6\text{H}_7\text{N}$	102.6 to 185.2	7.32010	1731.515	206.049
Benzene	C_6H_6	14.5 to 80.9	6.89272	1203.531	219.888
<i>n</i> -Butane	$n\text{-C}_4\text{H}_{10}$	-78.0 to -0.3	6.82485	943.453	239.711
<i>i</i> -Butane	$i\text{-C}_4\text{H}_{10}$	-85.1 to -11.6	6.78866	899.617	241.942
1-Butanol	$\text{C}_4\text{H}_{10}\text{O}$	89.2 to 125.7	7.36366	1305.198	173.427
2-Butanol	$\text{C}_4\text{H}_{10}\text{O}$	72.4 to 107.1	7.20131	1157.000	168.279
1-Butene	C_4H_8	-77.5 to -3.7	6.53101	810.261	228.066
Butyric acid	$\text{C}_4\text{H}_8\text{O}_2$	20.0 to 150.0	8.71019	2433.014	255.189
Carbon disulfide	CS_2	3.6 to 79.9	6.94279	1169.110	241.593
Carbon tetrachloride	CCl_4	14.1 to 76.0	6.87926	1212.021	226.409
Chlorobenzene	$\text{C}_6\text{H}_5\text{Cl}$	62.0 to 131.7	6.97808	1431.053	217.550
Chlorobenzene*	$\text{C}_6\text{H}_5\text{Cl}$	0 to 42	7.10690	1500.0	224.0
Chlorobenzene*	$\text{C}_6\text{H}_5\text{Cl}$	42 to 230	6.94504	1413.12	216.0
Chloroform	CHCl_3	-10.4 to 60.3	6.95465	1170.966	226.232
Chloroform*	CHCl_3	-30 to 150	6.90328	1163.03	227.4
Cyclohexane	C_6H_{12}	19.9 to 81.6	6.84941	1206.001	223.148
Cyclohexanol	$\text{C}_6\text{H}_{12}\text{O}$	93.7 to 160.7	6.25530	912.866	109.126
<i>n</i> -Decane	$n\text{-C}_{10}\text{H}_{22}$	94.5 to 175.1	6.95707	1503.568	194.738
1-Decene	$\text{C}_{10}\text{H}_{20}$	86.8 to 171.6	6.95433	1497.527	197.056
1,1-Dichloroethane	$\text{C}_2\text{H}_4\text{Cl}_2$	-38.8 to 17.6	6.97702	1174.022	229.060
1,2-Dichloroethane	$\text{C}_2\text{H}_4\text{Cl}$	-30.8 to 99.4	7.02530	1271.254	222.927
Dichloromethane	CH_2Cl_2	-40.0 to 40	7.40916	1325.938	252.616
Diethyl ether	$\text{C}_4\text{H}_{10}\text{O}$	-60.8 to 19.9	6.92032	1064.066	228.799
Diethyl ketone	$\text{C}_5\text{H}_{10}\text{O}$	56.5 to 111.3	7.02529	1310.281	214.192
Diethylene glycol	$\text{C}_4\text{H}_{10}\text{O}_2$	130.0 to 243.0	7.63666	1939.359	162.714
Dimethyl ether	$\text{C}_2\text{H}_6\text{O}$	-78.2 to -24.9	6.97603	889.264	241.957
Dimethylamine	$\text{C}_2\text{H}_7\text{N}$	-71.8 to 6.9	7.08212	960.242	221.667
<i>N,N</i> -Dimethylformamide	$\text{C}_3\text{H}_7\text{NO}$	30.0 to 90.0	6.92796	1400.869	196.434
1,4-Dioxane	$\text{C}_4\text{H}_8\text{O}_2$	20.0 to 105.0	7.43155	1554.679	240.337
Ethanol	$\text{C}_2\text{H}_6\text{O}$	19.6 to 93.4	8.11220	1592.864	226.184
Ethanolamine	$\text{C}_2\text{H}_7\text{NO}$	65.4 to 170.9	7.45680	1577.670	173.368
Ethyl acetate	$\text{C}_4\text{H}_8\text{O}_2$	15.6 to 75.8	7.10179	1244.951	217.881
Ethyl acetate*	$\text{C}_4\text{H}_8\text{O}_2$	-20 to 150	7.09808	1238.710	217.0
Ethyl chloride	$\text{C}_2\text{H}_5\text{Cl}$	-55.9 to 12.5	6.98647	1030.007	238.612
Ethylbenzene	C_8H_{10}	56.5 to 137.1	6.95650	1423.543	213.091

Compound	Formula	Range (°C)	A	B	C
Ethylene glycol	$\text{C}_2\text{H}_6\text{O}_2$	50.0 to 200.0	8.09083	2088.936	203.454
Ethylene oxide	$\text{C}_2\text{H}_4\text{O}$	0.3 to 31.8	8.69016	2005.779	334.765
1,2-Ethylenediamine	$\text{C}_2\text{H}_8\text{N}_2$	26.5 to 117.4	7.16871	1336.235	194.366
Formaldehyde	HCHO	-109.4 to -22.3	7.19578	970.595	244.124
Formic acid	CH_2O_2	37.4 to 100.7	7.58178	1699.173	260.714
Glycerol	$\text{C}_3\text{H}_8\text{O}_3$	183.3 to 260.4	6.16501	1036.056	28.097
<i>n</i> -Heptane	$n\text{-C}_7\text{H}_{16}$	25.9 to 99.3	6.90253	1267.828	216.823
<i>i</i> -Heptane	$i\text{-C}_7\text{H}_{16}$	18.5 to 90.9	6.87689	1238.122	219.783
1-Heptene	C_7H_{14}	21.6 to 94.5	6.91381	1265.120	220.051
<i>n</i> -Hexane	$n\text{-C}_6\text{H}_{14}$	13.0 to 69.5	6.88555	1175.817	224.867
<i>i</i> -Hexane	$i\text{-C}_6\text{H}_{14}$	12.8 to 61.1	6.86839	1151.401	228.477
1-Hexene	C_6H_{12}	15.9 to 64.3	6.86880	1154.646	226.046
Hydrogen Cyanide	HCN	-16.4 to 46.2	7.52823	1329.49	260.418
Methanol	CH_3OH	14.9 to 83.7	8.08097	1582.271	239.726
Methanol*	CH_3OH	-20 to 140	7.87863	1473.11	230.0
Methyl acetate	$\text{C}_3\text{H}_6\text{O}_2$	1.8 to 55.8	7.06524	1157.630	219.726
Methyl bromide	CH_3Br	-70.0 to 3.6	7.09084	1046.066	244.914
Methyl chloride	CH_3Cl	-75.0 to 5.0	7.09349	948.582	249.336
Methyl ethyl ketone	$\text{C}_4\text{H}_8\text{O}$	42.8 to 88.4	7.06356	1261.339	221.969
Methyl isobutyl ketone	$\text{C}_6\text{H}_{12}\text{O}$	21.7 to 116.2	6.67272	1168.408	191.944
Methyl methacrylate	$\text{C}_5\text{H}_8\text{O}_2$	39.2 to 89.2	8.40919	2050.467	274.369
Methylamine	CH_5N	-83.1 to -6.2	7.33690	1011.532	233.286
Methylcyclohexane	C_7H_{14}	25.6 to 101.8	6.82827	1273.673	221.723
Naphthalene	C_{10}H_8	80.3 to 179.5	7.03358	1756.328	204.842
Nitrobenzene	$\text{C}_6\text{H}_5\text{NO}_2$	134.1 to 210.6	7.11562	1746.586	201.783
Nitromethane	CH_3NO_2	55.7 to 136.4	7.28166	1446.937	227.600
<i>n</i> -Nonane	$n\text{-C}_9\text{H}_{20}$	70.3 to 151.8	6.93764	1430.459	201.808
1-Nonene	C_9H_{18}	66.6 to 147.9	6.95777	1437.862	205.814
<i>n</i> -Octane	$n\text{-C}_8\text{H}_{18}$	52.9 to 126.6	6.91874	1351.756	209.100
<i>i</i> -Octane	$i\text{-C}_8\text{H}_{18}$	41.7 to 118.5	6.88814	1319.529	211.625
1-Octene	C_8H_{16}	44.9 to 122.2	6.93637	1355.779	213.022
<i>n</i> -Pentane	$n\text{-C}_5\text{H}_{12}$	13.3 to 36.8	6.84471	1060.793	231.541
<i>i</i> -Pentane	$i\text{-C}_5\text{H}_{12}$	16.3 to 28.6	6.73457	992.019	229.564
1-Pentanol	$\text{C}_5\text{H}_{12}\text{O}$	74.7 to 156.0	7.18246	1287.625	161.330
1-Pentene	C_5H_{10}	12.8 to 30.7	6.84268	1043.206	233.344
Phenol	$\text{C}_6\text{H}_5\text{O}$	107.2 to 181.8	7.13301	1516.790	174.954
1-Propanol	$\text{C}_3\text{H}_8\text{O}$	60.2 to 104.6	7.74416	1437.686	198.463
2-Propanol	$\text{C}_3\text{H}_8\text{O}$	52.3 to 89.3	7.74021	1359.517	197.527
Propionic acid	$\text{C}_3\text{H}_6\text{O}_2$	72.4 to 128.3	7.71423	1733.418	217.724
Propylene oxide	$\text{C}_3\text{H}_6\text{O}$	-24.2 to 34.8	7.01443	1086.369	228.594
Pyridine	$\text{C}_5\text{H}_5\text{N}$	67.3 to 152.9	7.04115	1373.799	214.979
Styrene	C_8H_8	29.9 to 144.8	7.06623	1507.434	214.985
Toluene	C_7H_8	35.3 to 111.5	6.95805	1346.773	219.693
1,1,1-Trichloroethane	$\text{C}_2\text{H}_3\text{Cl}_3$	-5.4 to 16.9	8.64344	2136.621	302.769
1,1,2-Trichloroethane	$\text{C}_2\text{H}_3\text{Cl}_3$	50.0 to 113.7	6.95185	1314.410	209.197
Trichloroethylene	C_2HCl_3	17.8 to 86.5	6.51827	1018.603	192.731
Vinyl acetate	$\text{C}_4\text{H}_6\text{O}_2$	21.8 to 72.0	7.21010	1296.130	226.655
Water*	H_2O	0 to 60	8.10765	1750.286	235.000
Water*	H_2O	60 to 150	7.96681	1668.210	228.000
<i>m</i> -Xylene	$m\text{-C}_8\text{H}_{10}$	59.2 to 140.0	7.00646	1460.183	214.827
<i>o</i> -Xylene	$o\text{-C}_8\text{H}_{10}$	63.5 to 145.4	7.00154	1476.393	213.872
<i>p</i> -Xylene	$p\text{-C}_8\text{H}_{10}$	58.3 to 139.3	6.98820	1451.792	215.111

Lecture 18

6.4c Vapor-Liquid Equilibrium Calculations for Ideal Solutions

When a liquid is heated slowly at constant pressure, the temperature at which the first vapor bubble forms is the **bubble-point temperature** of the liquid at the given pressure. When a gas (vapor) is cooled slowly at constant pressure, the temperature at which the first liquid droplet forms is the **dew-point temperature** at the given pressure. Calculating bubble-point and dew-point temperatures can be a complex task for an arbitrary mixture of components. However, if the liquid behaves as an **ideal solution** (one for which Raoult's or Henry's law is obeyed for all components) and the gas phase can also be considered ideal, the calculations are relatively straightforward.

Suppose an ideal liquid solution follows Raoult's law and contains species A, B, C, ... with known mole fractions x_A , x_B , x_C , If the mixture is heated at a constant pressure P to its bubble-point temperature T_{bp} , the further addition of a slight amount of heat will lead to the formation of a vapor phase. Since the vapor is in equilibrium with the liquid, and we now assume that the vapor is ideal (follows the ideal gas equation of state), the partial pressures of the components are given by Raoult's law, Equation 6.4-1.

$$p_i = x_i p_i^*(T_{bp}), \quad i = A, B, \dots \quad (6.4-3)$$

where p_i^* is the vapor pressure of component i at the bubble-point temperature. Moreover, since we have assumed that only A, B, C, ... are present in the system, the sum of the partial pressures must be the total system pressure, P ; hence,

$$P = x_A p_A^*(T_{bp}) + x_B p_B^*(T_{bp}) + \dots \quad (6.4-4)$$

The bubble-point temperature may be calculated by trial and error as the value of T_{bp} that satisfies this equation; all that is needed is a set of relationships for $p_i^*(T)$, such as the Antoine equation or vapor-pressure charts or tables. Once T_{bp} is known, the composition of the vapor phase can easily be determined by evaluating the partial pressures of each component from Equation 6.4-3 and determining each vapor-phase mole fraction as $y_i = p_i/P$.

The pressure at which the first vapor forms when a liquid is decompressed at a constant temperature is the **bubble-point pressure** of the liquid at the given temperature. Equation 6.4-4 can be used to determine such a pressure for an ideal liquid solution at a specific temperature, and the mole fractions in the vapor in equilibrium with the liquid can then be determined as

$$y_i = \frac{p_i}{P_{\text{bp}}} = \frac{x_i p_i^*(T)}{P_{\text{bp}}} \quad (6.4-5)$$

The dew-point temperature of a gas (vapor) may be found using a method similar to that for bubble-point temperature estimation. Again, suppose a gas phase contains the condensable components A, B, C, ... and a noncondensable component G at a fixed pressure P . Let y_i be the mole fraction of component i in the gas. If the gas mixture is cooled slowly to its dew point, T_{dp} , it will be in equilibrium with the first liquid that forms. Assuming that Raoult's law applies, the liquid-phase mole fractions may be calculated as

$$x_i = \frac{y_i P}{p_i^*(T_{\text{dp}})}, \quad i = \text{A, B, C, ...} \quad \text{excluding } G \quad (6.4-6)$$

At the dew point of the gas mixture, the mole fractions of the liquid components (those that are condensable) must sum to 1:

$$x_A + x_B + x_C + \dots = 1$$

\Downarrow
Equation 6.4-6

$$\frac{y_A P}{p_A^*(T_{\text{dp}})} + \frac{y_B P}{p_B^*(T_{\text{dp}})} + \dots = 1 \quad (6.4-7)$$

The value of T_{dp} can be found by trial and error once expressions for $p_i^*(T)$ have been substituted. The composition of the liquid phase may then be determined from Equation 6.4-6.

The **dew-point pressure**, which relates to condensation brought about by increasing system pressure at constant temperature, can be determined by solving Equation 6.4-7 for P :

$$P_{dp} = \frac{1}{\frac{y_A}{p_A^*(T)} + \frac{y_B}{p_B^*(T)} + \frac{y_C}{p_C^*(T)} + \dots} \quad (6.4-8)$$

Liquid mole fractions may then be calculated from Equation 6.4-6 with T_{dp} replaced by the system temperature, T .

EXAMPLE 6.4-3

Bubble- and Dew-Point Calculations

1. Calculate the temperature and composition of a vapor in equilibrium with a liquid that is 40.0 mole % benzene–60.0 mole % toluene at 1 atm. Is the calculated temperature a bubble-point or dew-point temperature?
2. Calculate the temperature and composition of a liquid in equilibrium with a gas mixture containing 10.0 mole % benzene, 10.0 mole % toluene, and the balance nitrogen (which may be considered noncondensable) at 1 atm. Is the calculated temperature a bubble-point or dew-point temperature?
3. A gas mixture consisting of 15.0 mole % benzene, 10.0 mole % toluene, and 75.0 mole % nitrogen is compressed isothermally at 80°C until condensation occurs. At what pressure will condensation begin? What will be the composition of the initial condensate?

SOLUTION

Let A = benzene and B = toluene.

1. Equation 6.4-4 may be written in the form

$$f(T_{\text{bp}}) = 0.400p_A^*(T_{\text{bp}}) + 0.600p_B^*(T_{\text{bp}}) - 760 \text{ mm Hg} = 0$$

The solution procedure is to choose a temperature, evaluate p_A^* and p_B^* for that temperature from the Antoine equation using constants from Table B.4, evaluate $f(T_{\text{bp}})$ from the above equation, and repeat the calculations until a temperature is found for which $f(T_{\text{bp}})$ is sufficiently close to 0.

Trial-and-error searches of this sort are easy to do using spreadsheet programs. Enter a guessed value of T_{bp} in one cell and the formula for $f(T_{\text{bp}})$ (including the Antoine equation for each vapor pressure) in an adjacent cell, then vary the value in the first cell until the value in the second cell is sufficiently close to zero. If the spreadsheet program has a *goalseek* tool, the

calculation is even easier: simply instruct the program to vary the value in the first cell to drive the value in the second cell to zero. (See Appendix A.2c.)

Several numerical techniques for accelerating trial-and-error searches of this sort are discussed in Appendix A.2. One of them, the *regula-falsi* method, is used by goalseek tools in many spreadsheet programs. This procedure has been used to generate the trial temperatures shown here for the third and subsequent trials.

T (°C)	p_A^* (mm Hg)	p_B^* (mm Hg)	$f(T_{\text{bp}})$	T_{new} (°C)
80	757.66	291.21	-282.21	
100	1350.49	556.32	113.99	94.25
94.25	1152.23	465.71	-19.68	95.09
95.09	1179.91	478.26	-1.08	95.14
95.14	1181.43	478.95	-0.06	95.14

The solution is taken to be $T_{\text{bp}} = 95.1^\circ\text{C}$. At this temperature, Equation 6.4-1 yields

$$p_A = 0.400 \text{ (1181 mm Hg)} = 472.5 \text{ mm Hg}$$

$$p_B = 0.600 \text{ (479 mm Hg)} = 287.5 \text{ mm Hg}$$



$$P = (472.5 + 287.5) \text{ mm Hg} = 760 \text{ mm Hg}$$

Furthermore, from Equation 6.4-5,

$$y_A = \frac{472.5}{760.0} = \boxed{0.622 \text{ mol benzene/mol}}$$

$$y_B = 1 - y_A = \boxed{0.378 \text{ mol toluene/mol}}$$

Since the composition of the liquid was given, this was a **bubble-point** calculation.

2. Equation 6.4-7 may be written as

$$f(T_{\text{dp}}) = \frac{(0.100)(760 \text{ mm Hg})}{p_A^*(T_{\text{dp}})} + \frac{(0.100)(760 \text{ mm Hg})}{p_B^*(T_{\text{dp}})} - 1.00 = 0$$

A trial and error procedure similar to that in part (1) leads to the result $T_{\text{dp}} = 52.4^\circ\text{C}$, at which temperature $p_A^* = 297.4 \text{ mm Hg}$ and $p_B^* = 102.1 \text{ mm Hg}$. Then, from Equation 6.4-6,

$$x_A = \frac{0.100(760 \text{ mm Hg})}{p_A^*(52.4^\circ\text{C})} = \boxed{0.256 \text{ mol benzene/mol}}$$

$$x_B = 1 - x_A = \boxed{0.744 \text{ mol toluene/mol}}$$

The composition of the vapor was given and that of the liquid was calculated; therefore, this was a **dew-point** calculation.

3. The vapor pressures of benzene and toluene at 80°C are determined from the Antoine equation to be 757.7 mm Hg and 291.2 mm Hg, respectively. Assuming that nitrogen is insoluble in the condensate, Equation 6.4-8 gives

$$P = \frac{1}{(0.150/757.7 \text{ mm Hg}) + (0.100/291.2 \text{ mm Hg})} = \boxed{1847 \text{ mm Hg}}$$

$$x_A = \frac{y_A P}{p_A^*} = \frac{0.150(1847 \text{ mm Hg})}{757.7 \text{ mm Hg}} = \boxed{0.366 \text{ mol benzene/mol}}$$

$$x_B = 1 - x_A = \boxed{0.634 \text{ mol toluene/mol}}$$

6.4d Graphical Representation of Vapor-Liquid Equilibrium

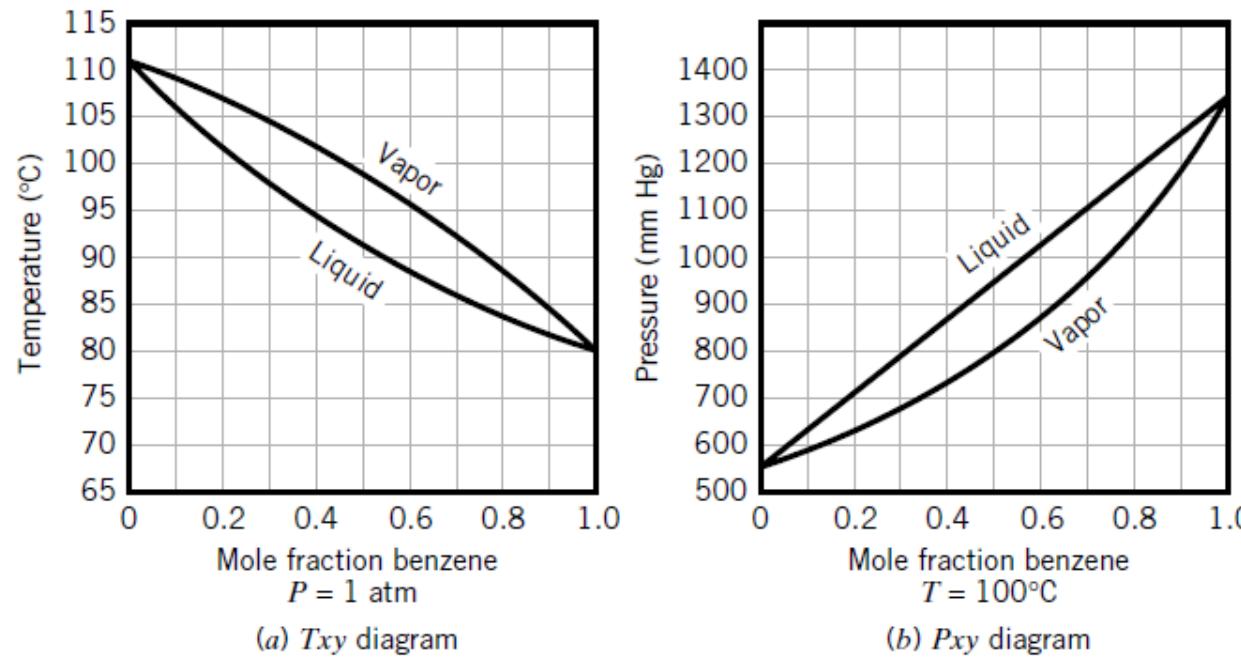


Figure 6.4-1 T_{xy} and P_{xy} diagrams for benzene–toluene system.

What happens as a liquid mixture is continuously vaporized is easily seen from the T_{xy} diagram. Consider the benzene–toluene system again, and suppose heat is added to a 55 mole % benzene and 45 mole % toluene liquid mixture at a fixed pressure of 1 atm. As Figure 6.4-1a shows, the mixture will begin to boil at 90°C , and the vapor generated will contain 77% benzene. However, once a small amount of liquid has been vaporized, the remainder no longer contains 55% benzene; it contains less, since the vapor produced is relatively rich in this component. Consequently, the temperature of the system steadily rises as more and more liquid is vaporized, and the compositions of both phases change continuously during the process.

EXAMPLE 6.4-4

Bubble- and Dew-Point Calculations Using Txy Diagrams

1. Using the Txy diagram, estimate the bubble-point temperature and the equilibrium vapor composition associated with a 40 mole% benzene–60 mole% toluene liquid mixture at 1 atm. If the mixture is steadily vaporized until the remaining liquid contains 25% benzene, what is the final temperature?
2. Using the Txy diagram, estimate the dew-point temperature and the equilibrium liquid composition associated with a vapor mixture of benzene and toluene containing 40 mole% benzene at 1 atm. If condensation proceeds until the remaining vapor contains 60% benzene, what is the final temperature?

SOLUTION

1. From Figure 6.4-1a, for $x_B = 0.40$, $T_{bp} \approx 95^\circ\text{C}$ and $y_B \approx 0.62$. (This matches the result of the much lengthier solution of the previous example.) When $x_B = 0.25$, $T_{bp} \approx 100^\circ\text{C}$. The temperature thus rises by 5°C as the vaporization proceeds.
2. From Figure 6.4-1a, for $y_B = 0.40$, $T_{dp} \approx 102^\circ\text{C}$ and $x_B \approx 0.20$. When $y_B = 0.60$, $T_{bp} \approx 96^\circ\text{C}$.

Note: The precision associated with graphical calculations is less than that of numerical calculations, as reflected in this example by the use of the \approx . However, the simplicity and clarity in following the process path make graphical calculations quite useful.

EXAMPLE 6.4-5

Boiling Point of a Mixture

A mixture that is 70 mole% benzene and 30 mole% toluene is to be distilled in a batch distillation column. The column startup procedure calls for charging the reboiler at the base of the column and slowly adding heat until boiling begins. Estimate the temperature at which boiling begins and the initial composition of the vapor generated, assuming the system pressure is 760 mm Hg.

SOLUTION

From the *Txy* diagram, the mixture will boil at approximately 87°C . The initial vapor composition is approximately [88 mole% benzene and 12 mole% toluene].

Lecture 19

6.5 Solutions of Solids in Liquids

6.5a Solubility and Saturation

The **solubility** of a solid in a liquid is the maximum amount of that substance that can be dissolved in a specified amount of the liquid at equilibrium. This physical property varies considerably from one solute–solvent pair to another: for example, 100 g of water at 20°C can dissolve 222 g of AgNO₃, 0.003 g of AgCO₃, and 0.00002 g of AgBr. The limit may also depend strongly on temperature: the solubility of AgNO₃ in 100 g of water increases from 222 g at 20°C to 952 g at 100°C. *Perry's Chemical Engineers' Handbook* (see footnote 1) on pp. 2-7 through 2-47 and 2-121 through 2-124 gives the solubilities of many substances in water, ethyl alcohol, and diethyl ether at specified temperatures.

A solution that contains as much of a dissolved species as it can *at equilibrium* is said to be **saturated** with that species. *A solution in equilibrium with solid solute must be saturated with that solute; if it were not, more solute would dissolve.*

If a saturated solution is cooled, the solubility of the solute generally decreases; in order for the cooled solution to return to equilibrium, some solute must come out of solution as solid crystals. The crystallization rate may be slow, however, so that a metastable condition can exist in which the concentration of the solute is higher than the equilibrium value at the solution temperature. Under such conditions, the solution is said to be **supersaturated** and the difference between actual and equilibrium concentrations is referred to as **supersaturation**. All problems involving solid–liquid separations in this text assume that equilibrium exists between the solid and liquid phases, so that supersaturation need not be considered.

EXAMPLE 6.5-1

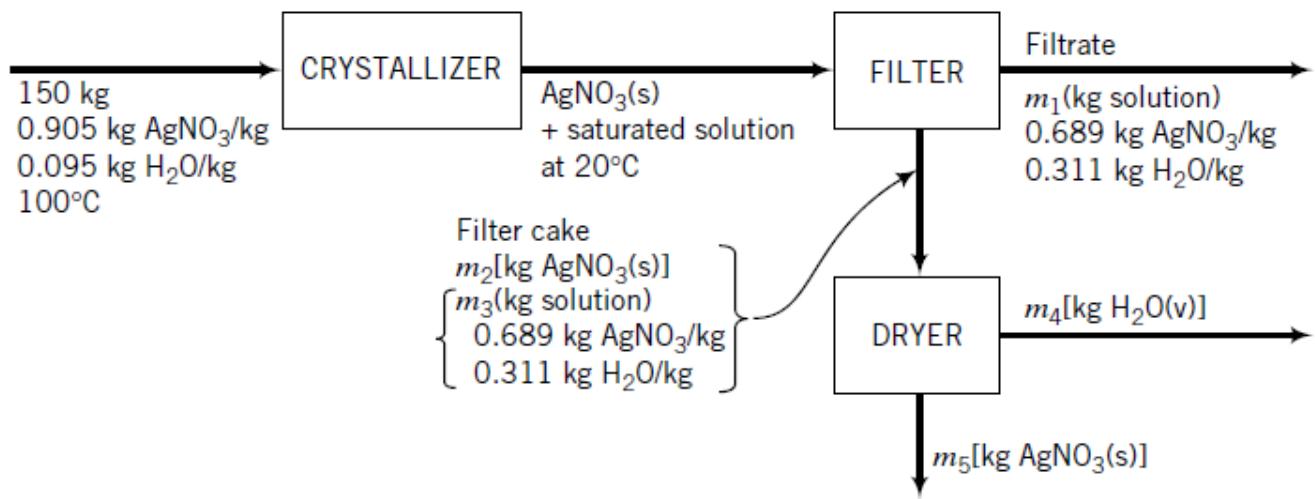
Crystallization and Filtration

One hundred fifty kilograms of a saturated aqueous solution of AgNO_3 at 100°C is cooled to 20°C , thereby forming AgNO_3 crystals, which are filtered from the remaining solution. The wet filter cake, which contains 80% solid crystals and 20% saturated solution by mass, passes to a dryer in which the remaining water is vaporized. Calculate the fraction of the AgNO_3 in the feed stream eventually recovered as dry crystals and the amount of water that must be removed in the drying stage.

SOLUTION

Basis: 150 kg Feed

Both the filtrate and the liquid retained in the filter cake are in equilibrium with solid AgNO_3 crystals and must therefore be saturated with AgNO_3 at 20°C . The compositions of saturated solutions of silver nitrate at 100°C and 20°C are given at the beginning of this section and are used in the flowchart.



Solubilities

100°C: $\frac{952 \text{ g AgNO}_3}{100 \text{ g H}_2\text{O}} \Rightarrow \frac{952 \text{ g AgNO}_3}{(100 + 952) \text{ g}} = 0.905 \text{ g AgNO}_3/\text{g}$



0.095 g H₂O/g

20°C: $\frac{222 \text{ g AgNO}_3}{100 \text{ g H}_2\text{O}} \Rightarrow \frac{222 \text{ g AgNO}_3}{(100 + 222) \text{ g}} = 0.689 \text{ g AgNO}_3/\text{g}$



0.311 g H₂O/g

Composition of the Filter Cake

$$m_2 = 0.8(m_2 + m_3) \implies m_2 = 4m_3$$

H_2O Balance About the Crystallizer and Filter $(0.095 \times 150) \text{ kg H}_2\text{O} = 0.311m_1 + 0.311m_3$

Mass Balance About the Crystallizer and Filter

$$150 \text{ kg} = m_1 + m_2 + m_3$$

The simultaneous solution of these three equations yields

$$m_1 = 20 \text{ kg}$$

$$m_2 = 104 \text{ kg}$$

$$m_3 = 26 \text{ kg}$$

Overall AgNO_3 Balance $(0.905 \times 150) \text{ kg AgNO}_3 = 0.689m_1 + m_5$

$$\downarrow m_1 = 20 \text{ kg}$$

$$m_5 = 122 \text{ kg AgNO}_3 \text{ crystals recovered}$$

Percentage Recovery $\frac{122 \text{ kg AgNO}_3 \text{ recovered}}{(0.905 \times 150) \text{ kg AgNO}_3 \text{ fed}} \times 100\% = \boxed{89.9\%}$

Overall Mass Balance $150 \text{ kg} = m_1 + m_4 + m_5$

$$\downarrow m_1 = 20 \text{ kg}$$

$$\downarrow m_5 = 122 \text{ kg}$$

$$m_4 = \boxed{8 \text{ kg H}_2\text{O removed in the dryer}}$$

6.5b Solid Solubilities and Hydrated Salts

The Gibbs phase rule shows that specifying temperature and pressure for a two-component system at equilibrium containing a solid solute and a liquid solution fixes the values of all other intensive variables. (Verify this statement.) Furthermore, because the properties of liquids and solids are only slightly affected by pressure, a single plot of solubility (an intensive variable) versus temperature may be applicable over a wide pressure range.

The solubility plots shown in Figure 6.5-1 illustrate how the effect of temperature on solubility can vary from system to system. Increasing the temperature from 0°C to 100°C barely changes NaCl solubility but increases the solubility of KNO₃ by more than a factor of 10. For Na₂SO₄, solubility increases up to about 40°C and decreases thereafter.

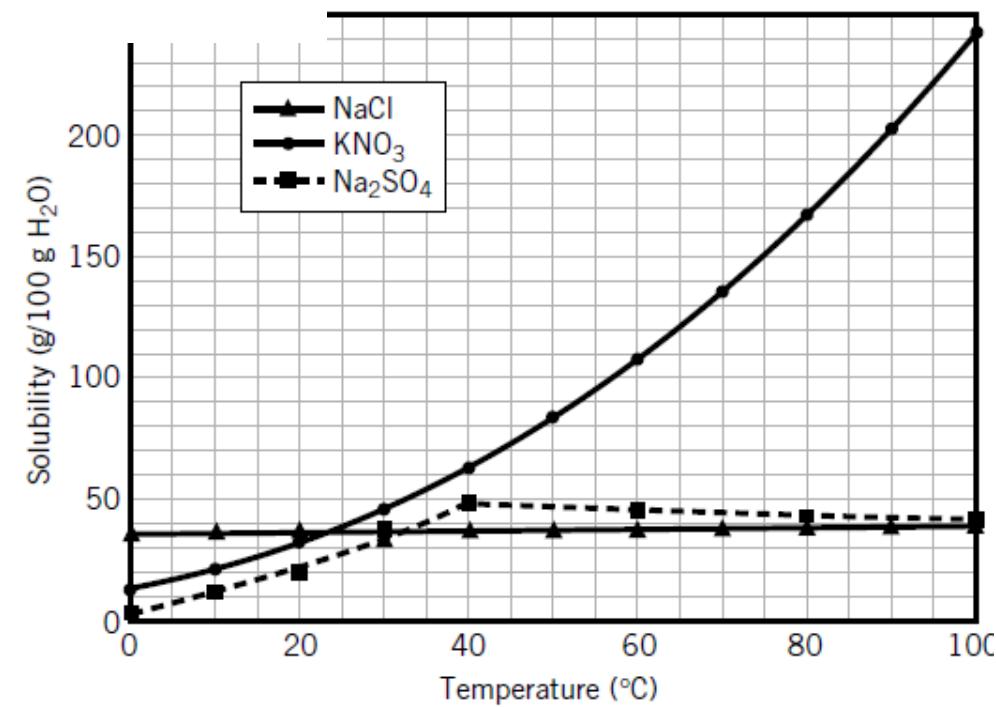


Figure 6.5-1 Solubilities of inorganic solutes.

EXAMPLE 6.5-2

Material Balances on a Crystallizer

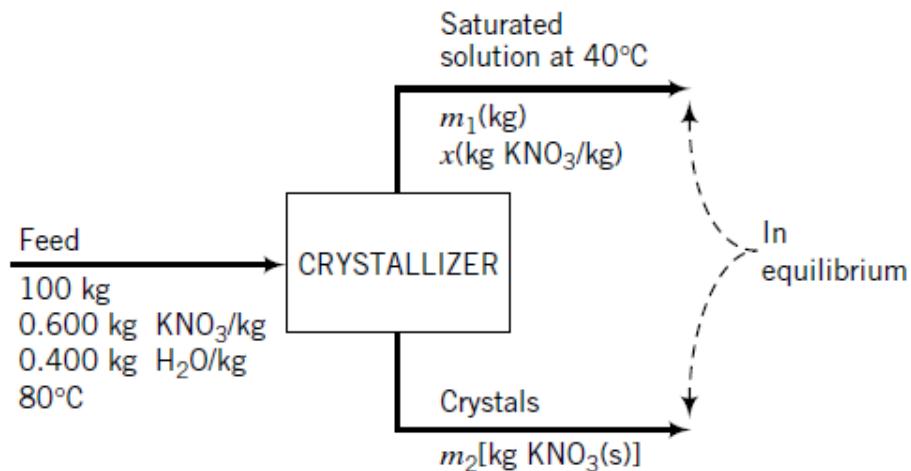
An aqueous potassium nitrate solution containing 60.0 wt% KNO_3 at 80°C is fed to a cooling crystallizer in which the temperature is reduced to 40°C. Determine the temperature at which the solution reaches saturation and the percentage of the potassium nitrate in the feed that forms crystals.

The feed concentration must be converted to a solute/solvent ratio to use Figure 6.5-1. Since 100.0 g of the solution contains 60.0 g KNO_3 and 40.0 g H_2O , the desired ratio is

$$\frac{60.0 \text{ g } \text{KNO}_3}{40.0 \text{ g } \text{H}_2\text{O}} = 1.50 \frac{\text{g } \text{KNO}_3}{\text{g } \text{H}_2\text{O}} = \frac{150 \text{ g } \text{KNO}_3}{100 \text{ g } \text{H}_2\text{O}}$$

From Figure 6.5-1, the saturation temperature of this solution is 74°C.

Here is a flowchart of the process for an assumed basis of 100 kg feed.



There are three unknowns on the chart (m_1 , x , m_2). We will assume that the solution leaving the crystallizer is saturated at 40°C. Accordingly, the value of x may be determined from the known solubility of KNO₃ at that temperature, and the remaining two variables may be determined from material balances. From Figure 6.5-1, the solubility at 40°C is roughly 63 kg KNO₃/100 kg H₂O. The calculations follow.

$$x = \frac{63 \text{ kg KNO}_3}{(63 + 100) \text{ kg solution}} = 0.386 \text{ kg KNO}_3/\text{kg}$$

H₂O Balance

100 kg	$0.400 \text{ kg H}_2\text{O}$	$= \frac{m_1(\text{kg})}{\text{kg}}$	$(1 - 0.386) \text{ kg H}_2\text{O}$	$\Rightarrow m_1 = 65.1 \text{ kg}$
--------	--------------------------------	--------------------------------------	--------------------------------------	-------------------------------------

Mass Balance

$$100 \text{ kg} = m_1 + m_2 \xrightarrow{m_1 = 65.1 \text{ kg}} m_2 = 34.9 \text{ kg KNO}_3(\text{s})$$

The percentage of the potassium nitrate in the feed that crystallizes is therefore

$$\frac{34.9 \text{ kg KNO}_3 \text{ crystallized}}{60.0 \text{ kg KNO}_3 \text{ fed}} \times 100\% = \boxed{58.2\%}$$

Table 6.5-1 Hydrated MgSO₄ Salts

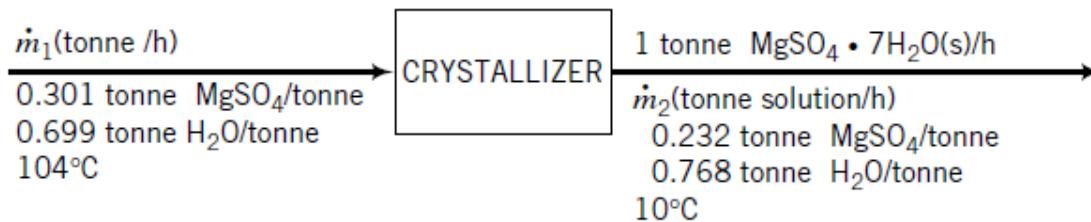
Form	Name	Wt% MgSO ₄	Conditions
MgSO ₄	Anhydrous magnesium sulfate	100.0	> 100°C
MgSO ₄ ·H ₂ O	Magnesium sulfate monohydrate	87.0	67 to 100°C
MgSO ₄ ·6 H ₂ O	Magnesium sulfate hexahydrate	52.7	48 to 67°C
MgSO ₄ ·7 H ₂ O	Magnesium sulfate heptahydrate	48.8	2 to 48°C
MgSO ₄ ·12 H ₂ O	Magnesium sulfate dodecahydrate	35.8	-4 to 2°C

EXAMPLE 6.5-3**Production of a Hydrated Salt**

An aqueous solution of magnesium sulfate at 104°C containing 30.1 wt% MgSO₄ is fed to a cooling crystallizer that operates at 10°C. The stream leaving the crystallizer is a slurry of solid magnesium sulfate heptahydrate particles [MgSO₄·7H₂O(s)] suspended in a liquid solution. Tabulated solubility data for magnesium sulfate [*Perry's Chemical Engineers' Handbook* (see footnote 1), p. 18-35] show that a saturated solution at 10°C contains 23.2 wt% MgSO₄. Determine the rate at which solution must be fed to the crystallizer to produce 1 metric ton (1 tonne, 1000 kg) of magnesium sulfate heptahydrate per hour.

Basis: 1 tonne $MgSO_4 \cdot 7H_2O(s)$ Produced/h

We assume that the solution leaving the crystallizer is in equilibrium with the solid crystals and is therefore saturated with $MgSO_4$. A flowchart of the crystallizer follows:



There are two unknowns on the chart (\dot{m}_1 and \dot{m}_2) and two independent molecular species on which balances may be written ($MgSO_4$ and H_2O), so that the problem can be solved. The atomic weights on the inside back cover may be used to show that the molecular weight of anhydrous magnesium sulfate is 120.4 and that of the heptahydrate salt is 246.4. The balances follow.

Total Mass Balance

$$\dot{m}_1 = 1 \text{ tonne/h} + \dot{m}_2$$

$MgSO_4$ Balance

$$0.301\dot{m}_1 \left(\frac{\text{tonne } MgSO_4}{\text{h}} \right) = \frac{1 \text{ tonne } MgSO_4 \cdot 7H_2O}{\text{h}} \quad \begin{array}{|c} 120.4 \text{ tonne } MgSO_4 \\ \hline 246.4 \text{ tonne } MgSO_4 \cdot 7H_2O \end{array}$$
$$+ \frac{\dot{m}_2(\text{tonne solution/h})}{\text{tonne solution}} \quad \begin{array}{|c} 0.232 \text{ tonne } MgSO_4 \\ \hline \end{array}$$

Solving these two equations simultaneously yields $\boxed{\dot{m}_1 = 3.71 \text{ tonne/h}}$ and $\dot{m}_2 = 2.71 \text{ tonne/h}$.

6.5c Colligative Solution Properties

Physical properties of a solution generally differ from the same properties of the pure solvent. Under certain conditions, the changes in the values of several properties—such as vapor pressure, boiling point, and freezing point—depend only on the concentration of solute in the solution, and not on what the solute and solvent are. Such properties are referred to as **colligative solution properties**. (A fourth colligative property—osmotic pressure—will not concern us in this text.)

Consider a solution in which the solute mole fraction is x and the vapor pressure of the pure solvent at the solution temperature is p_s^* . Applying Raoult's law (Equation 6.4-1) to the solution, we obtain for the partial pressure of the solvent

$$p_s(T) = (1 - x)p_s^*(T) \quad (6.5-1)$$

If the liquid is pure solvent ($x = 0$), this equation predicts that the partial pressure of the solvent vapor equals the vapor pressure of the solvent, as we would expect. Since the solute is nonvolatile, the solvent is the only component of the liquid solution that is also in the vapor. The pressure exerted by this vapor is referred to as the *effective* solvent vapor pressure:

$$(p_s^*)_e = p_s = (1 - x)p_s^* \quad (6.5-2)$$

Since x —and hence $(1 - x)$ —is less than one, the effect of the solute is to lower the effective solvent vapor pressure. The **vapor pressure lowering**, defined as the difference between the vapor pressure of the pure component and the effective vapor pressure of the solvent, is

$$\Delta p_s^* = p_s^* - (p_s^*)_e = xp_s^* \quad (6.5-3)$$

The lowering of solvent vapor pressure has two important consequences. *The solvent in a solution at a given pressure boils at a higher temperature and freezes at a lower temperature than does the pure solvent at the same pressure.* The validity of these statements can be seen by referring to Figure 6.5-2, a phase diagram for an arbitrary solute–solvent system. Shown on this figure are the vapor–liquid and solid–liquid equilibrium curves for a pure solvent (solid curves) and for a solution of a fixed solute concentration (dashed curves). The solution vapor–liquid and solid–liquid equilibrium curves lie below the solvent curves, reflecting the fact that the effective vapor pressure at a given temperature and freezing point at a given pressure for the solution are lower than those of the pure solvent. The higher the solute concentration, the greater is the separation between the pure solvent and the solution curves.

The effect of the solute on the solution boiling point is easy to see from the diagram. Recall that the boiling point of a liquid at a given pressure is the intersection of a horizontal line at that pressure with the vapor–liquid equilibrium curve. At pressure P_0 , the pure solvent boils at temperature T_{b0} , while the solution boils at a higher temperature, T_{bs} .

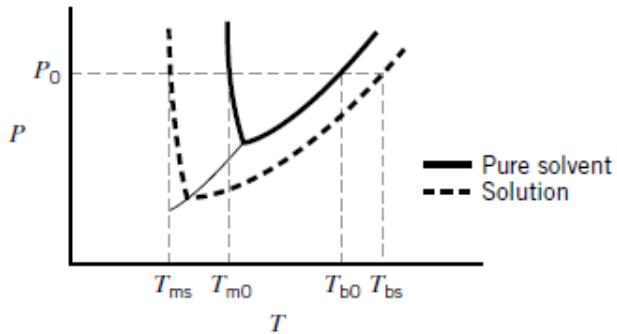


Figure 6.5-2 Phase-equilibrium curves for pure solvent and solution.

Since we know how the solution vapor pressure varies with concentration (the relationship being given by Equation 6.5-2) and temperature (through the Clausius–Clapeyron equation, Equation 6.1-3), we can determine the relationships between concentration and both boiling point elevation and freezing point depression. The relationships are particularly simple for dilute solutions ($x \rightarrow 0$, where x is solute mole fraction).

$$\Delta T_b = T_{bs} - T_{b0} = \frac{RT_{b0}^2}{\Delta \hat{H}_v} x \quad (6.5-4)$$

$$\Delta T_m = T_{m0} - T_{ms} = \frac{RT_{m0}^2}{\Delta \hat{H}_m} x \quad (6.5-5)$$

In these equations, $\Delta \hat{H}_v$ refers to the heat of vaporization of the pure solvent at its boiling point T_{b0} , and $\Delta \hat{H}_m$ denotes the heat of fusion of the pure solvent at its melting point T_{m0} . These properties of the solvent can be looked up in data tables, such as Table B.1 of this text. Their physical significance is discussed in Chapter 8. The derivation of Equation 6.5-4 is dealt with in Problem 6.87 at the end of this chapter.

EXAMPLE 6.5-4

Colligative Property Calculations

A solution of 5.000 g of a solute in 100.0 g of water is heated slowly at a constant pressure of 1.00 atm and is observed to boil at 100.421°C. Estimate the molecular weight of the solute, the effective solvent vapor pressure at 25°C, and the solution freezing point at 1 atm. The necessary properties of water can be found in Table B.1.

If the values of the normal boiling point and heat of vaporization of pure water (from Table B.1) and the gas constant are substituted into Equation 6.5-4, the result is

$$\Delta T_b(\text{K}) = \frac{[8.314 \text{ J}/(\text{mol}\cdot\text{K})](373.16 \text{ K})^2 x}{40,656 \text{ J/mol}} = 28.5x$$

From the measured boiling point elevation, $\Delta T_b = 0.421$ K, we may deduce that the mole fraction of the solute in the solution is $x = 0.421/28.5 = 0.0148$. But since the solution is known to contain $(5.000/M_s)$ mol of solute, where M_s is the solute molecular weight, and $100.0\text{ g}/18.016\text{ g/mol} = 5.551$ mol of water, we may write

$$0.0148 = (5.000\text{ g}/M_s)/(5.000\text{ g}/M_s + 5.551\text{ mol})$$



$M_s = 60.1\text{ g/mol}$

From Equation 6.5-2 the effective solvent vapor pressure at 25°C is determined from the vapor pressure of pure water at this temperature (found in Table B.3) as

$$(p_s^*)_e = (1.000 - 0.0148)(23.756\text{ mm Hg}) = \boxed{23.40\text{ mm Hg}}$$

Finally, substituting values of the melting point and heat of fusion of water (from Table B.1) and the gas constant into Equation 6.5-5, we obtain

$$\Delta T_m = \frac{[8.314\text{ J}/(\text{mol}\cdot\text{K})](273.16\text{ K})^2(0.0148)}{(6009.5\text{ J/mol})} = 1.53\text{ K} = 1.53^\circ\text{C}$$



$$T_{ms} = (0.000 - 1.53)^\circ\text{C} = \boxed{-1.53^\circ\text{C}}$$

Table B.1 (Continued)

Compound	Formula	Mol. Wt.	SG (20°/4°)	T_m (°C) ^b	$\Delta\hat{H}_m(T_m)$ ^{c,j} kJ/mol	T_b (°C) ^d	$\Delta\hat{H}_v(T_b)$ ^{e,j} kJ/mol	T_c (K) ^f	P_c (atm) ^g	$(\Delta\hat{H}_f^\circ)^{h,j}$ kJ/mol	$(\Delta\hat{H}_c^\circ)^{i,j}$ kJ/mol
Sodium thiosulfate	Na ₂ S ₂ O ₃	158.11	1.667	—	—	—	—	—	—	-1117.1(c)	—
Sulfur (rhombic)	S ₈	256.53	2.07	113	10.04	444.6	83.7	—	—	0(c)	—
Sulfur (monoclinic)	S ₈	256.53	1.96	119	14.17	444.6	83.7	—	—	+0.30(c)	—
Sulfur dioxide	SO ₂	64.07	—	-75.48	7.402	-10.02	24.91	430.7	77.8	-296.90(g)	—
Sulfur trioxide	SO ₃	80.07	—	16.84	25.48	43.3	41.80	491.4	83.8	-395.18(g)	—
Sulfuric acid	H ₂ SO ₄	98.08	1.834 ^{18e}	10.35	9.87	Decomposes at 340°C		—	—	-811.32(l) -907.51(aq)	—
Toluene	C ₇ H ₈	92.13	0.866	-94.99	6.619	110.62	33.47	593.9	40.3	+12.00(l) +50.00(g)	-3909.9(l) -3947.9(g)
Water	H ₂ O	18.016	1.00 ^{4°}	0.00	6.0095	100.00	40.656	647.4	218.3	-285.84(l) -241.83(g)	—
<i>m</i> -Xylene	C ₈ H ₁₀	106.16	0.864	-47.87	11.569	139.10	36.40	619	34.6	-25.42(l) +17.24(g)	-4551.9(l) -4594.5(g)
<i>o</i> -Xylene	C ₈ H ₁₀	106.16	0.880	-25.18	13.598	144.42	36.82	631.5	35.7	-24.44(l) +18.99(g)	-4552.9(l) -4596.3(g)
<i>p</i> -Xylene	C ₈ H ₁₀	106.16	0.861	13.26	17.11	138.35	36.07	618	33.9	-24.43(l) 17.95(g)	-4552.91(l) -4595.2(g)
Zinc	Zn	65.38	7.140	419.5	6.674	907	114.77	—	—	0(c)	—



Lecture 20

6.6 Equilibrium Between Two Liquid Phases

6.6a Miscibility and Distribution Coefficients

If water and methyl isobutyl ketone (MIBK) are mixed at 25°C, a single phase results if the mixture contains more than either 98% water or 97.7% MIBK by mass; otherwise, the mixture separates into two liquid phases, one of which contains 98% H₂O and 2% MIBK and the other 97.7% MIBK and 2.3% H₂O. Water and MIBK are examples of **partially miscible** liquids; they would be termed **immiscible** if one phase contained a negligible amount of water and the other a negligible amount of MIBK.

If a third substance is added to a two-phase liquid mixture, it distributes itself according to its relative solubility in each phase. For example, acetone is soluble in both water and chloroform—two nearly immiscible liquids—but much more so in chloroform. If a mixture of acetone and water is contacted with chloroform, a substantial portion of the acetone enters the chloroform-rich phase. Separation of the acetone and water may then be accomplished easily by allowing the mixture to settle and separating the two phases. This example illustrates the separation process of **liquid extraction**.

Suppose A and S are two nearly immiscible liquids and B is a solute distributed between the phases of an A–S mixture. The **distribution coefficient** (also known as **partition ratio**) of component B is the ratio of the mass fraction of B in the S phase to that in the A phase. *Perry's Chemical Engineers' Handbook* (see footnote 1) on pp. 15-10 through 15-14 lists distribution coefficients for a number of ternary (three-component) liquid systems. Example 6.6-1 illustrates the use of this physical property in a material balance calculation.

EXAMPLE 6.6-1**Extraction of Acetone from Water**

Two hundred cubic centimeters of an acetone–water mixture that contains 10.0 wt% acetone is mixed with 400.0 cm³ of chloroform at 25°C, and the phases are then allowed to settle. What percentage of the acetone is transferred from the water to the chloroform?

SOLUTION**Basis: Given Quantities**

The densities of the pure substances are given in Table B.1:

Acetone (A)	0.792 g/cm ³
Chloroform (C)	1.489 g/cm ³
Water (W)	1.000 g/cm ³

Since density data for the acetone–water system are not readily available, let us use Equation 5.1-1 to estimate the density of the feed solution:

$$\frac{1}{\bar{\rho}} = \frac{x_A}{\rho_A} + \frac{x_W}{\rho_W} = \left(\frac{0.100}{0.792} + \frac{0.900}{1.000} \right) \frac{\text{cm}^3}{\text{g}} = 1.026 \frac{\text{cm}^3}{\text{g}}$$

↓

$$\bar{\rho} = 0.974 \text{ g/cm}^3$$

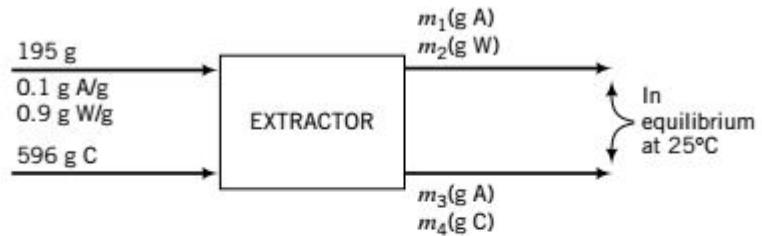
The mass of the solution fed is therefore

$$\frac{200.0 \text{ cm}^3}{\text{cm}^3} \Big| \frac{0.974 \text{ g}}{\text{cm}^3} = 195 \text{ g}$$

and that of the chloroform is

$$\frac{400.0 \text{ cm}^3}{\text{cm}^3} \Big| \frac{1.489 \text{ g}}{\text{cm}^3} = 596 \text{ g}$$

Let us next assume that chloroform and water are immiscible. (How to deal with partial miscibility is discussed in Section 6.6b.) In drawing the flowchart for this problem, it is advisable to label the quantities of each component in each of the two output streams, rather than the total stream masses and component mass fractions. (Labeling in the latter manner results in having to solve four simultaneous equations in four unknowns.)



The distribution coefficient for the A-C-W system is given on p. 15-12 of *Perry's Chemical Engineers' Handbook* (see footnote 1) as 1.72. If x denotes mass fraction of acetone,

$$K = \frac{(x)_{\text{C phase}}}{(x)_{\text{W phase}}} = \frac{m_3/(m_3 + m_4)}{m_1/(m_1 + m_2)} = 1.72 \quad (6.6-1)$$

This provides one equation in the four unknowns m_1 , m_2 , m_3 , and m_4 . The others are provided by material balances.

C Balance $596 \text{ g} = m_4$

W Balance $(0.900)(195 \text{ g}) = m_2 \implies m_2 = 175.5 \text{ g}$

A Balance $(0.100)(195 \text{ g}) = m_1 + m_3$

Substituting the known values of m_2 and m_4 into the first equation yields (with the acetone balance) two equations in two unknowns, which may be solved to obtain

$$m_1 = 2.7 \text{ g A in water phase}$$

$$m_3 = 16.8 \text{ g A in chloroform phase}$$

The percentage of acetone transferred is therefore

$$\frac{16.8 \text{ g acetone in chloroform phase}}{(0.100 \times 195) \text{ g acetone fed}} \times 100\% = \boxed{86.1\%}$$

6.6b Phase Diagrams for Ternary Systems

The behavior of partially miscible ternary (three-component) systems may be represented on a **triangular phase diagram**, which may take the form of an equilateral triangle (as shown in Figure 6.6-1 for H₂O–MIBK–acetone at 25°C) or a right triangle. The latter is easier to construct on rectangular axes, but the two forms are equally easy to use. In both cases, each apex of the triangle represents a single component and edges represent binary solutions. For example, edge *b* on Figure 6.6-1 represents solutions of H₂O and acetone. Point *K* represents a mixture that is 20.0 wt% MIBK, 65.0% acetone, and 15.0% water. Any mixture whose composition falls in region *A*, such as at point *K*, is a single-phase liquid, whereas any mixture whose *overall* composition falls in region *B* separates into two phases.

The lines shown within region *B*—called **tie lines**—connect compositions of the two liquid phases in equilibrium with each other. For example, if MIBK, water, and acetone are blended so that a mixture with overall composition at point *M* (55.0 wt% water, 15.0% acetone, 30.0% MIBK) results, the mixture separates into phases having compositions given by points *L* (85 wt% water, 12% acetone, 3% MIBK) and *N* (4 wt% water, 20% acetone, 76% MIBK). When a mixture does not fall on a tie line, interpolation between the lines is necessary to determine the composition of each phase.

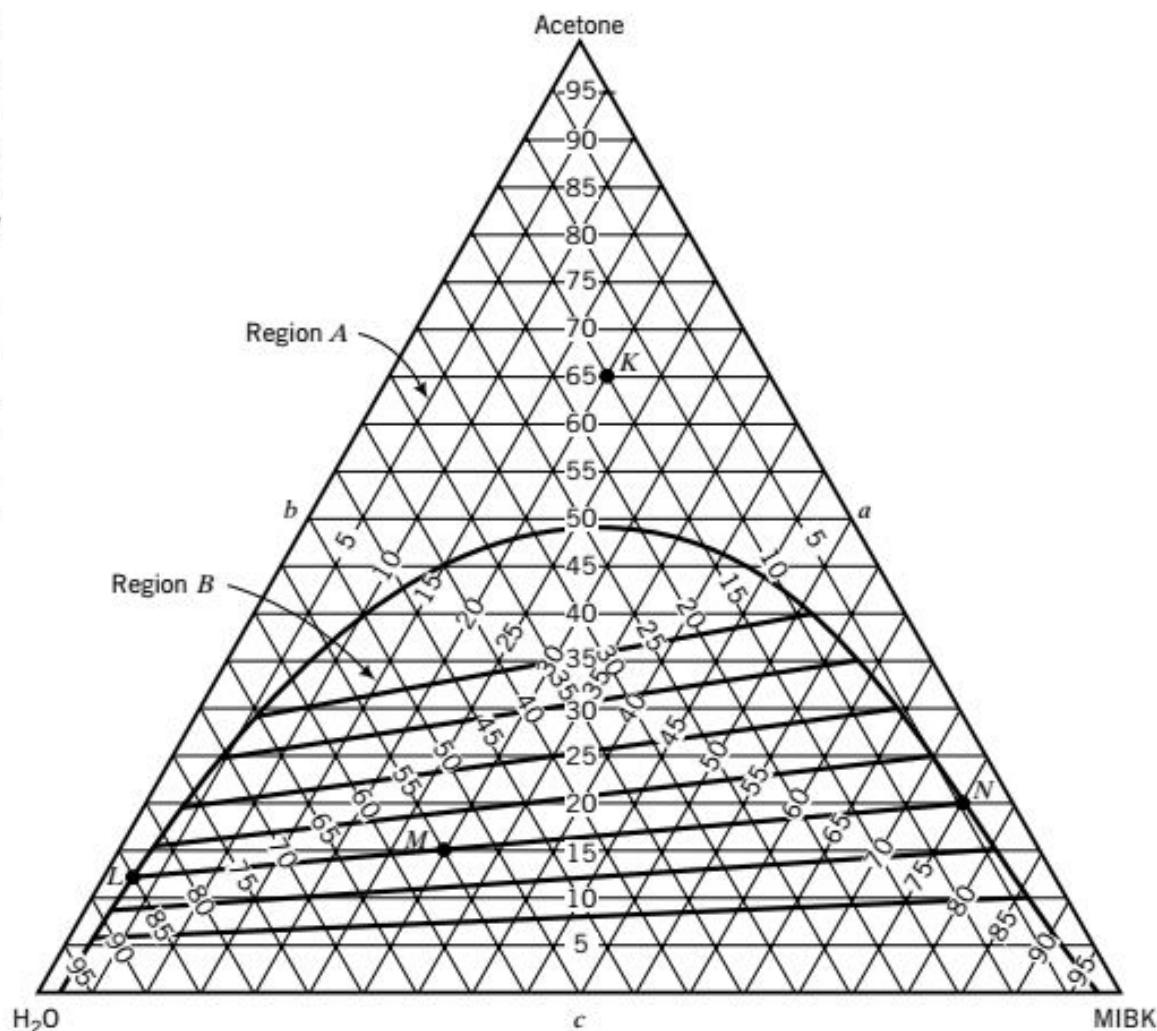
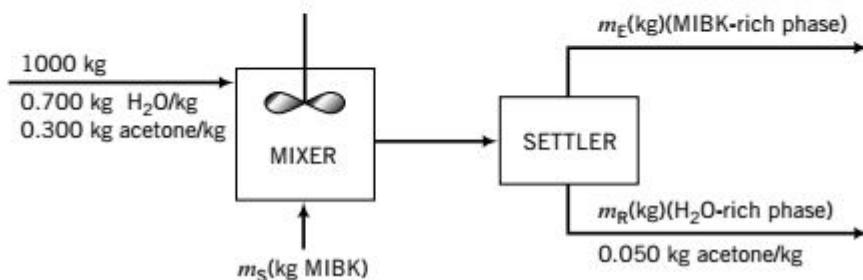


Figure 6.6-1 Triangular phase diagram for water–acetone–methyl isobutyl ketone (composition in wt%) at 25°C. (From D. F. Othmer, R. E. White, and E. Trueger, *Ind. Eng. Chem.* 33: 1240, 1941.)

EXAMPLE 6.6-2**Extraction of Acetone from Water: Use of the Phase Diagram**

One thousand kilograms of a 30.0 wt% solution of acetone in water and a second stream of pure methyl isobutyl ketone (MIBK) is fed to a mixer. The mixture is then fed to a settler where two phases form and are withdrawn separately at 25°C. How much MIBK must be fed to the process to reduce the acetone concentration in the water-rich phase to 5 wt%, assuming that the fluids remain in the settler long enough for equilibrium to be achieved?

**SOLUTION**

Since the two product streams are in equilibrium, their compositions must lie on the phase envelope and must be connected by a tie line. Accordingly, the composition of m_R is 5% acetone, 93% H₂O, and 2% MIBK and that of m_E is 10% acetone, 87% MIBK, and 3% H₂O. Overall balances can now be used to determine m_E , m_R , and m_S .

Mass Balance

$$m_S + 1000 \text{ kg} = m_E + m_R$$

Acetone Balance

$$(0.30)(1000 \text{ kg}) = 0.10m_E + 0.05m_R$$

H₂O Balance

$$(0.70)(1000 \text{ kg}) = 0.03m_E + 0.93m_R$$

Solving these three equations yields (before rounding for significant figures)

$$m_E = 2667 \text{ kg}$$

$$m_R = 667 \text{ kg}$$

and

$$\boxed{m_S = 2334 \text{ kg MIBK}}$$