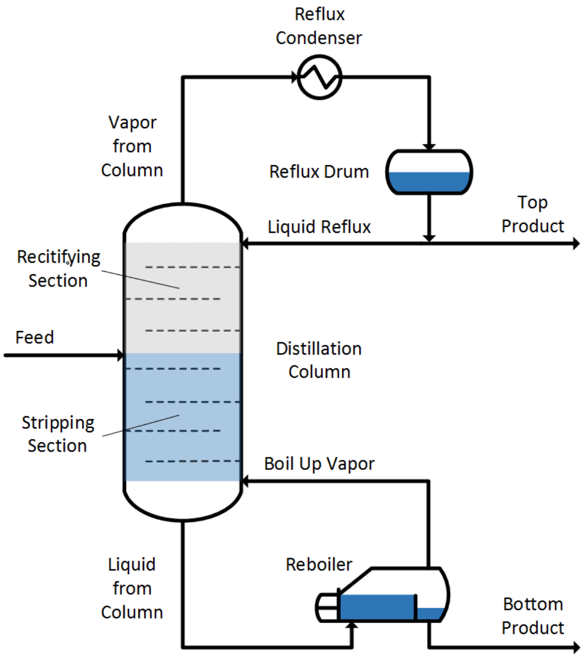
5. Two-Component Gas/Two-Component Liquid System

Distilling moonshine from a fermented grain mixture is an example of a binary vapor-liquid equilibrium in which water and ethanol are the primary components in the system and are present in both the vapor and the liquid.

The primary result of vapor-liquid equilibrium is that the more volatile component (i.e., the component with the larger vapor pressure also has the lowest boiling point temperature at a given temperature) tends to accumulate in the vapor phase while the less volatile component tends to accumulate in the liquid phase.

Distillation columns, which are used to separate a mixture into its components, are based on this principle. A distillation column is composed of several trays that provide contact between liquid and vapor streams inside the column. At each tray, the concentration of the more volatile component is increased in the vapor stream leaving the tray, and the concentration of the less volatile component is increased in the liquid leaving the tray. In this manner, applying several trays in series, the more volatile component is concentrated in the overhead stream from the column while the less volatile component is concentrated in the bottom product. To design and analyze distillation, you must be able to quantitatively describe vapor-liquid equilibrium for these systems.



5.1 Ideal Solution Relations

For a solution to behave as an ideal solution:

- All of the molecules of all types should have the same size.
- All of the molecules should have the same intermolecular interactions.

Most solutions are not ideal, but some real solutions are nearly ideal.

Raoult's law

Raoult's law is used for a solvent in an ideal solution. The best-known relation for ideal solutions is

$$p_i = x_i p_i^*(T)$$

p_i = partial pressure of component i in the vapor phase
x_i = mole fraction of component i in the liquid phase

$p_i^*(T)$ = vapor pressure of component i at T.

Raoult's law is used primarily for a component whose mole fraction spans the full range from 0 to 1 for solutions of components quite similar in chemical nature, such as straight-chain hydrocarbons.

Henry's law

A relation between the partial pressure of a gas in the gas phase and the mole fraction of the gas in the liquid phase at equilibrium. Henry's law is for a gas dissolved in a solvent. Henry's law is used primarily for a component whose mole fraction approaches zero, such as a dilute gas dissolved in a liquid:

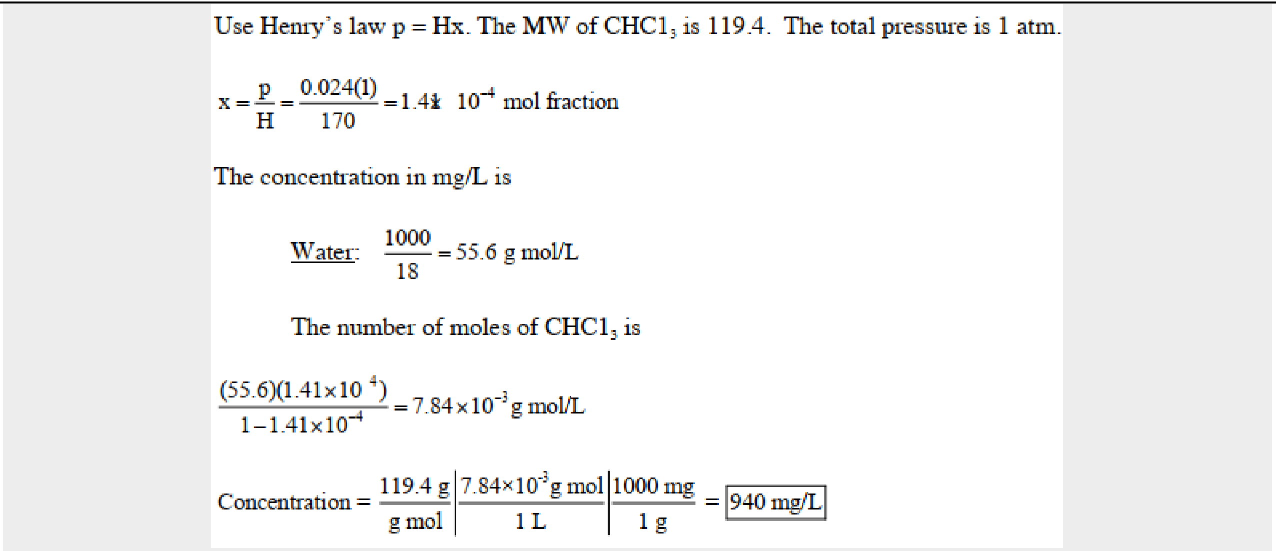
$$p_i = H_i x_i$$

where p_i is the partial pressure in the gas phase of the dilute component at equilibrium at some temperature, and H_i is *Henry's law constant*. Note that in the limit where $x_i \to 0$, $p_i \to 0$. Values of H_i can be found in several handbooks.

Henry's law is quite simple to apply when you want to calculate the partial pressure of a gas that is in equilibrium with the gas dissolved in the liquid phase.

Example 1 Henry's law

Determine the equilibrium concentration in milligrams per liter of chloroform in water at 20°C and 1 atm, assuming that gas and liquid phases are ideal and the mole fraction of the chloroform in the gas phase is 0.024. The Henry constant for chloroform is H = 170 atm/mol fraction.



Use Henry's law p = Hx. The MW of $CHC1_3$ is 119.4. The total pressure is 1 atm.

$$x = \frac{p}{H} = \frac{0.024(1)}{170} = 1.41\times 10^{-4} \text{ mol fraction}$$

The concentration in mg/L is

Water: $\frac{1000}{18} = 55.6$ g mol/L

The number of moles of $CHC1_3$ is

$$\frac{(55.6)(1.41\times 10^{-4})}{1-1.41\times 10^{-4}} = 7.84\times 10^{-3} \text{ g mol/L}$$

$$\text{Concentration} = \frac{119.4 \text{ g}}{\text{g mol}}\left|\frac{7.84\times 10^{-3}\text{ g mol}}{1 \text{ L}}\right|\frac{1000 \text{ mg}}{1 \text{ g}} = \boxed{940 \text{ mg/L}}$$

5.2 Vapor-Liquid Equilibria Phase Diagrams

Experimental data usually are presented as pressure as a function of composition at a constant temperature, or temperature as a function of composition at a constant pressure. For a pure component, vapor-liquid equilibrium occurs with only one degree of freedom:

$$F = 2 - P + C = 2 - 2 + 1 = 1$$

At 1 atm pressure, vapor-liquid equilibrium will occur at only one temperature: the normal boiling point. However, if you have a binary solution, you have two degrees of freedom:

$$F = 2 - 2 + 2 = 2$$

For a system at a fixed pressure, both the phase compositions and the temperature can be varied over a finite range.

Phase diagrams for ideal solutions

Figures 1 and 2 show the vapor-liquid envelope for a binary mixture of benzene and toluene, which is **essentially ideal**.

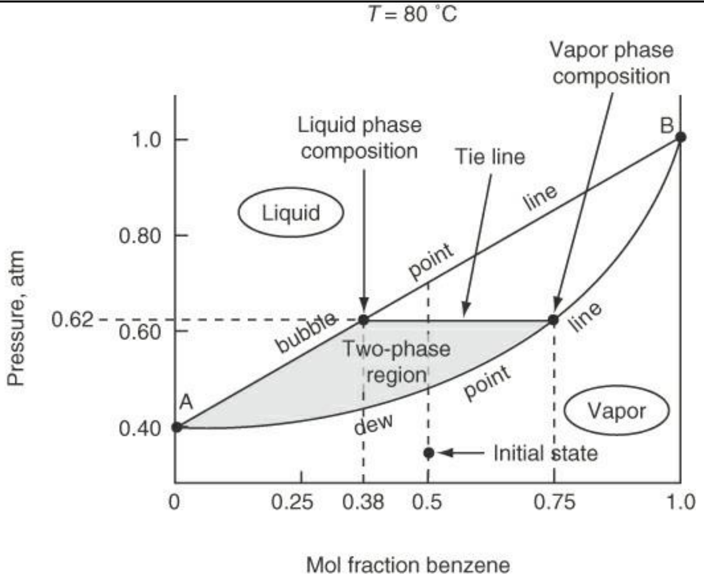


Figure 1 Phase diagram for a mixture of benzene and toluene at 80°C. At 0 mol fraction of benzene (point A), the pressure is the vapor pressure of toluene at 80°C. At a mole fraction of benzene of 1 (point B), the pressure is the vapor pressure of benzene at 80°C. The tie line shows the liquid and vapor compositions that are in equilibrium at a pressure of 0.62 atm (and 80°C).

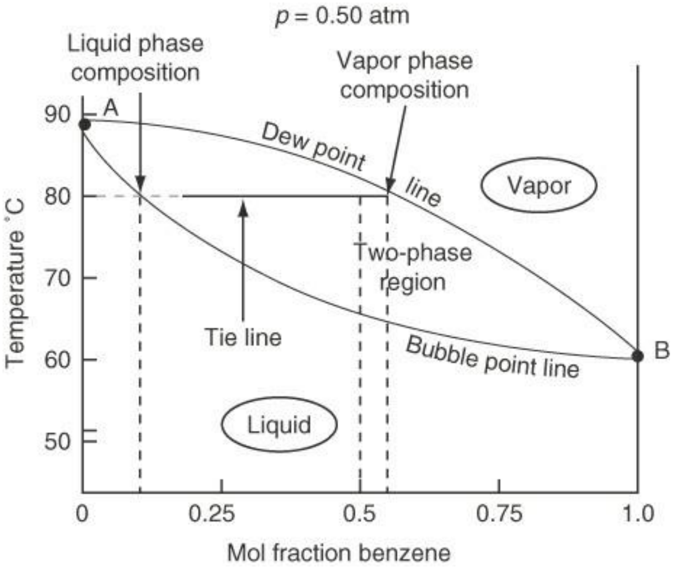


Figure 2 Phase diagram for a mixture of benzene and toluene at 0.50 atm. At 0 mole fraction of benzene (point A), the temperature is that when the vapor pressure of toluene is 0.50 atm. At a mole fraction of benzene of 1 (point B), the temperature is that when the vapor pressure of benzene is 0.50 atm. The tie line shows the liquid and vapor compositions that are in equilibrium at a temperature of 80°C (and 0.50 atm).

You can interpret the information on the phase diagrams as follows: Suppose you start in Figure 1 at a 50-50 mixture of benzene-toluene at 80°C and 0.30 atm in the vapor phase. Then you increase the pressure on the system until you reach the dew point at about 0.47 atm, at which point the vapor starts to condense. At 0.62 atm the mole fraction in the vapor phase will be about 0.75, and the mole fraction in the liquid phase will be about 0.38 as indicated by the tie line. As you increase the pressure from 0.70 atm, all of the vapor will have condensed to a liquid.

Phase diagrams for nonideal solutions

Figure 3 shows the temperature composition diagram for isopropanol in water at 1 atm. Note the minimum boiling point at a mole fraction of isopropanol of about 0.68, a point called an **azeotrope** (a point at which on a y_i versus-x_i plot the function of (y_i/x_i) crosses the function $y_i = x_i$, a straight line) and **azeotrope** is a constant boiling mixture with identical compositions in the liquid and vapor phases.. An azeotrope makes separation by simple distillation difficult because it creates a pinch point when the dew point and the bubble point overlap so that separation between the more volatile and the less volatile components does not occur.

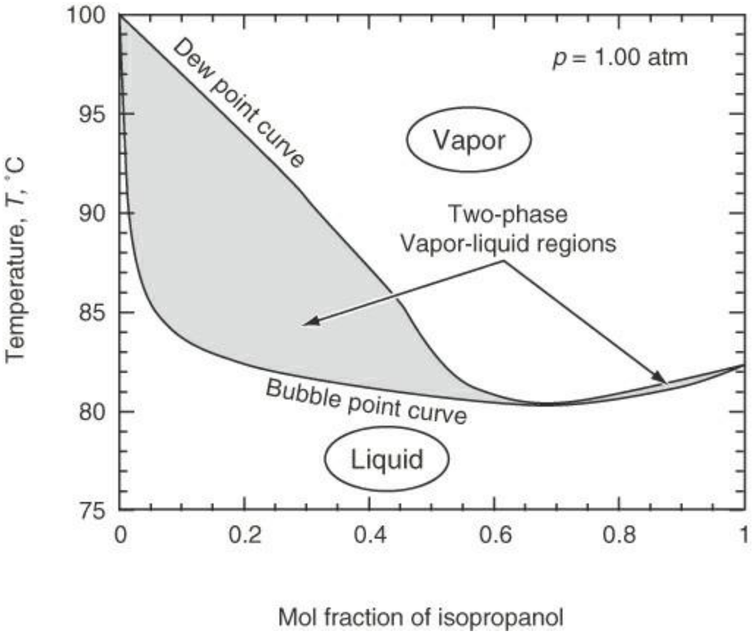


Figure 3 Phase diagram for a nonideal mixture of isopropanol and water at 1 atm

5.3 K-value (Vapor-Liquid Equilibrium Ratio)

For nonideal as well as ideal mixtures that comprise two (or more) phases, it proves to be convenient to express the ratio of the mole fraction in one phase to the mole fraction of the same component in another phase in terms of a **distribution coefficient** or **equilibrium ratio *K***, usually called a ***K*-value**. For example:

$$\text{Vapor-liquid ratio of component } i = \frac{y_i}{x_i} = K_i$$

***K*-value** A parameter (distribution coefficient) is used to express the ratio of the mole fraction in one phase to the mole fraction of the same component in another phase.

If $p_i = y_i\, p_{\text{total}}$ applies to the gas phase and the ideal Raoult's law $p_i = x_i p_i^*(T)$ applies to the liquid phase, then for an *ideal system.* The equation below gives reasonable estimates of K_i values at low pressures for components well below their critical temperatures but yields values too large for components above their critical temperatures, at high pressures, and/or for polar compounds. For ideal solutions, you can calculate values of K using Equation:

$$K_i = \frac{y_i}{x_i} = \frac{p_i^*(T)}{p_{\text{total}}}$$

5.4 Bubble Point and Dew Point Calculations

1. Calculate the bubble point temperature of a liquid mixture given the total pressure and liquid composition. To calculate the **bubble point temperature** (given the total pressure and liquid composition), you can write the above Equation as $y_i = K_i x_i$. Also, you know that $\Sigma y_i = 1$ in the vapor phase. Thus, for a binary:

$$1 = K_1 x_1 + K_2 x_2$$

in which the K_i are functions of solely the temperature. For an ideal solution,

$$p_{\text{total}} = p_1^* x_1 + p_2^* x_2$$

and you might use Antoine's equation for p^*_i. Once the bubble point temperature is determined, the vapor composition can be calculated from

$$y_i = \frac{p_i^* x_i}{p_{\text{total}}}$$

A degree-of-freedom analysis for the bubble point temperature for a binary mixture shows that the degrees of freedom are zero:

$$\text{Total variables} = 2\times2+2 = 6 \text{ variables: } x_1,\ x_2;\ y_1,\ y_2;\ p_{\text{total}};\ T$$

$$\text{Independent equations} = 2+1 = 3 \text{ equations:}$$

$$y_1 = K_1 x_1,\ \ y_2 = K_2 x_2;\ \ y_1 + y_2 = 1$$

2. Calculate the dew point temperature of a vapor mixture given the total pressure and vapor composition. To calculate the **dew point temperature** (given the total pressure and vapor composition), you can write ***$x_i = y_i/K_i$*,** and you know $\Sigma x_i = 1$ in the liquid phase. Consequently, you want to solve the equation:

$$1 = \frac{y_1}{K_1} + \frac{y_2}{K_2}$$

in which the *K*s are functions of temperature as explained for the bubble point temperature calculation. For an ideal solution,

$$1 = p_{\text{total}}\left[\frac{y_1}{p_1^*} + \frac{y_2}{p_2^*}\right]$$

The degree-of-freedom analysis is similar to that for the bubble point temperature calculation.

6 Multicomponent Vapor-Liquid Equilibrium

Multicomponent vapor-liquid equilibrium pertains to systems that contain three or more components in the vapor or liquid phases. Vapor-liquid equilibrium calculations for multicomponent systems are performed in a manner analogous to the ones for binary systems.

For bubble point calculations, $\sum y_i = 1$; therefore, the bubble point equation can be written in terms of the known liquid compositions (*x_i*) and the component *K*-values (*K_i*):

$$\sum_i^n x_i K_i = 1$$

For dew point calculations, $\sum x_i = 1$; therefore, the dew point equation can be written in terms of the known vapor composition (*y_i*) and the component *K*-values (*K_i*):

$$\sum_i^n \frac{y_i}{K_i} = 1$$

Note that both **the bubble point and dew point equations are, in general, nonlinear equations with temperature as the only unknown**.

Example 1: Raoult's law

A gas containing nitrogen, benzene, and toluene is in equilibrium with 40 mole% benzene and 60 mole% toluene liquid mixtures at 100 °C and 10 atm. Estimate the gas phase composition (mole fractions) using Raoult's law.

Antoine equation constants	A	B	C	Pressure (mm Hg) Temperature (K)
Benzene	15.9008	2788.51	- 52.36	
Toluene	16.0137	3096.52	- 53.67	

Solution

$$\ln p^* = A - \frac{B}{T + C}$$

$$p_T^* = Exp\left[16.0137 - \frac{3096.52}{-53.67 + 373}\right] = 553.8 \ \text{mmHg}$$

$$p_B^* = Exp\left[15.9008 - \frac{2788.51}{-52.36 + 373}\right] = 1344.9 \ \text{mmHg}$$

$$p_i = p_i^* x_{i,} \quad p_i = p_T y_i$$

$$y_B p_T = x_B p_B^*$$

Raoult's law $y_B = \frac{0.4 \times 1344.9}{10 \times 760} = 0.071$

$$y_T = \frac{0.6 \times 553.8}{10 \times 760} 0.044$$

$$y_{N_2} = 1 - 0.071 - 0.044 = 0.885$$

Example 2

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 $p^*_{H_2O}(75^\circ C) = 289 \text{ mm Hg}$.

Solution

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

$$y_{H_2O} = p^*_{H_2O}(75^\circ C)/P$$

$$y_{H_2O} = \frac{289 \text{ mm Hg}}{760 \text{ mm Hg}} = \boxed{0.380 \frac{\text{mol } H_2O}{\text{mol}}}$$

$$y_{\text{dry air}} = 1 - y_{H_2O} = \boxed{0.620 \frac{\text{mol dry air}}{\text{mol}}}$$

Example 3

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 are the system pressure and the composition of the vapor?

(Henry's law constant for ethane in water at 20°C as 2.63 x 10^4 atm/mole fraction).

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.

$$x_{C_2H_6} = \frac{y_{C_2H_6}P}{H_{C_2H_6}} = \frac{(0.0100)(20.0 \text{ atm})}{2.63 \times 10^4 \text{ atm/mole fraction}} = \boxed{7.60 \times 10^{-6} \frac{\text{mol } C_2H_6}{\text{mol}}}$$

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

$$\ln p^* = A - \frac{B}{C+T}$$

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

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

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

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

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

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

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

Problem

1. Two-Component Gas/Two-Component Liquid Systems

a) Water in an enclosed vessel at 17°C contains a concentration of dissolved oxygen of 6.0 mg/L. At equilibrium, determine the concentration of oxygen in the space above the water in mole fraction and the total pressure in kilopascals. Henry's law constant is 4.07×10^6 kPa/mol fraction.

b) A tank contains a liquid composed of 60 mol % toluene and 40 mol % benzene in equilibrium with the vapor phase and air at 1 atm and 60°F.

a. What is the concentration of hydrocarbons in the vapor phase?
b. If the lower flammability limit for toluene in air is 1.27% and benzene is 1.4%, is the vapor phase flammable?

b) Fuel tanks for barbecues contain propane and *n*-butane. At 120°F, in an essentially full tank of liquid that contains liquid and vapor in equilibrium and exhibits a pressure of 100 psia, what is the overall (vapor plus liquid) mole fraction of butane in the tank?

c) Methanol has a flash point at 12°C at which temperature its vapor pressure is 62 mm Hg. What is the flash point (temperature) of a mixture of 75% methanol and 25% water? Hint: The water does not burn.

d) What are (a) the pressure in the vapor phase and (b) the composition of the vapor phase in equilibrium with a liquid mixture of 20% pentane and 80% heptane at 50°F? Assume the mixture is an ideal one at equilibrium.

e) Two kilograms of a mixture of 50-50 benzene and toluene is at 60°C. As the total pressure on the system is reduced, at what pressure will boiling commence? What will be the composition of the first bubble of liquid?

f) The normal boiling point of propane is –42.1°C and the normal boiling point of n-butane is –0.5°C.

a. Calculate the mole fraction of the propane in a liquid mixture that boils at –31.2°C and 1 atm.

b. Calculate the corresponding mole fraction of the propane in the vapor at –31.2°C.

c. Plot the temperature versus propane mole fraction for the system of propane and butane.

g) Calculate the bubble point of a liquid mixture of 80 mol % *n*-hexane and 20 mol % *n*-pentane at 200 psia.

h) Calculate the dew point of a vapor mixture of 80 mol % *n*-hexane and 20 mol % *n*pentane at 100 psia.

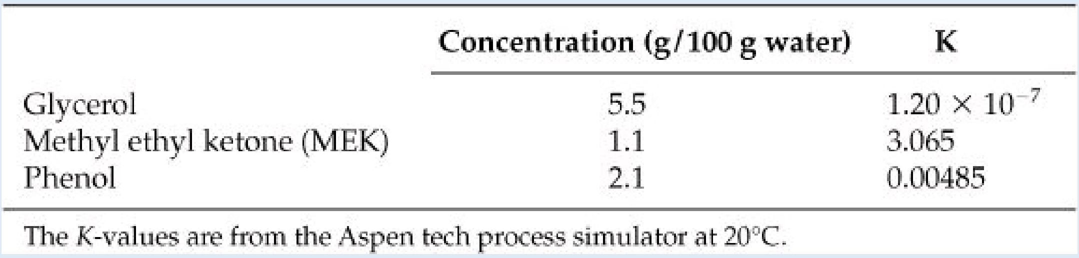
i) A mixture of 50 mol % benzene and 50 mol % toluene is contained in a cylinder at 39.36 in. Hg absolute. Calculate the temperature range in which a two-phase system can exist.

j) A liquid mixture of *n*-pentane and *n*-hexane containing 40 mol % *n*-pentane is fed continuously to a flash separator operating at 250°F and 80 psia. Determine (a) the quantity of vapor and liquid obtained from the separator per mole of feed, and (b) the composition of both the vapor and the liquid leaving the separator.

k) If the pressure in the headspace (gas space) in a bioreactor is 110 kPa and 25°C, and the oxygen concentration in the headspace is enriched to 39.7%, what is the mole fraction of the dissolved oxygen in the liquid phase? What is the percent excess? oxygen dissolved in the liquid phase compared with the saturation value that could be obtained from air alone dissolved in the liquid

7.6 Multicomponent Vapor-Liquid Equilibrium

a) Three separate waste discharge streams from a plant into a river contain the following respective chemicals in the water:



	Concentration (g/100 g water)	K
Glycerol	5.5	1.20×10^{-7}
Methyl ethyl ketone (MEK)	1.1	3.065
Phenol	2.1	0.00485

The *K*-values are from the Aspen tech process simulator at 20°C.

Estimate the concentration of the respective compounds in the gas phase above each discharge stream at 20°C. Will volatilization from the discharge stream be significant?