7.3.5 Equilibrium Pressure Above Liquid Mixtures

For liquid mixtures containing two or more components, the partial pressures of the components in an equilibrium vapor phase are functions of the liquid phase composition as well as the temperature.

For some simple situations, the functional relationship between partial pressure and mole fraction is satisfactorily expressed as

$$\overline{P}_i = C_i x_i$$

Where, C_i is a temperature-dependent constant. The total pressure is now the sum of the partial pressures. The numerical value and significance of C_i depends on the nature of the solution.

When the solution consists of substances with nearly identical molecules, the partial pressure in the equilibrium vapor may be predicted by *Raoult's Law,*
This expression is obtained by setting $C_i = P_{vi}$, the vapor pressure of substance i at the temperature of the liquid. The above equation (7.35 in the textbook) is certainly correct in the limit as x_i nears one, that is, as the liquid solution becomes nearly pure substance i.

$$\overline{P}_i = P_{vi} x_i$$

Suppose a liquid mixture containing C components is in equilibrium with a vapor phase. The phase rule can be applied to this system. Since P = 2, the number of degrees of freedom is

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

If the composition of the mixture is known, C-1 degrees of freedom are used up. If the temperature is also fixed, then there is no degree of freedom left and all intensive variables of the system assume definite values. Specifically, there is a unique pressure, which depends on the prescribed composition of the liquid mixture and the temperature, at which the vapor phase is in equilibrium with the liquid. This pressure is the bubble-point pressure of the liquid mixture.

It is an interesting problem to calculate the bubble-point pressure and the composition of the vapor for a liquid mixture. The design of distillation equipment, which plays a key role in many chemical processes and in petroleum and natural gas refining operations, requires that the designer be able to solve this problem. At each point in a distillation column, the vapor can be assumed to be in equilibrium with the liquid with which it is in contact.

If the liquid mixture behaves in the idealized manner as required by Raoult's Law (Equation 7.35), the calculation can be carried out easily. Each vapor pressure is

evaluated at the system temperature and the total pressure, P, is the sum of the partial pressures. That is,

$$P = x_1 P_{v1} + x_2 P_{v2} + \ldots + x_c P_{vc}$$

The mole fraction of the ith component in the gas phase y_i can be calculated, in turn, from partial pressure P_i and the total pressure. That is,

$$y_i = P_i/P$$

For binary mixtures,

$$y_1 = \frac{x_1 P_{v1}}{x_1 P_{v1} + x_2 P_{v2}} = \frac{x_1}{x_1 + (P_{v2}/P_{v1})x_2} \tag{7.39}$$

By substituting $(x_2 = 1 - x_1)$ in the above equation and defining a new variable $\alpha_{21} = P_{V2}/P_{V1}$, we get

$$y_1 = \frac{x_1}{x_1 + \alpha_{21}(1 - x_1)} = \frac{x_1}{x_1(1 - \alpha_{21}) + \alpha_{21}} \tag{7.40}$$

The parameter α_{21} is known as the *relative volatility* and it is a function of temperature.

It is fairly simple to use Equation 7.40 and

$$P = x_1 P_{v1} + x_2 P_{V2} = x_1(P_{v1} - P_{V2}) + P_{V2} \tag{7.42}$$

to prepare a pressure-composition phase diagram for a binary vaporliquid equilibrium system. The benzene-toluene system is very well represented by these equations.

By substituting $x_2 = 1 - x_1$ in Equation 7.39 and then solving for x_1, we can get an expression for x_1 in terms of y_1 and y_2.

$$x_1 = \frac{y_1}{y_1 + (P_{v1}/P_{v2})y_2}$$

Some mixtures which cannot be described by Raoult's Law will still conform to Equation 7.34. The solubilities of gases in liquid solvents are often correlated by *Henry's Law,*

$$P_i = H_i \, x_i$$

which is obtained by letting $C_i = H_i$, the Henry's constant for the solute gas i in the solvent liquid. Henry's constant is a function of temperature and cannot be calculated from first principles. It must be obtained from experimental data. At 28°C, H_i for O_2 in water is, for example, 4.68×10^4 atm, and for N_2 in water is 8.45×10^4 atm . Use of Henry's law is generally restricted to very dilute solutions.

Henry's Law and Raoult's Law are reasonable models for the limiting behavior of the solute gas and the solvent, respectively, in dilute solutions. The only reservation is that the solute should not dissociate or associate in the solvent. In a binary mixture described by these models the pressure is given by

$$P = H_1 x_1 + P_{V2}(1 - x_1)$$

Where, substance 1 is the solute gas and substance 2 is the solvent. This equation can be solved for the solubility of the gas at a given temperature and pressure, i.e.

$$X_1 = (P - P_{V2}) / (H_1 - P_{V2}) \cdot \qquad (7\ 45)$$

Example Problem (2000 Final)
A vessel contains a two-phase (vapour and liquid) mixture of butane, pentane and hexane at 21 °C. The mole fraction of butane in the vapour phase is 0.35. The liquid phase contains 45 mol% pentane. Some useful properties of these components are provided in the following table.

Component	Vapour pressure at 21 °C atm	Temperature at which $P_v = 2$ atm, °C
Butane	2.14	18.8
Pentane	0.58	58.0
Hexane	0.17	93.0

(a) Under the specified conditions, what is the number of remaining degrees of freedom?
(b) Assuming that the system obeys Raoult's law, calculate the pressure in the vessel.
(c) Calculate the vapour pressure of pentane at 45 °C.

(a) $F = C + 2 - P = 3 + 2 - 2 = 3$
Degrees of freedom already used = 1 for T, 1 for y_1, and 1 for x_2, i.e. total of 3.
Remaining degrees of freedom = **0**

(b) Raoult's law states:

$$\overline{p}_i = P_{vi}x_i$$

$$\overline{p}_1 = P_{v1}x_1 = 2.14x_1$$
$$\overline{p}_2 = P_{v2}x_2 = 0.58 * 0.45 = 0.261$$
$$\overline{p}_3 = P_{v3}x_3 = 0.17(1 - x_1 - x_2) = 0.17(1 - x_1 - 0.45) = 0.17(0.55 - x_1)$$

$$y_1 = \frac{\overline{p}_1}{\overline{p}_1 + \overline{p}_2 + \overline{p}_3} = \frac{2.14x_1}{2.14x_1 + 0.261 + 0.17(0.55 - x_1)}$$

The value of y_1 is given to be 0.35, therefore,

$$\frac{2.14x_1}{2.14x_1 + 0.261 + 0.17(0.55 - x_1)} = 0.35$$

Solve for x_1 to get $x_1 = 0.0856$.
$x_3 = 1 - 0.0856 - 0.45 = 0.464$

Now that the mole fractions are known in the liquid phase, the partial pressures can be determined.

$$\overline{p}_1 = P_{v1}x_1 = 2.14 * 0.0856 = 0.183 \, atm$$
$$\overline{p}_2 = P_{v2}x_2 = 0.58 * 0.45 = 0.261 \, atm$$
$$\overline{p}_3 = P_{v3}x_3 = 0.17 * 0.464 = 0.079 \, atm$$

The pressure in the vessel is equal to the sum of all partial pressures.

P = 0.183 + 0.261 + 0.079= **0.523 atm**.

Estimating the vapour pressure at 45 °C, requires developing a relationship between P_v and T from the available information.

$$\ln P_v = \frac{-A}{T} + B$$

$$\ln(0.58) = \frac{-A}{294.15} + B$$

$$\ln(2) = \frac{-A}{331.15} + B$$

$$\ln\left(\frac{2}{0.58}\right) = A\left[\frac{1}{294.15} - \frac{1}{331.15}\right]$$

A = 3259
B = 10.53

At 45 °C:

$$\ln P_v = \frac{-3259}{318.15} + 10.53 = 0.286$$

P_v = **1.33 atm**