Chapter 6 – New Exercises and Solutions

E6.1(c) At 90°C, the vapour pressure of methylbenzene is 53.3 kPa and that of 1,3-dimethylbenzene is 18.0 kPa. What is the composition of a liquid mixture that boils at 90°C when the pressure is 0.40 atm? What is the composition of the vapour produced?

E6.1(c) An expression for composition of the solution in terms of its vapour pressure is required. This is obtained from Dalton's law and Raoult's law as follows

$$p = p_A + p_B \text{ [Dalton's law]} = x_A p_A^* + (1 - x_A) p_B^*$$

Solving for x_A, $x_A = \dfrac{p - p_B^*}{p_A^* - p_B^*}$

For boiling under 0.40 atm (40.5 kPa) pressure, the combined vapour pressure, p, must be 40.5 kPa;

hence $x_A = \dfrac{40.5 - 18.0}{53.3 - 18.0} = \boxed{0.637}$, $x_B = \boxed{0.373}$

The composition of the vapour is given by eqn 6.5

$$y_A = \frac{x_A p_A^*}{p_B^* + (p_A^* - p_B^*) x_A} = \frac{0.637 \times 53.3}{18.0 + (53.3 - 18.0) \times 0.637} = \boxed{0.839}$$

and $y_B = 1 - 0.839 = \boxed{0.161}$

E6.2(c) The vapour pressure of pure liquid A at 293 K is 68.8 kPa and that of pure liquid B is 82.1 kPa. These two compounds form ideal liquid and gaseous mixtures. Consider the equilibrium composition of a mixture in which the mole fraction of A in the vapour is 0.612. Calculate the total pressure of the vapour and the composition of the liquid mixture.

E6.2(c) The vapour pressures of components A and B may be expressed in terms of both their composition in the vapour and in the liquid. The pressures are the same whatever the expression; hence the expressions can be set equal to each other and solved for the composition.

$$p_A = y_A p = 0.612 p = x_A p_A^* = x_A \times (68.8 \text{kPa})$$
$$p_B = y_B p = (1 - y_A) p = 0.388 p = x_B p_B^* = (1 - x_A) \times (82.1 \text{ kPa})$$

Therefore, $\dfrac{y_A p}{y_B p} = \dfrac{x_A p_A^*}{x_B p_B^*}$

Hence $\dfrac{0.612}{0.388} = \dfrac{68.8 x_A}{82.1(1 - x_A)}$

which solves to $x_A = \boxed{0.653}$, $x_B = 1 - x_A = \boxed{0.347}$

and, since $0.612 p = x_A p_A^*$

$$p = \frac{x_A p_A^*}{0.612} = \frac{(0.653) \times (68.8 \text{ kPa})}{0.612} = \boxed{73.4 \text{ kPa}}$$

E6.3(c) It is found that the boiling point of a binary solution of A and B with $x_A = 0.479$ is 88°C. At this temperature the vapour pressures of pure A and B are 130.1 kPa and 74.9 kPa, respectively. (a) Is this solution ideal? (b) What is the initial composition of the vapour above the solution?

E6.3(c) (a) Check to see if Raoult's law holds; if it does the solution is ideal.

$$p_A = x_A p_A^* = (0.479) \times (130.1 \text{kPa}) = 62.32 \text{kPa}$$

$$p_B = x_A p_B^* = (0.521) \times (74.9 \text{kPa}) = 39.0 \text{kPa}$$

$$p = p_A + p_B = 101.3 \text{ kPa} = 1 \text{atm}$$

Since this is the pressure at which boiling occurs, Raoult's law holds and the solution is ideal.

(b) $y_A = \dfrac{p_A}{p} [6.4] = \dfrac{62.32 \text{kPa}}{101.3 \text{kPa}} = \boxed{0.615}$ $\quad y_B = 1 - y_A = 1.000 - 0.615 = \boxed{0.385}$

E6.3(d) It is found that the boiling point of a binary solution of A and B with $x_A = 0.547$ is 105°C. At this temperature the vapour pressures of pure A and B are 89.1 kPa and 116.0 kPa, respectively. (a) Is this solution ideal? (b) What is the initial composition of the vapour above the solution?

E6.3(d) (a) If Raoult's law holds, the solution is ideal.

$$p_A = x_A p_A^* = (0.547) \times (89.1 \text{ kPa}) = 48.7\bar{4} \text{ kPa}$$

$$p_B = x_B p_B^* = (1 - 0.547) \times (116.0 \text{ kPa}) = 52.5\bar{6} \text{ kPa}$$

$$p = p_A + p_B = (48.74 + 52.56) \text{ kPa} = 101.3 \text{ kPa} = 1.000 \text{ atm}$$

Therefore, Raoult's law correctly predicts the pressure of the boiling liquid and the solution is ideal .

(b) $\quad y_A = \dfrac{p_A}{p} = \dfrac{48.74 \text{ kPa}}{101.3 \text{ kPa}} = \boxed{0.481}$

$$y_B = 1 - y_A = 1.000 - 0.481 = \boxed{0.519}$$

E6.4(c) Benzene and toluene form nearly ideal solutions. Consider a solution of 1.0 mol benzene and 3.0 mol toluene. At 20°C the vapour pressures of pure benzene and toluene are 9.9 kPa and 2.9 kPa, respectively. The solution is boiled by reducing the external pressure below the vapour pressure. Calculate (a) the pressure when boiling begins, (b) the composition of each component in the vapour, and (c) the vapour pressure when only a few drops of liquid remain. Assume that the rate of vaporization is low enough for the temperature to remain constant at 20°C.

E6.4(c) Let B = benzene and T = toluene. $z_B = 0.250$, $z_T = 0.750$

(a) Initially $x_B = z_B$ and $x_T = z_T$; thus

$$p = x_B p_B^* = + x_T p_T^* [6.3] = (0.250) \times (9.9 \text{ kPa}) + (0.750) \times (2.9 \text{ kPa})$$

$$= 1.9\bar{8} \text{ kPa} + 2.1\bar{8} \text{ kPa} = \boxed{4.2 \text{ kPa}}$$

(b) $y_B = \dfrac{p_B}{p}[6.4] = \dfrac{1.98 \text{ kPa}}{4.2 \text{ kPa}} = \boxed{0.47}$ $y_T = 1 - 0.47 = \boxed{0.53}$

(c) Near the end of the distillation

$$y_B = z_B = 0.250 \quad \text{and} \quad y_T = z_T = 0.750$$

Equation 6.5 may be solved for x_A [A = benzene = B here]

$$x_B = \dfrac{y_B p_T^*}{p_B^* + \left(p_T^* - p_B^*\right)y_B} = \dfrac{(0.250)\times(2.9 \text{ kPa})}{(9.9 \text{ kPa})+(2.9 \; - \; 9.9)\text{ kPa}\times(0.750)} = 0.16$$

$$x_T = 1 - 0.16 = 0.84$$

$$p(\text{final}) = x_B p_B^* + x_T p_T^* = (0.16)\times(9.9 \text{ kPa}) + (0.84)\times(2.9 \text{ kPa}) = \boxed{4.0 \text{ kPa}}$$

Thus in the course of the distillation the vapour pressure fell from 4.2 kPa to 4.0 kPa

E6.5(c) The following temperature/composition data were obtained for a mixture of octane (O) and methylbenzene (M) at 1.00 atm, where x is the mole fraction in the liquid and y the mole fraction in the vapour at equilibrium.

$\theta/°C$	110.9	112.0	114.0	115.8	117.3	119.0	121.1	123.0
x_M	0.908	0.795	0.615	0.527	0.408	0.300	0.203	0.097
y_M	0.923	0.836	0.698	0.624	0.527	0.410	0.297	0.164

The boiling points are 110.6°C and 125.6°C, for M and O respectively. Plot the temperature–composition diagram for the mixture. What is the composition of the vapour in equilibrium with the liquid of composition (a) $x_M = 0.750$ and (b) $x_O = 0.750$?

E6.5(c) The data are plotted in Fig. 6.3, p.111 of the Instructor's Manual. From the graph, the vapour in equilibrium with a liquid of composition (a) $x_M = 0.75$ is determined from the tie line labelled b in the figure extending from $x_M = 0.75$ to $\boxed{y_M = 0.82}$, (b) $x_O = 0.75$ is determined from the tie line labelled b in the figure extending from $x_M = 0.25$ to $\boxed{y_M = 0.36.}$

E6.6(c) State the number of components in the following systems. (a) Acetic acid $HC_2H_3O_2$ in water at equilibrium with water vapour but disregarding the fact that the salt is ionized. (b) The same, but taking into account the ionization of the acid. (c) The same as (b), but also taking into account the ionisation of water.

E6.6(c) (a) Though there are three constituents, acid, water, and water vapor, there is an equilibrium condition between liquid water and its vapor. Hence, C = 2.

(b) Disregarding the water vapor for the reasons in (a) there are five species: $HC_2H_3O_2$, H^+, $C_2H_3O_2^-$, H_2O, OH^-. There are also two equilibria, namely

$$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$$

$$H^+ + OH^- \rightleftharpoons H_2O$$
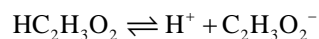
(These could all be written as Brønsted equilibria without changing the conclusions.) There is also one condition of electrical neutrality, namely

$$[H^+] = [OH^-] + [C_2H_3O_2^-]$$

Hence, the number of independent components is

$$C = 5 - (2+1) = \boxed{2}$$

E6.7(c) Ammonium chloride, NH_4Cl, decomposes when it is heated. Suppose that additional ammonia and HCl are also present in a closed container. How many components and phases are present?

E6.7(c) $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$
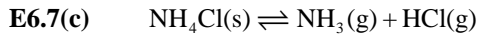
If ammonia and HCl are added before heating, $\boxed{C=2}$,because the number of components is equal to the number of species minus the number of restrictions between them. In this case the concentrations are arbitrary, but related by the equilibrium constant restriction, giving $C = 3 - 1 = 2$, and $\boxed{P=2}$ (s and g).

E6.10(c) Figure 6.40 is the phase diagram for silver and tin. Label the regions, and describe what will be observed when liquids of compositions (a) 40% Ag and (b)77% Ag are cooled to 200 K.
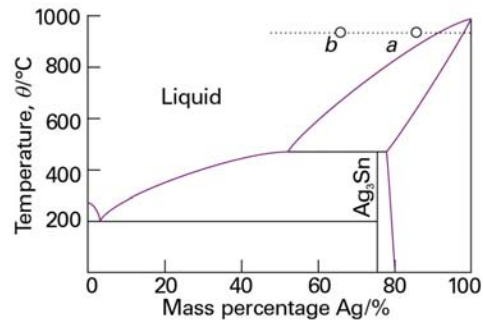

Fig. 6.40

E6.10(c) See Fig. 6.5, p. 116 of the Student's Solutions Manual. The phase diagram should be labeled as in Fig. 6.5. (a) Solid Ag_3Sn begins to precipitate at about 450 °C, and the sample solidifies completely at about 200 °C. (b) Solid Ag with dissolved Sn begins to precipitate at about 850 °C, and the liquid becomes richer in Sn. The peritectic reaction occurs about 460 °C, and as cooling continues Ag_3Sn and Ag are precipitated and become contaminated with Sn.