Department of Chemistry, Oregon State University

Physical Chemistry Assignment 5

due: 5 December 2014

1. The addition of 100 g of a compound to 750 g of CCl_4 lowered the freezing point of the solvent by 10.5 K. Calculate the molar mass of the solvent. $K_f = 30K \cdot kg/mol$.

2. What volumes of ethanol and water should be mixed to form 100 ml of a mixture which is fifty percent by mass of ethanol? $\bar{V}_{EtOH} = 57cm^3/mol$, $\bar{V}_{water} = 17cm^3/mol$

3. The vapor pressure of pure liquid A is at 293 K is 60 kPa, and that of pure liquid B is 80 kPa. These two compounds form ideal liquid and gaseous mixtures. Calculate the total pressure of the vapor and the composition of the gas and the liquid when (a) $x_A = 0.20$; and (b) $y_A = 0.40$.

4. Benzene and toluene form nearly ideal solutions. Consider an equi-molar solution of benzene and toluene . At $20°C$, the vapor pressures of benzene and toluene are 10 kPa and 4 kPa, respectively. The solution is boiled by reducing external pressure below the vapor pressure. Calculate (a) the pressure when boiling begins; (b) the composition of each component in the vapor, and (c) the vapor pressure when only a few drops of liquid remain.

5. The vapor pressure of water over the domain, $0°C$ to $100°C$, can be fit to

$$\ln P = -a/T + b \ln T + cT + d \tag{1}$$

   (a) Derive the equation relating the vapor pressure to the enthalpy of vaporization; and (b) calculate the enthalpy of vaporization in terms of a, b, c, d.

6. From Silbey, et. al, *Physical Chemistry*, Problem 6.17

7. State what substances exist at each of the labeled points in the binary T, z phase diagrams shown below. One point on the third diagram corresponds to AB(S),A(L),B(L), meaning that the AB(S) precipitate coexists with a liquid of A and B.

Problem set 5

1. $\Delta T = K_f m$, $\Delta T = 10.5\,K$, $K_f = 30\ K \cdot \frac{kg}{mol}$

$$M = \frac{10.5\,K}{30\ K \cdot kg/mol} = 0.35\ \frac{mols}{kg \cdot solvent} = \frac{100g \times \frac{1\ mole}{Mw}}{0.75\,kg}$$

$Mw = 381\ g/mole$

2.

$$100\ ml\ solution = n_{EtOH}\bar{V}_{EtOH} + n_{H_2O}\bar{V}_{H_2O}$$

$$\underset{cm^3}{100} = n(g) \times \frac{1\ mole}{46\ g/mole} \times \underbrace{57\frac{cm^3}{mol}}_{\bar{V}_{EtOH}} + n(g) \times \frac{1 mole}{18 g} \times 17\frac{cm^3}{mole}$$

$\bar{V}_{H_2O}$

solve for $n = 45.8\ g$ of each.

$$V_{EtOH} = 45.8\,g \times \frac{1\ mole}{46\,g} \times \frac{57\,cm^3}{mole} = 56.8\ ml$$

$$V_{H_2O} = \overset{45.8}{\cancel{18}}\,g \times \frac{1\ mole}{18\,g} \times \frac{17\ cm^3}{mol} = 43.2\ ml$$

3. $P_A^o = 60\,kPa$, $P_B^o = 80\,kPa$

Calculate the total pressure and X_A, Y_A.

a) $X_A = 0.20$, then $P = X_A P_A^o + (1 - X_A) P_B^o$

$$P = (0.20)(60\,kPa) + (0.80) \cdot 80\,kPa = 76\ kPa$$

$P_A = Y_A P = X_A P_A^o$, $Y_A = \frac{X_A P_A^o}{P} = \frac{(0.20)(60\ kPa)}{76\ kPa}$

$Y_A = 0.158$

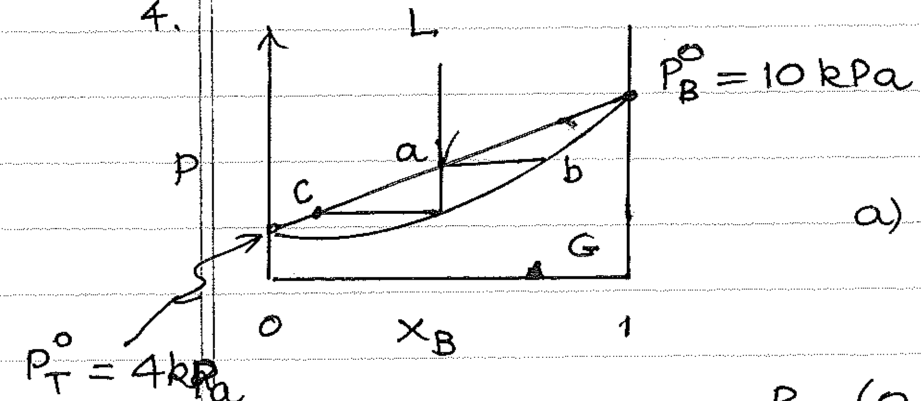
b) $Y_A = 0.40$, then

$$\frac{Y_A}{Y_B} = \frac{X_A P_A^o}{X_B P_B^o} = \frac{3}{4}\frac{X_A}{1-X_A} = \frac{Y_A}{1-Y_A} = \frac{0.4}{0.6}$$

$\therefore \frac{2}{3} = \frac{3}{4}\frac{X_A}{(1-X_A)}$, $X_A = \frac{8}{17}$

and $P = \left(\frac{8}{17}\right)\cdot 60\ kPa + \left(\frac{9}{17}\right)\cdot 80\ kPa = 70.6\ kPa$

4.



a) Boiling occurs @ $X_B = X(\text{benzene}) = 0.50$

$P = (0.50)\ 10\ kPa + (0.50)\ 4\ kPa$

$P = 7\ kPa$

b) composition of the vapor when $X_B = 1/2$

$$\frac{X_B P_B^o}{X_T P_T^o} = \frac{Y_B}{Y_T} = \frac{Y_B}{1-Y_B}$$

$X_B = X_T = 1/2$ so, $\frac{P_B^o}{P_T^o} = \frac{10}{4} = \frac{Y_B}{1-Y_B}$

$Y_B = \frac{2.5}{3.5} = \frac{5}{7}$

c) now the vapor is characterized by

$y_B = y_T = 1/2$ and

$$\frac{y_B}{1-y_B} = \frac{x_B P_B^o}{x_T P_T^o} = 1$$

and $2.5 \dfrac{x_B}{1-x_B} = 1 \Rightarrow x_B = 2/7$

$$P = \left(\frac{2}{7}\right)(10 \text{ kPa}) + \left(\frac{5}{7}\right) 4 \text{ kPa} = \frac{40}{7} \text{ kPa}$$

5.

a) $d\mu_L = -\bar{S}_L dT + \bar{V}_L dP = -\bar{S}_G dT + \bar{V}_G dP$

or $$\left(\frac{\partial P}{\partial T}\right)_{coex} = \frac{\bar{S}_G - \bar{S}_L}{\bar{V}_G - \underbrace{\bar{V}_L}_{\text{negligible}}} \simeq \frac{\Delta H(L \to G)/T}{RT/P}$$

$$\therefore \frac{dP}{dT} = \frac{P \Delta H}{RT^2}$$

$$\frac{dP}{P} = \frac{\Delta H}{RT^2} dT = d\ln P$$

$$\therefore d\ln P = \frac{\Delta H}{RT^2} dT$$

b) $\ln P = -\dfrac{a}{T} + b\ln T + cT + d$

$$d\ln P = \frac{a}{T^2} + \frac{b}{T} + c = \frac{\Delta H_{vap}}{RT^2}$$

$$\therefore \Delta H_{vap} = R\{a + bT + cT^2\}$$

6. Silbey, 6.17.

Max number of phases in 1, 2 + 3 component systems

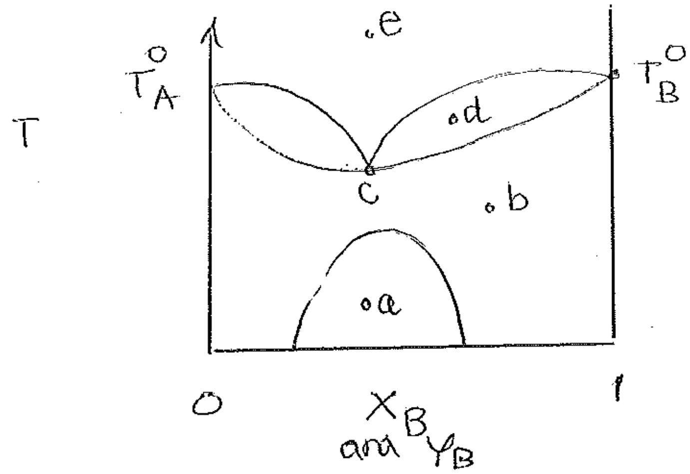
$F = 2 + C - P$

If $C = 1$, $P = 3$

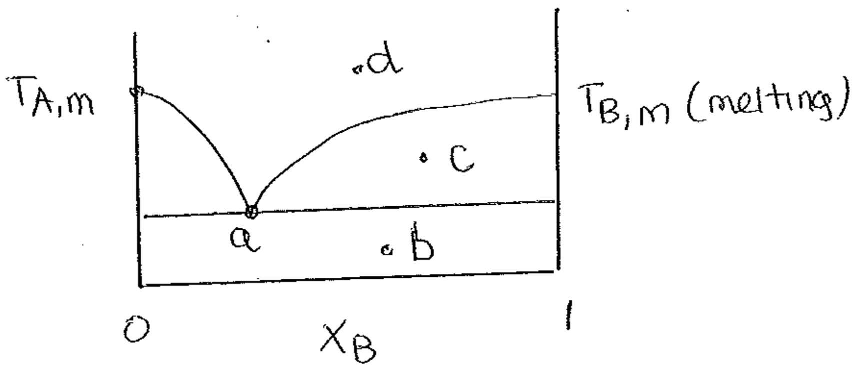
If $C = 2$, $P = 4$

If $C = 3$, $P = 5$

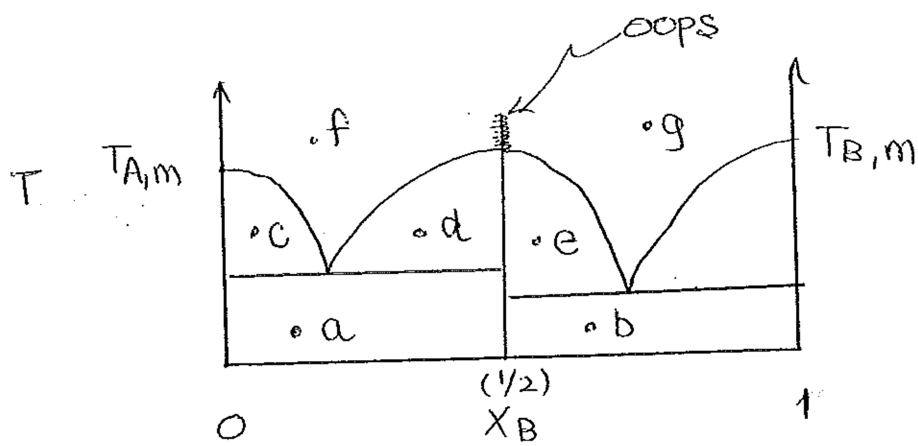
7. See attached page.



a, L, L equilibrium
b, one L-phase
c, azeotrope
d, L, G equilibrium
e, G phase



a, eutectic
b, solid
c, B(S), A(L), B(L)
d, A(L), B(L)



a, A(S), AB(S)
b, AB(S), B(S)
c, A(S), A(L), B(L)
d, AB(S), A(L), B(L)
e, AB(S), A(L), B(L)
f, A(L), B(L)
g, A(L), B(L)