CHEM 345 PROBLEM SET VIII

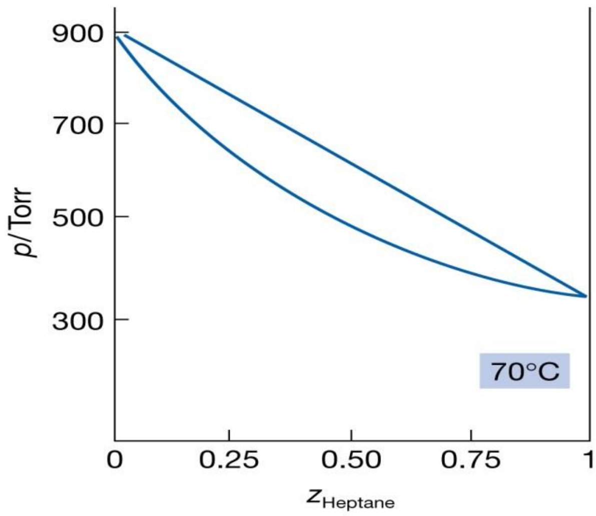
1. At 27^{0}C, one mole of m-xylene is mixed with three moles of p-xylene to form an ideal solution. Calculate Gibbs free energy, entropy and enthalpy of mixing per mole.

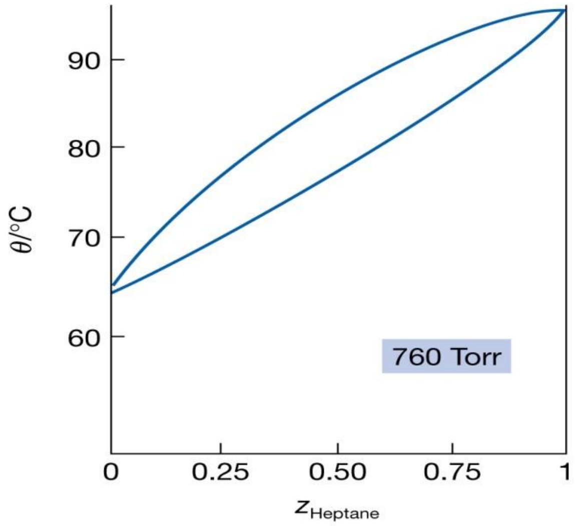
2. In a solution of water and alcohol, the mole fraction of water is 0.5. The partial pressures of water and alcohol over the solution are 13.5 and 27.6 torr, respectively. The vapor pressures of pure water and alcohol at the temperature of the solution are 17.5 and 43.6 torr, respectively. Calculate
   a. Activities of water and alcohol
   b. Activity coefficients of water and alcohol.

3. At 25^{0}C, two moles of cyclohexane are mixed with three moles of iso-octane. The activity coefficients of cyclohexane and iso-octane in the solution are found to be 1.049 and 0.996, respectively. Calculate Gibbs free energy of mixing per mole of the mixture. By how much is it greater than the corresponding value in an ideal solution of the same composition?

4. The vapour pressure of a pure liquid at 25^{0}C is 100 torr. Its mole fraction in the solution is 0.20. Its activity coefficient is 1.5. Calculate its vapour presure.

5. Given below are the phase diagrams of "ideal" solutions of hexane and heptane.
   a. Label the phases.
   b. For a solution of 1 mol of heptane and hexane each, estimate the vapour pressure at 70^{0}C when the vapourization (upon reduction of external P) just begins. What is the mole fraction of hexane in the liquid phase, and in the vapour phase?
   c. What is the vapour pressure of the solution at 70^{0}C when 1 drop of liquid remains? What are the mole fractions?





CHEM 345 PROBLEM SET IX

1. (Atkins 10th. Edition Exercise 5C.1 (b)) The following temperature-composition data were obtained for a mixture of two liquids A and B at 1.00 atm, where x is the mole fraction in the liquid phase and y is the mole fraction in the vapour in equilibrium.

$T/^0C$	125	130	135	140	145	150
x_A	0.91	0.65	0.45	0.30	0.18	0.098
y_A	0.99	0.91	0.77	0.61	0.45	0.25

The boiling points are 124^0C and 155^0C for A and B, repectively.

a) Plot the T versus composition diagram for the mixture.

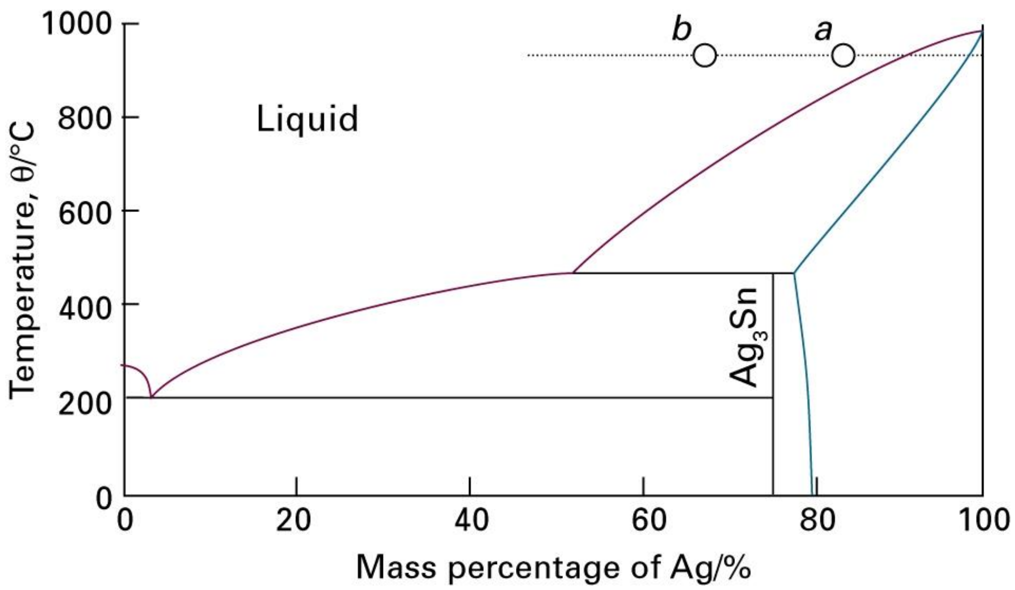
b) What is the composition of the vapour in equilibrium with the liquid of composition

i) $x_A = 0.50$ and ii) $x_A = 0.33$.

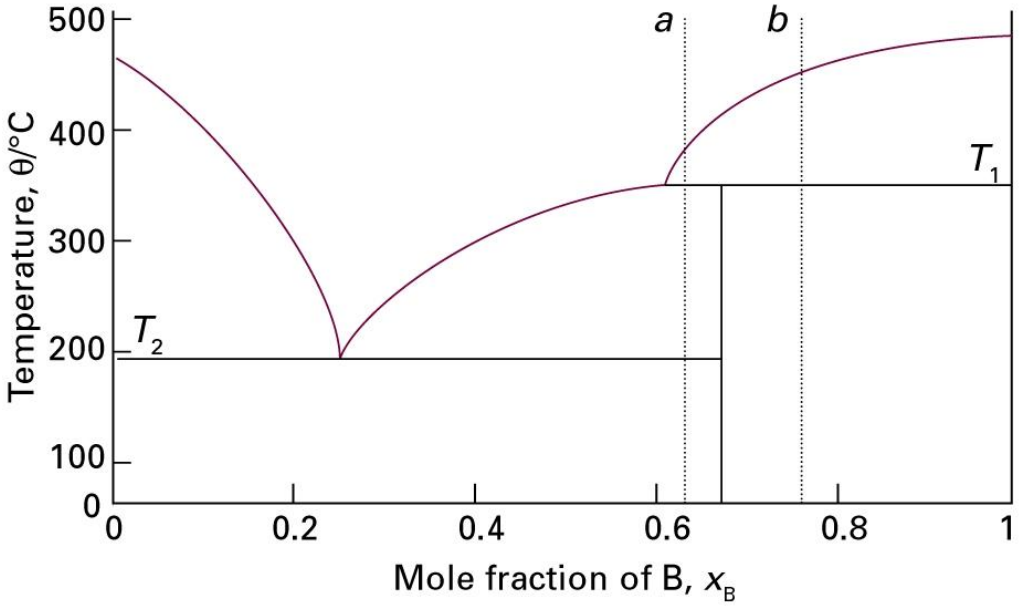
Phase Diagrams From Physical Chemistry By Atkins And De Paula;

Label the diagrams given below:

2.

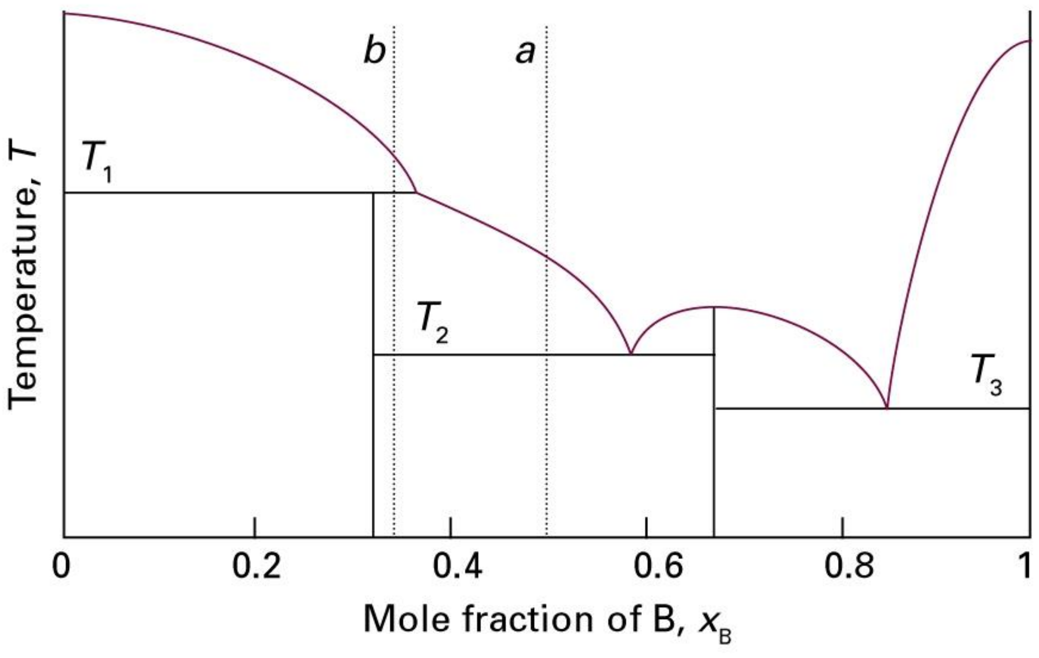


3.



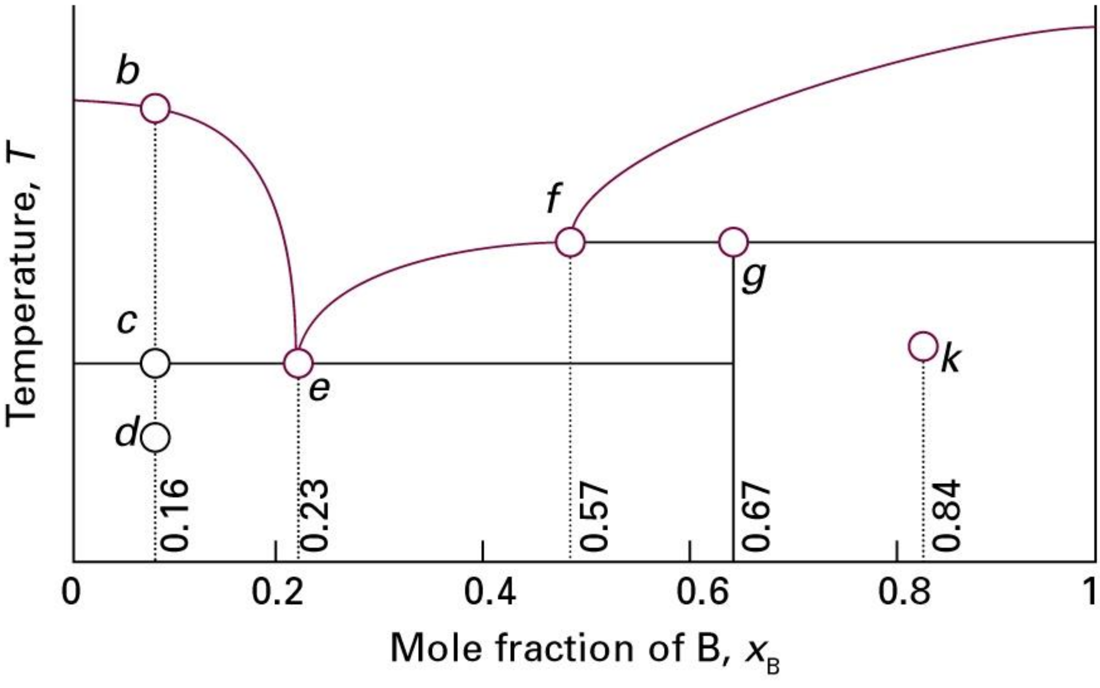
500
400
300
200
100
0
Temperature, θ/°C
a
b
T_1
T_2
0
0.2
0.4
0.6
0.8
1
Mole fraction of B, x_B

4.



Temperature, T
b
a
T_1
T_2
T_3
0
0.2
0.4
0.6
0.8
1
Mole fraction of B, x_B

5.

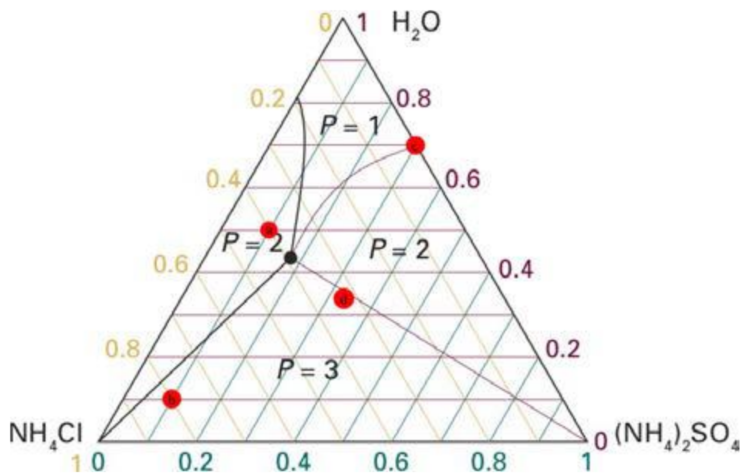


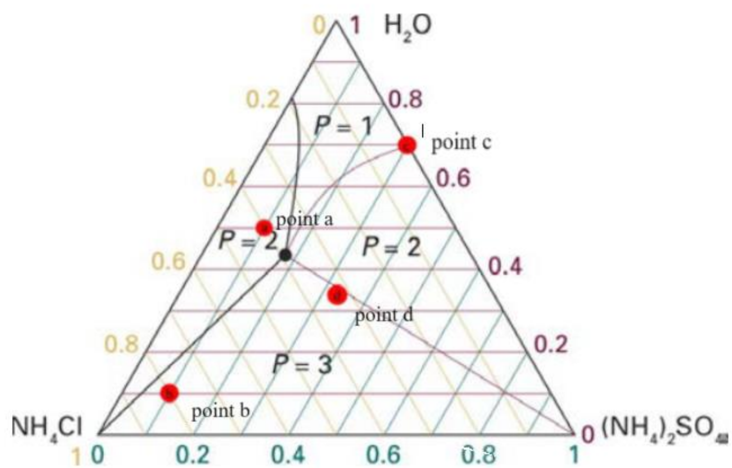
b
f
g
c
e
d
k
Temperature, T
0.16
0.23
0.57
0.67
0.84
0
0.2
0.4
0.6
0.8
1
Mole fraction of B, x_B

CHEM 345 PROBLEM SET X

1. Figure below shows the phase diagram for the ternary system $NH_4Cl/(NH_4)_2SO_4/H_2O$ at 25^0C. Identify the number of phases present for mixtures of compositions (i) (0.2, 0.4, 0.4), (ii) (0.4, 0.4, 0.2), (iii) (0.2, 0.1, 0.7), (iv) (0.4, 0.16, 0.44). The numbers are mole fractions of the three components in the order $(NH_4Cl,(NH_4)_2SO_4,H_2O)$.

   Also look for the number of phases present at points a, b, c and d.





2. Calculate I for a) a 0.050 molal solution of NaCl and for b) a Na_2SO_4 solution of the same molality.

3. Calculate the ionic strength of a solution that is 0.040 mol kg^{-1} in $K_3[Fe(CN)_6](aq)$, 0.030 mol kg^{-1} in KCl(aq), and 0.050 mol kg^{-1} in NaBr(aq).
4. Calculate the masses of (a) KNO_3 and, separately, (b) $Ba(NO_3)_2$ to add to a 0.110 mol kg^{-1} solution of $KNO_3(aq)$ containing 500 g of solvent to raise its ionic strength to 1.00.
5. Estimate the mean ionic activity coefficient and activity of NaCl in a solution that is 0.020 mol kg^{-1} NaCl (aq) and 0.035 mol kg^{-1} $Ca(NO_3)_2(aq)$.

CHEM 345 PROBLEM SET XI

1. The vapour pressure of water above mixtures of $CuCl_2.H_2O(s)$ and $CuCl_2.2H_2O(s)$ are given as a function of temperature:

$T/^0C$	17.9	39.8	60.0	80.0
P/atm	0.0049	0.0247	0.120	0.322

Calculate:

a) ΔH^0 for the reaction

$$CuCl_2.2H_2O(s) \rightleftharpoons CuCl_2.H_2O(s) + H_2O(g)$$

b) ΔG^0_r for the reaction at 60^0C.

c) ΔS^0_r for the reaction at 60^0C.

2. At 1237 K and a total pressure of 30 atm, the equilibrium in the reaction

$$CO_2(g) + C(s) \rightleftharpoons 2CO(g)$$

is such that 17 molar % of the gas is CO_2.

   a) What % would be CO_2 if the total pressure were 40 atm?

   b) At what pressure will 25% of the gas be CO_2?

3. The standard reaction enthalpy of

$$Zn(s) + H_2O(g) \rightarrow ZnO(s) + H_2(g)$$

is approximately constant at 224 kJ mol^{-1} from 920 *K* up to 1280 *K*. The ΔG^0_{reac} is 33 kJ mol^{-1} at 1280 *K*. Estimate the temperature at which the equilibrium constant becomes greater than 1.

4. For the reaction

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

At 300 K, K_p is 0.174. Calculate the apparent Molecular Weight of an equilibrium mixture of N_2O_4 and NO_2 formed by the dissociation of 1 mole of pure N_2O_4 at a total pressure of 1 atm and a temperature. (MWt for NO_2 = 46 g mol^{-1}, MWt for N_2O_4 = 92 g mol^{-1})