

UNIVERSITY OF MALTA

DEPARTMENT OF CHEMISTRY

CH237 - Chemical Thermodynamics and Kinetics

Tutorial Sheet 6

1. (a) Calculate the change in the chemical potential of a perfect gas when its pressure is increased isothermally:
- (i) from 1.8 atm to 29.5 atm at 40°C
  - (ii) from 92.0 kPa to 252.0 kPa at 50°C
- (b) The fugacity coefficient of a certain gas is:
- (i) 0.72 at 200K at 50bar;
  - (ii) 0.68 at 290K and 2.1Mpa
- Calculate the difference in the chemical potential from that of the perfect gas in the same states.
- (c) For a binary A/B mixture:
- (i) Define the chemical potential of A,  $\mu_A$ ,
  - (ii) Write an expression for  $dG$  if mixture A/B is an open system of constant composition.
  - (iii) Use this expression of  $dG$  to derive the Gibbs-Duhem equation, i.e.:
- $$d\mu_B = -\frac{n_A}{n_B}d\mu_A$$
- (iv) Write the equivalent Gibbs-Duhem equation for the partial molar volumes.
  - (v) Discuss the significance of these two Gibbs-Duhem equations.
2. (a) (i) The partial molar volume of acetone (propanone) and chloroform in a mixture in which the mole fraction of chloroform is 0.4693 are 74.166 cm<sup>3</sup> mol<sup>-1</sup> and 80.235 cm<sup>3</sup> mol<sup>-1</sup>, respectively. What is the volume of a solution of mass 1.000kg ?
- (ii) At 25°C, the density of a 50% (by mass) ethanol-water solution is 0.914 g cm<sup>-3</sup>. Given that partial molar volume of water in the solution is 17.4cm<sup>3</sup> mol<sup>-1</sup>, calculate the partial molar volume of the ethanol.
- (b) At 300K, the partial vapour pressures of HCl (i.e. the partial pressure of the HCl vapour) in liquid GeCl<sub>4</sub> are as follows:
- |                               |       |       |       |
|-------------------------------|-------|-------|-------|
| $x_{\text{HCl}}$              | 0.005 | 0.012 | 0.019 |
| $p_{\text{HCl}} / \text{kPa}$ | 32.0  | 76.9  | 121.8 |
- (i) Show that the solution obeys Henry's law in this range of mole fractions, and calculate Henry's law constant at 300K.
  - (ii) Predict the partial vapour pressure of HCl above its solution in liquid germanium tetrachloride of molality 0.10 mol kg<sup>-1</sup>.

- (c) Consider a container of volume  $V$  that is divided into two compartments of equal size, containing different gasses A (left compartment), and gas B (right compartment) both at the same temperature,  $\theta$ , and pressure,  $p$ . Assuming that the gases are perfect, calculate the entropy and Gibbs energy of mixing if the partition was to be removed, where:
- $V = 5.0\text{L}$ , A = nitrogen, B = hydrogen,  $\theta = 25^\circ\text{C}$ ,  $p = 1\text{ atm}$ ;
  - $V = 250\text{ mL}$ , A = argon, B = neon,  $\theta = 0^\circ\text{C}$ ,  $p = 100\text{kPa}$ .
- (d) Assuming that air is a mixture of nitrogen, oxygen, argon and carbon dioxide gases with mass percentages 75.52(N<sub>2</sub>), 23.15(O<sub>2</sub>), 1.28 (Ar) and 0.046(CO<sub>2</sub>). Calculate the entropy of mixing for the preparation of air if it was to be prepared from its pure and perfect gases.
- (e) (i) Calculate the Gibbs free energy, entropy and enthalpy of mixing when one mole of hexane is mixed with one mole of heptane at 298K. (Note: Treat the solution as ideal.)  
(ii) What proportions of hexane and heptane should be mixed (a) by mole fraction, (b) by mass, in order to achieve the greatest entropy of mixing?
- (f) Substances A and B are both volatile liquids with  $p_A^* = 300\text{ Torr}$ , and  $p_B^* = 250\text{ Torr}$ , and  $K_B = 200.00\text{ Torr}$  (= concentration expressed in mole fraction). When  $x_A = 0.9$ ,  $b_B = 2.22\text{ mol kg}^{-1}$  (= molality),  $p_A = 250\text{ Torr}$ , and  $p_B = 25\text{ Torr}$ . Calculate the activities and the activity coefficients of A and B. Use the mole fraction, Raoult's law basis for A and Henry's law basis (both mole fractions and molalities) for B.
- (g) A dilute solution of Br<sub>2</sub> in CCl<sub>4</sub> behaves as an ideal-dilute solution. The vapour pressure of pure CCl<sub>4</sub> is 33.85 Torr at 298K. The Henry's law constant when the concentration of Br<sub>2</sub> is expressed as a mole fraction is 122.36 Torr. Calculate the vapour pressure of each component, the total pressure, and the composition of the vapour phase when the mole fraction of Br<sub>2</sub> is 0.050, on the assumption that the conditions of the ideal-dilute solution are satisfied at this concentration.
- (h) By measuring the equilibrium between liquid and vapour phases of an acetone (A)- methanol (M) solution at 57.2°C at 1.0 atm, it was found that  $x_A = 0.400$  and  $y_A = 0.516$ . Calculate the activities and the activity coefficients of both components in this solution on the Raoult's law basis.  
*NOTE:* (i) The vapour pressure of the pure components at this temperature are:  $p_A^* = 786\text{ Torr}$ , and  $p_M^* = 551\text{ Torr}$ . (ii)  $x_J$  is the mole fraction of component J in the liquid, and  $y_J$  is the mole fraction of component J in the vapour.
- (i) The table below lists the vapour pressures of mixtures of iodoethane (I) and ethyl acetate (A) at 50°C. Find the activity coefficients of both components on (a) the Raoult's law basis, (b) the Henry's law basis with I as solute.

$x_I$	0	0.0579	0.1095	0.1918	0.2353	
$p_I$ /Torr	0	20.0	52.7	87.7	105.4	
$p_A$ /Torr	280.4	266.1	252.3	231.4	220.8	
$x_I$	0.3718	0.5478	0.6349	0.8253	0.9093	1.0000
$p_I$ /Torr	155.4	213.3	239.1	296.9	322.5	353.4
$p_A$ /Torr	187.9	144.2	122.9	66.6	38.2	0