

### Solution thermodynamics Assignment:

- The molar volume ( $\text{cm}^3 \cdot \text{mol}^{-1}$ ) of a binary liquid mixture at T and P is given by  
 $V = 120x_1 + 70x_2 + (15x_1 + 8x_2)x_1x_2$ 
  - Find expression for the partial molar volume of species 1 and 2 at T and P.
  - Show that the expression satisfies Gibbs-Duhem equation.
  - Show that  $\left(\frac{d\hat{v}_1}{dx_1}\right)_{x_1=1} = \left(\frac{d\hat{v}_2}{dx_1}\right)_{x_1=0} = 0$
- Find out the fugacity of the following
  - Cyclopentane at 110 °C and 275 bar. At 110 °C VAPOUR PRESSURE OF CYCLOPENTANE IS 5.276 BAR
  - 1-Butane AT 120 °C and 30 bar. Vapour pressure of 1 butane is 25.83 bar at 120 °C.
- The volume change of mixing ( $\text{cm}^3 \cdot \text{mol}^{-1}$ ) for the system ethanol (1)/methyl butyl ether (2) at 25 °C is given by  
 $\Delta V = x_1x_2 [-1.026 + 0.0220(x_1 - x_2)]$   
 Given that  $V_1 = 58.63 \text{ cm}^3 \cdot \text{mol}^{-1}$  and  $V_2 = 118.46 \text{ cm}^3 \cdot \text{mol}^{-1}$ , what volume of mixture is formed when 750  $\text{cm}^3$  of pure species 1 is mixed with 1500  $\text{cm}^3$  of species 2 at 25 °C? What would be volume if an ideal solution were formed?
- A 20 mol% LiCl/H<sub>2</sub>O is made by six different mixing process. Mixing is isothermal at 25 °C. Determine the heat effect in  $\text{J} \cdot \text{mol}^{-1}$  of the final solution for each case.
  - Mix LiCl (s) with H<sub>2</sub>O(l).
  - Mix H<sub>2</sub>O(l) with a 25 mol% LiCl/H<sub>2</sub>O solution.
  - Mix LiCl.H<sub>2</sub>O (s) with H<sub>2</sub>O (l).
  - Mix LiCl (s) with a 10 mole% LiCl/H<sub>2</sub>O solution.
  - Mix a 25 mol% LiCl/H<sub>2</sub>O) with a 10 mole% LiCl/H<sub>2</sub>O solution.
  - Mix a LiCl/H<sub>2</sub>O(s) with a 10 mole% LiCl/H<sub>2</sub>O solution.
- The following empirical two parameter expression has been proposed for correlation of excess properties of symmetric liquid mixtures:  

$$M^E = Ax_1x_2\left(\frac{1}{x_1+Bx_2} + \frac{1}{x_2+Bx_1}\right)$$
 Here, A and B are parameter that depend on T.  
 Determine the expression for  $\hat{M}_1^E$  and  $\hat{M}_2^E$   
 Determine the expression for  $(\hat{M}_1^E)$  and  $\hat{M}_2^E$  at infinite dilution.
- The molar enthalpy changes of mixing of methanol (1) - water (2) at a particular temperature is as follows

| $X_1$ | $\Delta h_m \text{ (kJ/mol)}$ | $X_1$ | $\Delta h_m \text{ (kJ/mol)}$ |
|-------|-------------------------------|-------|-------------------------------|
| 0.05  | - 0.342                       | 0.40  | - 0.887                       |
| 0.10  | - 0.599                       | 0.60  | - 0.718                       |
| 0.20  | - 0.871                       | 0.80  | - 0.455                       |
| 0.30  | - 0.917                       | 0.95  | - 0.127                       |

Determine the difference between partial molar and pure component enthalpies for methanol and water for  $X_1 = 0.35$  and  $X_2 = 0.65$ .

7. It is required to prepare 1 m<sup>3</sup> of methanol (1) water (2) solution at 25 °C with  $X_1 = 0.7779$ . the density of methanol (1) water (2) solution at 25 °C with  $X_1 = 0.7779$  is 0.825.959 kg/m<sup>3</sup>. The partial molar volume of water in the solution is  $15.686 \times 10^{-6}$  m<sup>3</sup>/mol. Determine volume of methanol and water. The density of methanol at 25 °C is 786.846 kg/ m<sup>3</sup>.
8. The van Laar constant A and B for a system ethanol (1) and benzene (2) at 50 °C are 1.7910 and 1.8262 respectively. Calculate the activity coefficient of the component in the solution containing 60 mol% ethanol.
9. Determine the bubble pressure and the composition of vapor if  $x_1 = 0.4$  for a liquid mixture of methanol (1) – benzene (2) at 60 °C by using NRTL equation.
10. In a binary mixture the activity coefficient ( $\gamma_1$ ) of component is given by
 
$$R \ln \gamma_1 = A x_2^2 + B x_2^3$$
 This equation is valid in the range of composition  $x_2 = 0$  to  $x_2 = 1$ . Derive an expression to find out the activity coefficient of component 2.
11. The system chloroform (1) and acetone (2) form a minimum boiling azeotrope at 64.5 °C and 760 torr. Determine the van Laar constants and P-x-y diagram for the system at 64.5 °C.
12. For a particular binary system, the activity coefficients are adequately represented by
 
$$\ln \gamma_1 = 0.5 x_2^2 \text{ and } \ln \gamma_2 = 0.5 x_1^2$$
 the saturation pressure of the component at 80 °C are given by  $P_1^S = 900$  Torr and  $P_2^S = 600$  Torr. Is it possible to exhibit azeotrope at 80 °C? If so, what is the azeotropic composition and what pressure is the azeotrope likely to form?