

**III B.Tech. I Semester Supplementary Examinations, April/May -2005**  
**CHEMICAL ENGINEERING THERMODYNAMICS-II**  
**(Chemical Engineering)**

Time: 3 hours

Max Marks: 80

Answer any FIVE Questions  
All Questions carry equal marks

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- What are various empirical relations to calculate latent heat accompanying a phase change?
  - How can you calculate the latent heat of vaporization at some temperature from the knowledge of its value at a single temperature?
- Calculate the standard heat at 250C for the following reaction,  
 $4HCL(g) + O_2(1) \rightarrow H_2Co(g)$
- Assuming the heat of vaporization of water to be constant at 539 cal  $g^{-1}$ , calculate the temperature at which water will boil under a pressure of 77.0 cm, the boiling point being 100.00°C at 76.0 cm. The specific volume of water vapour at 100°C and 76.5 cm pressure is 1664 cc. $g^{-1}$  and that of liquid water is 1.cc.  $g^{-1}$ . Explain the theoretical principles you used for calculation.
- Define the thermodynamic property change of mixing. How are the excess properties and property changes readily calculated one from the other? Illustrate your answer in terms of Gibbs energy, entropy, volume and enthalpy.
- If a system is governed by the following equation of state, derive expressions for residual Gibbs free energy, residual enthalpy and residual entropy  $P = \frac{RT}{v-b} \exp(-a/vRT)$  where a and b are functions of composition only.
- Using Van Laar equations, compute the y-x curve for ethyl alcohol water mixtures at a total pressure of 760 mm Hg. Base the computations upon the composition of the azeotropic mixture given below :  
mole percent alcohol = 89.43 ; t = 78.15°C ;  
vapor pressure of alcohol at 78.15°C = 755 mm Hg. ;  
vapor pressure of water at 78.15°C = 329 mm Hg.
- Why does immiseibility occur in liquid solution. How would you estimate the composition of the vapor phase in equation with two immiscible liquid phase?
- Derive an equation from the fundamentals to describe the effect temperature on 'K' in terms of  $\Delta H^\circ, \Delta \alpha \Delta \beta \Delta \gamma$  etc. Discuss the practical application of above derived equation with reference to any chemical reaction.

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1. (a) Define heat of mixing and heat of solution.  
(b) How is heat of solution of hydrates calculated?
2. What is the maximum temperature that can be reached by the combustion of methane with 20 percent excess air? Both the methane and air enter the burner at 25°C.
3. (a) Define the term, partial molar property. Give some examples.  
(b) The partial molar volume is defined as :  
$$\bar{V}_i = \left[ \frac{\delta(nV)}{\delta(n_i)} \right] P, T, n_j$$
  
Discuss the physical interpretation of this equation.  
(c) State the important thermodynamic properties of solution. How are they classified to distinguish the solution thermodynamics?
4. State the various models for the excess Gibbs energy. Discuss their salient features with special reference to Redlich / Kister expansion, the Margules equations and van Laar equations.
5. Calculate the fraction of liquid, liquid composition and vapor composition in a two phase system consisting of acetone(1)-acetonitrile (2) nitromethane (3) at 80°C and 110Kpa. The overall composition of the mixture is  $Z=0.45$ ,  $Z_2=0.35$  and  $Z_3=0.2$ . The vapor pressures of the components (1), (2) and (3) are 195.8 Kpa, 97.84 kPa and 50.32 kPa respectively.
6. (a) Explain Lewis-Randall rule and Henry's law. For a binary system, show that if Henry's law is applicable for one component; Lewis-Randall rule is applicable for the other component.  
(b) Explain Henry's law as a model for ideal behavior of a solute.
7. Prove that for a stable phase, the fugacity of each species of a binary system always increase with the composition.
8. (a) What are the criteria for chemical reaction equilibrium. Discuss in detail?  
(b) Derive an equation for reaction co-ordinate and explain how this equation can be used for practical purposes.

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1. (a) Discuss heat effects due to change of phase.  
(b) Discuss mixing heat effects.
2. Calculate the standard heat at 25°C for the following reaction,  
$$\text{C(s)} + \text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{(g)} + \text{Co(g)}$$
3. (a) State the equilibrium criteria usually applied by chemical engineers in the solution of phase-equilibrium problems.  
(b) Explain the term partial residual Gibbs Energy. With its help define fugacity coefficient of a species in solution and show that fugacity of a species 'i' in an ideal-gas mixture is equal to its partial pressure.
4. Define and explain the terms:  
Molar Gibbs Energy,  
Standard state Gibbs Energy,  
Partial Gibbs Energy,  
Excess Gibbs Energy and  
Residual Gibbs Energy  
Bring out the differences amongst them with simple thermodynamic relations.
5. Estimate residual enthalpy and residual entropy for an equimolar mixture of carbon dioxide (1)-nitrogen(2) at 400K and 135 bar pressure by the Redlich-Kwong equation.  
Dioxide :  $T_c = 304.2 \text{ K}$ ,  $P_c = 73.83 \text{ kPa}$ ,  $V_c = 94 \times 10^{-6} \text{ m}^3/\text{mol}$   
Nitrogen :  $T_c = 126.2 \text{ K}$ ,  $P_c = 34.0 \text{ kPa}$ ,  $V_c = 89 \times 10^{-6} \text{ m}^3/\text{mol}$ .
6. (a) Derive the Phase rule and Duhems theorem for reacting and non-reacting systems.  
(b) Draw the P-x,y, T-x,y and y-x diagrams for systems showing:
  - i. Positive deviations from Raoult's law
  - ii. Negative deviations from Raoult's law
  - iii. Azeotropism.
7. Develop equations that apply to the limiting case of binary LLE for which the  $\alpha$ -phase is very dilute in species 1 and the  $\beta$ -phase is very dilute in species 2.
8. (a) Discuss on effect of inerts, excess reactants on 'K'.

(b) The enthalpy change of reaction



If the equilibrium constant for the reaction at 2000 K is  $4.08 \times 10^4$ ,

Calculate the value of the equilibrium constant at 2500 K.

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1. (a) Define the following: Heat of reaction; Heat of formation  
(b) What is heat of combustion? What is difference between net value and gross value of heat of combustion?
2. What is the standard heat of combustion of n-pentane gas at 25<sup>0</sup>C, if the combustion products are  $H_2O(l)$  and  $CO_2(g)$ ?
3. (a) State Henrys Law and Define Henrys Constant. Discuss the relation of Henrys Law to Lewis-Randall rule through Gibbs Duhem equation.  
(b) Show graphically (not to scale) the composition dependence of fugacity for species i in a binary solution at constant temperature and pressure, to distinguish it from Henrys Law and Lewis Randall rule.
4. Discuss the enthalpy-concentration diagrams. What are the assumptions made in plotting these curves? Explain their utility and advantages. Discuss the effect of temperature and variation of these curves.
5. A vapour mixture containing 50 mole % pentane, 30 mole% hexane, 20 mole% heptane, enters a partial condenser, which is maintained at 60C. If it is desired to condense 60% of the vapour, determine the pressure at which the condenser is to be operated. Saturation pressures: pentane=1611.39 mm Hg hexane = 568.97 mmHg; heptane = 210.64 mmHg.
6. (a) Discuss the Phase behavior for Vapor / Liquid systems.  
(b) Discuss about Retrograde Condensation.
7. Show that Wilson equation is capable of representing LLE.
8. (a) Discuss the degree of conversion at 3500°C and 1.2 Mpa for the reaction  
 $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3$   
if a stoichiometric mixture of  $N_2$  and  $H_2$  is fed to the reactor which is maintained at constant temperature and pressure of 350°C and 1 bar.  
 $K_{350^\circ C} = 1.96 \times 10^{-4}$   
(b) Discuss the effect of pressure on 'K' and derive the equation.

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