

Code No: 07A50803

**R07****Set No. 2**

**III B.Tech I Semester Examinations, November 2010**  
**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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1. What do you mean by excess property? How is it different from residual properties? Derive the expression for partial excess Gibbs energy. [16]
2. If the heat capacity of a substance is correctly represented by an equation of the form  $C_p = A + BT + CT^2$  When sp. Mean heat capacity is assumed equal to  $C_p$  evaluated at the arithmetic mean of  $T_1$  and  $T_2$ , show the error results in  $C(T_2 - T_1)^2/12$  [16]
3. Estimate  $H^R$  and  $S^R$  for an equimolar mixture of methyl ethyl ketone (1) and Toluene (2) at  $50^\circ\text{C}$  and 25 kPa using van der Waals equation. The constants for van der Waals equation are (in SI units)
 
$$\begin{aligned} a_1 &= 2.01 \times 10^6 & b_1 &= 0.1341 \\ a_2 &= 2.487 \times 10^6 & b_2 &= 0.149 \end{aligned}$$
 [16]
4. Derive the equation for determining the fugacity coefficient of component in gaseous mixture from fundamental residual property relation? [16]
5. (a) Explain modified Raoult's law.  
 (b) The system acetone (A) and ethanol (E) at 0.1013 MPa total pressure is a non-azeotropic, completely miscible system. From the following point of equilibrium data, determine whether or not the system is ideal. The equilibrium concentration and temperature are  $x_A = 0.4$ ;  $y_A = 0.605$ ;  $T = 66^\circ\text{C}$ . Vapor pressures of acetone and ethanol are  $P_{A^0} = 0.1373$  MPa  $P_{E^0} = 0.0600$  MPa. [6+10]
6. (a) On what parameters do rate and equilibrium conversion of a chemical reaction depend upon? How rate and equilibrium conversion vary in various situations. Give a suitable example to explain above.  
 (b) Discuss of free energy change in the significance of free energy change with respect to chemical reaction equilibrium. [12+4]
7. Derive the general equation for determining fugacities of any component in a gaseous state and hence derive equation for fugacity of a component assuming as an ideal gas solution. [16]
8. Explain Pxy diagram and Txy diagram for a binary system of immiscible liquid. [16]

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1. (a) Prove  $y_i = \frac{n_{i0} + \theta_i \epsilon}{n_0 + \theta \epsilon}$ , all notations have their usual meaning.  
(b) Methanol is produced from synthesis gas according to the following reaction.  
 $\text{CO}_{(g)} + 2\text{H}_{2(g)} \rightleftharpoons \text{CH}_3\text{OH}_{(g)}$   
Calculate the equilibrium conversion at 2 bar and 2200°C, if stoichiometric quantities are used in the above reaction. Given  $K_{2200} = 1.9 \times 10^{-2}$ . [8+8]
2. Define internal energy. Show that it is a function of temperature only for an ideal gas. How it is different from all other types of energies. [16]
3. (a) The heat capacity of a substance will increase or decrease with increasing temperature. What are the reasons for your answers?  
Data:  $\Delta H_{C^0} \text{C}_2\text{H}_2(g) = -1299.61 \text{ kJ/mol}$   
 $\Delta H_{C^0} \text{C}_3\text{H}_8(c) = -2204.0 \text{ kJ/mol}$   
 $\Delta H_{C^0} \text{CO}(g) = -282.9 \text{ kJ/mol}$   
(b) Define heating value of a fuel. Define gross heating value and net heating value of a fuel. Differentiate them. [6+10]
4. (a) Discuss the use of Pitzer's correlations to estimate vapor-liquid equilibrium state.  
(b) Briefly explain the flash calculations and VLE using Redlich-Kwong equation of state. [6+10]
5. (a) Define Lewis - Randall rule and Rault's law. How are they different?  
(b) How fugacity of liquid is determined at any given pressure? Derive the expression for it. [8+8]
6. In a petroleum refining plant, an equimolar mixture of ethane (1) - propane (2) and normal butane (3) is fed to a flash separator in which the pressure is 5 bar and the temperature 130°C. Assuming ideal solution behavior, calculate the liquid to vapor ratio and composition of each phase. Given  $\log P_1^{sat} = -\frac{817.08}{T} + 4.4022$

$$\log P_2^{sat} = -\frac{1051.38}{T} + 4.5171$$

$$\log P_3^{sat} = -\frac{1267.56}{T} + 4.6176$$

where  $P^{sat}$  is in bar and T is in K .

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7. (a) Discuss the criteria for liquid-liquid equilibrium.  
(b) What is Eutectic composition?  
(c) Write a note on isosteric heat of adsorption. [8+4+4]
8. Derive the equation for volume change of mixing for real solution and hence for an ideal solution. [16]

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**R07****Set No. 1**

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1. Show that one of the conditions for a mixture to form a stable single phase binary liquid mixture is  $\frac{d^2}{dx_1^2} \left( \frac{G^E}{RT} \right) > \frac{-1}{x_1 x_2}$  [16]
2. Discuss in detail, the estimation of thermodynamic properties from cubic equation of state, along with equations. [16]
3. (a) Write Lewis Randall rule and Henry's law and discuss their applicability. Write their mathematical statement also.  
 (b) What is property change of mixing? Discuss it. [10+6]
4. Discuss the equilibrium constant dependence on temperature for the following cases:  
 (a) If  $\Delta H$  is constant for the given temperature range  
 (b) If  $\Delta H$  varies with temperature [16]
5. Prove  $T_2 = \frac{\Delta H}{\langle C_p \rangle} + T_1$ , when change is taking place from  $T_1$  to  $T_2$  [16]
6. (a) Prove for an ideal gas the difference between two sp. heats is constant  
 (b) Pure CO is mixed with 100% excess air and completely burnt at constant pressure. The reactants are originally at 400K. Determine the heat added or removed if the product leaves at 600K. The mean specific heats of components are CO(29.10), O<sub>2</sub>(29.7), N<sub>2</sub>(29.1), CO<sub>2</sub>(41.45) in J/mol.k  $\Delta H_{f298} = -283.028$  KJ/mol CO burnt [4+12]
7. Wilson's parameters for the system chloroform (1) - methanol (2) at 35 °C are given by  $(\lambda_{12} - \lambda_{11}) = -1.552 \frac{\text{kJ}}{\text{molK}}$  and  $(\lambda_{12} - \lambda_{22}) = 7.559 \frac{\text{kJ}}{\text{molK}}$

Estimate the VLE data for the system at 35°C

$$\text{if } V_1^L = 80.67 \times 10^{-6} \frac{\text{m}^3}{\text{mol}} \text{ and } V_2^L = 40.73 \times 10^{-6} \frac{\text{m}^3}{\text{mol}}$$

Vapor pressures are calculated from the Antoine equation  $\log_{10}^p = A - \frac{B}{t+C}$ , where P is in Torr and t is in °C whose constants are given as follows:

	A	B	C	
Chloroform	9.95465	1170.966	226.322	[16]
Methanol	8.08097	1582.271	239.726	

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8. Estimate  $\phi_1$  and  $\phi_2$  for an equimolar mixture of MEK (1)/Toluene (2) at 50°C and 25 Kpa .Assume all  $K_{ij}=0$ . Data as follows

$ij$	$T_{c_{ij}}(K)$	$P_{c_{ij}}(\text{bar})$	$V_{c_{ij}}(\text{cm}^3/\text{mol})$	$Z_{c_{ij}}$	$\omega_{ij}$
11	535.5	41.5	267	0.249	0.323
22	591.8	41.1	316	0.264	0.262
12	563.0	41.3	291	0.256	0.293

[16]

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1. (a) State the equilibrium criterion for two phases of a multi component system.  
 (b) With the help of a block diagram or flow chart, explain the various steps involved in the calculation of Dew pressure for a binary system. [4+12]
2. (a) Derive the equation for determining the latent heat of vaporization of water at sufficiently low pressure. Write the assumptions  
 (b) Write Trouton's rule, Riedel eqn. and Watson eqn. for rough determination of latent heat and discuss them. Explain the notation. [10+6]
3. (a) Define chemical potential for a pure component and for a component in a mixture. Why it is defined in terms of Gibbs free energy only?  
 (b) If a gas is brought from ideal condition (say  $p=0$ ) to real condition (sat  $p=p$ ) then prove  $G = G_i + RT \ln \phi$ , all notations have their usual meaning. [6+10]
4. (a) Write Gibbs Duhem equation at a constant temperature and pressure in terms of fugacity. What are the limitations of this equation?  
 (b) Write the modified Raoult's law. Write the steps to calculate activity coefficient using experimental low pressure VLE isothermal data. [6+10]
5. For the reaction  $\text{CO}_2(\text{g}) + 4\text{H}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g}) + \text{CH}_4(\text{g})$  Calculate the standard heat of reaction at 773K Data :  $\Delta H_{f298} = -164.987 \text{KJ}$

	A	B	C
Products :	H <sub>2</sub> O : 29.16	$14.49 \times 10^{-3}$	$-2.02 \times 10^{-6}$
	CH <sub>4</sub> : 13.41	$77.03 \times 10^{-3}$	$-18.74 \times 10^{-6}$
Reactants :	CO <sub>2</sub> : 26.75	$42.26 \times 10^{-3}$	$-14.25 \times 10^{-6}$
	H <sub>2</sub> : 26.88	$4.35 \times 10^{-3}$	$-0.33 \times 10^{-6}$

6. (a) Discuss phase rule for reacting systems.  
 (b) Ethanol may be formed by the reaction  $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{C}_2\text{H}_5(\text{OH})(\text{g})$  For which  $G = -9670 + 6.43T \ln T - 9.01T - 0.00665T^2$ , where T is in Kelvin. G is in cal/g-mol of ethanol. Calculate the equilibrium constant for this reaction at 200°C. [6+10]
7. Derive the relations to estimate the enthalpy and entropy departures for a fluid obeying the following equation of state  

$$\left(P + \frac{a}{TV^2}\right)(V - b) = RT$$
 Where a and b are constants characteristic of the fluid and all other terms have their usual meaning. [16]

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8. The concentration of benzoic acid dissolved in layers of benzene and water at equilibrium are, in units of grams acid per liter of solution:

Inwater	2.89	1.95	1.5	0.98	0.79
InBenzene	97.0	41.2	25.2	10.5	7.37

Analyze the data and decide whether the benzoic acid is almost completely dissociated in the water? [16]

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