

Seat No.: \_\_\_\_\_

Enrolment No. \_\_\_\_\_

**GUJARAT TECHNOLOGICAL UNIVERSITY**

**BE - SEMESTER-V(New) • EXAMINATION – WINTER 2016**

**Subject Code:2150503**

**Date:19/11/2016**

**Subject Name:Chemical Engineering Thermodynamics - II**

**Time:10:30 AM to 01:00 PM**

**Total Marks: 70**

**Instructions:**

1. Attempt all questions.
2. Make suitable assumptions wherever necessary.
3. Figures to the right indicate full marks.

	<b>Marks</b>
<b>Q.1      Short Questions</b>	<b>14</b>
1 Define reaction coordinate and write physical significance of $\Delta\varepsilon = 1$ .	
2 Write two distinctive features of the equilibrium state at given temperature and pressure.	
3 The water – gas shift reaction carried out at 1100 K and 1 bar. The initial mixture consist of 1 mole H <sub>2</sub> O vapor and 1 mole of CO. If 2 mole of N <sub>2</sub> is included in the reactants, what is the effect on equilibrium composition?	
4 A system of two miscible non-reacting species which exists as an azeotrope in vapor – liquid equilibrium. Determine the number of degrees of freedom.	
5 How the fugacity of each component in a binary system affected with its mole fraction for a stable phase at constant pressure and temperature?	
6 Gibbs free energy of a pure fluid approaches _____ as the pressure tends to zero at constant temperature.	
7 Define chemical potential.	
8 Write the applicability of NRTL equation for liquid solutions.	
9 State Raoult’s law and write its application.	
10 Define activity coefficient of species in the solution.	
11 Write the equation and limitation of Henry’s law.	
12 Define bubble point temperature.	
13 Write the stability conditions for species in a binary solution at constant temperature and pressure.	
14 All irreversible processes occurring at constant T and P proceeds in such direction as to cause _____ in the Gibbs energy of the system.	
<b>Q.2 (a) Write a brief note on excess properties.</b>	<b>03</b>

(b) Estimate the fugacity of iso-butane at 15 atm and 87 °C using the compressibility factor correlation  $Z = 1 + \frac{BP}{RT}$ , given that the second virial coefficient  $B = 4.28 \times 10^{-4} \text{ m}^3/\text{mol}$ . **04**

(c) The enthalpy of a binary liquid mixture of species 1 and 2 at fixed T and P is represented by the equation:  $H = 400 X_1 + 600 X_2 + X_1 X_2 (40X_1 + 20X_2)$ , where H is in J/mol. Determine expressions for  $\bar{H}_1$  and  $\bar{H}_2$  as functions of  $X_1$ , numerical values for the pure species enthalpies  $H_1$  and  $H_2$ , and numerical values of partial enthalpies at infinite dilution  $\bar{H}_1^\infty$  and  $\bar{H}_2^\infty$ . **07**

**OR**

(c) At 300 K and 1 bar, the volumetric data for a liquid mixture of benzene and cyclohexane are represented by:

$$V = 109.4 \times 10^{-6} - 16.8 \times 10^{-6} X - 2.64 \times 10^{-6} X^2$$

where X is the mole fraction of benzene and V has the units of  $\text{m}^3/\text{mol}$ . Find the expressions for the partial molar volumes of benzene and cyclohexane.

**Q.3 (a)** State and discuss the Duhem's theorem for non – reacting systems. **03**

(b) Write a brief note on T – x – y diagram for partially miscible system. **04**

(c) Define azeotropes and explain minimum boiling and maximum boiling azeotropes with suitable examples and neat diagrams. **07**

**OR**

**Q.3 (a)** Write a brief note on solid – vapor equilibrium. **03**

(b) Discuss the Gamma / Phi formulation for vapor – liquid equilibrium. **04**

(c) Explain the methodology adopted for flash calculation of vapor – liquid mixture involving high pressure and multicomponent systems. **07**

**Q.4 (a)** Discuss Wohl's three suffix equations used to determination of activity coefficient for vapor – liquid equilibria at low pressure. **03**

(b) Discuss the Redlich – Kister zero area method applied to test the consistency of experimental VLE data. **04**

(c) Prove that if Raoult's law is valid for one component of a binary solution over the whole concentration range, it must also apply to the other components. **07**

**OR**

**Q.4 (a)** Discuss Margules three suffix equations used to determination of activity coefficient for vapor – liquid equilibria at low pressure. **03**

(b) Construct P – x – y diagram for the cyclohexane (1) – benzene (2) system at 40 °C. The vapor pressure of cyclohexane and benzene at 40 °C are 24.62 kPa **04**

and 24.41 kPa respectively. Use the following expressions for the liquid - phase activity coefficients:

$$\ln \gamma_1 = 0.458 X_2^2 \text{ and } \ln \gamma_2 = 0.458 X_1^2$$

- (c) The following values refer to the Wilson parameters for the system of acetone (1) – water (2): **07**

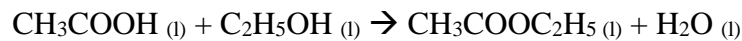
$a_{12} = 1225.31 \text{ J/mol}$ ,  $a_{21} = 6051.01 \text{ J/mol}$ ,  $V_1 = 74.05 \times 10^{-6} \text{ m}^3/\text{mol}$  and  $V_2 = 18.07 \times 10^{-6} \text{ m}^3/\text{mol}$ . The vapor pressure are given by the equations:

$$\ln P_1^{\text{sat}} = 14.3915 - \frac{2795.817}{T - 43.198} \text{ and } \ln P_2^{\text{sat}} = 16.262 - \frac{3799.887}{T - 46.854}$$

where P is in kPa and T is in K. Calculate the equilibrium pressure and composition of vapor in equilibrium with a liquid of composition  $x_1 = 0.43$  at 349 K.

- Q.5 (a)** Explain effect of temperature, pressure and total stoichiometric number on equilibrium constant. **03**

- (b) Acetic acid is esterified in the liquid phase with ethanol at 100 °C and atmospheric pressure to produce ethyl acetate and water according to the reaction: **04**



If initially there is one mole of each acetic acid and ethanol, estimate the mole fraction of ethyl acetate in the reacting mixture at equilibrium. The values of  $\Delta H^\circ_{298}$  and  $\Delta G^\circ_{298}$  for the above reaction are 13110 J and 9270 J respectively. Assume that the heat of reaction is independent of temperature and the liquid mixture behaves as ideal solution.

- (c) For an ideal gas, the exact mathematical expressions can be developed for the effect of T and P on the reaction co-ordinate at equilibrium. For conciseness we let  $\prod_i (y_i)^{\nu_i} = K_y$ . Then we can write the mathematical relations: **07**

$$\left( \frac{\partial \epsilon_e}{\partial T} \right)_P = \left( \frac{\partial K_y}{\partial T} \right)_P \frac{d\epsilon_e}{dK_y} \text{ and } \left( \frac{\partial \epsilon_e}{\partial P} \right)_T = \left( \frac{\partial K_y}{\partial P} \right)_T \frac{d\epsilon_e}{dK_y}$$

Using above equation, show that

$$(i) \left( \frac{\partial \epsilon_e}{\partial T} \right)_P = \frac{K_y}{RT^2} \frac{d\epsilon_e}{dK_y} \Delta H^\circ \quad (ii) \left( \frac{\partial \epsilon_e}{\partial P} \right)_T = \frac{K_y}{P} \frac{d\epsilon_e}{dK_y} (-v)$$

**OR**

- Q.5 (a)** Discuss the relation between equilibrium constant to composition for homogeneous liquid phase reaction. **03**

- (b) Consider a vessel which initially contains only  $n_0$  moles of water vapor. If decomposition occurs according to the reaction:  $\text{H}_2\text{O} \rightarrow \text{H}_2 + 0.5\text{O}_2$  Find expressions which relate the number of moles and mole fraction of each chemical species to the reaction co-ordinate and fractional decomposition of water vapor. **04**
- (c) The ammonia synthesis reaction written as:  $0.5\text{N}_2(\text{g}) + 1.5\text{H}_2(\text{g}) \rightarrow \text{NH}_3(\text{g})$  with 0.5 mole nitrogen and 1.5 mole hydrogen as the initial amounts of reactants and with the assumption that the equilibrium mixture is an ideal gas, show that reaction coordinate at equilibrium is: **07**

$$\varepsilon_e = 1 - \frac{1}{(1 + 1.299 \text{ KP})^{0.5}}$$

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