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GUJARAT TECHNOLOGICAL UNIVERSITY

BE - SEMESTER–V (NEW) EXAMINATION – SUMMER 2019

Subject Code: 2150503 **Date: 31/05/2019**

Subject Name: Chemical Engineering Thermodynamics - II

Time: 02:30 PM TO 05:00 PM **Total Marks: 70**

Instructions:

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

Q.1	**(a)**	Discuss the phase rule and Duhem's theorem.	**03**
	(b)	Derive the expression of vapor composition at equilibrium using flash vaporization.	**04**
	(c)	Derive the equation for criteria for phase equilibrium in terms of chemical potential for a mixture of N components and π phases.	**07**
Q.2	**(a)**	At 303 K the vapour pressures of benzene (1) and toluene (2) are 15.75 kPa and 4.89 kPa respectively. Determine the partial pressure and composition of the benzene vapour in equilibrium with a liquid mixture consisting of equal weight of the two components.	**03**
	(b)	A 30 mol% methanol-water solution is to be prepared. How many cubic meters of pure methanol (molar volume 40.727 x 10^{-6} m^3/mol) and pure water (molar volume 18.068 x 10^{-6} m^3/mol) are to be mixed to prepare 2 m^3 of the desired solution? The partial molar volumes of methanol and water in 30% solution are 38.632 x 10^{-6} m^3/mol and 17.765 x 10^{-6} m^3/mol respectively.	**04**
	(c)	Define fugacity coefficient. Discuss any two methods to evaluate fugacity coefficient in details.	**07**
		OR	
	(c)	Water (1)/hydrazine (2) system forms an azeotrope containing 58.5 mol% hydrazine at 393 K and 101.3 kPa. Calculate the equilibrium vapor composition for a solution containing 20 mol% hydrazine. The relative volatility of water with reference to hydrazine is 1.6 and may be assume to remain constant in the temperature range involved. Vapor pressure of hydrazine at 393 K is 124.76 kPa.	**07**
Q.3	**(a)**	Derive the Margules equations from the following expression: $$\frac{G^E}{x_1 x_2 RT} = A_{21}x_1 + A_{12}x_2$$	**03**
	(b)	Define partial molar properties and explain any one method in detail for evaluation of partial molar properties.	**04**
	(c)	The following values refer to the Wilson parameters for the system of acetone (1)/water (2): a_{12} = 1225.31 J/mol, a_{21} = 6051.01 J/mol, V_1 = 74.05 x 10^{-6} m^3/mol and V_2 = 18.07 x 10^{-6} m^3/mol. The vapour pressures are given by the equations: $$\ln P_1^{sat} = 14.3915 - \frac{2795.817}{T - 43.198} \quad \text{and} \quad \ln P_2^{sat} = 16.262 - \frac{3799.887}{T - 46.854}$$ where p_i^{sat} is in kPa and T is in K. Calculate the equilibrium pressure and composition of vapour in equilibrium with a liquid of composition x_1 = 0.43 at 349 K.	**07**

OR

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Q.3 **(a)** Discuss the area test for checking the consistency of experimental VLE data. **03**

(b) The experimental pressure-volume data for benzene at 675 K from a very low pressures up to 75 bar may be approximated by the equation V = 0.0554(1/P - 0.0046).Where V is in m^3/mol and pressure P is in bar. What is the fugacity of benzene at 1 bar and 675 K? **04**

(c) What is gamma-phi formulation of VLE? Draw block diagrams for the BUBL P and DEW P calculations. Write all necessary equations. **07**

Q.4 **(a)** Write a short note on group contribution methods. **03**

(b) Define azeotrope and explain the minimum boiling and maximum boiling azeotropes with suitable examples. **04**

(c) Prove "Henry's law applies to a species as it approaches infinite dilution in a binary solution, and the Gibbs/Duhem equation ensures the validity of the Lewis/Randall rule for the other species as it approaches purity. **07**

OR

Q.4 **(a)** Explain the Lewis-Randall rule and its significance. **03**

(b) Write a brief note on retrograde condensation and its application. **04**

(c) Using fundamental properties relations establish the expression of standard Gibbs free energy change of chemical reaction as a function of thermodynamic equilibrium constant. **07**

Q.5 **(a)** Write down Raoult's Law and Henry's Law explaining each term associated with them with their applicability. **03**

(b) Explain T-x-y diagram for partial miscible system. **04**

(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 $\prod (y_i)^{\nu_i} = K$. Then we can write the mathematical relations: **07**

$$\left(\frac{\partial \varepsilon_e}{\partial T}\right)_P = \left(\frac{\partial K_y}{\partial T}\right)_P \frac{d\varepsilon}{dK_y} \quad \text{and} \quad \left(\frac{\partial \varepsilon_e}{\partial T}\right)_T = \left(\frac{\partial K_y}{\partial T}\right)_T \frac{d\varepsilon_e}{dK_y}$$

Using above equations, show that

$$i)\left(\frac{\partial \varepsilon_e}{\partial T}\right)_P = \frac{K_y}{RT^2}\frac{d\varepsilon}{dK_y}\Delta H^0 \quad \text{and} \quad ii)\left(\frac{\partial \varepsilon_e}{\partial T}\right)_T = \frac{K_y}{P}\frac{d\varepsilon_e}{dK_y}(-v)$$

OR

Q.5 **(a)** Write a brief note on solid - vapor equilibrium. **03**

(b) The ammonia synthesis reaction written as: 0.5 $N_{2(g)}$ + 1.5 $H_{2(g)} \rightarrow NH_{3(g)}$ with 0.5 mol nitrogen and 1.5 mol hydrogen as the initial amounts of reactants and with the assumption that the equilibrium mixture is an ideal gas, show that: **04**

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

(c) Estimate the equilibrium constant at 1000 K and 0.1 MPa for the reaction : $CO_{2(g)} + H_{2(g)} \rightarrow CO_{(g)} + H_2O_{(g)}$ taking into account the variation of ΔH^o with temperature. **07**

Component	a	$b \times 10^3$	$e \times 10^{-5}$	ΔG^o_{298} (J/mol)	ΔH^o_{298} (J/mol)
CO_2	45.369	8.688	-9.619	-394359	-393509
H_2	27.012	3.509	0.690	-	-
CO	28.068	4.631	-0.258	-137169	-110525
H_2O	28.85	12.055	1.006	-228572	-241818

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