

GUJARAT TECHNOLOGICAL UNIVERSITY**BE- SEMESTER-IV (NEW) EXAMINATION – WINTER 2020****Subject Code:3140507****Date:24/02/2021****Subject Name:Chemical Engineering Thermodynamics II****Time:02:30 PM TO 04:30 PM****Total Marks:56****Instructions:**

1. Attempt any FOUR questions out of EIGHT questions.
2. Make suitable assumptions wherever necessary.
3. Figures to the right indicate full marks.

- Q.1** (a) Write down Raoult's law and Henry's law explaining each term associated with them with their applicability. **03**
- (b) Write a brief note on retrograde condensation and its application. **04**
- (c) Define azeotrope and explain the minimum boiling and maximum boiling azeotropes with suitable examples. **07**
- Q.2** (a) Discuss the phase rule and Duhem's theorem. **03**
- (b) At 303 K, 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. **04**
- (c) Define partial molar properties. Discuss various methods for evaluation of partial molar properties. **07**
- Q.3** (a) Estimate activity coefficient of methanol for chloroform (1) / methanol (2) system at 35°C. The vapour pressures of chloroform and methanol at 35° are 39.54 kPa and 27.95 kPa respectively. The mole fraction of methanol in the liquid mixture is 0.25. Margules' parameters are $A_{12} = 0.738$, $A_{21} = 1.868$. **03**
- (b) Discuss the area test for checking the thermodynamic consistency of experimental VLE data. **04**
- (c) The enthalpy at 300 K and 1 bar of a binary liquid mixture is represented by the following 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^∞ and \bar{H}_2^∞ . **07**
- Q.4** (a) Methanol (1) / acetone (2) system is described by the Van Laar activity coefficient model. At 60°C, the model parameters are $A_{12} = 0.47$ and $A_{21} = 0.78$. Estimate the activity coefficient of methanol for a solution containing 15 mol% of methanol. **03**
- (b) Consider a vessel which initially contains only n_0 moles of water vapor. If decomposition occurs according to the reaction: $H_2O \rightarrow H_2 + 0.5O_2$. 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) Using fundamental property relations, establish the expression of standard Gibbs free energy change of a chemical reaction as a function of the thermodynamic equilibrium constant. **07**
- Q.5** (a) Define K-value and explain its importance in vapour-liquid equilibrium calculations. **03**

- (b) Derive the expression of vapour composition at equilibrium using flash vapourization. **04**
 (c) Derive the Gibbs – Duhem equation for a binary solution in terms of activity and activity coefficient. **07**
- Q.6** (a) Write a brief note on ideal solutions. **03**
 (b) Derive the Margules² equations from the expression $\frac{G^E}{x_1 x_2 RT} = A_{21}x_1 + A_{12}x_2$. **04**
 (c) The experimental pressure volume data for benzene at 675 K from a very low pressure to about 75 bar may be approximated by the equation, $V = 0.0561(1/P - 0.0046)$, where V is in m³/mol and P is in bar. What is fugacity of benzene at 1 bar and 675 K ? **07**
- Q.7** (a) Discuss the Gamma/Phi formulation for vapor-liquid equilibrium. **03**
 (b) Discuss criteria of chemical reaction equilibrium with neat sketch. **04**
 (c) The vapour pressures of acetone (1) and acetonitrile (2) can be evaluated by the following Antoine equations: **07**
- $$\ln p_1^{\text{sat}} = 14.5463 - \frac{2940.46}{T - 35.93} \quad \text{and} \quad \ln p_2^{\text{sat}} = 14.2724 - \frac{2945.47}{T - 49.15}$$
- where T in K and p_i^{sat} in kPa. Assuming that the solution formed is ideal, calculate:
- x_1 and y_1 at 327 K and 65 kPa
 - T and y_1 at 65 kPa and $x_1 = 0.4$
- Q.8** (a) Discuss about liquid-liquid equilibrium (LLE). **03**
 (b) Develop expressions for the mole fractions of reacting species as functions of the reaction coordinate for: **04**
- A system initially containing 2 mol of NH₃ & 5 mol of O₂ and undergoing the reaction

$$4\text{NH}_{3(g)} + 5\text{O}_{2(g)} \rightarrow 4\text{NO}_{(g)} + 6\text{H}_2\text{O}_{(g)}$$
 - A system initially containing 3 mol of H₂S & 5 mol of O₂ and undergoing the reaction

$$2\text{H}_2\text{S}_{(g)} + 3\text{O}_{2(g)} \rightarrow 2\text{H}_2\text{O}_{(g)} + 2\text{SO}_{2(g)}$$
- (c) Explain effect of temperature, pressure and total stoichiometric number on equilibrium constant. **07**

GUJARAT TECHNOLOGICAL UNIVERSITY**BE - SEMESTER-IV (NEW) EXAMINATION – WINTER 2021****Subject Code:3140507****Date:05/01/2022****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.
4. Simple and non-programmable scientific calculators are allowed.

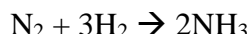
- Q.1** (a) Discuss the criteria of chemical reaction equilibrium. **03**
 (b) Explain in brief T-x-y diagram for binary solutions. **04**
 (c) Discuss and derive the various forms of Gibbs-Duhem Equation. **07**
- Q.2** (a) Define: 1. Partial Molar Properties 2. Raoult's law 3. Activity coefficient **03**
 (b) Derive van't Hoff equation which predicts the effect of temperature on the equilibrium constant. **04**
 (c) Discuss in brief Minimum and maximum boiling azeotropes with diagrams. **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 activity coefficients and 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 assumed to remain constant in the temperature range involved. The vapor pressure of hydrazine at 393 K is 124.76 kPa. **07**
- Q.3** (a) Write a short note on Activity in solution. **03**
 (b) Prove that if Henry's Law is obeyed by component 1 in a binary solution over certain concentration range, Lewis-Randall rule (Raoult's law) will be obeyed by component 2 over the same concentration range. **04**
 (c) Derive the relationship equation for equilibrium constant and standard free energy change. **07**

OR

- Q.3** (a) Discuss the Lewis-Randall rule and its significance. **03**
 (b) Derive the equation for effect of temperature on the chemical potential. **04**
 (c) In the synthesis of ammonia, stoichiometric amounts of nitrogen and hydrogen are sent to a reactor where the following reaction occurs: **07**



The equilibrium constant for the reaction at 675 K may be taken equal to 2×10^{-4} . Determine the % conversion of nitrogen to ammonia at 675 K and 20 bar.

- Q.4** (a) Discuss various methods for evaluation of equilibrium constant. **03**
 (b) Discuss the thermodynamic consistency of experimental VLE data using the slopes of $\ln \gamma$ curves for a binary solution. **04**
 (c) Define excess property. Derive the relationship between excess Gibbs free energy and activity coefficient. **07**

OR

- Q.4** (a) Discuss in brief phase rule for reacting systems. **03**
 (b) State and explain Wilson equation for activity coefficient in a binary mixture. **04**

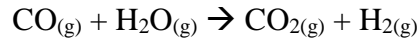
- (c) The Enthalpy at 300 K and 1 bar of a binary liquid mixture is **07**

$$H = 400x_1 + 600x_2 + x_1x_2(40x_1 + 20x_2)$$

Where H is in J/mol. For the stated temperature and pressure, determine:

1. Expressions for \overline{H}_1 and \overline{H}_2 in terms of x_1
2. Numerical values for pure components enthalpies H_1 and H_2
3. Numerical values for the partial molar enthalpies at infinite dilution.

- Q.5 (a)** A gas mixture which contained 1 mol CO, 1 mol water vapor and 1 mol CO_2 is undergoing the following reaction at a temperature of 1100 K and a pressure of 1 bar. **03**



The equilibrium constant for the reaction is $K=1$. Assume that the gas mixture behaves as ideal gas. Calculate the fractional dissociation of steam.

- (b) Discuss the determination of Fugacity of pure gases by using compressibility factor method. **04**
- (c) Discuss the criteria of phase equilibrium for a homogeneous closed system. Also develop criteria of equilibrium under various sets of constraints. **07**

OR

- Q.5 (a)** Define equilibrium constant K of a chemical reaction. How it is related to K_f and K_P ? **03**

- (b) The density of gaseous ammonia at 473 K and 50 bar is 24.3 kg/m^3 . Estimate its fugacity. **04**

- (c) Construct P-x-y diagram for the cyclohexane(1)-benzene(2) system at 313 K given that at 313 K the vapor pressures are $P_1^S = 24.62 \text{ kPa}$ and $P_2^S = 24.41 \text{ kPa}$. The liquid phase activity coefficients are given by **07**

$$\ln \gamma_1 = 0.458 x_2^2 \quad \ln \gamma_2 = 0.458 x_1^2$$

GUJARAT TECHNOLOGICAL UNIVERSITY**BE - SEMESTER-IV (NEW) EXAMINATION – SUMMER 2021****Subject Code:3140507****Date:11/09/2021****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.
4. Simple and non-programmable scientific calculators are allowed.

		MARKS
Q.1	(a) Explain the significance of studying phase equilibria.	03
	(b) Liquid A and B forms an azeotrope containing 46.1 mole percent A at 101.3 kPa and 345 K. The vapour pressure of A is 84.8 kPa and B is 78.2 kPa at 345 K. Calculate activity coefficient for A and B at an azeotropic condition.	04
	(c) Write a short note on flash vaporization.	07
Q.2	(a) Write a brief note on ideal solutions and non-ideal solutions.	03
	(b) Explain the residual volume method for calculating fugacity of pure gaseous component.	04
	(c) A mixture of A and B confirms closely to Raoult's law. At 373 K, the vapour pressure of A and B are 106 and 74 kPa respectively. Determine the composition of the vapour and liquid in equilibrium at 173 K and 101.3 kPa.	07
	OR	
	(c) The vapour pressure of acetone (1) and acetonitrile (2) at 327 K are 85.12 kPa and 39.31 kPa respectively. Assuming that the solutions formed by these are ideal, calculate the total pressure and y_1 at 327 K and $x_1 = 0.5$.	07
Q.3	(a) Discuss about partial molar properties.	03
	(b) What is vaporisation equilibrium constant? How do you estimate the bubble-point temperature of a multicomponent system?	04
	(c) A Gibbs free energy of a binary liquid mixture of Benzene (1) and Toluene (2) at fixed temperature and pressure is represented by the equation: $G = 40X_1 + 30X_2 + X_1X_2$ Where G is in J/mol. Determine chemical potential of benzene and toluene for an equimolar mixture.	07
	OR	
Q.3	(a) Write Lewis-Randall rule and its significance.	03
	(b) What is Poynting correction?	04
	(c) The fugacity of component 1 in binary liquid mixture of components 1 and 2 at 298 K and 20 bar is given by $\bar{f}_1 = 50x_1 - 80x_1^2 + 40x_1^3$ where \bar{f}_1 is in bar and x_1 is the mole fraction of component 1. Determine: a) The fugacity (f_1) of pure component 1 b) The fugacity coefficient (ϕ_1) c) The activity coefficient (γ_1) for an equimolar mixture	07
Q.4	(a) Define fugacity and fugacity coefficient.	03
	(b) Discuss Wilson equation with merits and demerits.	04

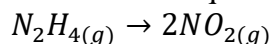
- (c) From vapour–liquid equilibrium measurements for ethanol–benzene system at 318 K and 40.25 kPa it is found that the vapour in equilibrium with a liquid containing 38.4% (mol) benzene contained 56.6% (mol) benzene. The system forms an azeotrope at 318 K. At this temperature, the vapour pressures of ethanol and benzene are 22.9 and 29.6 kPa respectively. Determine the composition and total pressure of the azeotrope. Assume that van Laar equation is applicable for the system. **07**

OR

- Q.4** (a) Define activity and activity co efficient. **03**
 (b) Discuss any one group contribution method to determine Activity coefficients. **04**
 (c) Discuss various methods for checking the consistency of experimental VLE data. **07**
- Q.5** (a) Explain gamma-phi formulation of VLE. **03**
 (b) Define the reaction coordinate. **04**
 (c) Derive from the first principles, $\Delta G^0 = -RT \ln K$. **07**

OR

- Q.5** (a) Discuss about liquid – liquid equilibrium (LLE). **03**
 (b) Write in brief a note on feasibility of chemical reaction. **04**
 (c) Calculate the equilibrium constant at 298 K of the reaction **07**



Given that the standard free energy of formation at 298 K are 97540 J/mol for N₂O₄ and 51310 J/mol for NO₂.

GUJARAT TECHNOLOGICAL UNIVERSITY**BE - SEMESTER-IV (NEW) EXAMINATION – SUMMER 2022****Subject Code:3140507****Date:08-07-2022****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.
4. Simple and non-programmable scientific calculators are allowed.

		MARKS
Q.1	(a) State and explain Duhem's Theorem.	03
	(b) Evaluate the fugacity coefficient at 5 bar for a gas that follows the equation of state $PV = RT(1 - 0.005 P)$, where P is pressure in bar.	04
	(c) In the laboratory of mass transfer, will it be possible to prepare 0.12m ³ of alcohol-water solution by mixing 0.04m ³ alcohol with 0.08m ³ pure water? If not possible, Assess the volume which should have been mixed in order to prepare a mixture of the same strength and of the required volume? Density of ethanol and water are 789kg/m ³ and 997kg/m ³ respectively. Data: The partial molar volumes of ethanol and water at the desired compositions are: Ethanol = 53.6×10^{-6} m ³ /mol; Water = 18×10^{-6} m ³ /mol.	07
Q.2	(a) Derive the equation for determination of fugacity of pure gases using any two methods.	03
	(b) Prove that for a multi component system, chemical potential of each component is the same in all phases.	04
	(c) Molar volume of binary solution is expressed as: $H = 400x_1 + 600x_2 + (40x_1 + 20x_2)x_1x_2$ (i) Acquire the expression for partial molar enthalpies. (ii) Compute pure component enthalpy (iii) Compute enthalpy at infinite dilution.	07
	OR	
	(c) Prove that if Henry's law is obeyed by component 1 in a binary solution over certain concentration range, Lewis–Randall rule (Raoult's law) will be obeyed by component 2 over the same concentration range.	07
Q.3	(a) For a binary solution consider M_1 and M_2 are properties of component 1 and component 2 in a solution. Derive equations to calculate partial properties of component 1 and component 2 in a solution.	03
	(b) The activity coefficients for component 2 in a binary solution can be represented by $\ln \gamma_2 = Ax_1 + Bx_1^2$, where A and B are concentration independent parameters. Derive an expression for $\ln \gamma_1$.	04
	(c) The ethanol-benzene system forms azeotrope with azeotropic composition of 44.8mol% ethanol with boiling point of 341.4K at 101.3kPa. At this temperature the vapor pressure of benzene is 68.9kPa and the vapor pressure of ethanol is 67.4kPa. Compute the activity co-efficient in a solution of Ethanol-Benzene containing 20mol% ethanol using Van Laar equation.	07
	OR	
Q.3	(a) State applications and limitations of Wilson and NRTL equation.	03

- (b) Write steps to determine Bubble point temperature using Raoult's Law. **04**
- (c) A certain experiment was carried out in the laboratory. The results of the data are as shown below. Verify whether the following data are thermodynamically consistent or not? **07**

x_1	0	0.2	0.4	0.6	0.8	1.0
γ_1	0.576	0.655	0.748	0.856	0.950	1.0
γ_2	1.0	0.985	0.930	0.814	0.626	0.379

- Q.4** (a) Explain Liquid-Liquid Equilibrium with suitable example. **03**
- (b) Define azeotrope and explain maximum and minimum boiling azeotrope with a neat diagram. **04**
- (c) Assuming Raoult's law to be valid for the system benzene (1)–ethyl benzene (2) and the vapour pressures are given by the Antoine equation: **07**

$$\ln P_i^{\text{sat}} = \left[A - \left(\frac{B}{T+C} \right) \right], \text{ where } P \text{ is in kPa and } T \text{ is in K.}$$

Species, i	A	B	C
1	13.8858	2788.51	-52.41
2	14.0045	3279.47	-60.00

Construct the P-x-y diagram at 100°C.

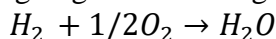
OR

- Q.4** (a) What is retrograde condensation and write its application in chemical industry. **03**
- (b) Two suffix Margules equation is the simplest expression for excess Gibbs free energy. $G^E = \beta x_1 x_2$ where β is an empirical constant. Derive the expression for the activity coefficient of component 1 that results from this equation. **04**
- (c) Assuming the validity of Raoult's law, Evaluate for the system of Acetone (1), Acetonitrile (2) and Nitromethane (3), given the mole fraction of component $x_1 = 0.30$ and $x_2 = 0.40$ and temperature $T = 75^\circ\text{C}$, Compute y_1 and P. **07**

$$\ln P_i^{\text{sat}} = \left[A - \left(\frac{B}{T+C} \right) \right], \text{ where } P \text{ is in kPa and } T \text{ is in K.}$$

Component	A	B	C
Acetone(1)	14.3916	2795.82	230.0
Acetonitrile (2)	14.2724	2945.47	224.0
Nitromethane (3)	14.2043	2972.64	209.0

- Q.5** (a) Describe phase rule for reacting systems **03**
- (b) The water–gas shift reaction takes place at 373K, $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ **04**
The equilibrium constant K_P for this reaction at 537K = 9.8×10^{-4} . The heats of formation at 298K are: $\text{CO} = -110,525\text{J/mol}$, $\text{CO}_2 = -393,509\text{ J/mol}$, $\text{H}_2\text{O} = -241,818\text{ J/mol}$. Calculate the equilibrium constant at 1000 K.
- (c) A gas mixture containing 1.25 moles hydrogen, 0.75 moles oxygen and 0.25 mole water initially, is undergoing the following reaction: **07**



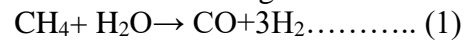
- (i) Derive expressions for the mole fractions of various components in the reaction mixture in terms of the extent of reaction.
- (ii) Explain how the conversion of limiting reactant is related to the extent of reaction.

OR

- Q.5** (a) How would you predict the feasibility of a chemical reaction from the value of standard free energy change? **03**
- (b) What is the effect of temperature on equilibrium constant? Using Van't Hoff equation predict the effect of increasing temperature on endothermic and exothermic reactions. **04**

(c) Consider a system in which the following reactions occur:

07



If 3mol CH_4 and 4mol H_2O are initially present, Compute the mole fraction of the product gases for $\varepsilon_1 = 0.25$ and $\varepsilon_2 = 0.5$