Enrolment No./Seat No_____

GUJARAT TECHNOLOGICAL UNIVERSITY

BE - SEMESTER–IV EXAMINATION – SUMMER 2025

Subject Code:3140507 **Date:23-05-2025**

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)**	Define fugacity, fugacity co efficient, and activity	**03**
	(b)	Derive the equation for determination of fugacity of pure gases using any two methods.	**04**
	(c)	For a system in which the following reaction occurs, $CH_{4(g)} + H_2O_{(g)} \rightarrow CO_{(g)} + 3H_{2(g)}$ Assume there are present initially 2mol of CH_4, 1mol of H_2O, 0.5mol of CO, and 3.5mol of H_2. Determine an expression for the mole fraction yi as function of εe	**07**
Q.2	**(a)**	Write a brief note on Ideal solutions	**03**
	(b)	Define azeotrope and explain maximum boiling azeotrope with a neat diagram.	**04**
	(c)	Estimate activity coefficient of methanol for chloroform (1) / methanol (2) system at 35°C. The vapour pressures of chloroform and methanol at 35°C are 39.54kPa and 27.95kPa respectively, when the mole fraction of methanol in the liquid mixture is 0.4. Margules' parameters are $A_{12} = 0.738$, $A_{21} = 1.868$.	**07**
		OR	
	(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: (i) The fugacity f_1 of pure component 1 (ii) The fugacity coefficient ϕ_1 (iii) The Henry's law constant K_1 (iv) The activity coefficient Υ_1.	**07**
Q.3	**(a)**	Discuss the criteria of phase equilibrium for a homogeneous closed system.	**03**
	(b)	What is partial molar property? Discuss the physical significance and importance of partial molar property.	**04**
	(c)	The molar volume of a binary solution at 300 K and 1 bar is given by: $V = 500x_1 + 1000x_2 + x_1x_2(50\ x_1 + 40x_2)$ cm^3/mol For the stated temperature and pressure, determine: (i) Expressions for $\bar{V}_1$ and $\bar{V}_2$ in terms of x_1 (ii) Numerical values for the partial molar volumes at infinite dilution $\overline{V_1^\infty}$ and $\overline{V_2^\infty}$	**07**
		OR	

Q.3 **(a)** What is retrograde condensation and explain its application in chemical industry. **03**

(b) State applications and limitations of Wilson and NRTL equation. **04**

(c) The vapour pressures of acetone (1) and acetonitrile (2) can be evaluated by the Antoine equations **07**

$$\ln P_1^S = 14.5463 - \frac{2940.46}{T - 35.93}$$

$$\ln P_2^S = 14.2724 - \frac{2945.47}{T - 49.15}$$

Where T is in K and P is in kPa. Assuming that the solutions formed by these are ideal, calculate x1, and y1 at 327 K and 65 kPa

Q.4 **(a)** Determine the fugacity and fugacity coefficient of steam at 623 K and 1000 kPa using enthalpy and entropy values from steam tables. Assume that steam behaves ideally at 101.3 kPa and 623K, H = 3176 kJ/kg; S = 8.38 kJ/kg K. Data from steam tables: At 1000kPa and 623K, **03**

H = 3159 kJ/kg; S = 7.3 kJ/kg K.

(b) The Henry's law constant for oxygen in water at 298 K is 4.4*10 4bar. Estimate the solubility of oxygen in water at 298 K for a partial pressure of oxygen at 0.25 bar. **04**

(c) Write steps to determine Bubble point temperature using Raoult's Law. **07**

OR

Q.4 **(a)** What do you mean by the 'extent of reaction'? How is it related to the mole fraction of the species in the reaction mixture? **03**

(b) Discuss any one group contribution method to determine activity coefficients **04**

(c) The water-gas-shift reaction is carried out under the different sets of conditions described below. Calculate the fraction of steam reacted in each case. Assume the mixture behaving as an ideal gas. **07**

$CO_{(g)} + H_2O_{(g)} \rightarrow CO_{2(g)} + H_{2(g)}$

(i) The reactants consist of 1mol of water vapour and 1mol of carbon monoxide. The equilibrium constant K= 1 for the reaction at temperature of 1100 K and the pressure of 1 bar.

(ii) Same as (i) except that 3 mol of N2 is included in the reactants.

(iii)The reactants are 2 mol of CO and 1 mol of H2O; other conditions are the same as in (i).

Q.5 **(a)** Describe phase rule for reacting systems **03**

(b) Explain any one method for checking the consistency of experimental VLE data. **04**

(c) Explain how the equilibrium constant for liquid reaction is evaluated. **07**

OR

Q.5 **(a)** Calculate the equilibrium constant at 298K of the reaction **03**

$N_2O_{4(g)} \rightarrow 2NO_{2(g)}$

Given that the standard free energies of formation at 298K are 97,540 J/mol for N2O4 and 51,310 J/mol for NO2.

(b) Explain effect of temperature and pressure on equilibrium constant. **04**

(c) Using the fundamental properties relation for single phase reaction, show that $\Delta G0 = -RT \ln K$ **07**

****

Enrolment No./Seat No_____

GUJARAT TECHNOLOGICAL UNIVERSITY

BE - SEMESTER–IV (NEW) EXAMINATION – SUMMER 2024

Subject Code:3140507 Date:08-07-2024

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.**
5. **Notation used have their conventional meanings.**

Q.1 **(a)** Write down Raoult's Law and Henry's Law and explain each term associated with them with their applicability. **03**

(b) Consider a system in which following reactions occur: **04**

$CH_{4(g)} + H_2O_{(g)} \rightarrow CO_{(g)} + 3H_{2(g)}$ and

$CH_{4(g)} + 2H_2O_{(g)} \rightarrow CO_{2(g)} + 4H_{2(g)}$

If there are 2 moles of CH_4 and 3 moles of H_2O present initially then derive the expressions for the mole fractions of the components in terms of extent of the reactions.

(c) Derive Margules equations for determination of activity coefficients of a binary system from the expression: **07**

$$\frac{G^E}{x_1 x_2 RT} = A_{21}x_1 + A_{12}x_2$$

Q.2 **(a)** Discuss the Gamma/Phi formulation for vapor-liquid equilibrium. **03**

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

(c) The vapour pressures of acetone (1) and acetonitrile (2) can be evaluated by the Antoine equations: **07**

$$lnP_1^{sat} = 14.5463 - \frac{2940.46}{T - 35.93} \quad \text{and} \quad lnP_2^{sat} = 14.2724 - \frac{2945.47}{T - 49.15}$$

where T in K and P_i^{sat} in kPa. Assuming that the solution formed is ideal, calculate:

i) P and y_1 at 327 K and $x_1 = 0.4$

ii) P and x_1 at 327 K and $y_1 = 0.4$

iii) x_1 and y_1 at 327 K and 65 kPa

OR

(c) Derive from the first principles, $\Delta G^0 = -RTlnK$ **07**

Q.3 **(a)** Explain modified Raoult's law with all its terms. **03**

(b) Discuss about liquid-liquid equilibrium (LLE). **04**

(c) Explain the minimum boiling and maximum boiling azeotropes with suitable examples. **07**

OR

Q.3 **(a)** Define and explain K-value and its importance in vapour-liquid equilibrium calculations. **03**

(b) Describe the phenomena of retrograde condensation. **04**

(c) Derive the expression used to estimate fraction of initial mixture that is vaporized at equilibrium using flash vaporization calculation. **07**

Q.4 **(a)** Discuss about partial molar properties. **03**

(b) Explain that if Henry's law is obeyed by component 1 in a binary solution over certain concentration range, Lewis-Randall rule will be obeyed by component 2 over the same concentration range. **04**

(c) Derive the Gibbs – Duhem equation for a binary solution in terms of activity and activity coefficient. **07**

OR

Q.4 **(a)** Discuss Wilson equations with their merits and demerits. **03**

(b) Discuss the area test for checking the thermodynamic consistency of experimental vapour-liquid equilibrium (VLE) data. **04**

(c) Discuss the effect of temperature and pressure on chemical potential. **07**

Q.5 **(a)** Discuss the concept of group contribution methods to determine activity coefficients. **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) Explain the effect of temperature and pressure on equilibrium constant. **07**

OR

Q.5 **(a)** Discuss the feasibility of chemical reactions. **03**

(b) Consider a vessel which initially contains only n_o moles of water vapor. If decomposition occurs according to the reaction: $H_2O \rightarrow H_2 + \frac{1}{2}O_2$ **04**

Derive the 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.

(c) The ammonia synthesis reaction written as: **07**

$$\frac{1}{2}N_{2(g)} + \frac{3}{2}H_{2}{}_{(g)} \rightarrow NH_{3(g)}$$

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, derive the following expression:

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

****

Seat No.: _____ Enrolment No._____

GUJARAT TECHNOLOGICAL UNIVERSITY

BE - SEMESTER– IV(NEW) EXAMINATION – SUMMER 2023

Subject Code:3140507 Date:25-07-2023

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**	Write a short note on fugacities of solids and liquids.	**03**
	B	Define the terms: 1.Acivity 2. Fugacity coefficient 3. Residual property 4. fugacity	**04**
	C	Derive the relation between equilibrium constant and standard free energy change.	**07**
Q-2	**A**	Show the P-x-y, T-x-y and x-y curves for the minimum boiling azeotrope.	**03**
	B	Discuss the flash vaporization calculation for vapor and liquid phase equilibrium.	**04**
	C	State the various methods for determination of fugacity of pure gases. Discuss any two methods in detail.	**07**
		OR	
	C	The two-suffix Margules equation for excess Gibbs free energy is $G^E = Ax_1\, x_2$ Where A is empirical constant. Derive the expression for the activity coefficient.	**07**
Q-3	**A**	Discuss the different conditions under which the Lewis-Randall rule becomes applicable.	**03**
	B	Discuss van Laar equation for activity coefficient.	**04**
	C	Discuss and prove the tangent-intercept method to determine partial molar properties.	**07**
		OR	
Q-3	**A**	Define and explain partial molar property and chemical potential.	**03**
	B	Derive the equation which shows the effect of temperature on chemical potential.	**04**
	C	Derive the various forms of Gibbs Duhem equation.	**07**
Q-4	**A**	Discuss Roult's law and ideal solutions.	**03**
	B	Calculate the standard free energy change at 298 K in the gas-phase alkylation of isobutene with ethylene to form neohexane $C_4H_{10\,(g)} + C_2H_{4\,(g)} \rightarrow C_6H_{14\,(g)}$ The free energies of formation at 298 K are -21000 J/mol, 68460 J/mol and -9950 J/mol for isobutane, ethylene and neohexane respectively.	**04**
	C	Laboratory alcohol containing 96% alcohol and 4% water is to be diluted to a solution containing 56% alcohol and 44% water. All percentages are on weight basis. The partial specific volumes are as follows: In 96% alcohol solution, $\overline{V_w} = 0.816 * 10^{-3}$ m^3/kg, $\overline{V_E} = 1.273 * 10^{-3}$m^3/kg. In 56% alcohol solution, $\overline{V_w} = 0.953 * 10^{-3}$ m^3/kg, $\overline{V_E} = 1.243 * 10^{-3}$m^3/kg. The density of water may be taken as 0.997 * 10^3 kg/m^3, (a) How much water should be added to 2 * 10^{-3} m^3 of the laboratory alcohol? (b) What is the volume of the dilute alcohol obtained?	**07**
		OR	
Q-4	**A**	State phase rule for reacting system. Discuss with example.	**03**
	B	A gas mixture containing 3 mol CO_2, 5 mol H_2 and 1 mol water is undergoing the following reactions	**04**

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$
$$CO_2 + H_2 \rightarrow CO + H_2O$$

Develop expressions for the mole fraction of the species in terms of the extent of reaction.

C Prove that if Raoult's law is valid for constituent of a binary solution over the whole concentration range, it must also apply to the other constituents. **07**

Q-5 **A** Explain and discuss the feasibility of a reaction. **03**

B An equimolar solution of benzene and toluene is totally evaporated at a constant temperature of 363 K. At this temperature, the vapor pressures of benzene and toluene are 135.4 and 54 kPa respectively. What are the pressures at the beginning and at the end of the vaporization process? **04**

C In the synthesis of ammonia, stoichiomeric amounts of nitrogen and hydrogen are sent to reactor where the following reaction occurs **07**

$$N_2 + 3H_2 \rightarrow 2\ NH_3$$

The equilibrium constant for the reaction at 675 K may be taken equal to 0.0002. Determine the % conversion of nitrogen to ammonia at 675 K and 20 bar.

OR

Q-5 **A** Explain boiling point diagram for binary solution. **03**

B Define: 1. Extent of reaction 2. Bubble point 3. Azeotrope 4. Henry's law **04**

C Explain and derive the criteria of chemical reaction equilibrium. **07**

Seat No.: _____ Enrolment No._____

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 Duhemn 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 expresses as: $H = 400x_1 + 600\,x_2 + (40x_1 + 20\,x_2)x_1\,x_2$ (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**

$\ln P_i^{sat} = \left[A - \left(\frac{B}{T+C}\right)\right]$, where P is in kPa and T 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°C, Compute y_1 and P. **07**

$\ln P_i^{sat} = \left[A - \left(\frac{B}{T+C}\right)\right]$, where P is in kPa and T 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, $CO + H_2O \rightarrow CO_2 + H_2$ **04**
The equilibrium constant K_P for this reaction at 537K = 9.8×10^{-4}. The heats of formation at 298K are: CO = –110,525J/mol, CO_2 = –393,509 J/mol, H_2O= –241,818 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**

$$H_2 + 1/2O_2 \rightarrow H_2O$$

(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**

$$CH_4 + H_2O \rightarrow CO + 3H_2 \text{..... (1)}$$

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \text{ .....(2)}$$

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 $\varepsilon_2 = 0.5$