CHEMICAL ENGINEERING THERMODYNAMICS
(CHE2203)

Time Allotted : 2½ hrs **Full Marks : 60**

Figures out of the right margin indicate full marks.

Candidates are required to answer Group A and any 4 (four) from Group B to E, taking one from each group.

Candidates are required to give answer in their own words as far as practicable.

Group – A

1. Answer any twelve: **12 × 1 = 12**

Choose the correct alternative for the following

(i) The dead state of a system is
(a) the state at which system is in pressure and temperature equilibrium with the surroundings
(b) the state at which system is in chemical equilibrium with the surroundings
(c) the state at which system must have zero velocity and minimum potential energy
(d) All of these

(ii) As pressure tends to zero, fugacity coefficient value tends to
(a) unity (b) zero
(c) infinity (d) compressibility coefficient

(iii) In which of the following process maximum increase in entropy is observed?
(a) dissolution of salt in water (b) condensation of water
(c) sublimation of naphthalene (d) melting of ice

(iv) For a real solution comprising of two components A and B, the activity coefficient of A (γ_A)
(a) is zero (b) may be positive or negative
(c) is always positive (d) is always negative

(v) For an ideal liquid solution, which of the following is unity?
(a) Activity (b) Fugacity
(c) Activity coefficient (d) Fugacity coefficient

(vi) Which of the following is true for excess property M^E? (M^{ig} thermodynamic property of ideal gas, M^{id} thermodynamic property of ideal solution) (Symbols bear usual significance)
(a) $M^E = M - \sum x_i M_i$ (b) $M^E = M - \sum x_i \overline{M_i}$
(c) $M^E = M - M^{ig}$ (d) $M^E = \Delta M - \Delta M^{id}$

(vii) For partially miscible liquid system the applicable VLE equation is generally_____.
(a) Wilson equation (b) NRTL
(c) UNIQUAC (d) All of the above

(viii) For a concentrated solution the osmotic pressure can be given by _____ (symbols have their usual meaning).

(a) $\pi = -\frac{RT}{\bar{V}_{Solvent}} ln(\gamma_{Solvent} x_{Solvent})$ (b) $\pi = -\frac{RT}{\bar{V}_{Solute}} ln(\gamma_{Solute} x_{Solute})$

(c) $\pi = \frac{x_{Solute} RT}{\bar{V}_{Solvent}}$ (d) $\pi = \frac{x_{Solvent} RT}{\bar{V}_{Solute}}$

(ix) For a specific reaction, which of the following statements can be made about equilibrium constant

(a) it always remains same at different reaction condition
(b) it increases if the concentration of one product is increased
(c) it changes with change in temperature
(d) it may be changed by addition of catalyst

(x) For a chemical reaction at equilibrium, which of the following statements is correct?

(a) The concentrations of reactants and products become zero.
(b) The forward reaction stops completely.
(c) The rate of the forward reaction equals the rate of the reverse reaction.
(d) The equilibrium constant becomes zero.

Fill in the blanks with the correct word

(xi) A system from which finite quantities of heat can be removed without affecting its temperature is called _____.

(xii) A solution that does not obey _____ over the entire range of composition is called a non-ideal solution.

(xiii) For non-electrolyte mixtures containing non-polar fluids _____ VLE model may be appropriate.

(xiv) During bubble point 'T' calculation the degrees of freedom for the system is same as the number of _____.

(xv) In UNIFAC or UNIQUAC the intermolecular forces that are responsible for enthalpy of mixing is represented by _____.

Group - B

2. (a) What is the physical significance of a thermodynamic property called 'Exergy'? Derive the second law efficiency expression for heat engine and heat pump.

[(CO1)(Remember/LOCQ)]

(b) Derive the following relation of μ_{J-T}, Joule-Thompson coefficient from the thermodynamic property relation: (Symbols bear usual significance) $\mu_{J-T} = \frac{v}{C_p}(\alpha T - 1)$ where, α is isobaric thermal volume expansion coefficient.

[(CO4)(Evaluate/HOCQ)]

(2 + 4) + 6 = 12

3. (a) The experimental pressure – volume data for benzene at 400^0C from very low pressure up to 75 atm may be represented by the equation:

$V = RT\left(\frac{1}{P} - 0.0046\right)$ m³/kmol, where P is in atmosphere. What is the fugacity (expressed in atm) of benzene at 400⁰C and 1 atm? *[(CO1)(Analyse/IOCQ)]*

(b) From the following compressibility factor data for hydrogen (H_2) at 0⁰C determine fugacity of hydrogen at 1000 atm.

P, atm	100	200	300	400	500	600	700	800	900	1000
Z	1.06	1.138	1.209	1.283	1.356	1.431	1.504	1.577	1.649	1.720

[(CO1)(Evaluate/HOCQ)]

6 + 6 = 12

Group - C

4. (a) At atmospheric pressure ethyl alcohol and water forms azeotrope at 78.15⁰C and contains 89.43 mol% alcohol. Find the composition of alcohol vapour in equilibrium with a liquid analysing 60 mol% alcohol at this temperature.
Data: Vapour pressures of ethyl alcohol and water at 78.15⁰C are respectively 755 mmHg and 329mm Hg. *[(CO3)(Evaluate/IOCQ)]*

(b) The excess enthalpy (heat capacity) for a liquid mixture of components 1 and 2 at fixed P and T is represented by the equation:

$H^E = x_1x_2(40x_1+20x_2)$

Where H^E is in j/mol. Determine $\bar{H}_1^E$ and $\bar{H}_2^E$ as functions of x_1. *[(CO3)(Analyse/IOCQ)]*

7 + 5 = 12

5. (a) Derive an expression to determine partial molar thermodynamic property of a component in a binary solution. *[(CO3)(Understand/LOCQ)]*

(b) Calculate the partial molar volume of methanol and water in a 40 mol% methanol solution given the following data at 1 bar and 298 K. (x is the mole fraction of methanol)

x	0	0.114	0.197	0.249	0.495	0.692	0.785	0.892	1.0
$V \times 10^6$, m³/mol	18.1	20.3	21.9	23.0	28.3	32.9	35.2	37.9	40.7

[(CO3)(Analyse/IOCQ)]

4 + 8 = 12

Group - D

6. (a) Liquids A and B form an azeotrope containing 46.1 mole per cent A at 101.3 kPa and 345 K. At 345 K, the vapour pressure of A is 84.8 kPa and that of B is 78.2 kPa. Calculate the vanLaar constants, where the equation is given by

$ln\,\gamma_1 = A_{12}\left[1 + \frac{A_{12}x_1}{A_{21}x_2}\right]^{-2}$ and $ln\,\gamma_2 = A_{21}\left[1 + \frac{A_{21}x_2}{A_{12}x_1}\right]^{-2}$. *[(CO3)(Analyse/HOCQ)]*

(b) Write a pseudocode for the bubble point pressure calculation for binary liquid mixtures following NRTL activity model. The model is given as

$ln\,\gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1+x_2G_{21}}\right)^2 + \frac{G_{12}\tau_{12}}{(x_2+x_1G_{12})^2}\right]$ and

$ln\,\gamma_2 = x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2+x_1G_{12}}\right)^2 + \frac{G_{21}\tau_{21}}{(x_1+x_2G_{21})^2}\right]$, where $G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$ and $\tau_{ij} = \frac{b_{ij}}{RT}$.

[(CO3)(Apply/IOCQ)]

6 + 6 = 12

7. (a) Mention the stability criterion for a single phase liquid to be sustained after liquid-liquid mixing along with its mathematical expression. *[(CO3)(Remember/LOCQ)]*

(b) For a binary liquid mixture show that the essential feature for binary VLE is given by $\frac{dy_1}{dx_1} > 0$. *[(CO3)(Analyse/HOCQ)]*

4 + 8 = 12

Group - E

8. (a) Estimate the maximum conversion of ethylene to ethanol by vapour phase hydration at 250^0C and 35 bars for an initial steam to ethylene ratio of 5. The reaction is: $C_2H_4(g) + H_2O(g) = C_2H_5OH(g)$

Data: The equilibrium constant (K) = 9.841×10^{-3}

Material	Fugacity coefficient
Ethylene	0.977
Water vapour	0.896
Ethanol	0.837

[(CO3)(Evaluate/HOCQ)]

(b) Estimate the standard free energy change and equilibrium constant at 700 K for the reaction

A (g) + 3 B (g) = 2 R(g)

Given that the standard heat of reaction and standard free energy of reaction at 298 K

ΔH^0 = -92200 J / mole and ΔG^0 = - 33000 J / mole

The heat capacity (J/mole K) data are given below as function of temperature (K)

$C_P = \alpha + \beta T$

Component	A	B	R
α	27.27	27.01	29.75
$\beta \times 10^3$	4.93	3.51	25.11

[(CO4)(Evaluate/IOCQ)]

7 + 5 = 12

9. (a) Discuss the effect of pressure and presence of inerts on equilibrium composition of chemical reaction. Using van't Hoff equation, predict the effect of increasing temperature on endothermic and exothermic reactions. *[(CO3)(Understand/LOCQ)]*

(b) Calculate the equilibrium constant at 298 K of the reaction $N_2 + 3H_2 = 2NH_3$, given that the free energy of formation of ammonia at 298 K is -16500 J/mol.

[(CO4)(Evaluate/IOCQ)]

(4 + 4) + 4 = 12

Cognition Level	LOCQ	IOCQ	HOCQ
Percentage distribution	22.92	42.71	34.37