CHEMICAL ENGINEERING THERMODYNAMICS
(CHEN 2203)

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) For a system in equilibrium, at a given temperature and pressure
(a) the entropy must be maximum
(b) the enthalpy must be minimum
(c) the Gibb's free energy must be minimum
(d) all of these.

(ii) If second law efficiency of a process is 100%, it means the process is
(a) isenthalpic (b) isothermal (c) reversible (d) irreversible.

(iii) Fugacity has the same dimension as that of
(a) Gibb's free energy (b) pressure
(c) temperature (d) volume.

(iv) For a real gas, the chemical potential is given by
(a) RTdlnP (b) RTdlnf (c) Rdlnf (d) None of the above

(v) An aqueous solution of ethanol contains 60 mole % ethanol. If the partial molar volumes of ethanol and water are 57.5ml/mole and 16.0 ml/mole respectively, the molar volume of the mixture is
(a) 40.9 ml/mole (b) 73.5 ml/mole
(c) 41.5 ml/mole (d) none of the above.

(vi) If an ideal solution is formed by mixing two pure liquids in any proportion, then the _____ of mixing is zero.
(a) enthalpy (b) volume
(c) both (a) and (b) (d) neither (a) nor (b)

(vii) Activity co-efficient is a measure of the
(a) departure from ideal solution behavior
(b) departure of gas phase from ideal gas law
(c) vapour pressure of liquid
(d) none of the above.

(viii) Van Laar equation predicts the activity co-efficient from experimental data
(a) True (b) False
(c) True for ideal solution only (d) None of these.

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

(x) Chemical potential is a/an
(a) extensive property
(b) intensive property
(c) force which drives the chemical system to equilibrium
(d) both (b) and (c).

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) The maximum work available with a system at elevated temperature and pressure is called _____.

(xiii) For a given liquid at a specified temperature, activity is _____ to fugacity.

(xiv) The partial molar free energy is equal to the _____ for a pure substance.

(xv) _____ equation predicts the activity co-efficient from experimental data.

Group - B

2. (a) A rigid evacuated tank is connected to supply line carrying an ideal gas at fixed temperature and pressure. If the valve between the tank and the supply line is opened, gas flows into the tank till the pressure inside the tank become equal to the supply line pressure. Determine an expression to calculate the temperature of the gas in the tank after the filling operation. *[(CO1)(Evaluate/HOCQ)]*

(b) What is residual property of a pure substance? Establish the following relation of a substance: $G^R = RT \ln \phi$ (Symbols bear usual significance). *[(CO1)(Analyze/IOCQ)]*

6 + (2 + 4) = 12

3. (a) Calculate the fugacity of CO at 400 bar 273 K from the data given below at 273 K:

P, bar	25	50	100	200	400	800	1000
Z	0.989	0.9792	0.9741	1.0196	1.2482	1.8057	2.0819

[(CO1)(Evaluate/LOCQ)]

(b) Establish the following thermodynamic relation from the fundamental property relation: $dh = c_p dT + v(1 - T\alpha)dP$ where, α is isobaric thermal volume expansion coefficient. *[(CO1) (Analyze/IOCQ)]*

7 + 5 = 12

Group - C

4. (a) Define chemical potential. Express chemical potential as a criterion of phase equilibrium. *[(CO3)(Understand/LOCQ)]*

(b) It is required to prepare in a chemical laboratory, 1000 dm^3 of a solution containing 60 mol% ethanol (A) and 30 mol% water (B). From the data given below determine the volumes of A and B to be mixed to get the required solution.

Data:

Liquid Component	Molar volume of pure component, dm^3/mol	Partial Molar volume of pure component, dm^3/mol
A	0.0579	0.0575
B	0.018	0.016

[(CO3)(Evaluate/IOCQ)]

(2 + 4) + 6 = 12

5. (a) For a binary solution of components A and B, activity coefficient is given by

$$\ln \gamma_A = -(3x_1x_2^2 + 1.8x_2^2) \text{ and } \ln \gamma_B = -(2.6x_1^3 + x_1^2x_2)$$

Does it follow Gibbs-Duhem equation? *[(CO3)(Evaluate/HOCQ)]*

(b) Discuss how partial molar properties can be evaluated using graphical technique. *[(CO3)(Analyse/IOCQ)]*

6 + 6 = 12

Group - D

6. (a) At atmospheric pressure ethyl alcohol and water forms azeotrope at 78.15^{0}C 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 78.15^{0}C are respectively 755 mmHg and 329mm Hg. *[(CO2)(Evaluate/HOCQ)]*

(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)(Evaluate/HOCQ)]

7 + 5 = 12

7. (a) Show that the Wilson equation

$$G^E/RT = -x_1 \ln(x_1 + x_2\lambda_{12}) - x_2 \ln(x_2 + x_1\lambda_{21})$$

satisfies the stability criteria for all values of $\lambda_{12}, \lambda_{21}$ and x_1. *[(CO4)(Evaluate/IOCQ)]*

(b) Draw and explain the Pressure – Composition (P – x – y) diagram of a Binary system. *[(CO4)(Remember/LOCQ)]*

7 + 5 = 12

Group - E

8. (a) Ethanol can be manufactured by the hydration of ethylene according to the reaction:

$$C_2H_4\,(g) + H_2O\,(g) = C_2H_5OH\,(g)$$

The feed to the reactor in which the above reaction takes place is a gas mixture containing 25 mol% ethylene and 75 mol% of steam. Estimate the product composition if the reaction occurs at 393 K and 101.3 kPa. A value of ΔG^0 at 393 K is given 4530 J/mol. *[(CO5) (Analyse/IOCQ)]*

(b) A gas mixture containing 3 mol CO_2, 5 mol H_2 and 1 mol water is undergoing the following reactions:

$$CO_2 + 3H_2 = CH_3OH + H_2O$$
$$CO_2 + H_2 = CO + H_2O$$

Develop an expression for the mol fraction of CO_2 in terms of the extent of reaction. *[(CO5)(Evaluate/LOCQ)]*

8 + 4 = 12

9. (a) Prove that for a chemical reaction the standard free energy change(ΔG^0) and equilibrium constant (K) are related by the relation:

$$\Delta G^0 = - RT \ln K$$ *[(CO5)(Analyse/IOCQ)]*

(b) Calculate the equilibrium constant at 298K of the reaction

$$N_2O_4(g) = 2NO_2(g)$$

Given that the standard free energies of formation at 298K are 97540 J/mol for N_2O_4 and 51310 J/mol for NO_2. *[(CO5)(evaluate/LOCQ)]*

8 + 4 = 12

Cognition Level	LOCQ	IOCQ	HOCQ
Percentage distribution	27.08	47.92	25.00

Course Outcome (CO):

After the completion of the course students will be able to

1. Understand the basic knowledge that allows the students to solve problems relating fugacity of pure components as well as in mixture.
2. Apply the concept of chemical potential as criterion of phase equilibrium.
3. Apply concept of partial molar properties in solution thermodynamics.
4. Understand the basic knowledge that allows the students to solve problems on equilibrium of different phases involving no chemical reaction.
5. Understand the basic knowledge that allows the students to solve problems on chemical reaction equilibrium.

**LOCQ: Lower Order Cognitive Question; IOCQ: Intermediate Order Cognitive Question; HOCQ: Higher Order Cognitive Question.*