THERMODYNAMICS II
(CHEN 2203)

Time Allotted : 3 hrs **Full Marks : 70**

Figures out of the right margin indicate full marks.

Candidates are required to answer Group A and any 5 (five) from Group B to E, taking at least one from each group.

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

Group – A
(Multiple Choice Type Questions)

1. Choose the correct alternative for the following: **10 × 1 = 10**

(i) Work done in free expansion process is
(a) zero (b) minimum (c) maximum (d) can't be determined.

(ii) A gas deviates from ideal behaviour when it is subject to
(a) high temp & low pressure (b) high temp. & high pressure
(c) low temp. & high pressure (d) low temp. & low pressure.

(iii) The free energy change for a chemical reaction is given by
(a) RT lnK (b) –RTlnK (c) RlnK (d) -RlnK.

(iv) In a homogeneous solution, activity co-efficient of a component depends on
(a) pressure (b) temperature (c) composition (d) all of these.

(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) The throttling process is a/an
(a) isobaric process
(b) irreversible steady flow process
(c) irreversible isothermal process
(d) reversible adiabatic process.

(viii) For an exothermic reaction, the increase in temperature results in
(a) increase of K (b) decrease of K
(c) no change of K (d) can't be predicted.
K is reaction equilibrium constant.

(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 the equilibrium yield in a gas phase reaction, diluting the reaction mixture with an inert gas
(a) has the same effect as that of an increase in pressure
(b) has the same effect as that of an decrease in pressure
(c) has no correlation with change in pressure
(d) always produces unfavorable results.

Group- B

2. (a) A two stage adiabatic compressor with inter-stage cooler is to be used to compress an ideal gas stream from pressure P_1 to P_2 ($P_2>P_1$). The inter-stage cooler keeps the inlet temperature of gas to both the compressors same. Show that, for minimum power requirement of the compressor assembly inter-stage pressure is the geometric mean of P_1 and P_2. [(CO1)(Apply/IOCQ)]

(b) Now determine the minimum power requirement with the following data: P_1 = 1 atm, P_2 = 10 atm, inlet temperature of the gas (γ = 1.4) is 27°C flowing at a mass flow rate of 1 kg/s. (Molecular weight of the gas = 29). [(CO1)(Evaluate/HOCQ)]

7 + 5 = 12

3. (a) Prove the following relation:

$\ln f/P = \int_0^P (z-1)dP/P$. [(CO1)(Remember/LOCQ)]

(b) Calculate the fugacity of CO_2 gas at 100^{0}C and 50 atm pressure given:

Pressure (P), atm	0	14	22	30	44	58	68
Z	1	0.95	0.92	0.89	0.84	0.79	0.76

[(CO1)(Evaluate/HOCQ)]

6 + 6 = 12

Group - C

4. (a) Deduce Gibbs – Duhem equation. [(CO3)(Analyse/IOCQ)]

(b) It is required to prepare 2000 ml of a solution consisting of 30 mol% A and 70 mol% water. What volume of pure A and pure water at 25^{0}C must be mixed to form the 2000 ml solution also at 25^{0}C
Data: Partial molar volume of A at 25^{0}C = $\overline{V_1}$ = 38.632 ml/mol

Partial molar volume of water at 25^0C = $\overline{V_2}$ = 17.765 ml/mol
For the pure species at 25^0C
Molar volume of A = V_1 = 40.727 ml/mol
Molar volume of water = V_2 = 18.068 ml/mol. [(CO3)(Evaluate/HOCQ)]

6 + 6 = 12

5. (a) For a binary liquid mixture at constant temperature and pressure excess Gibbs energy is given by
$G^E/RT = -(0.4\,x_1 + 0.5\,x_2)\,3x_1x_2$
Does it follow Gibbs-Duhem equation? [(CO3)(Analyse/IOCQ)]

(b) It is required to prepare 3 m^3 of a 60 mole% ethanol – water mixture. Determine the volumes of ethanol and water to be mixed in order to prepare the required solution. Given:

Component	Partial molar volume, m^3/mole	Molar volume of pure component, m^3/mole
Ethanol	57.5×10^{-6}	57.9×10^{-6}
Water	16.0×10^{-6}	18.0×10^{-6}

[(CO3)(Evaluate/HOCQ)]

6 + 6 = 12

Group - D

6. (a) The azeotrope of the ethanol-benzene system has a composition of 44.8 mol% ethanol with a boiling point of 341.4K. At this temperature the vapour pressures of benzene and ethanol are respectively 68.9 kPa and 67.4 kPa. Find the vapour composition of benzene in equilibrium with a solution containing 10 mol% ethanol and rest benzene at 341.4K. [(CO2)(Evaluate/HOCQ)]

(b) Discuss in details the characteristics of liquid – liquid equilibrium.
[(CO3)(Analyse/IOCQ)]

6 + 6 = 12

7. (a) The enthalpy of a binary liquid system of components 1 and 2 at constant temperature and pressure is given by $H = 400x_1 + 600x_2 + x_1x_2(40x_1 + 20x_2)$ j/mol Calculate and plot partial molar enthalpy as a function of x_1.
[(CO4)(Analyse/IOCQ)]

(b) Show by stability analysis that Liquid Liquid Equilibrium is predicted by the expression $G^E/RT = Ax_1x_2$ A ≥ 2. [(CO4)(Analyse/IOCQ)]

6 + 6 = 12

Group - E

8. (a) How is equilibrium constant of chemical reaction defined? What are the factors on which equilibrium constant of chemical reaction depend?
[(CO4,5)(Remember/LOCQ)]

(b) A gas mixture containing 2 mol CH_4, 3 mol H_2O and 1 mol H_2 is undergoing the following reactions:

CH_4 (g) + H_2O (g) ↔ CO (g) + $3H_2$ (g)
CH_4 (g) + $2H_2O$ (g) ↔ CO_2 (g) + $4H_2$ (g)
Determine the expression for mole fraction of each species in terms of extent of reaction. [(CO5)(Analyze/IOCQ)]

7 + 5 = 12

9. An equimolar mixture of CH_4(g) and H_2O(g) enters a reactor which is maintained at 1000 K and 5 bar. The following reaction is likely to occur in the reactor:
$CH_4(g) + H_2O(g) = CO(g) + 3H_2(g)$
Estimate the conversion of CH_4 into the product at the reactor condition. Given:
$C_p = A + BT$

Component	A	Bx10^3
CH_4(g)	17.45	60.45
H_2(g)	27.01	3.51
H_2O(g)	28.85	12.06
CO(g)	28.07	4.63

At 298K:

Component	$H_f^0, kJ/mol$	$G_f^0, kJ/mol$
CH_4(g)	-74.94	-50.66
CO(g)	-110.53	-137.37
H_2O(g)	-242.00	-228.60

[(CO5)(Evaluate/HOCQ)]

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Cognition Level	LOCQ	IOCQ	HOCQ
Percentage distribution	13.5	43.8	42.7

Course Outcome (CO):

Course Outcomes: To introduce the concepts of fugacity, activity coefficient, vapour - liquid equilibrium, reaction equilibrium, and introduction to molecular thermodynamics. After completion of the course students will be able to:

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