

**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) 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) An ideal gas at temperature T_1 and pressure P_1 is compressed isothermally to a pressure P_2 ($>P_1$) in a closed system. Which of the following is true of the gas at two states?
(a) $U_1 = U_2$, $G_1 > G_2$
(b) $H_1 = H_2$, $G_1 < G_2$
(c) $U_1 > U_2$, $G_1 = G_2$
(d) $H_1 < H_2$, $G_1 = G_2$
- (iii) 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
- (iv) If an ideal solution is formed by mixing two pure liquids in any proportion, then the volume change of mixing is
(a) positive
(b) negative
(c) zero
(d) infinite
- (v) At equilibrium condition, the chemical potential of a material in different phases in contact with each other is equal. The chemical potential (μ) in real gas is given by _____, when 'f' is the fugacity for real gas and standard fugacity (f°)=1 (the gas behaves ideally).
(a) $\mu^\circ + RT \ln(f)$
(b) $\mu^\circ + R \ln(f)$
(c) $\mu^\circ + T \ln(f)$
(d) $\mu^\circ + (R/T) \ln(f)$

- (vi) Solute in a dilute solution obeys _____.
 (a) Raoult's law (b) Henry's law
 (c) Amagat's law (d) either (A) or (B)
- (vii) 5 moles of liquid X and 10 moles of liquid Y make a solution having a total vapour pressure 9 kPa. The vapour pressures of pure X and pure Y are 8.5 kPa and 10 kPa respectively. The solution _____.
 (a) shows positive deviation
 (b) shows negative deviation
 (c) is ideal
 (d) has volume greater than the individual volume
- (viii) The free energy change for a chemical reaction is given by
 (a) $RT \ln K$ (b) $-RT \ln K$
 (c) $R \ln K$ (d) $-R \ln K$
- (ix) For an exothermic reaction, the increase in temperature results in (K is reaction equilibrium constant)
 (a) increase of K (b) decrease of K
 (c) no change of K (d) can't be predicted
- (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 a decrease in pressure
 (c) has no correlation with change in pressure
 (d) always produces unfavorable results.

Fill in the blanks with the correct word

- (xi) According to phase rule, triple point of a pure substance is _____.
 (xii) The unit of fugacity is the same as that of the _____.
 (xiii) The constant boiling mixture are called _____.
 (xiv) In UNIQUAC model the structural units in a solution is called _____.
 (xv) The chemical equilibrium is _____ in nature.

Group - B

2. (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/HOCQ)]

- (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

3. (a) An ideal gas at P_i and T_i enters a reversible and adiabatic nozzle with negligible inlet velocity and leaves at a pressure P_e . Derive an expression to estimate the exit velocity of the gas. [[CO1](Analyse/LOCQ)]
- (b) A boiler produces steam at 1 MPa and 300°C. The steam from the boiler is used to operate a turbine. The turbine exhausts steam into an evacuated tank of volume 100 m³. The turbine operates till the pressure in the tank rises to 1 MPa at which point the temperature of steam in the tank is 250°C. Assuming that the turbine and the tank are adiabatic, determine the work delivered by the turbine. Given, steam at 1MPa and 250°C: $v = 0.232 \text{ m}^3/\text{kg}$; $h = 2939.45 \text{ kJ/kg}$. Steam at 1MPa and 300°C: $h = 3052.1 \text{ kJ/kg}$. [[CO1](Evaluate/HOCQ)]

6 + 6 = 12

Group - C

4. (a) What is Gibbs-Duhem equation? What are the major fields of application of Gibbs-Duhem equation? [[CO3](Understand/LOCQ)]
- (b) It is required to prepare 2000ml of a solution consisting of 30 mol% A and 70 mol% water. What volume of pure A and pure water at 25°C must be mixed to form the 2000 ml solution also at 25°C.

Data: Partial molar volume of A at 25°C = $\bar{V}_1 = 38.632 \text{ ml/mol}$

Partial molar volume of water at 25°C = $\bar{V}_2 = 17.765 \text{ ml/mol}$

For the pure species at 25°C, Molar volume of A = $V_1 = 40.727 \text{ ml/mol}$, Molar volume of water = $V_2 = 18.068 \text{ ml/mol}$. [[CO3](Analyse/IOCQ)]

(3 + 3) + 6 = 12

5. (a) What is Lewis-Randall rule of solution or mixture? How it is different from Henry's law? [[CO3](Understand/LOCQ)]
- (b) Establish logically that if Henry's law is applicable for solute in a solution then Lewis-Randall rule will be applicable for the solvent of the solution. [[CO3](Analyse/HOCQ)]

- (c) The fugacity of component 1 in binary liquid mixture of a 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 the fugacity and fugacity coefficient of pure component 1. Also evaluate the activity coefficient and Henry's law constant of component 1 in the solution. [[CO3](Evaluate/IOCQ)]

(2 + 2) + 3 + 5 = 12

Group - D

6. (a) What is meant by colligative property of a solution? If a solution is infinitely dilute, what will be the value of the vapour pressure of the solvent 'S', when the pure solvent vapour pressure is equal to 12.4 kPa at 50°C? – Justify your answer. [[CO3](Remember/LOCQ,Apply/IOCQ)]

- (b) Show that for 1 mole of a solute the excess enthalpy is linearly varying with temperature, when the molar specific heat is constant. [[CO3](Analyse/HOCQ)]
(2 + 4) + 6 = 12
7. (a) What is meant by non-randomness in VLE model like NRTL? What does combinatorial part represents in UNIQUAC model? [[CO3](Remember/LOCQ)]
- (b) For binary system n-pentanol(1)/n-hexane(2), the Wilson equation constants are $a_{12} = 7192$ kJ/kmol, $a_{21} = 697$ kJ/kmol. Assuming the vapor phase to be an ideal gas, determine the composition of the vapor in equilibrium with a liquid containing 20 mole% n-pentanol at 30°C. Also calculate the equilibrium pressure. Given vapour pressure of n-pentanol at 30°C is 0.4 kPa and that for n-hexane is 24.9 kPa. Molar volume of n-pentanol = 0.108 m³/kmol and n-hexane=0.130 m³/kmol. [[CO3](Apply/IOCQ)]
(2 + 2) + 8 = 12

Group - E

8. (a) For the vapour phase reaction $P_4 \rightleftharpoons 2P_2$ carried out at 2000 K, the equilibrium reaction mixture contains 80 mol% P_2 . Find the total pressure of the system. Note that the stoichiometric quantity of reactant was fed to the reactor. Data: At 2000 K, $\Delta G^0 = 225400 + 7.90 T \ln T - 209.4T$ [[CO3](Evaluate/HOCQ)]
- (b) A gas mixture containing 2 mole nitrogen, 7 moles hydrogen and 1mole ammonia initially is undergoing the following reaction:

$$N_2 + 3H_2 = 2NH_3$$
Derive an expression for the mole fraction of NH_3 in terms of the extent of reaction. [[CO4](Analyse/IOCQ)]
8 + 4 = 12
9. (a) Derive a relation between chemical reaction equilibrium constant with the standard Gibb's free energy change of the reaction. [[CO3](Analyse/LOCQ)]
- (b) A gaseous mixture containing 30% CO , 50% H_2 and the rest is inert gas is sent to a reaction chamber for methanol synthesis. The following reaction occurs at 635 K and 310 bar.

$$CO(g) + 2H_2(g) = CH_3OH(g)$$
Assuming that the gas mixture behaves like an ideal gas mixture, calculate the percent conversion of CO given that $K_f = 5 \times 10^{-5}$ and $K_\phi = 0.35$. [[CO4](Evaluate/HOCQ)]
6 + 6 = 12

Cognition Level	LOCQ	IOCQ	HOCQ
Percentage distribution	27.1	35.4	37.5