

B. Tech-5 (Chem. Engg)
Chemical Engineering Thermodynamics

Full Marks : 70

Time : 3 hours

Answer all questions.

The figures in the right-hand margin indicate marks.

Symbols carry usual meaning.

1. Answer *all* questions : 2 × 10
- (a) Define first law of thermodynamics and mention its limitations.
 - (b) What is a quasi-static process ? Give example.
 - (c) What is the physical significance of virial coefficients ?
 - (d) What does the Kelvin-Planck statement of the second law of thermodynamics say ?
 - (e) What is the effect of temperature and pressure on the activity coefficient of a component in a solution ?

(Turn Over)

(2)

- (f) Define activity and activity coefficient.
- (g) Define Raoult's law. Mention its limitations.
- (h) What is an azeotrope and how many types of azeotropes are there ?
- (i) Define reaction coordinate. What is its effect on temperature and pressure ?
- (j) What is the standard Gibbs free energy change of a chemical reaction and how it is related to the equilibrium constants ?
2. (a) With proper assumption derive van der Waals equation of state. 4
- (b) Reported values for the virial coefficients of *n*-octane vapor at 456.37 K are $B = -0.326 \text{ m}^3 \text{ mol}^{-1}$, $C = -24 \times 10^{-3} \text{ m}^6 \text{ mol}^2$. Calculate V and Z for *n*-octane vapor at 456.37 K and 10 bar by
- (i) The ideal gas equation
- (ii) Pressure explicit virial expression with 2nd term
- (iii) Pressure explicit virial expression with 3rd term. 6

(3)

Or

- (a) With neat sketch explain the PT and TV diagram of pure substance. 4
- (b) One mole of air, initially at 423.15 K and 8 bar, undergoes the following mechanically reversible changes. It expands isothermally to a pressure such that when it is cooled at constant volume to 323.15 K its final pressure is 3 bar. Assuming air is an ideal gas for which $C_p = 7/2R$ and $C_v = 5/2R$, calculate W, Q, dU and dH. 6
3. One mole of an ideal gas, initially at 303.15 K and 1 bar, is changed to 403.15 K and 10 bar by three different mechanically reversible processes.
- (a) The gas is first heated at constant volume until its temperature is 403.15 K; then it is compressed isothermally until its pressure is 10 bar.
- (b) The gas is first heated at constant pressure until its temperature is 403.15 K; then it is compressed isothermally to 10 bar.

(4)

- (c) The gas is first compressed isothermally to 10 bar, then it is heated at constant pressure to 403.15 K.

Calculate Q , W , dU and dH in each case. Take $C_p = 7/2 R$ and $C_v = 5/2 R$. 10

Or

- (a) With neat sketch write the working principle of Carnot engine. 4

- (b) A vessel, divided into two parts by a partition, contains 4 mol of nitrogen gas at 348.15 K and 30 bar on one side and 2.5 mol of argon gas at 403.15 K and 20 bar on the other. If the partition is removed and the gases mix adiabatically and completely. What is the change in entropy? Assume nitrogen to be an ideal gas with $C_v = 5/2 R$ and argon to be an ideal gas with $C_v = 3/2 R$. 6

4. (a) Derive the expression of Gibbs Duhem equation for a solution containing multi component mixture. 5

(5)

(b) The molar enthalpy of a binary solution at constant T and P is given by the relation

$$\bar{H} = 500X_1 + 1000X_2 + (50X_1 + 40X_2) X_1X_2$$

Where H is in J/mol. Determine \bar{H}_1 and \bar{H}_2 as function of X_1 and the numerical values of the pure component H_1 and H_2 . Also determine the partial molar enthalpies at infinite dilution. 5

Or

Calculate the fugacity and fugacity coefficient for one mole liquid n-octane and vapor at 427.85 K and 0.215 MPa. Assume that n-octane follows the van der Waals equation of state. The van der Waals constants a and b are $3.789 \text{ Pa}(\text{m}^3/\text{mol})^2$ and $2.37 \times 10^{-4} \text{ m}^3/\text{mol}$ respectively. Use iterative method. 10

5. Mixtures of n-pentene (1) and n-heptane (2) conform to ideal solution behavior. The vapor pressures of pure components are adequately described by the Antoine equation. Prepare

- (i) P-x-y diagram at 70 °C
- (ii) T-x-y diagram at a pressure of 101.325 kPa (760 Torr).

The Antoine constant for n-pentene (1) and n-heptane (2) are given by 10

(6)

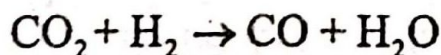
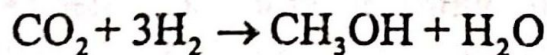
Component	A	B	C
n-pentene (1)	6.84268	1043.206	233.344
n-heptane (2)	6.89386	1264.370	216.640

Or

Derive the expression of fugacity and fugacity coefficient for a component in a mixture which obeys van der Waals equation of state. 10

6. (a) Write the effect of operating condition on degree of conversion at equilibrium. 5

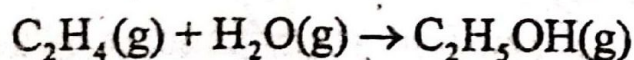
(b) A system formed initially of 2 mol CO₂, 5 mol H₂ and 1 mol CO undergoes the reactions



Develop expressions for the mole fractions of the reacting species as function of the reaction coordinates for the two reactions. 5

Or

Ethanol can be produced according to the reaction



Formula	A	B × 10 ³	C × 10 ⁶	D × 10 ⁹	E × 10 ⁻³
C ₂ H ⁴ (g)	4.196	154.565	-81.076	16.813	-
H ₂ O(g)	28.850	12.055	-	-	1.006
C ₂ H ₅ OH(g)	20.691	205.346	-99.793	18.825	-

10

Heat capacities constant for C₂H⁴, H₂O and C₂H₅OH are

Formula	ΔH ^f (kJ/mol)	ΔG ^f (kJ/mol)
C ₂ H ⁴ (g)	52.335	68.245
H ₂ O(g)	-241.818	-228.572
C ₂ H ₅ OH(g)	-235.100	-168.490

If an equimolar mixture of ethylene and water vapor is fed to a reactor which is maintained at 1000 K and 1 bar determine the degree of conversion and the composition of the reaction mixture at equilibrium, assuming that the reaction mixture behaves like an ideal gas. Data :
Standard enthalpies and Gibbs free energies of formation of C₂H⁴, H₂O and C₂H₅OH