Total Pages—7

(Set-SP)

# 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 : $2 \times 10$

(*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* )

(*f*) Define activity and activity coefficient.

(*g*) Define Raoults 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 standards 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 $m^3$ $mol^{-1}$, C = $-24 \times 10^{-3}$ $m^6$ $mol^2$. 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

*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 $C_v = 5/2\,R$, 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.

(*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

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

$$H = 500X_1 + 1000X_2 + (50X_1 + 40X_2)X_1X_2$$

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 $Pa(m^3/mol)^2$ and $2.37 \times 10^{-4}$ $m^3/mol$ 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

| 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 $CO_2$, 5 mol $H_2$ and 1 mol CO undergoes the reactions

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$

$$CO_2 + H_2 \rightarrow CO + H_2O$$

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

$$C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(g)$$

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 $C_2H_4$, $H_2O$ and $C_2H_5OH$

| Formula | $\Delta H_f^0$ (kJ/mol) | $\Delta G_f^0$ (kJ/mol) |
|---|---|---|
| $C_2H_4(g)$ | 52.335 | 68.245 |
| $H_2O(g)$ | –241.818 | –228.572 |
| $C_2H_5OH(g)$ | –235.100 | –168.490 |

Heat capacities constant for $C_2H_4$, $H_2O$ and $C_2H_5OH$ are

| Formula | A | $B \times 10^3$ | $C \times 10^6$ | $D \times 10^9$ | $E \times 10^{-5}$ |
|---|---|---|---|---|---|
| $C_2H_4(g)$ | 4.196 | 154.565 | –81.076 | 16.813 | - |
| $H_2O(g)$ | 28.850 | 12.055 | - | - | 1.006 |
| $C_2H_5OH(g)$ | 20.691 | 205.346 | –99.793 | 18.825 | - |

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