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

Full Marks: 70

Time: 3 hours

Answer six questions including Q.No.1 which is compulsory.

The figures in the right-hand margin indicate marks.

Symbols carry usual meaning.

1. Answer all:

 2×10

- (a) State the limitations of first law of thermodynamics wit example.
- (b) An egg, initially at rest, is dropped onto a concrete surface and breaks. With the egg treated as the system, what is the sign of W, Q and ΔE_p .
- (c) Calculate ΔU and ΔH for 1 kg of water when it is vaporized at the constant temperature of 373.15 K and the constant pressure of 101.325

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kPa. The specific volumes of liquid and vapour water at the conditions are 0.00104 and 1.673 m³ kg⁻¹. For this change, heat in the amount of 2256.9 kJ is added to the water.

- (d) One mole of an ideal gas is compressed in a piston cylinder assembly from the initial state 0.1 MPa and 300 K till its volume is reduced to 1/15 of the original volume. The process of compression can be approximated as a polytropic process with n = 1.2. Determine the final temperature, pressure and work done on the gas.
- (e) State Kelvin-Plank and Clausius statement of second law of thermodynamics.
- (f) Define partial molar properties of a component in a solution.
- (g) Define activity and activity coefficients of a component in a solution.
- (h) Define Raoults law and its limitations.
- (i) State third law of thermodynamics.
- (j) Write the effect of temperature on equilibrium constant in a reaction mixture. (Continued)

- 2. (a) With neat sketch explain the PT and TV diagram of pure substance.
 - (b) Reported values for the virial coefficients of isopropanol vapor at 473.15 K (200 °C) are:

 $B = -0.3888 \,\mathrm{m}^3 \,\mathrm{kmol}^{-1}$

 $C = -26 \times 10^{-3} \,\mathrm{m}^6 \,\mathrm{kmol}^{-2}$

Calculate V and Z for isopropanol vapour at 473.15 K (200 °C) and 10 bar by:

- (i) The ideal gas equation
- (ii) Virial equation with 2nd term
- (iii) Virial equation with 3rd term.
- 3. Air is compressed from an initial condition of 1 bar and 298.15 K (25 °C) to a final state of 5 bar and 298.15 K (25 °C) by three different mechanically reversible processes in a closed system:
 - (i) Heating at constant volume followed by cooling at constant pressure
 - (ii) Isothermal compression
 - (iii) Adiabatic compression followed by cooling at constant volume.

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Assume air to an ideal gas with the constant heat capacities, $C_v = (5/2)R$ and $C_p = (7/2)R$. Calculate the work required, heat transferred and the changes in internal energy and enthalpy of the air for each process. At 298.15 K and 1 bar the molar volume of air is 0.02479 m³/mol. 10

- 4. (a) Derive the expression of Gibbs Duhem equation for a solution containing multi component mixture.
 - (b) The molar enthalpy of a binary solution at constant T and P is given by the relation $h = 500x_1 + 1000x_2 + (50x_1 + 40x_2)x_{12}$ where h is in J/mol. Determine $\overline{h_1}$ and $\overline{h_2}$ 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. Derive the expression of fugacity and fugacity coefficient for a component in a mixture which obeys van der Waals equation of state.
- 6. Mixture of Benzene (1) and Tolune (2) conform to ideal solution behaviour. The vapor pressure of pure components are adequately described by the Antoine equation. Prepare:

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(Continued)

- (a) P-x-y diagram at 95 °C
- (b) T-x-y diagram at a pressure of 101.325 kPa (760 Torr).

Antoine constant A B C
Benzene 6.87987 1196.760 219.161
Tolune 6.95087 1342.310 219.187

7. (a) A system formed initially of 2 mol CO₂, 5 mol H₂ 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.

- (b) Write the effect of operating condition on degree of conversion at equilibrium.
- 8. Write short notes on any two:
 - (a) Virial equation of state

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- (b) van der Waals equation of state
- (c) Acentric factor
- (d) Chemical potential.

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