



- (e) A monobasic acid "A" has molecular weight  $M$ . The specific gravity is mentioned on the bottle of the acid "A" is  $Y$  g/cc and purity of the acid is  $Z\%$  by weight. Find out the normality of the acid "A" in terms of  $M$ ,  $Y$  and  $Z$ .
- (f) Explain Hess's Law of constant heat summation with an example.
- (g)  $C_p$  is always greater than  $C_v$ . (3×5)

2. Derive the following relations :

(a)  $C_p - C_v = [(\partial U / \partial V)_T + P](\partial V / \partial T)_p$

(b)  $(\partial H / \partial P)_T = V - T(\partial V / \partial T)_p$

(c)  $(\partial T / \partial V)_S = -(\partial P / \partial S)_V$

(d)  $TP^{-R/C_p, m} = \text{Constant}$  (4×3)

3. (a) Make a rough sketch of the following cycle on T-S diagram :

Step A. Isothermal expansion (at  $T_1$ ) from  $P_1$  to  $P_2$ .

Step B. Isochoric heating from  $P_2, T_1$  to  $P_3, T_3$ .

Step C. Isobaric cooling from  $P_3, T_3$ , to  $P_1, T_1$ .

Find out the slope in each step.

- (b) Write a short note on abnormal colligative properties of solutions and van't Hoff factor ?
- (c) One mole of an ideal gas is allowed to expand isothermally at  $27^\circ\text{C}$  until its volume is tripled. Calculate  $\Delta S_{\text{sys}}$  and  $\Delta S_{\text{univ}}$  under the following conditions :
- (i) Expansion is carried out reversibly.
- (ii) Expansion is a free expansion. (4×3)

4. (a) For a certain gas, the following is true :

$$C_{v,m} = a + bT + cT^2 \quad \text{and} \quad P(V_m - B) = RT$$

Derive an expression for the entropy change of 1.0 mole of this gas that accompanies a change in its state from  $T_i, V_{i,m}$  to  $T_f, V_{f,m}$ .

- (b) Define molal depression constant. Derive thermodynamically an expression relating the freezing point depression of a solution with its molality.
- (c) The bond enthalpy of  $H_2(g)$  is  $436 \text{ kJ mol}^{-1}$  and that of  $N_2(g)$  is  $941.3 \text{ kJ mol}^{-1}$ . Calculate the average bond enthalpy of an N-H bond in ammonia.  $\Delta H_f^\circ (NH_3) = -40.0 \text{ kJ mol}^{-1}$ . (3×4)

5. (a) For a binary system show that

$$dv_1 = -\frac{n_2}{n_1} dv_2. \text{ What is the physical significance of this expression ?}$$

- (b) Explain the terms osmosis and osmotic pressure. Using the concept of chemical potential, derive an expression for the osmotic pressure of the solution in terms of its concentration.
- (c) An ideal gas is allowed to expand reversibly and isothermally at 298K from a pressure of 1 bar to 0.05 bar. (i) What is the change in molar Gibbs energy? (ii) What would be the change if the process occurs irreversibly? (3×4)

6. Differentiate between :

- (i) Differential and Integral enthalpy of solution.
- (ii) Bond enthalpy and Bond dissociation enthalpy.
- (iii) Exact and Inexact differential. (3×4)

7. (a) Prove that :

(i)  $(\partial H / \partial P)_T = 0$  for an ideal gas

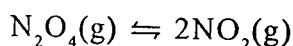
(ii)  $(\partial U / \partial V)_p + P = C_p (\partial T / \partial V)_p$

- (b) 5.13% (wt/v) solution of cane sugar is isotonic with a 0.9% (wt/v) solution of an unknown solute. Calculate molar mass of the solute. Molecular weight of cane sugar = 342 g/mol.
- (c) The volume of an aqueous solution of sodium chloride at 25°C was found to obey the relation :

$$V/\text{cm}^3\text{kg}^{-1} = 1003 + 16.62 (\text{m}/\text{mol kg}^{-1}) + 1.77(\text{m}/\text{mol kg}^{-1})^{3/2} + 0.12 (\text{m}/\text{mol kg}^{-1})^2$$

Find the partial molar volume of the components at  $m=0.1 \text{ mol kg}^{-1}$  by explicit differentiation. (3×4)

8. (a) At a total pressure of 2 atmospheres and 673K the equilibrium constant  $K_p$  for the following reaction is  $1.64 \times 10^{-4}$ . Calculate  $K_c$  and  $K_x$ .



- (b) 100 g of water at 100°C is placed in thermal contact with 1 kg of ice at 0°C and the system is allowed to come into equilibrium. Calculate the entropy change for the original 100 g of water, for the original 1 kg of ice and for the total system. Take the specific heat capacity of water to be  $4.18 \text{ JK}^{-1}\text{g}^{-1}$  and the enthalpy of fusion of ice to be  $333 \text{ Jg}^{-1}$ .
- (c) A salt solution fails to quench thirst: Justify with reasons. (4,6,2)

9. (a) State and explain third law of thermodynamics. How is it useful in calculating the absolute entropy of a substance ?
- (b) What do you understand by maximum flame temperature ? Prove that it is given by following relation :

$$T_f = T_0 + (-\Delta H_{T_0}) / \sum C_{P(\text{Products})}$$

- (c) Explain the effect of addition of inert gas at equilibrium by deriving equilibrium constant ( $K_p$ ) under the following conditions :
- (i) When pressure is constant.
- (ii) When volume is constant. (4,4,4)