(ii) Residual entropy

(iii) Le Chatelier's principle (5,5,2.5×2)

[This question paper contains 8 printed pages.]

Your Roll No.....

Sr. No. of Question Paper : 7007 **K**

Unique Paper Code : 2172512302

Name of the Paper : DSC: Chemical Energetics and Equilibria

Name of the Course : **B.Sc. (Prog.)**

Semester : III

Duration : 2 Hours Maximum Marks : 60

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt **FOUR** questions in all. Question No. **1** is compulsory.
3. The questions should be numbered in accordance to the number in the question paper.
4. Use of Scientific Calculator is permitted.

P.T.O.

Values of constant :

$R = 8.314\ J\ K^{-1}\ mol^{-1}$ or $1.987\ cal\ K^{-1}\ mol^{-1}$ or $0.082\ atm\ dm^3 K^{-1}\ mol^{-1}$

$K_b = 1.380649 \times 10^{-23}\ J\ K^{-1}$

$F = 96500\ C\ mol^{-1}$

$N_A = 6.022 \times 10^{23}\ mol^{-1}$

1. Answer **any five** questions. Each question carries equal marks

   (a) What are extensive variables? Identify the extensive variables among the following. specific heat capacity, molar volume, enthalpy, chemical potential, free energy.

   (b) The Joule coefficient of an ideal gas is zero. Explain.

   (c) The enthalpy of neutralization of strong acid with strong base is constant. Give reason.

   (i) 25.0 cm^3 of distilled water

   (ii) 10.0 cm^3 of 0.1M HCl (5×3)

6. (a) Define solubility product of sparingly soluble salt. What is the solubility of $Ag_2(CrO_4)$ in water if the value of solubility product is $K_s = 1.3 \times 10^{-11}\ M^3$.

   (b) At 1105 K, the value of $K°_p$ for a reaction $SO_2(g) + ½\ O_2 \leftrightarrow SO_3(g)$ is 0.63. Calculate

   (i) the standard free energy change for this reaction at 1105K

   (ii) the free energy change at 1105 K for the reaction

   $SO_2(1\ bar) + ½\ O_2(25\ bar) \leftrightarrow SO_3(2\ bar)$

   (c) Write short notes on any **two** :

   (i) Common ion effect

(c) Prove that the change in Gibbs free energy at constant temperature and pressure is equal to the net amount of non-mechanical work done.

(5×3)

5. (a) Derive the expression of equilibrium constant of a weak electrolyte AB in terms of degree of dissociation a and concentration c. Also prove that $\alpha \rightarrow 1$ as $c \rightarrow 0$.

(b) The pH of pure water at 40°C is found to be 6.765. What is the value of pK_w? What will be the nature of the solution at 40°C having $[H^+] = 0.54 \times 10^{-7}M$. What will be the pOH of the solution.

(c) A buffer is made by adding 25.0 cm^3 of 0.1M Sodium acetate to 50.0 cm^3 of 0.1M acetic acid ($pK_a = 4.75$). Write the Henderson-Hasselbalch equation and determine pH of the solution. What would be the pH if this buffer is added to:

(d) At constant temperature and pressure, Gibbs free energy attains a minimum value at equilibrium ($dG_{T,p} = 0$). Justify this statement.

(e) What are buffer solutions? Give one example of acidic buffer and basic buffer.

(f) Draw the pH metric titration curve of strong acid vs strong base. What is the pH at equivalence point? (3×5)

2. (a) Applying the first law of thermodynamics, prove that heat is an inexact differential.

(b) Describe the Joule's experiment. Write the mathematical expression that the energy of a gas is a function of temperature only.

(c) 7.0 g of N2 at 25°C is subjected to reversible isothermal expansion from initial pressure of 0.505 MPa to final pressure of 0.202 MPa. Calculate q, w, ΔU and ΔH. (5×3)

3. (a) State Hess's law of constant heat summation. Describe the Born Haber Cycle for the determination of lattice energy of NaCl.

(b) Define integral enthalpy of solution. Enthalpy of neutralization of HCl by NaOH is -57.32 kJ mol^{-1} and by NH_4OH is -51.34 kJ mol^{-1}. Calculate enthalpy of dissociation of NH_4OH.

(c) On the basis of following data, evaluate the standard enthalpy of formation of tungsten carbide (WC).

(i) $W(s) + 3/2O_2(g) \rightarrow WO_3(s)$

$\Delta_r H_{298k} = -837.47$ kJ mol^{-1}

(ii) $WC(s) + 5/2O_2(g) \rightarrow WO_3(s) + CO_2(g)$

$\Delta_r H_{298k} = -1195.79$ kJ mol^{-1}

(iii) $C(graphite) + O_2(g) \rightarrow CO_2(g)$

$\Delta_r H_{298k} = -393.51$ kJ mol^{-1}

(5×3)

4. (a) Define heat capacity. Prove that for an ideal gas

$C_{p,m} - C_{vm} = R$ (for 1 mole of an ideal gas)

(b) Derive the expression for change in entropy function when the amount n mole of an ideal gas undergoes change from temperature T_1 and volume V_1 to temperature T_2 to volume V_2.