CHEMISTRY

Paper—I

| Time Allowed : Three Hours | Maximum Marks : 200 |

INSTRUCTIONS

Candidates should attempt Question Nos. 1 and 5 which are compulsory, and any THREE of the remaining questions, selecting at least ONE question from each Section.

All questions carry equal marks.

Marks allotted to parts of a question are indicated against each.

Answers must be written in ENGLISH only.

Assume suitable data, if considered necessary, and indicate the same clearly.

Unless otherwise indicated, symbols and notations have their usual meanings.

<u>Important Note</u>

All parts/sub-parts of a question being attempted are to be answered contiguously on the answer-book. That is, where a question is being attempted, all its constituent parts/sub-parts must be answered before moving on to the next question.

Pages left blank, if any, in the answer-book(s) must be clearly struck out. Answers that follow pages left blank may not be given credit.

Section—A

1. Answer all the five parts below. Answers to be brief and to the point : 8×5=40

   (a) Chromium in a sample can be quantitatively estimated by converting it

into sodium dichromate, and titrating the acidified solution with a standard solution of ferrous sulfate. Write down the stoichiometrically balanced equation for the reaction.

(b) The quantum efficiency of H_2-Cl_2 reaction is 10^4–10^6 but that of H_2-Br_2 reaction is only 0·01 even though the mechanism is the same. The H_2-I_2 reaction does not occur photo-chemically. Explain giving reasons.
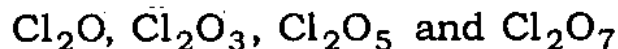
(c) Discuss the effect of temperature on rate of reaction. It is observed that for the reaction

$$2NO + O_2 \rightarrow 2NO_2$$
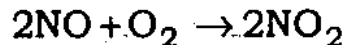
Rate $= k[NO]^2[O_2]$.

The rate of this reaction decreases with increase of temperature. Explain giving the mechanism of reaction.

(d) Which oxide is most acidic and why?

$$Cl_2O, \ Cl_2O_3, \ Cl_2O_5 \ and \ Cl_2O_7$$

(e) The bond in AB is estimated to be 15% ionic and the A—B bond distance is 1·76 Å. What is the dipole moment in AB?

2. *(a)* What is the difference between a fuel cell and a battery? Describe the mechanism of electricity generation in—

    (i) proton exchange membrane fuel cell (PEMFC) using proton-conducting polymer membrane as the electrolyte;

    (ii) solid oxide fuel cell (SOFC) using yttria-stabilized zirconia (YSZ) as the electrolyte.   **20**

(b) What are ion-selective electrodes?   **3**

(c) What is meant by glass electrode? Draw its labelled diagram and give the corresponding electrode reactions. What is it generally used for?   **12**

(d) The pressure of a real gas is less than that of an ideal gas. Give reason(s).   **5**

3. *(a)* What will be the pH of an aqueous solution containing an equimolal concentration of oxalic acid and NaOH?   **10**

(b) With the help of an appropriate diagram, discuss the structure of electrode/electrolyte interface.   **10**

(c) Explain the phase diagram for the Na_2SO_4-H_2O system, giving clearly the number of components, phases and degrees of freedom at each point in the system.   **20**

4. **(a)** When 18 g of liquid water is vaporized at 100 °C at 1·00 atm, how much work is done?

Data provided are :

$$\Delta H_{vap}(H_2O) = 9 \cdot 7 \text{ kcal mol}^{-1}$$

$$\Delta H_{fus}(H_2O) = 1 \cdot 4 \text{ kcal mol}^{-1}$$

$$R = 0 \cdot 0820 \text{ litre atm mol}^{-1} \text{ deg}^{-1}$$
$$= 1 \cdot 99 \text{ cal mol}^{-1} \text{ deg}^{-1}$$

$$D\,[H_2O\,(l)] = 1 \cdot 00 \text{ g cm}^{-3}$$ 15

(b) How many σ- and π-bonds are there in the tetracyanoethylene? 10

(c) What type of hybridization does the sulphur atom adopt in sulphur hexafluoride? (F, $Z = 9$; S, $Z = 16$) 10

(d) Calculate the potential of the following cell and write down the cell reaction :

$$Fe \,|\, Fe^{+2}\,(0 \cdot 004\ M) \,||\, Cd^{2+}\,(0 \cdot 001\ M)\,|\, Cd$$
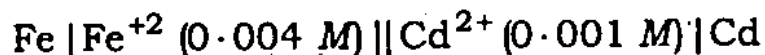
Given :

$$E^{\circ}_{Fe\,|\,Fe^{+2}} = +0 \cdot 441$$

$$E^{\circ}_{Cd\,|\,Cd^{2+}} = +0 \cdot 403$$ 5

Section—B

5. Answer all the five parts below. Answers to be brief and to the point : $8 \times 5 = 40$

(a) Briefly describe the various kinds of crystal defects.

(b) There are carbonyl-containing metal coordination complexes and metal clusters. How do they differ structurally?

(c) What are graphenes? Are they different from other allotropes of carbon? If so, how?

(d) Which of the oxides listed below cannot act as a reducing agent?

$$NO_2, \; SO_2, \; CO_2 \text{ and } ClO_2$$

(e) How many of the following have same bond order?

$$H_2^+, \; H_2^-, \; H_2^{-2} \text{ and } H_2$$
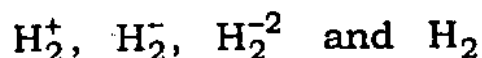
6. (a) Tripositive lanthanide ions show characteristic colors in the crystalline salts. These colors are unaffected by the alteration of the anion. Explain.   10

(b) What is the preferred geometry for the transition state formed during ligand substitution reaction of a square planar complex?

Indicate with diagram the position of the trans, the leaving and the entering group in the transition state. What influence does the trans group have on the rate of the reaction?   10

(c) What are 2-electron 3-centered bonds? Explain with an example. 5

(d) Give the mechanism for an enzyme-catalyzed reaction and derive the rate expression. What are the Michaelis-Menten constant and the Michaelis-Menten equation? 15

7. (a) What are the main assumptions on which an equation for adsorption isotherm was derived by Langmuir and what are its drawbacks? Derive the expression and explain how the equation accounts for adsorption at high pressure and low pressure. 20

(b) Ferredoxins are known to act as electron transfer agents. What is the correct structure of ferredoxin? 8

(c) Explain, with examples, the mechanism for the Na^+/K^+ pump responsible for maintaining appropriate concentration of Na^+ and K^+ in the cells. 12

8. (a) A definite amount of $BaCl_2$ was dissolved in aqueous HCl solution of unknown concentration. 20 ml of this solution was treated with 21·4 ml of $N/10$ NaOH for the complete neutralization. Further 20 ml of this solution was added to 50 ml of

$N/10$ Na_2CO_3 and the precipitate was filtered off. The filtrate reacted with 10·5 ml of 0·08 N H_2SO_4 (phenolphthalein was used as an indicator). Find the strength of $BaCl_2$ and HCl solution. 20

(b) Explain Heisenberg's uncertainty principle. Give the Schrödinger equation for the system of a particle in a one-dimensional box. Derive an expression for the wave function and energy of the system. 5+10=15

(c) Differentiate between nucleophilicity and basicity. 5

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