INDIAN FOREST SERVICE (MAIN)EXAM- 2023

CHEMISTRY

PAPER—I

Time Allowed : Three Hours

Maximum Marks : 200

QUESTION PAPER SPECIFIC INSTRUCTIONS

Please read each of the following instructions carefully before attempting questions

There are EIGHT questions in all, out of which FIVE are to be attempted.

Question Nos. **1** and **5** are compulsory. Out of the remaining SIX questions, THREE are to be attempted selecting at least ONE question from each of the two Sections A and B.

Attempts of questions shall be counted in sequential order. Unless struck off, attempt of a question shall be counted even if attempted partly. Any page or portion of the page left blank in the Question-cum-Answer Booklet must be clearly struck off.

All questions carry equal marks. The number of marks carried by a question/part is indicated against it.

Answers must be written in ENGLISH only.

Unless otherwise mentioned, symbols and notations have their usual standard meanings.

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

Neat sketches may be drawn, wherever required.

$h = 6 \cdot 626 \times 10^{-34}$ J s

$k_B = 1 \cdot 38 \times 10^{-23}$ J K^{-1}

$R = 8 \cdot 314$ J K^{-1} mol^{-1}

$\pi = 3 \cdot 14$

$c = 3 \times 10^8$ m s^{-1}

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

$N_A = 6 \cdot 023 \times 10^{23}$ mol^{-1}

1 atm = 101325 Pa

$m_e = 9 \cdot 1 \times 10^{-31}$ kg

SECTION—A

1. *(a)* An oxygen atom has a total of eight electrons. Write the four quantum numbers (in tabular form) for each of the eight electrons in the ground state. 8

(b) Use the Born-Haber cycle to calculate the enthalpy of formation of LiF. Use the following data in the calculation :

$$\Delta H_{sub} = 161 \text{ kJ/mol}$$

$$\Delta H_{dis} = 79 \text{ kJ/mol}$$

$$\Delta H_{ion} = 531 \text{ kJ/mol}$$

$$\Delta H_{EA} = -328 \text{ kJ/mol}$$

$$\Delta H_{xtal} = -1239 \text{ kJ/mol}$$ 8

(c) Iron(II) oxide, FeO, crystal has a cubic structure and each edge of the unit cell is 5·0 Å. Taking density of oxide as 4·0 $g\,cm^{-3}$, calculate the number of Fe^{2+} and O^{2-} ions present in each unit cell. 8

(d) Derive the following thermodynamic relations :

(i) $S = -\left(\frac{\delta A}{\delta T}\right)_V$ *(ii)* $P = -\left(\frac{\delta A}{\delta V}\right)_T$

(iii) $S = -\left(\frac{\delta G}{\delta T}\right)_P$ *(iv)* $V = \left(\frac{\delta G}{\delta P}\right)_T$ 8

(e) *(i)* What is meant by ionic atmosphere? How can we eliminate it?

(ii) Differentiate between Faraday current and Diffusion current. 4+4=8

2. *(a)* *(i)* Find the wavelength of light emitted when 5×10^{-28} g particles in a 3 Å one-dimensional box goes from $n = 2$ to $n = 1$ level.

(ii) Verify $H\psi = E\psi$ for the particle in a one-dimensional box. 8+7=15

(b) Draw the molecular orbital diagram for NO molecule. Predict the magnetic behaviour and bond order. Comment on the stability of NO^+ ion. 15

(c) Calculate the bond order of the following molecules :

O_2 and CO 10

3. *(a)* *(i)* The density of NaCl is 2·17 g cm^{-3}. Calculate the interionic distance. (F. wt. of NaCl = 58·45)

(ii) The ionic radii of Rb^+, Br^- and I^- ions are 1·47 Å, 1·95 Å and 2·16 Å respectively. Predict the most probable type of geometry exhibited by RbBr and RbI on the basis of radius ratio rule. 5+5=10

(b) The density of LiF is 2·601 g cm^{-3}. The (111) first-order reflection in the X-ray diffraction from LiF occurs at 8°44′ when X-rays of wavelength 70·8 pm are used. If there are four LiF molecules per unit cell, calculate Avogadro's number. LiF crystallizes in the cubic system. Li = 6·939, F = 18·998. 10

(c) What is the difference between pressures (in atm) calculated using ideal gas equation and the van der Waals' gas equation of 7·0 moles of CO_2 gas confined in a volume of 10·4 L at 47 °C?

(Given : $a = 3 \cdot 59$ atm L^2/mol^2 and $b = 0 \cdot 0427$ L/mol) 10

(d) Show that the pressure of a gas obeying the relation

$$\left(P + \frac{a}{V_m^2}\right)(V_m) = RT$$

is a state function. 10

4. *(a)* Assuming $N_2(g)$ is behaving ideally at 25 °C and 1 bar pressure, calculate the translational contribution to entropy (S_m°) of this gas. 10

(b) *(i)* Show that the slope of μ versus T curve for a pure substance (existing in three phases—solid, liquid and gas) is always negative and is equal to $-S_m$.

(ii) Draw a schematic diagram of μ versus T curve for the above-mentioned three phases and show that for a pure substance, the slope follows the order

$$\left(\frac{\delta\mu\,(s)}{\delta T}\right)_P > \left(\frac{\delta\mu\,(l)}{\delta T}\right)_P \gg \left(\frac{\delta\mu\,(g)}{\delta T}\right)_P$$

Locate the melting point and boiling point of the substance on the diagram. 5+5=10

(c) *(i)* The following cell has a resistance of 5·00 Ω. Calculate its potential when it is producing a current of 0·100 A :

$$Cd\left|Cd^{2+}(0 \cdot 0100\ M)\right|\left|Cu^{2+}(0 \cdot 0100\ M)\right|Cu$$

Given :

$$E_{Cu} = 0 \cdot 278 \text{ V}$$

$$E_{Cd} = -0 \cdot 462 \text{ V}$$

(ii) Calculate the potential required to generate a current 0·100 A in the reverse direction of the cell.

Given :

$$E_{Cd} = -0 \cdot 462 \text{ V}$$

$$E_{Cu} = 0 \cdot 278 \text{ V}$$

$$I = 0 \cdot 100 \text{ A}$$

$$R = 5 \cdot 00 \ \Omega$$

5+5=10

(d) (i) Write the working principle of ion-selective electrode with an example.

(ii) Using the Debye-Hückel limiting law, calculate the activity coefficients of sodium and sulfate ions, and the mean ionic activity coefficient of a 0·01 molal solution of sodium sulfate in water at room temperature.

5+5=10

SECTION—B

5. (a) Starting with pure A (of concentration a) in the reversible reaction

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$

derive the following relation :

$$t = \frac{1}{k_2(K+1)} \ln \frac{k_a}{k_a - (K+1)x}$$

where K is equilibrium constant and other symbols have their usual meanings. 8

(b) State the structural differences between the macrocyclic rings present in chlorophyll and hemoglobin. How does the light-emitting behaviour of the macrocyclic ring present in chlorophyll change without and with metal ion in the cavity? Why does the change occur? 8

(c) In a book, it is written that the structures of both Fe_3O_4 and Mn_3O_4 are normal spinel. With the help of CFSE, establish whether the structures written in the book are correct or not. 8

(d) Draw all the possible isomers (diastereoisomers + enantiomers) for $[Ni(H_2NCH_2COO)_2(H_2O)_2]$. 8

(e) Give one reaction each to show the amphoteric behaviour of Zn(II) and Al(III) salts in sulfur dioxide. 8

6. *(a)* For a reaction between two gaseous species A and B at 1000 °C represented as

$$2A(g) + 2B(g) \rightarrow C(g) + 2D(g)$$

the following kinetic data are collected at this temperature :

Sl. No.	$[A]$ (M)	$[B]$ (M)	*Initial rate* (M/sec)
1.	4×10^{-3}	$1\cdot5\times10^{-3}$	$1\cdot2\times10^{-5}$
2.	8×10^{-3}	$1\cdot5\times10^{-3}$	$4\cdot8\times10^{-5}$
3.	8×10^{-3}	3×10^{-3}	$9\cdot6\times10^{-5}$

Determine—

(i) the rate law;

(ii) the rate constant;

(iii) the rate of the reaction when $[A] = 12\cdot0\times10^{-3}$ M and $[B] = 6\cdot0\times10^{-3}$ M. 15

(b) In a photochemical reaction, it usually takes 1·5 eV to 2·0 eV to put a molecule into an excited state. What is the maximum wavelength of light capable of exciting the molecule? Which part of electromagnetic spectrum it belongs? Also, calculate the energy per mole (in kJ/mole) associated with photon of that light. 15

(c) *(i)* Write five characteristic features of a catalyst.

(ii) Discuss the important features, conditions and range of applicability of Freundlich adsorption isotherm. 10

7. *(a)* What is cytochrome P-450? How do you justify its name? State the oxidation state and spin state of the active metal centre present in the resting enzyme and any two important functions of P-450. During its enzymatic pathway, state the colour and origin of the colour of the radical cation intermediate and the role of the axial thiolate ligand present in its structure. What do you understand by peroxide shunt in the activity of cyt P-450? 15

(b) Discuss the structure of $Mn_2(CO)_{10}$. 15

(c) In $[Pt^0(\eta^2\text{-PhC}{\equiv}\text{CPh})(PPh_3)_2]$, the C—C bond length is 1·32 Å and C—C—Ph bond angle is 140°. Write the structure and justify the bonding. 10

8. *(a)* Define oxidative-addition reaction. Taking suitable example, explain the following mechanisms for the oxidative-addition reaction :

(i) Concerted mechanism

(ii) S_N2 mechanism 10

(b) Discuss the following reactions with suitable example in liquid ammonia :

(i) Acid-base reaction

(ii) Ammonolysis

(iii) Redox reaction 15

(c) (i) Arrange the following in decreasing order of basicity giving explanation :

$Ce(OH)_3$, $Lu(OH)_3$, $Gd(OH)_3$ and $Nd(OH)_3$

Which one of these is most likely to dissolve in hot conc. NaOH solution? Why? 7

(ii) Among Ce^{III}, Eu^{III}, Tb^{III} and Yb^{III} ions, for which one, the calculated magnetic moment is zero? Why? Among these ions, for which two ions, appreciably higher intensity bands are found in the lower energy UV-region than the other two? Explain your answer mentioning the transition. 8

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