I.F.S. EXAM-2016

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
$N_A = 6{\cdot}023 \times 10^{23}$
1 atm = 101325 Pa

SECTION—A

1. *(a)* Explain why—

(i) the bond angle in F_2O is smaller than that in H_2O;

(ii) certain substances like CO and N_2O are associated with residual entropy even at 0 K. 5+5

(b) *(i)* Assuming that the activation energy and pre-exponential factor are temperature independent, obtain the expression relating the activation energy (E_a) and the rate parameters $k(T_1)$ and $k(T_2)$ for the same reaction at temperatures T_1 and T_2.

(ii) Calculate the ionic strength of a solution that contains 0·01 mol kg^{-1} H_2SO_4 and 0·02 mol kg^{-1} sodium chloride. 5+5

(c) The heat of the reaction

$$Fe_2O_3(s) + 3H_2(g) \rightarrow 2Fe(s) + 3H_2O(l)$$

at 25 °C was found to be −8·4 kcal. What will be the heat of the reaction at 120 °C? The molar heat capacities at constant pressure and at 25 °C for iron oxide, hydrogen, iron and water are 25·0 cal deg^{-1} mol^{-1}, 6·9 cal deg^{-1} mol^{-1}, 6·1 cal deg^{-1} mol^{-1} and 18·0 cal deg^{-1} mol^{-1} respectively. 10

(d) *(i)* How many crystal systems are there? Name the crystal systems wherein the unit cell axes are mutually perpendicular. Give one example in each case.

(ii) What is the equation for the distance between the planes (110) for a crystal with mutually perpendicular axes? 5+5

2. *(a)* Explain the following : 5+5+10

(i) The dipole moment of CF_4 is less than that of CH_2F_2.

(ii) Carbon dioxide has a linear structure whereas sulphur dioxide is a bend molecule.

(iii) The bond order of NO is lower than that of NO^+. Comment on their magnetic behaviour.

(b) A molecule has only two translational and two vibrational energy levels. Show that the molecular partition function can be written as the product of two partition functions. 10

(c) Explain the adsorption theory of catalysis. What are the various steps involved in it? Give one example to support your answer. 10

3. *(a)* *(i)* Discuss the principle of polarographic analysis. Explain the meaning and significance of half-wave potential ($E_{1/2}$). If $E_{1/2}$ values of two electroactive species are too close, how can these be separated?

(ii) "Magnetic susceptibility measurements are of little use in structural elucidation of lanthanide complexes." Justify the statement. 10+10

(b) *(i)* Just define the terms phase, component and degree of freedom involved in the statement of phase rule.

(ii) How many components are there in an aqueous solution of NaCl and KBr? If to this solution KCl and NaBr are added, how many components will be there? 5+5

(c) The 'relaxation time' for a reversible first-order reaction $C \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} D$ is 100 microsecond and the equilibrium constant is $1{\cdot}0 \times 10^2$. Find k_1 and k_{-1}. 10

4. *(a)* *(i)* State and explain Einstein law of photochemical equivalence. How is low quantum yield explained?

(ii) The volume of nitrogen gas at 1 atmosphere and 273 K required to cover one gram of silica gel is $0{\cdot}129\ dm^3$. Calculate the surface area of the gel if each nitrogen molecule occupies an area of $16{\cdot}2 \times 10^{-10}\ m^2$. (Given $N_A = 6{\cdot}023 \times 10^{23}$) 10+10

(b) Consider a galvanic cell that uses the reaction

$$Cu(s) + 2Fe^{3+}(aq) \rightarrow 2\,Fe^{2+}(aq) + Cu^{2+}(aq)$$

Given, $E^{\circ}_{Fe^{3+}/Fe^{2+}} = +0{\cdot}77\ V$ and $E^{\circ}_{Cu^{2+}/Cu} = +0{\cdot}34\ V$.

(i) Calculate the standard cell potential.

(ii) Obtain the cell potential at 25 °C that has the following concentration values :

$$[Fe^{3+}] = 1{\cdot}0 \times 10^{-4}\ M;\quad [Cu^{2+}] = 0{\cdot}25\ M;\quad [Fe^{2+}] = 0{\cdot}2\ M$$

(Given, $F = 96500\ C$, $R = 8{\cdot}314\ J\,K^{-1}\,mol^{-1}$) 10

(c) Set up the Schrödinger wave equation (three dimensions). Comment on the nature of the equation and various terms involved. Explain the significance of ψ and ψ^2. 10

SECTION—B

5. *(a)* Explain the following briefly : 5+5

(i) Fluorescence

(ii) Chemiluminescence

(b) Explain the following terms : 5+5

(i) Chelate effect

(ii) Lability

(c) Explain why—

(i) the absorption spectra of actinides (ions) are independent of the nature of the ligand attached to them;

(ii) Co^{2+} salts are stabler than those of Co^{3+} salts, but solutions of Co^{2+} complexes get readily oxidized to Co^{3+} complexes. (At. No. of Co is 27) 5+5

(d) *(i)* Draw neat diagrams of the shapes of *d*-orbitals.

(ii) Explain the pattern of splitting of *d*-orbitals in a square-planar ligand field. Label each energy level. 5+5

6. *(a)* *(i)* Explain crystal field stabilization energy (CFSE). What are the factors that affect its magnitude?

(ii) Calculate CFSE and magnetic moments in case of

$$FeCl_3 \cdot 6H_2O \quad \text{and} \quad K_4Fe(CN)_6$$ 10+10

(b) *(i)* Write the general expressions for the filling of electrons in $4f$ and $5f$ block elements.

(ii) What do you understand by 'lanthanide contraction'? How does it affect the chemistry of $4f$ and $5d$ block elements? 5+5

(c) *(i)* Write the IUPAC nomenclature of the following :

(1) $K_3[Fe(CN)_5 \cdot NO]$

(2) $[Co(NO_2)_3 \cdot (NH_3)_3]$

(ii) Why Ce^{3+} ion $(4f^1)$ is colourless, whereas Ti^{3+} $(3d^1)$ solution is purple in colour? 5+5

7. *(a)* *(i)* What are carbonyls? How are they formed? Show that the molecule $Ni(CO)_4$ has a tetrahedral structure.

(ii) Write the structure of $Fe_2(CO)_9$. Show that each iron atom in the structure conforms to the 18*e* rule. 10+10

(b) Describe the structural features of 'ferredoxin' molecule. What is its role in photosynthesis? 10

(c) Draw labelled structures of all the possible isomers of dichloro-*bis* (ethylenediamine) cobalt(III) ion. Does a *meso*-form exist? Give reason to support your answer. 10

8. *(a)* *(i)* Discuss the solvent behaviour of liquid NH_3 in respect of the following :

(1) Alkali metals

(2) Urea

(3) BF_3

(4) Amides (—NH_2)

(5) $Zn(NH_2)_2 + 2NH_4Cl$

(ii) What is 'superacid'? Give two chemical properties to justify this nomenclature. 10+10

(b) *(i)* Starting with $[PtCl_4]^{2-}$, prepare diamine dichloroplatinum(II). Name the isomer formed.

(ii) Choose the relevant starting material and write all the steps to get the other geometrical isomer of the above product. 4+6

(c) *(i)* What do you understand by an 'oxidative addition' reaction?

(ii) How does it differ from an 'insertion reaction'? Give example in each case. 5+5

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