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.*

*Questions no. **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.

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.

*Answers must be written in **ENGLISH** only.*

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

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

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

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

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

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

$\pi = 3{\cdot}14$

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

1 atm = 101325 Pa

SECTION A

Q1. (a) For an acceptable solution, the wavefunction, $\phi(x)$ and its derivative, $d\phi(x)/dx$, has to be continuous. Why is this condition imposed on the wavefunction ? *8*

(b) Between NH_3 and NF_3, which one possesses higher dipole moment ? Explain. *8*

(c) Mention point defects which can arise for MgO as an impurity in Al_2O_3. How many Mg^{2+} ions must be added to form each of these defects ? *8*

(d) What is the pH of pure water at 37°C ? *8*
(Given : $\Delta_r H^0$ (enthalpy of ionization) at 25°C = 55·82 kJ mol^{-1})

(e) Calculate the mean ionic activity coefficient of 0·002 M aqueous solution of potassium ferricyanide at 25°C. *8*
(Given A = 0·509)

Q2. (a) Find the radial and angular nodes in H-orbitals, $\psi_{3pz}(r, \theta, \phi)$ and $\psi_{3px}(r, \theta, \phi)$. *10*

(b) The lattice energies (U_0) for the formation of NaCl and hypothetical $NaCl_2$ from Cl_2 gas and Na-metal are –757 kJ mol^{-1} and –2180 kJ mol^{-1} and their enthalpies of formation (ΔH_f) are – 381 kJ mol^{-1} and + 2530 kJ mol^{-1}, respectively. From these data, calculate the 2^{nd} ionization energy of Na. *15*
(Given that $\Delta H_{EA \text{ for Cl}}$ and $\Delta H_{(\text{atomization of } Cl_2 \rightarrow 2Cl)}$ are – 349 kJ mol^{-1} and + 242 kJ mol^{-1}, respectively)

(c) (i) Prove that the minimum value of R_A/R_X = 0·155 will provide a 3 : 3 coordination for A and X ions in AX compound (A is the cation, X is the anion, R_A is the radius of cation, R_X is the radius of anion). *10*

(ii) Zinc blende lattice is face-centered cubic. However, each atom is tetrahedrally bonded to four nearest neighbours. Explain how a Zinc blende lattice can be a face-centered cubic lattice. *5*

Q3. (a) Draw the MO diagram of BeH_2. Sketch the electron density boundary surface for $\sigma_g(\psi_1)$ and $\sigma_u^*(\psi_6)$. Show the combination of atomic orbitals of H atoms and Be atom for the σ_g and σ_u^* orbitals. *10*

(b) (i) 1 g of ice at T = 0°C and 10 g of water at T = 100°C are mixed in an adiabatic container. What is the temperature within the container when its content reaches equilibrium ? Express your answer in K.

For H_2O, the change in enthalpy on melting,

ΔH_{melt} = 6·01 kJ/mole and C_p = 75·3 J/(mol K). *10*

(ii) Which of the following substances would obey Trouton's rule most closely : hydrogen fluoride, toluene, methanol ? Explain with reasoning. *5*

(c) Draw the phase diagram of Sulphur system and indicate the existence of the following metastable equilibria : $S_R \rightleftharpoons S_V$ and $S_L \rightleftharpoons S_V$. Explain the reasons behind these equilibria. *15*

Q4. (a) What is excluded volume ? Explain with illustration. Show that the excluded volume per molecule is four times the actual volume of the gas molecule. *10*

(b) Deduce the expression for rotational partition function of a rigid heteronuclear diatomic rotator. *15*

(c) (i) What is ionic atmosphere ? How do relaxation and electrophoretic effects retard the velocity of central ion in the ionic atmosphere ? Explain with illustration. *10*

(ii) The EMF of a cell set-up by using hydrochloric acid solution, standard calomel electrode and quinhydrone electrode was found to be 0·1595 V at 25°C. Calculate the pH of hydrochloric acid solution. *5*

(Given the electrode potential of calomel electrode = 0·244 V, and that of quinhydrone electrode = 0·699 V)

SECTION B

Q5. (a) Consider two possible mechanisms for the synthesis of HI. The first is

$$H_2 + I_2 \xrightarrow{k} 2HI$$

and the second is

$$I_2 \xrightarrow{k_1} 2I$$

$$2I \xrightarrow{k_2} I_2$$

$$2I + H_2 \xrightarrow{k_3} 2HI.$$

Derive the expressions for the rate of formation of HI for both mechanisms. Under what conditions will both the mechanisms lead to the same type of kinetic equation ? *8*

(b) Obtain the expression for fraction of surface sites adsorbed by gas molecules from Langmuir theory of adsorption. *8*

(c) Explain why $[Co(H_2O)_6]^{2+}$ is stable but $[Co(NH_3)_6]^{2+}$ is readily oxidized to $[Co(NH_3)_6]^{3+}$ in air. *8*

(d) For the complex $[V(H_2O)_6]^{3+}$, how many absorption bands are expected in principle in its UV-Vis spectra and why ? Show the ground state to excited state transition for each band. *8*

(e) Write an equation to show self-ionization of fluorosulphuric acid. What happens when it is mixed with SbF_5 ? Write the equation. By what name is the mixture known and why ? How does the mixture react with Me_3CH ? *8*

Q6. (a) How does singlet excited state differ from triplet excited state ? Explain with the help of an energy level diagram. *10*

(b) Differentiate between active transport and passive transport through the cell membrane. What type of transport occurs in $Na^+ - K^+$ pump ? How does this pump function ? Explain with mechanism. *15*

(c) (i) Draw the crystal field splitting diagram of d-orbitals in octahedral and tetrahedral fields. In which case would the energy difference (Δ) between the two states be lower ? Why would it be so ? 8

(ii) Calculate the spin only magnetic moment for $Ni^{2+}(d^8)$ in octahedral and tetrahedral complexes. In which case is the experimental value expected to be much higher than the calculated spin only value ? Give reasons. 7

Q7. (a) Draw various types of adsorption isotherm curves involved in monolayer and multilayer formation. Explain these curves based on Brunauer-Emmett-Teller Theory. 10

(b) (i) Give a mechanism for substitution reaction in square planar complexes. Hence, give an explanation for 'Trans effect'. 10

(ii) What do you understand by 'fluxional molecule' ? Taking an example of your choice, show how the fluxional behaviour can be characterized with the help of a spectroscopic technique. 5

(c) (i) What is the common oxidation state of lanthanides ? Name two lanthanides which can exist in an oxidation state lower than the common one. What is this oxidation state ? Name one lanthanide which can exist in a higher oxidation state than the common one. What is this oxidation state ? Give an explanation for the existence of these uncommon oxidation states in each case. 8

(ii) Explain why the f $\rightarrow$ f transitions in lanthanide ions are much sharper and lower in intensity as compared to d $\rightarrow$ d transitions. 7

Q8. (a) What do you understand by 'Cooperativity' (Cooperative interaction) and 'Bohr effect' with respect to the oxygen transport in hemoglobin ? 10

(b) (i) A small piece of Na is dissolved in liquid NH_3 and then the solution was made saturated by dissolving more and more Na. In relation to the above experiment, answer the following : 10

I. What are the colours of the dilute solution and the concentrated solution ?

II. What is the composition of the dilute solution ?

III. How does the molar conductivity and magnetic susceptibility change from dilute to saturated solution ? Give possible explanation for the changes.

(ii) What happens when the dilute solution of Na in NH_3 is reacted with (I) O_2, and (II) $Fe(CO)_5$? Give equations. 5

(c) (i) For a hypothetical isomerization that is first order in both directions with $k_f = 17{\cdot}7\ min^{-1}$ and $k_r = 32{\cdot}2\ min^{-1}$, find the equilibrium composition if the initial concentration of A is equal to $0{\cdot}150\ mol\ L^{-1}$ and the initial concentration of B is equal to zero. Find the half-life and the relaxation time. 10

(ii) Can the activation energy of a reaction be zero or negative ? Explain your answer. 5