Civil Services (Main) Examination, 2014

CHEMISTRY

(Paper I)

Time Allowed : Three Hours **Maximum Marks : 250**

QUESTION PAPER SPECIFIC INSTRUCTIONS

(Please read each of the following instructions carefully before attempting questions)

There are EIGHT questions divided in two Sections.
Candidate has to attempt FIVE questions in all.
Question Nos. 1 and 5 are compulsory and out of the remaining, any THREE are to be attempted choosing at least ONE question from each Section.
The number of marks carried by a question/part is indicated against it.
Wherever any assumptions are made for answering a question, they must be clearly indicated.
Word limit in questions, wherever specified, should be adhered to.
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.

SECTION 'A'

1. (a) Calculate the radius ratio (r_c/r_a) in an octahedral lattice. Explain why lithium salts crystallize in octahedral lattice, although radius-ratio values are much below the expected ratio. **10**

(b) Point out the main features of the Valence Bond and Molecular Orbital theories. For the H_2 molecule, write down the wave function using (i) Valence Bond theory (ii) Molecular Orbital theory Suggest improvements to the wave functions. **10**

(c) Calculate the entropy change involved in the isothermal reversible expansion of 5 moles of an ideal gas from a volume of 20 L to a volume of 200 L at 300 K. **10**

(d) The density of acetone at 30 °C is 0.8310 gmL^{-1}. Calculate the surface tension of acetone, given that the parachor values of C, H, O and the double bond are 8.2, 16.3, 19.5 and 21.5 respectively. **10**

(e) For a particle confined in a one-dimensional box of length L ($0 \le x \le L$), calculate the values of the average position ($\langle x \rangle$) and momentum ($\langle p \rangle$). **10**

2. (a) Deduce the Born-Landé equation for 'lattice energy'. What modifications are imposed on this for better results? **10**

(b) Draw the molecular orbital diagrams for N_2 and NO. Based on the diagrams, find the bond orders and comment on the magnetic properties of the two. **20**

(c) How high will a liquid rise in a capillary tube of 0.4 mm diameter, if its density is 1.3×10^3 kgm^{-3} and surface tension 8.5×10^{-2} Nm^{-1}? (g=9.8 ms^{-2}) **10**

(d) During the electrolysis of a solution of potassium chloride between platinum electrodes, 0.0145 g of the chloride were lost from the anodic compartment and 0.0875 g of silver was deposited in a silver coulometer connected in series with the cell. Determine the transport number of K^+ and Cl^- ions. **10**

3. (a) Draw the radial part of the wave function and radial probability distribution for hydrogen atom for 1s, 2s and 2p orbitals. **10**

(b) What is the basic difference between Schottky and Frenkel defects in ionic crystals? How do solids with such defects differ from non-stoichiometric compounds? **10**

(c) Draw and explain curves showing the variation of first and second ionization energies for the elements from H to Ne. **20**

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(d) The enthalpy of decomposition of gaseous water per mole at 20 °C and 1 atm pressure is 243.05 kJ. Calculate its value at 80 °C, given the following data: $C_p(H_2O)=44.26$, $C_p(H_2)=29.56$, $C_p(O_2)=32.15$ JK^{-1} mol^{-1} **10**

4. (a) What do you mean by the terms 'eigen functions and eigen values'? Which of these functions is/are eigen functions of the d/dx operator? (i) $\exp(ax)$, (ii) $\exp(ax^2)$, (iii) $\sin(x)$, (iv) $25\,x^2$ What is/are the eigen value/s? **20**

(b) Calculate the number of components, and number of phases, and evaluate the number of degrees of freedom for the following equilibria: (i) An iceberg floating in a lake, considering the lake, iceberg and atmosphere as one system. (ii) $N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$ (iii) Pure partly frozen acetic acid (iv) $NaCl(s)-KCl(s)-H_2O(l)-H_2O(g)$ system (v) $NaBr(s)-KCl(s)-H_2O(l)-H_2O(g)$ system **20**

(c) Show that for a gas obeying the van der Waals equation:

$$C_p - C_v = R(1+2a/RTV)$$ **10**

SECTION 'B'

5. (a) (i) Specify the basis of the Irving-Williams series and arrange the Cu^{2+}, Fe^{2+}, Zn^{2+} and Ni^{2+} ions according to this series. (ii) Specify the basis of the trans effect and arrange Cl^-, NH_3, CN^- and H_2O in this sequence. **10**

(b) What are the salient features and limitations of the Crystal Field Theory? Show the splitting of the d^6 ion in weak and strong fields in an octahedral environment. **10**

(c) Explain 'lanthanide contraction' underlying its relevance in periods other than 4f. **10**

(d) Calculate ΔH^*, ΔG^* and ΔS^* for the second order reaction, $2\ NO_2(g) \rightarrow 3\ NO(g)+O_2(g)$ at 400 K. Given: Arrhenius factor $A=2.5\times10^9\ S^{-1}$ and the energy of activation is 121 kJ mol^{-1}. **10**

(e) Distinguish between the following: (i) Photochemical and dark reactions (ii) Fluorescence and phosphorescence **10**

6. (a) In the following sequence of reactions, identify the products (A – H). (i) $SiCl_4+CH_3MgCl \rightarrow A \xrightarrow{\text{controlled pyrolysis}} B$ (ii) $PCl_5+NH_4Cl \xrightarrow{\text{heating in (120°–150°C)}} C \xrightarrow{\text{heating in } 25°C} D$ (iii) $SCl_2+NH_3 \xrightarrow{90°C} E \xrightarrow{\text{hydrolysis}} F$ (iv) $KI+F_2 \xrightarrow{\text{conc. alkali}} G \xrightarrow{\text{hydrolysis in } 300°C} H$ **20**

(b) How are iron-proteins classified? What are the various functions performed by iron in biological systems? **10**

(c) For the photochemical reaction $A \rightarrow B$, 1.5×10^{-5} moles of B were formed on absorption of 6.2 J at 360 nm. Calculate the quantum efficiency. **10**

(d) Discuss the geometrical and optical isomerism in octahedral complexes of the type $M(A-A)_3$ and $M(A-B)_3$, where A – A and A – B are bidentate ligands. **10**

7. (a) Point out the special structural features of the following compounds: (i) $K[Pt(C_2H_4)Cl_3]$ (ii) $K_2[Re_2Cl_8]$ (iii) $(\eta^5-C_5H_5)Fe$ (iv) $[IrCl(Co)(PPh_3)_3]$ **10**

(b) Decomposition of a gas is of second order. It takes 60 min. for 60% of the gas to be decomposed, when its initial concentration is 4.5×10^{-2} mol L^{-1}. Calculate the specific reaction rate. **10**

(c) Comment on the spectroscopic and magnetic properties of 4f elements. **10**

(d) Show the various photochemical processes and their approximate rate constants on a Jablonski diagram. **10**

(e) Draw the contours of the five d orbitals. Show how σ, π and δ bonds are formed with metal d-orbital participation. **10**

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8. **(a)** "SiO_4 tetrahedra form the framework of all silicates, including silica (SiO_2)." Justify this statement with appropriate framework structures of ortho, pyro, cyclic, infinite chain, sheet and silica. **20**

(b) Calculate the room temperature (300 K) ratio of the rate constants for two reactions that have the same A value but have E_a values that differ by (i) 5 kJ mol^{-1} (ii) 50 kJ mol^{-1}. **20**

(c) Derive Langmuir's Adsorption Isotherm and explain how it could be used for determination of the surface area of an adsorbent.
Some Useful Constants (printed at the head of Section A): (R=8.3 J k^{-1} mol^{-1}; g=9.8 m s^{-2}; 1F=96,500 C; N_A=6.0×10^{23} mol^{-1}; h=6.6×10^{-34} J s^{-1}; c=3.0×10^8 m s^{-1}) **10**

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