Civil Services (Main) Examination, 2006

CHEMISTRY

(Paper I)

Time Allowed : Three Hours **Maximum Marks : 300**

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.

SECTION 'A'

1. Answer any three of the following:

(a) Explain how paramagnetism of O_2 molecule can be accounted for by Molecular Orbital (MO) theory whereas Valence Bond (VB) theory predicts it to be diamagnetic. **20**

(b) Given evidence to establish that sodium chloride (NaCl) has fcc structure but caesium chloride (CsCl) has bcc structure. **20**

(c) Lanthanides are generally trivalent but Ce^{4+} and Eu^{2+} are more stable. Explain this observation. **20**

(d) Why ethylenediamine forms much stronger complexes with transition metals as compared to NH_3, even though both are N-donors? **20**

2. (a) Define bond order, bond strength and bond length, and differentiate between them. Explain with suitable examples as to how these are interrelated with each other. **30**

(b) What is ferrocene? Draw its structure and explain its characteristic bonding features. **15**

(c) Explain the difference between homogeneous and heterogeneous catalysis with a suitable example for each. **15**

3. (a) Write salient features of stop-flow and relaxation methods for studying fast reactions. **20**

(b) What do you understand by thermodynamic and kinetic stability of complexes? Give suitable examples for each. **20**

(c) Explain the following briefly: (i) Metal atom clusters (ii) Fuel cells (iii) BET isotherm (iv) Quantum yield **20**

4. (a) Explain the difference between consecutive and chain reaction. The rate constant for the reaction $C_2H_6 \rightarrow 2CH_3$ is 1.57×10^{-3} s^{-1} at 1000 K. Calculate the rate constant for the backward reaction, if $\Delta_f G$ for $CH_3(g)$ is 159.74 kJ mol^{-3}, K_p=1.083×10^{-11} and R=0.0831 L bar K^{-1} mol^{-1}. **30**

(b) What are fluxional molecules? How are these characterized? **15**

(c) Draw the structures of cytochromes and ferredoxins explaining their functions in biological systems. **15**

SECTION 'B'

5. Answer any three of the following:

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(a) Compare the solvent behaviour of liquid ammonia with that of water especially with regard to solvolysis, redox and complexometric reactions. **20**

(b) Electronic spectra of coordination compounds cannot be explained by valence bond theory and it is essential to consider splitting in d-orbitals. Justify. **20**

(c) What do you understand by entropy of a system? How it increases with increasing temperature & ΔS becomes zero at absolute zero temperature? **20**

(d) Explain the free energy change in a Galvanic cell generating positive e.m.f. What happens when it is drained off? **20**

6. (a) Draw the shapes of d-orbitals. How do these split up in the presence of octahedral and tetrahedral fields? Explain the relationship between CFSE for the two geometries. Calculate the magnetic moments of $FeSO_4 \cdot 6H_2O$ and $[Ni(NH_3)_6]SO_4$ and predict their geometry. **30**

(b) Explain the basic principle of polarography. Write Ilkovic equation explaining all the terms and show that diffusion current is directly proportional to concentration. **15**

(c) What do you understand by liquefaction of gases? Explain critical temperature and critical pressure. Draw schematic diagram for liquefaction of air. **15**

7. (a) Explain Aufbau principle, Hund's rule of maximum multiplicity and Pauli's exclusion principle. What is their significance in writing electronic configuration? Give suitable examples. **20**

(b) Explain Hess's law. Calculate the enthalpy change for the reaction $HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$ Given that $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$ $\Delta H = -184.6$ kJ mol^{-1}; $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$ $\Delta H = 92.2$ kJ mol^{-1}; $Cl_2(g) + N_2(g) + 4H_2(g) \rightarrow 2NH_4Cl(s)$ $\Delta H = -628.8$ kJ mol^{-1} **20**

(c) How liquid crystals are different from solid crystals? Compare their characteristic features. **20**

8. (a) How metal carbonyls are synthesized? What are the characteristic features of metal-carbon bonding in carbonyls? Draw the structures of $Ni(CO)_4$, $Fe(CO)_5$ and $Cr(CO)_6$. **25**

(b) Explain ionization, coordination, linkage and optical isomerism in coordination compounds with a suitable example for each. **20**

(c) What do you understand by imperfection in crystals? Explain various types of defects and resulting change in properties. **15**

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