Civil Services (Main) Examination, 2000

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 the difference between 1s and 2s orbitals and also between 2s and 2p orbitals. **20**

(b) What is the node in an atomic orbital and what role does it play in determining broadly the relative stability of various types of atomic orbitals with the same principal quantum number? **20**

(c) What is the bond order in CO molecule according to the molecular orbital theory? Also describe how the theory explains (1) coordination through carbon and (ii) negligible dipole moment of the molecule. **20**

(d) Apply molecular orbital theory to explain paramagnetism of B_2 molecule. **20**

2. (a) E (Standard state pH = 7) for the electrode reaction $CH_3CHO+2H^{+}+2e^{-} \rightarrow CH_3CH_2OH$ is −0.197 volt. Calculate E at pH = 6 when ethanol and acetaldehyde are present at 10^{-5} M, temperature = 25 °C. **20**

(b) What changes do you expect in a cathodic polarogram if the d.m.e. is replaced with some solid stationary electrode while solution conditions remain the same? Also explain why. **20**

(c) State and explain the law of corresponding states. For large number of substances, the quantity RT_c/P_cV_c lies between 3.4 and 3.7. Comment on the fact. **20**

3. (a) Employing d.m.e. as the indicator electrode, sometimes it is possible to estimate a very dilute solution of some metal ion amperometrically even when there is no apparent chemical interaction between it and the titrant. Elaborate the statement taking an example. **20**

(b) What is an electrometric indicator and how does it facilitate the amperometric estimation of some metal species at d.m.e.? Give an example. **20**

(c) Pb^{++} ions when titrated with $Cr_2O_7^{-2}$ amperometrically at d.m.e. at 0.0 V in an acidic medium, yield a curve which shows only non-faradic current in the beginning and faradic current appears (and then increases regularly as the titration progresses) only after the null point has been reached. however, a V-shaped curve is obtained when the same titration is carried out at −1.2 V. Explain why it is so. **20**

4. (a) Radius ratio of two types of ions is the determining factor for the ultimate crystal structure. Elaborate the statement taking examples of NaCl, BeO and CsCl. [Ionic radii values in Å = Na^{+}, 0.98; Be^{++}, 0.30; Cs^{+}, 1.67; O^{2-}, 1.45; Cl^{-}, 1.81] **20**

(b) Explain the crystal structure of CdI_2. **20**

English version compiled from published transcriptions and cross-checked across sources; not a facsimile of the official UPSC question paper.

Optional Province · optionalprovince.com

(c) A unit cube in the sodium chloride crystal contains 14 chlorine and 13 sodium ions and yet it contains four molecules of NaCl. Explain. **20**

SECTION 'B'

5. Answer any three of the following:

(a) $Ni(CO)_4$ contains metal in zero-valent state and yet it is quite stable. Why? **20**

(b) Lanthanides are responsible for the extreme similarity in the chemistry of zirconium and hafnium and also for the fact that their separation from each other has been a difficult task. Comment. **20**

(c) Lanthanides have little tendency to form complexes but when they form they can attain high coordination number of 7 or 8 even. Comment. **20**

(d) Lanthanides have little tendency to form complexes but their compounds are generally brilliantly coloured. Any explanation? **20**

6. (a) How many bands are expected in the electronic spectrum of $[V(H_2O)_6]^{3+}$ and why? **20**

(b) Explain, applying crystal field theory, why $[Co(NH_3)_6]^{2+}$ is easily oxidized to $[Co(NH_3)_6]^{3+}$ **20**

(c) Furnish explanation for the general inertness of square planar complexes of Pd (II) and Pt (II). **20**

7. (a) What role photosensitizers can play in the decay of photo-excited states? Explain with an example. **20**

(b) How is phosphorescence important in the decay of some photochemically excited molecules? Explain. **20**

(c) What is the explanation for $FeCl_4^-$ and HgI_4^{2-} being tetrahedral on the basis of crystal field theory? **20**

8. (a) Explain the following facts from the standpoint of adsorption properties of reactant and product molecules (i) Decomposition of NH_3 on W is zero order (ii) Decomposition of N_2O on Au is first order (iii) Recombination of H atoms on Au is second order **20**

(b) A certain reaction is 20% complete in 15 minutes at 40 °C and in 3 minutes at 60 C, Estimate its activation energy. **20**

(c) Show that for a first-order reaction the time required for 99.9% of reaction to take place is ten times of that required for one-half the reaction. **20**

Optional Province · optionalprovince.com