

CHEMISTRY

Paper—I

Time Allowed : Three Hours

Maximum Marks : 200

INSTRUCTIONS

Please read each of the following instructions carefully before attempting questions.

There are ELEVEN questions divided under SIX Sections.

Candidate has to attempt SIX questions in all.

The ONLY question in Section—A is compulsory.

Out of the remaining TEN questions, the candidate has to attempt FIVE, choosing ONE from each of the other Sections B, C, D, E and F.

The number of marks carried by a question/part is indicated against it.

All parts and sub-parts of a question are to be attempted together in the answer book.

Attempts of questions shall be counted in sequential order. Unless struck off, attempt of a question shall be counted even if attempted partly.

Answers must be written in ENGLISH only.

Neat sketches are to be drawn to illustrate answers, wherever required.

Unless otherwise mentioned, symbols and notations have their usual standard meanings.

Any page or portion of the page left blank in the answer book must be clearly struck off.

Section—A

(Compulsory Section)

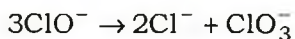
1. Answer *all* the following : 5×10=50

(a) Lithium does not occur with sodium and potassium though all belong to group I. Explain. 5

(b) How does bond order change in the cases (i) O_2 to O_2^- and (ii) N_2 to N_2^+ ? Show with MO diagram. 5

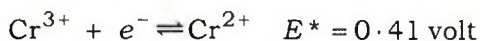
(c) Why HF is a strong acid in liquid ammonia but is a weak acid in water? 5

(d) Consider the following reaction :



Name the type of such reactions and give name and example of the reverse type. 5

(e) Which of the two ions Fe(II) and Cr(III) would be easily oxidized? 5



E^* is standard reduction potential.

(f) Explain why H_2 molecule exists but He_2 does not. 5

(g) Explain packing fraction. 5

- (h) Explain briefly geometrical isomerism. Draw the structures of various geometrical isomers of the following complexes : 5
- (i) $[\text{PtCl}_2(\text{NH}_3)_2]$
- (ii) $[\text{Pt}(\text{NO}_2)(\text{C}_5\text{H}_5\text{N})(\text{NH}_3)(\text{NH}_2\text{OH})]$
- (i) Identify the ground term symbol of set of terms 1G , 3F , 3P , 1F . Specify the spin (S) and angular momenta (L) of ground state and also the possible total angular momentum (J) value. 5
- (j) In which of the following, the EAN rule is not followed? Explain : 5
- (i) $\text{Co}_2(\text{CO})_8$
- (ii) $\text{V}(\text{CO})_6$

Section—B

Attempt *any one* question

2. (a) Explain briefly the liquid-drop model of a nucleus. Show that usually $^{238}_{92}\text{U}$ is an α -emitter and not a β -emitter. 15
- (b) Explain the concept of VSEPR theory and illustrate its efficacy in predicting gross geometrical structures of BeF_2 , NH_3 and CCl_4 . 15

3. (a) Write down all the term symbols for d^2 -configuration. Identify the term symbol for ground state and show how it is split up by spin-orbit coupling. 10
- (b) Explain 'mass defect' and 'binding energy'. How are they related? 10
- (c) Explain the structure of Cu(II) acetate dihydrate. 10

Section—C

Attempt *any one* question

4. (a) Show diagrammatically the crystal field splitting of d -orbitals in octahedral and tetrahedral environment. Show that
- $$\Delta_{td} = \frac{4}{9} \Delta_{oct} \quad 15$$
- (b) The $\log k$ value of Cr-EDTA complex is 23.0, still Cr(III) cannot be titrated with EDTA directly. Explain. 5
- (c) Explain the structure and bonding in $Fe_3(CO)_9$. 10
5. (a) What is diagonal relationship in the periodic table? Discuss with reference to lithium, magnesium, beryllium and aluminium. 10

- (b) Explain why the magnetic moment of Gd^{3+} ($Z = 64$) complexes can be obtained by spin-only formula but not of Tb^{3+} ($Z = 65$) complexes. 10
- (c) Discuss the bonding of CO in metal carbonyls. Find EAN of metal atoms in $\text{Ni}(\text{CO})_4$ and $\text{Fe}(\text{CO})_5$. Also give their structures. 10

Section—D

Attempt *any one* question

6. (a) Explain briefly tetragonal distortion of octahedral complexes. In which of the following complexes, it is observed?
 $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{MnF}_6]^{4-}$, $\text{Co}(\text{II})$ in strong field, $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ and $\text{Mn}(\text{III})$ in weak field 10
- (b) Explain the Lewis concept of acids and bases. 10
- (c) What is $\text{p}K_a$ value of a weak acid? How is it related to its pH? Explain. 10
7. (a) Differentiate between thermodynamic and stoichiometric stability constant. Under which condition the two will be identical? 10

- (b) Calculate the magnetic moment of $[\text{Mn}(\text{CN})_6]^{3-}$ and $[\text{MnBr}_4]^{2-}$. 10
- (c) Write down a brief note on peroxy acids. 10

Section—E

Attempt *any one* question

8. (a) What are fluorocarbons? Give their method of preparation, properties and commercial applications. 15
- (b) Explain which of the following has the shortest bond length : 10
- $\text{NO}, \text{NO}^-, \text{NO}^+, \text{NO}^{++}$
- (c) Write the structure of diborane. 5
9. (a) Explain the structures of different types of silicates. 15
- (b) Balance the following ionic reaction by 'ion electron' method in acidic medium : 7
- $\text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cr}^{3+}$
- (c) Write down the ionic oxidation reaction for the liberation of iodine from potassium iodide in acidic medium by potassium dichromate. 8

Section—F

Attempt *any one* question

10. (a) Name all the elements belonging to group 14 and comment on the group trend in properties in respect of—
- (i) metallic character;
 - (ii) chemical reactivity;
 - (iii) stability of tetrahalides;
 - (iv) basicity of oxides. 10
- (b) Explain the configuration and oxidation states of 'lanthanides'. 10
- (c) How is Cu^{2+} estimated iodometrically? Explain the reactions involved. 10
11. (a) Comment on the following : 15
- (i) SnCl_2 dissolves in HCl but not in ammonia.
 - (ii) CO_2 is a molecular gas but SiO_2 is a solid.
 - (iii) SnCl_2 shows reducing behaviour, PbCl_2 does not.
- (b) How are nuclear radiations detected and measured? Discuss one method. 15

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