

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 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.

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 Question-cum-Answer Booklet must be clearly struck off.

SECTION 'A'

1. Answer all of the following : 5×10=50
- 1.(a) How lithium hydride can be prepared ? Write the product of the reaction between lithium hydride and carbon dioxide. Whether it (LiH) is electrovalent or covalent compound ? Explain.
- 1.(b) Write IUPAC nomenclature of the following coordination compounds :
- (i) $[\text{CoCl}(\text{CN})(\text{NO}_2)(\text{NH}_3)_3]$
- (ii) $[\text{Pt}(\text{Py})_4][\text{PtCl}_4]$
- 1.(c) A complex with the formula $\text{CoCl}_3 \cdot 4\text{NH}_3$ gives precipitate with AgNO_3 with reference to one chloride ion. Answer the following :
- (i) What is the primary valency of cobalt ?
- (ii) What is the secondary valency of cobalt ?
- (iii) Draw the possible geometrical isomers of the compound.
- 1.(d) All Bronsted-Lowry acids are Lewis acids also. But all Lewis acids are not Bronsted-Lowry acids. Explain.
- 1.(e) Iodine and bromine are added to a solution containing I^- and Br^- ions. What reaction would occur ? Explain.
- The electrode potentials for the reactions are :
- $\text{I}_2 + 2\text{e}^- \longrightarrow 2\text{I}^-$, $E^\circ = +0.54 \text{ V}$
- $\text{Br}_2 + 2\text{e}^- \longrightarrow 2\text{Br}^-$, $E^\circ = +1.08 \text{ V}$

- 1.(f) What is 18-electron rule ? Using the 18-electron rule predict the 'n' value for the following compounds :
- $[\eta^6(\text{C}_6\text{H}_6) \text{Cr}(\text{CO})_n]$
 - $[\eta^4(\text{C}_4\text{H}_4)_2 \text{Mn}(\text{Cl})(\text{CO})_n]$
- 1.(g) A wooden article of old age shows 40% as much ^{14}C activity as a fresh piece of wood. Calculate the age of the article.
($t_{1/2}$ of $^{14}\text{C} = 5760$ years)
- 1.(h) What is the usual order of preference of the alkali metal ions for a cation exchanging resin ? Explain.
- 1.(i) Draw the structure of borazine. With the help of its reaction with HCl, explain why chemical properties of borazine are quite different from those of benzene.
- 1.(j) Atomic radii of two of the lanthanides are considerably higher than the other lanthanides. Identify those two lanthanides and explain the observation.

SECTION 'B'

(Attempt any *one* question)

- 2.(a) Define the electron affinity. Explain the general trends of electron affinity in periodic table. Electron affinities of beryllium, magnesium, calcium and nitrogen are practically close to zero. Explain. 10
- 2.(b) Explain the basicities of the following acids and justify the answer by drawing the structures : 10
- Orthophosphoric acid
 - Pyrophosphoric acid
 - Metaphosphoric acid
- 2.(c) Write the product(s) formed from the following reactions : 10
- $3\text{PCl}_3 + \text{SO}_3 \longrightarrow$
 - $\text{HPO}_4 + \text{H}_2\text{O} \longrightarrow$
 - $\text{TeO}_2 + 2\text{SeF}_4 \longrightarrow$
 - $8\text{HI} + \text{H}_2\text{SO}_4 \longrightarrow$
 - $\text{PCl}_5 + \text{H}_2\text{O} \longrightarrow$
- 3.(a) Write the important points of VSEPR theory. Draw the shape of the following molecules by using VSEPR theory : 10
- SF_4
 - XeOF_4
 - IF_5
- 3.(b) Draw the Born-Haber Cycle for the formation of NaCl crystal and write the two important uses of the Cycle. 10
- 3.(c) Draw the molecular orbital energy level diagrams for nitric oxide and carbon monoxide. Explain the magnetic behaviour of the molecules also. 10

SECTION 'C'

(Attempt any *one* question)

- 4.(a) Calculate ground state terms for the following electronic configurations : 10
(i) d^3 (ii) d^4 (iii) d^8 (iv) f^3 and (v) f^7
- 4.(b) Arrange the following metal compounds in the increasing order of their molar extinction coefficient values. Explain the reasons. 10
 KMnO_4 , $[\text{Co}(\text{NH}_3)_6]^{2+}$, $[\text{MnBr}_4]^{2-}$ and $[\text{CoCl}_4]^{2-}$
- 4.(c) Calculate the crystal field stabilization energy value for the complex $[\text{Cr}(\text{NH}_3)_6]^{2+}$. The crystal field splitting energy and pairing energy are found to be 150 kJ mol^{-1} and 120 kJ mol^{-1} respectively. 10
- 5.(a) What is Jahn-Teller effect? Calculate Jahn-Teller stabilization energy for Cu(II) complex in an octahedral field. 10
- 5.(b) What is premature end point? Explain this with reference to ferrous and dichromate titration in acidic medium. 10
- 5.(c) Draw the basicity order of CH_3^- , NH_2^- , OH^- and F^- anions. Justify your answer. 10

SECTION 'D'

(Attempt any *one* question)

- 6.(a) Balance the following equation by ion-electron method in basic medium : 10
$$\text{P}_4 \longrightarrow \text{H}_2\text{PO}_2^- + \text{PH}_3$$
- 6.(b) Distinguish between disproportionation and comproportionation reactions. Classify the following reactions into disproportionation or comproportionation reactions. Explain the reasons. 10
(i) $3\text{Cl}_2 + 6\text{NaOH} \longrightarrow \text{NaClO}_3 + 5\text{NaCl} + 3\text{H}_2\text{O}$
(ii) $3\text{HClO}_2 \longrightarrow 2\text{HClO}_3 + \text{HCl}$
(iii) $\text{AgCl}_2 + \text{Ag} \longrightarrow 2\text{AgCl}$
- 6.(c) Write oxidation half reaction and reduction half reaction and calculate EMF of the following cell at 298 K : 10
 $\text{Fe(s)}/\text{Fe}^{2+}(\text{aq})(0.001 \text{ M})//\text{H}^+(\text{aq})(1 \text{ M})/\text{H}_2(\text{g})(1 \text{ atm}), \text{Pt}.$
Standard reduction potentials of $\text{Fe}^{2+}/\text{Fe} = -0.44 \text{ V}$ and $\text{H}^+/\frac{1}{2}\text{H}_2 = 0.0 \text{ V}.$
- 7.(a) Explain band theory with an example. Using the band theory distinguish between conductors, semiconductors and insulators. 15
- 7.(b) Give the synthesis of the mixed metal carbonyl nitrosyls from the following compounds : 5
(i) $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{H}$ and
(ii) CrCl_3 and $\text{Na}^+ \text{C}_5\text{H}_5^-$
- 7.(c) Explain Structure and Bonding of ferrocene. 10

SECTION 'E'

(Attempt any *one* question)

- 8.(a) Briefly discuss the 'shell model' of nucleus and hence explain the concept of 'magic numbers' for the stability of nucleus. 15
- 8.(b) Explain the concept of Nuclear Binding Energy and hence the binding energy curve. How does the curve give information about nuclear fission and nuclear fusion as energy source. 10
- 8.(c) What are x and y in the following nuclear reactions ? Justify their formation. 5
- $${}^{11}_6\text{C} \longrightarrow {}^{11}_5\text{B} + x$$
- $${}^{14}_6\text{C} \longrightarrow {}^{14}_7\text{N} + y$$
- 9.(a) What happens, when the following salts are strongly heated ? Give balanced equations. 15
- (i) Li_2CO_3 (ii) LiNO_3 (iii) MgCO_3 (iv) $\text{Mg}(\text{NO}_3)_2$ (v) NaNO_3 (vi) Na_2CO_3
- From these reactions, can you suggest (with reasons) a relationship between any two of these metal ions ? Suggest one more property in favour of this relationship. 15
- 9.(b) Write the formula and draw the structure of the compound which is formed when $\text{Be}(\text{OH})_2$ is evaporated with acetic acid. 5
- 9.(c) Calculate the effective nuclear charge (Z_{eff}) for the last electron in sodium (Na) atom. (Atomic number of Na = 11) 10

SECTION 'F'

(Attempt any *one* question)

- 10.(a) State the method of preparation of diborane from BF_3 . Draw its structure and discuss its bonding. What happens when diborane is reacted with (i) water (ii) excess ammonia at low temperature. 15
- 10.(b) Give one example each of (i) orthosilicate (ii) pyrosilicate (iii) cyclic silicate and (iv) chain silicate and draw their structures. 15
- 11.(a) Calculate the magnetic moment of $\text{Ce}^{3+}(\text{f}^1)$ and $\text{Yb}^{3+}(\text{f}^{13})$ considering spin-orbit coupling. Comment on the difference (if any) in the ground. State terms and values of the moment, of the two ions. 15
- 11.(b) Explain why $5 \times 3 = 15$
- (i) Atomic radii of Zr and Hf are virtually identical.
- (ii) The most common oxidation state of Cu is +2 but that of Ag is +1.
- (iii) Gold forms Au^- ion under suitable conditions but Cu or Ag does not.