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.

Neat sketches are to be drawn to illustrate answers, wherever required. These shall be drawn in the space provided for answering the question itself.

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

Assume suitable data, if necessary, and indicate the same clearly.

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 (QCA) Booklet must be clearly struck off.

*Answers must be written in **ENGLISH** only.*

SECTION A

(Compulsory Section)

Answer all of the following : *5×10=50*

Q1. (a) Match the following : *5*

(i)	Mg_2SiO_4	(A)	Spinel
(ii)	$Be_3Al_2Si_6O_8$ (Beryl)	(B)	Zeolite
(iii)	$M_q^{m+}[Si_{x-y}P_{1-x}Al_{1-y}O_4]$	(C)	Orthosilicate
(iv)	$MgAl_2O_4$	(D)	Aluminophosphate
(v)	$Ca(OH)(PO_4)_3$	(E)	Cyclosilicate
		(F)	Hydroxyapatite
		(G)	Intercalation Compound

(b) Determine the ground state terms for the following compounds using L-S coupling scheme : *5*

(i) $[Cr(NH_3)_6]^{3+}$ and (ii) $[Mn(H_2O)_6]^{3+}$

(c) How many stereoisomers are possible for the square-planar complexes (i) Ma_2bc and (ii) Mabcd (a, b, c and d are unidentate ligands) ? Draw the structures. *5*

(d) Calculate the concentration of carbonate ions in 0·10 M H_2CO_3 (aq). (Given : $K_{a_1} = 4{\cdot}3 \times 10^{-7}$, $K_{a_2} = 4{\cdot}6 \times 10^{-11}$) *5*

(e) A 25 mL solution containing Cl^- was treated with excess $AgNO_3$ solution to precipitate 0·830 g of AgCl. What was the molarity of Cl^- in the unknown solution ? (At. wt. of Ag = 107·87, Cl = 35·453) *5*

(f) A sample of 0·6128 g of iron ore is dissolved in HCl and all the iron is reduced to Fe^{2+} ions. This solution required 38·4 mL of 0·0198 M $KMnO_4$ to titrate under acidic conditions. Calculate the mass percent of iron in the ore. (Given atomic weight of iron = 55·85) *5*

(g) Explain the masking process and demasking process. How can the concentration of nickel(II) be determined in the presence of Cu^{2+} ? *5*

(h) Consider the 18-electron rule and determine the value of n for the following compounds : *5*

(i) $K_2Fe(CO)_n$ and (ii) $MnCl(CO)_n$

(i) What is Carbon-14 dating ? Why is this method used to determine the age of the ancient articles made of wood ? *5*

(j) Arrange the following metal ions in the increasing order of their oxidising power. Give reasons. *5*

Sc^{3+}, Ti^{4+}, V^{5+}, Cr^{6+} and Mn^{7+}

SECTION B

Attempt any *one* question :

Q2. (a) Perovskite mineral contains calcium, titanium and oxygen.

(i) Draw the unit cell of perovskite with titanium at the centre of the unit cell.

(ii) Draw the unit cell of perovskite with calcium at the centre of the unit cell.

(iii) Find the formula of perovskite in both the unit cell representations.

(iv) What is the coordination number of titanium in each representation of the unit cell ? *10*

(b) The conductivity of silicon semiconductor is small compared to metals. Propose two methods to increase the conductivity of silicon, with examples. Draw the energy level diagrams illustrating the two methods. *10*

(c) (i) The crystalline form of fullerene has a face-centred cubic array of C_{60} molecules. What is the basis of this unit cell ?

(ii) What are the products likely to form when Ta_2O_5 is heated at 700°C in the flow of NH_3 gas ? *4*

(d) Match the following : *6*

(i)	Schottky defects	(A)	ReO_3
(ii)	Frenkel defects	(B)	$Ti_{1-x}O$
(iii)	Non-Stoichiometric compound	(C)	Silver halides
(iv)	Semiconductor	(D)	CaF_2
(v)	Corundum structure	(E)	GaAs
(vi)	Conductor at room temperature	(F)	Ti_2O_3

Q3. (a) Identify the electron configurations which cause strong distortions and weak distortions for d^1 to d^9 metals in the case of strong and weak field octahedral complexes. Give reasons. *10*

(b) Discuss the factors which affect the crystal field splitting energy values. *10*

(c) Calculate the magnetic moment values for the following complexes based on the unpaired electrons present : *10*

(i) $[Fe(NH_3)_6]^{3+}$

(ii) $[CoBr_6]^{3-}$ and $[CuCl_4]^{2-}$

SECTION C

Attempt any *one* question :

Q4. (a) How does the VBT account for the following facts ? *10*

(i) $[NiCl_4]^{2-}$ is paramagnetic and tetrahedral.

(ii) $[Ni(CO)_4]$ is diamagnetic and tetrahedral.

(b) Identify the type of selection rules observed for the following compounds in their electronic absorption spectra. Justify your answer. *10*

(i) $[Co(NH_3)_6]^{2+}$

(ii) $[NiBr_4]^{2-}$

(iii) $[MnBr_4]^{2-}$

(iv) $[Mn(H_2O)_6]^{2+}$

(v) $KMnO_4$

(c) Draw and explain the crystal field splitting energy diagram of $[Ni(CN)_4]^{2-}$ complex. *10*

Q5. (a) 50 mL of 0·1 M HCl was titrated against 0·1 M NaOH. Calculate the pH at the start of titration and after addition of 10 mL, 50 mL and 60 mL of NaOH. *10*

(b) The phenolphthalein indicator gives pink colour in presence of dilute alkali, while in presence of excess of concentrated alcoholic alkali, the pink colour disappears. Explain by drawing the structures. *10*

(c) Write the reactions involved in the volumetric titration of weak base with strong acid. Explain using titration curve. *10*

SECTION D

Attempt any *one* question :

Q6. (a) A 2·0000 gm of a rock sample contains lead, iron and copper. This sample is dissolved to form a solution containing the three metals. Gravimetric estimation of the metals yielded 0·3188 gm of $PbSO_4$, 0·7282 gm of Fe_2O_3 and 0·4787 gm of CuCNS. Calculate the percentages of the three metals in the rock sample. *10*

(Given atomic weights : Pb = 207·19, S = 32·07, O = 16·01, Fe = 55·85, Cu = 63·54, N = 14·01, C = 12·01)

(b) Explain nucleation and particle growth. What are the techniques that promote particle growth ? *10*

(c) Give the principles involved in gravimetric volatilization methods. How are the carbonate content of dolomite, and carbon and hydrogen content of organic compounds determined using this method ? *10*

Q7. (a) Calculate the reduction potential of the following half-cell reaction at 25°C.

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

The concentrations are $[MnO_4^-] = 0{\cdot}1$ M, $[Mn^{2+}] = 0{\cdot}010$ and pH = 3·0.

The standard reduction potential of the reaction at 25°C, $E^\circ = 1{\cdot}51$ V. *10*

(b) Answer the following : *10*

(i) What is the difference between iodimetry and iodometry ?

(ii) Why is iodine used in a solution containing excess I^- ?

(iii) Why is starch used as an indicator in titrations involving iodine ?

(iv) Is starch a redox indicator ?

(v) In iodometric titrations, the contents of the reaction mixture are usually kept in dark after adding KI solution. Why ?

(c) A piece of 1·06 g of copper metal is dropped in 250 mL of 0·20 M $AgNO_3$ solution. Will all the copper dissolve in this solution ? Write the net reaction equation. *10*

(Given atomic weight of Cu = 63·54 and atomic weight of Ag = 107·87)

SECTION E

Attempt any *one* question :

Q8. (a) Write the formation constant (K_f) and conditional formation constant (K_f') for metal – EDTA complex. Calculate the conditional (effective) formation constant for Fe^{3+} in a solution of 0·10 M FeY^- at pH 4·00 and at pH = 1·00. *10*

(Given : K_f for FeY^- is $1·3 \times 10^{25}$

$\alpha_{Y^{4-}} \rightarrow$ at 4·00 pH is $3·8 \times 10^{-9}$

$\alpha_{Y^{4-}} \rightarrow$ at 1·00 pH is $1·9 \times 10^{-18}$)

(b) Give the stepwise chemical equations and calculate the overall stability constant β_2 for the formation of $[Ag(NH_3)_2]^+$ from $[Ag(H_2O)_4]^+$. *10*

(Given : $K_1 = 2·1 \times 10^3$, $K_2 = 8·2 \times 10^3$)

(c) Explain the metal ion – indicator – EDTA reactions. What are the important criteria to be satisfied by metal ion indicator for visual detection of end points ? *10*

Q9. (a) Determine the total valency electrons of metal and number of metal-metal bonds present in the following compounds, which obey the 18-electron rule. Draw structures. *10*

(i) $CO_2(CO)_8 : (CO)_3\,Co(\mu - CO)_2\,Co(CO)_3$

(ii) $(\eta^5 - C_5H_5)\,(CO)\,Fe(\mu - CO)_2\,Fe(CO)\,(\eta^5 - C_5H_5)$

(b) Draw the structures of $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$. Explain hybridization and bonding present in them. *15*

(c) Which one of the given complexes will undergo ligand substitution faster with PPh_3 ? Why ? *5*

$[V(CO)_6]$ and $[V(CO)_6]^-$

SECTION F

Attempt any *one* question :

Q10. (a) Calculate the rate of disintegrations that occur in the first second(s) from 1·0 mol of a radioactive material with $t_{1/2}$ = 12000 years, $t_{1/2}$ = 12 hours and $t_{1/2}$ = 12 seconds. *15*
Avogadro number = $6{\cdot}022 \times 10^{23}$ $mole^{-1}$

(b) Complete the following nuclear reactions : *5*

(i) $^{238}_{92}U \longrightarrow ? + {}^{234}_{90}Th$

(ii) $^{234}_{91}Pa \longrightarrow ? + {}^{234}_{92}U$

(iii) $^{14}_{6}C \longrightarrow ? + {}^{14}_{7}N$

(iv) $^{22}_{11}Na \longrightarrow ? + {}^{22}_{10}Ne$

(v) $^{210}_{84}Po \longrightarrow ? + {}^{206}_{82}Pb$

(c) What is the principle involved in Geiger–Müller counter which is used to measure the radioactivity levels ? *10*

Q11. (a) The atomic size increases from 3d to 4d metals. However, the atomic size is similar between 4d and 5d metals. Give reasons. *10*

(b) How is magnetic data useful to distinguish between strong field and weak field octahedral complexes of d^1 to d^9 metals ? *10*

(c) How are lanthanides separated by ion-exchange method ? Explain. *10*