NEW

2017

M.Sc. Part–I Examination

CHEMISTRY

PAPER—III

Full Marks : 100

Time : 4 Hours

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Illustrate the answers wherever necessary.

(Inorganic)

Answer any *five* questions,
taking at least *two* from Group–A and B.
Answer any *five* questions from Group–C.

Group–A

1. (a) What are the essential and beneficial metals ? Discuss the biological function of (A) zinc (B) Nitrogen (C) iron and (D) calcium. 2+4

(b) Discuss the function two iron proteins which involved in transport and storage of iron in higher animal. 3+3

(c) Write notes on carbonic anhydrase. 3

2. (a) What is chelate effect? Discuss the function of entropy effect on chelate effect? How will you determine the composition of complex by slop ratio method? 2+3+4

(b) Write down the associative mechanism for L_5MX complex. Derive rate for it? 6

3. (a) Write short notes on :

(i) Vaska's complex ;

(ii) Irving williams series ;

(iii) Creutz Taube complex. 3×3

(b) Following the 18e rule as a guide, determine the 'x' in the following complexes :

(i) $[(CO)_3Ni - Co(CO)_3]^x$

(ii) $[CpMn(CO)_x]_2$ (concider Mn = Mn double bond)

(iii) $[Co(CO)_3]^x$

(iv) $[\eta^5 - C_6H_6)Mn(CO)_2(CH_3)]^x$ $4\times1\frac{1}{2}$

4. (a) What do you mean by fluxionality? Explain with example. 2+3

(b) Write down the schoenflies symbols and the list of symmetry element present for the following molecular point group :

(i) Methyl chloride

(ii) Methylene bromide

(iii) Sodium acetylide

(iv) Phosphorous pentachloride. 4

(c) What are the essential criteria for a collection of entities must have to form a group. 2

(d) State and explain the Great Orthogonality Theorem. 4

5. (a) What do you mean by symmetry operation? Write down the all symmetry element present in IF_6 molecule indicating from where they are passing? 2+4

(b) What point symmetry is obtained by adding or deleting from each of the following groups in the indicated symmetry operation?

(i) C_2 plus i

(ii) D_{3d} Minus S_6

(iii) C_{3h} minus S_6^5

(c) What is the conventional designation for the group of operation generated by a S_n axis when n is odd. Write out all the operation generated by S_5 and S_8 axes and express each one in conventional notation. 3+2+3

Group–B

6. (a) What is reducible and irreducible representation ? How they can be differentiated ? 2+2

(b) Find the point group of the following :

(i) Cyclohexane (chair form), (ii) $[Ni(CN)_5]^{3-}$,

(iii) NH_4^+, (iv) HCHO. $4\times\frac{1}{2}$

(c) Find matrix representation of C_{3v} point group. 4

(d) Give Hermann-Mauguin (H – M) notation for D_3h, D_2h, C_{3v} and C_2h point group. Write down the number of faces, vertices and edges for dodecahedron and isooctahedron. 2+3

7. (a) Draw the electronic spectrum of $[V(H_2O)_6]^{3+}$ complex. Explain the only two peaks are resolved, γ_1 = 17,250 cm^{-1}, γ_2 = 25,000 cm–1. Why is a transition from a t_{2g} to e_g orbital spin allowed in $[V(H_2O)_6]^{3+}$? 4+2

(b) Calculate the ground state term symbol for d^3, d^8, d^{10} electronic system ? 3

(c) Deduce the character table for D_4 by using Great Orthogonality Theorm. 6

8. (a) Calculate a value for μ_{eff} for $[Ni(en)_3]^{2+}$ taking into account spin-orbit coupling. Compare your answer with μ(spin-only) and the value of 3.16 μB observed experimentally for $[Ni(en)_3][SO_4]$, given that Δ_{oct} = 11,500 cm^{-1}, γ = 315 cm^{-1}. Write down the increasing order of F^-, SCN^-, CN^-, S^{2-}, I^- under the guideline of Nephelauxetic effect. 3

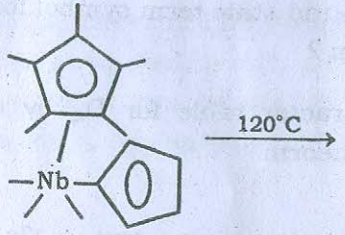
(b) Explain why an electronic transition for high-spin $[Mn(H_2O)_6]^{2+}$ 2p is spin-forbidden, but for $[Co(H_2O)_6]^{2+}$ is spin-allowed. 2

(c) Draw the MO diagram of octahedral $[Mo(CO)_6]$ (indicating both sigma and p interaction with proper symmetry). 3

(d) Synthesize cis and trans isomer of $[PtCl_2(NO_2)(NH_3)]^-$. 6

9. (a) Predict the product

(i) Fe(g) +  (g) ⟶

(ii) 

(iii) $Na[Mn(CO)_5]$ +  $\longrightarrow$ A $\xrightarrow{h\nu}$ B

(iv) $Cp_2Ni + Na(Hg) \xrightarrow{EtOH}$

(v) $RhCl_3 + C_2H_4 + EtOH \longrightarrow$

(vi) $Fe_2(CO)_9 + CH_2 = C = CH_2 \longrightarrow$ 6

(b) The alkene complex $Fe(PMe_3)_4\eta^2$-propane at low temperature shows four peaks in it ^{31}P NMR spectra. Draw structure of the complex. When the sample is warmed four peaks in ^{31}P NMR spectra converted to two peaks in same intensity — explain this phenomenon. 3

(c) Calculate the number of metal bond in $Co_3(CO)_9CH$, $Ru_6C(CO)_{17}$, $[Fe_4(CO)_{12}(\mu_4 - C)^{2-}$, $Fe_5C(CO)_{15}$ 4

(d) Discuss the fluxional behaviour of $[Ru(\eta^4 - C_8H_8)(CO)_3]$. 2

10. (a) What do you mean by accuracy ? What is determinate error ? Write short notes on (i) personal error and (ii) Methodic error. 1+2+4

(b) Write down the principle of paper chromatography. What is Rf value discuss the significance of it ? 4+4

Group–C

11. Answer any *five* of the following : 5×5

(i) A borane molecule has its STYX no 3203 predict the formula of the molecule and draw the possible structure ?

(ii) Predict the core structure of $CpFe(C_2B_9H_{11})]^-$ and $[(Ph_3P)_2(H)IrB_9H_{11}]$.

(iii) Discuss the role of distal and proximal histidine residue in haemoglobin and myoglobin ? Explain the trigger mechanism ?

(iv) Discuss the reactivity of Fisher and Schrock type carbine towards electrophiles and nucleophiles ?

(v) Explain the diamagnetism of Ruthenium Red-complex.

(vi) Deduce the following oxides as normal or inverse spinel with explanation $NiFe_2O_4$ and Fe_3O_4.

(vii) Discuss nitrogen fixation mechanism.

(viii) Calculate the STYX number of B_4H_{10} and write the probable structure.
