

OLD

2017

M.Sc. Part-I Examination

CHEMISTRY

PAPER—III

Full Marks : 75

Time : 3 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 each group.

**Group-A**

1. (a) How Bohr effect helps the function of haemoglobin ?  
2
- (b) Discuss the storage and transfees of  $\text{Ca}^{2+}$  in biological system. What do you mean by  $\text{Na}^+ - \text{K}^+$  pump and how does it work ?  
4

(Turn Over)

- (c) Write notes on carbonic anhydride. 3
- (d) What is chelation therapy? How chelation therapy be applied for removal of lead ( $Pb^{2+}$ ) contaminated human body? 1+2
- (e) Explain the formation of hemation and discuss how this can be prevented? 3
2. (a) Arrange in order of increasing lability :  
 $[K(H_2O)_6]^+$ ,  $[Ir(H_2O)_6]^{2+}$ ,  $[Al(H_2O)_6]^{3+}$ ,  $[Fe(H_2O)_6]^{3+}$  2
- (b) What do you mean by template effect? How will you determine the composition of a complex by Job's method? 1+3
- (c) What are the roles of masking and demasking agents during the complexometric titration? 3
- (d) Write notes on "Macrocyclic effect". 3
- (e) What do you mean by fluxionality? Why NMR spectroscopy is used to detect the fluxional behaviour — explain. 1+2

3. (a) The absorption spectra of  $[Ni(H_2O)_6]^{2+}$  shows three transitions around 8500, 15000 and 26000  $cm^{-1}$ . Assign these transitions. 3
- (b)  $CrO_4^{2-}$  is coloured other than d - d transition — explain. 3
- (c) The C - C bond distance ( $1.37 \text{ \AA}$ ) in  $K^+[PtCl_3(C_2H_4)]^-$  is slightly longer than in the free ethylene ( $1.34 \text{ \AA}$ ) — explain. 4
- (d) Give examples of Fischer and Schrock type of carbonyl complexes & explain their bonding. 5
4. (a) Write notes on :  
 (i) Tungsten Bronze,  
 (ii) Vasca's complex,  
 (iii) Ruthenium red,  
 (iv) Dioxygen as ligand. 4×2
- (b) Why borazine is nicknamed as "inorganic benzene"? 3
- (c) Assuming 18 electron rule to be valid find the number of Os - Os bonds in  $Os_4(CO)_{14}$ . 2
- (d) Although  $V(CO)_6$  is a 17 electron system, yet it does not dimerise — explain. 2

5. (a) Prove that for HCHO molecule  $n - \pi^*$  transition is symmetry forbidden whereas  $\pi - \pi^*$  transition is symmetry allowed. 4
- (b) What are the essential criteria for a collection of entities must have to form a group? 3
- (c) Show that the order of a group is an integral multiple of the order of its sub-group. 3
- (d) State the "rearrangement theorem". Does the relation  $A^2 = B^2 = E$ , holds good for the following Abelian group. {E, A, B}, where E is the identity element. 2+3

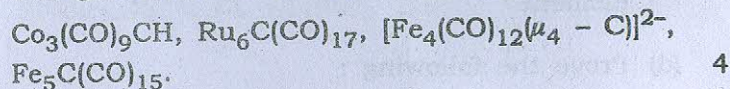
### Group-B

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)  $[\text{Ni}(\text{CN})_5]^{3-}$
- (iii)  $\text{NH}_4^+$
- (iv) HCHO.  $4 \times \frac{1}{2}$
- (c) Find matrix representation of  $C_{3v}$  point group. 4

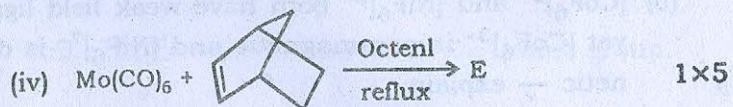
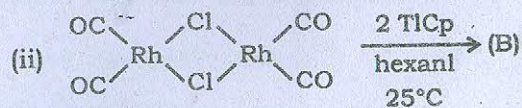
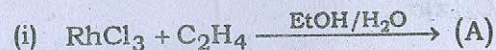
- (d) Give Hermann - Mauguin (H - M) notation for  $D_{3h}$ ,  $D_{2h}$ ,  $C_{3v}$  and  $C_{2h}$  point group. Write down the number of faces, vertices and edges for dodecahedron and isoctahedron. 2+3
7. (a) Calculate all the IR and Raman active modes present in  $\text{H}_2\text{O}$  molecule. 3
- (b) Define class. Find the number of classes in  $\text{NH}_3$  molecule using similarity transformation. 5
- (c) Prove that no classes of a group can share a common element. 3
- (d) Prove the following :
- (i)  $S_2 = i$
- (ii)  $\sigma_d = C_4(z)\sigma_{xz}$
- (iii)  $C_2(z) = C_2(y)C_2(x)$
- (iv)  $S_4^5 = S_4^1$  4×1
8. (a) Using an Orgel diagram explain the electronic spectral transition for  $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$  in weak octahedral field indicating the spectroscopic ground state. 4
- (b)  $[\text{CoF}_6]^{3-}$  and  $[\text{NiF}_6]^{2-}$  both have weak field ligand  $\text{F}^-$ , yet  $[\text{CoF}_6]^{3-}$  is paramagnetic and  $[\text{NiF}_6]^{2-}$  is diamagnetic — explain. 2

- (c)  $\text{Mn}^{2+}(\text{aq})$  is faintly coloured whereas  $\text{aq. solution of } \text{MnO}_4^-$  is deeply coloured — explain. 2
- (d) In  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ , two water molecules undergo exchange with bulk solvent molecule much more rapidly than the other four — justify. 4
- (e) The stability of  $[\text{Ni}(\text{en})_3]^{2+}$  is much greater than  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  — explain. 3

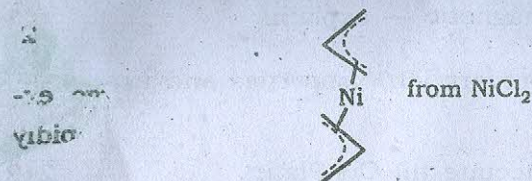
9. (a) Deduce the structure of metal clusters using Wade-Mingos-Lauher rule of the following :



(b) Predict the product :



(c) How will you synthesise the following?



(d) The addition of excess  $\text{HCl}$  to a  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  solution changes the colour from pink to blue, however this change is not observed for  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  on addition of  $\text{HCl}$  — explain. 4

10. (a) Is  $p_y \rightarrow p_x$  is an allowed transition in a  $T_d$  molecule? — Explain. Given below the character table for  $T_d$  point group. 3

$T_d$	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
$A_1$	1	1	1	1	1		$x^2 + y^2 + z^2$
$A_2$	1	1	1	-1	-1		
E	2	-1	2	0	0		$(x^2 - y^2, 2z^2 - x^2 - y^2)$
$T_1$	3	0	-1	1	-1	$(R_x, R_y, R_z)$	
						$(x, y, z)$	
$T_2$	3	0	-1	-1	1		$(xz, yz, xy)$

- (b)  $\text{Ni}(\text{CO})_4$  is tetrahedral and  $\text{Ni}(\text{CN})_4^{2-}$  is sq. planar, but both are diamagnetic — explain. 3
- (c) Discuss the preparation, properties and uses of the following :
- (i) zincuranylacetate (ii) Cis-Platin. 2+2
- (d)  $\text{KMnO}_4$  is an oxidant in both acidic and alkaline media but  $\text{K}_2\text{Cr}_2\text{O}_7$  is an oxidant in acidic medium only — explain. 2
- (e) Electronic absorption spectrum of 4f block ions consists of broad bands — explain. 3
-