PG Odd Semester (CBCS) Exam., December—2017

CHEMISTRY

(1st Semester)

Course No. : CHMCC–101

(Inorganic Chemistry—I)

Full Marks : 70
Pass Marks : 28

Time : 3 hours

The figures in the margin indicate full marks for the questions

Answer **five** questions, taking **one** from each Unit

UNIT—I

1. *(a)* Work out the Schöenflies notations for the following species : 2×3=6

(i) N_2O

(ii) HPO_3^2

(iii) CH_2N_2 (diazomethane)

(b) Furnish the examples of molecules that possess— 1×4=4

(i) only ;

(ii) only C_2;

(iii) I_n symmetry point group;

(iv) C_V symmetry point group.

(c) Develop the matrix corresponding to C_2 operation in a C_{2v} point group and show that C_2 is its own inverse. 4

2. *(a)* Furnish symmetry point group for the following : 2×3=6

(i) SO_3

(ii) H_3O

(iii) Staggered $Fe(Cp)_2$

(b) Work out the point group of $[Co(en)_3]^3$ and comment on its optical activity. 4

(c) What is the order of an O_n point group? For a $[PtCl_6]^2$, what would be the consequence on symmetry if the axial Cl is replaced one at a time? 4

UNIT—II

3. *(a)* Describe the potential energy curve for the ionic solid (NaCl). Derive the relationship for the crystal energy ($E_{crystal}$) from equilibrium energy consideration. 6

(b) Construct the MO diagram of CO_2 molecule showing the electronic arrangement. Work out the number of bonding and antibonding electrons. 4

(c) State and explain Bent's rule and hence discuss the shape and bond angles in PCl_2F_3. 4

4. *(a)* On the basis of VSEPR theory, predict the shapes and explain the O—N—O bond angles for NO_2, NO_2, NO_2. Indicate the state of hybridization of the central atom. 6

(b) What is meant by absolute hardness? Use this approach to illustrate the HSAB properties among halogen molecules. 1+3=4

(c) Describe the Jahn-Teller distortion in $[Cu(H_2O)_6]^2$. 2

(d) When Ge is doped with Ga it becomes a *p*-type semiconductor. Explain. 2

UNIT—III

5. *(a)* Draw the topological diagram of B_5H_9 and B_5H_8. 2+2=4

(b) Calculate the number of skeletal electrons of the following cluster and nomenclate : 2+2=4

(i) B_4H_{10}

(ii) $Fe_3(CO)_{12}$

(c) Complete the following reactions and draw the structures of the final products : 2×3=6

(i) $B_5H_9 + NH_3 \longrightarrow A \xrightarrow{\frac{1}{2}\,B_2H_6} B$

(ii) *nido*-$B_{10}H_{14} + SEt_2 \longrightarrow A \xrightarrow{C_2H_2} B$

(iii) *closo*-1,7-$C_2B_6H_8 \xrightarrow[NaC_5H_5]{2e/th+,\ COCl_2} A$

6. *(a)* *(i)* Write the products when NH_4Cl reacts with PCl_5 in 1,1,2,2-tetrachloroethane at 146 °C. 2

(ii) Discuss the -bonding in cyclophosphazenes. 4

(b) What are silicates? Explain different types of silicate with examples. 6

(c) Write a short note on 'polyacid'. 2

UNIT—IV

7. *(a)* Write the sources and sinks of CO gases. Explain 'CO poisoning' in human. 4

(b) Explain how Pb-poisoning interferes with the heme synthesis. How is detoxification of Pb carried out? 3

(c) Discuss the passive transport of ions/substances across the cell membrane. 5

(d) Write a note on Spherands. 2

8. *(a)* How does arsenic pollution occur? Discuss the biochemical aspects of arsenic poisoning in human body. 6

(b) Illustrate the ion-transport mechanism through a cell membrane using model macrocyclic ligand. 4

(c) Write short notes on the following : 4

(i) Acid rain

(ii) Crown ether complex

UNIT—V

9. *(a)* The half-lives of substitution reactions of the pair of complexes are given as :

$t_{1/2}$ 1 min	$t_{1/2}$ > 1 day
$[Cr(CN)_6]^4$	$[Cr(CN)_6]^3$
$[Fe(H_2O)_6]^3$	$[Fe(CN)_6]^4$
$[Co(H_2O)_6]^2$	$[Co(NH_3)_5(H_2O)]^3$

Interpret the differences in half-lives. 2×3=6

(b) The following data have been obtained at 50 °C for aquation of $[Cr(NH_3)_5X]^2$ (K_{aq}) :

X	K_{aq} (10^4 sec^1)
NCS	0·11
Cl_3CCO_2	0·37
F_3CCO_2	0·50
Cl	1·75
Br	12·5
I	102
H_2O	13·7 (exchange)

What conclusion can be drawn about the mechanism of these reactions? Explain. 4

(c) What is associative reaction? Derive a rate law for an associative reaction. 4

10. *(a)* What is the significance of the following facts for the mechanism of substitution of X by Y at Co(III) in aqueous solution?

(i) The rates of aquation are always given by expression :

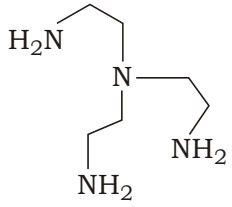
$$\text{rate} = k_{aq}\,[Co(NH_3)_5X]^2$$

(ii) No direct replacement of X by Y is ever observed. 3

(b) Base hydrolysis of

trans-$[Co(tren)(NH_3)Cl]^2$

is 10^4 times faster than the *cis*-form. Explain with mechanism : 5

tren = 

(c) How would you account for the observation that the rate of hydrolysis of $[Co(en)_2F_2]NO_3$ is greatly enhanced by either acid or base? It increases linearly with [H] below pH 2 or with [OH] above pH 6. 4

(d) In an inner sphere reaction between $[Cr(H_2O)_6]^2$ and $[Co(NH_3)_5X]^2$, the rate of the reaction decreases as X varies in the order I Br Cl F . Explain. 2

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