

2019

Time : As in Programme

Full Marks : 50

Answer all questions. The figures in the right-hand margin indicate marks.

1. (a) Write down the postulates of VSEPR theory and explain the limitations of the theory. 5+3
(b) Write down the shapes and structure of following species : 2×4
(i) :CCl_2 (ii) $\text{S}_2\text{O}_3^{2-}$
(iii) XeF_6 (iv) SbCl_6^{3-}

OR

- (a) State Wade's rule and classify the following compounds as Closo, Nido, Arachno etc. 4+4
(i) $\text{B}_4\text{H}_6(\text{CoCp})_2$
(ii) $\text{Fe}_4\text{C}(\text{CO})_{12}^{2-}$
(iii) Bi_5^{3+}
(iv) $\text{C}_2\text{B}_4\text{H}_6\text{Ni}(\text{PPh}_3)_2$
(b) Select the species with which $\cdot\text{CH}_3$ is isolobal and explain : 2
(i) $\text{Fe}(\text{CO})_5^\oplus$ (ii) $[\text{Cr}(\text{CO})_5]^\ominus$
 $\text{Cr}(\text{CO})_5$ $[\text{Mn}(\text{CO})_5]$
(iii) $\text{Re}(\text{CO})_5$
 $\text{W}(\text{CO})_5$

(2)

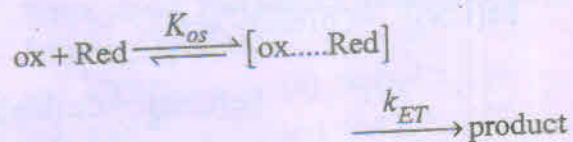
- (c) Determine styx number of the following Boranes : 3+3
(i) B_6H_{10} (ii) B_4H_{10}
2. (a) What do you mean by stepwise and overall formation constant? How are they related? 7
(b) Explain why — 2×5
(i) bpy can produce easily the tris chelate while 6,6'-dimethyl-bpy fails to produce, the tris chelate?
(ii) BF_4^- and ClO_4^- show only very poor complexing power?
(iii) The hard-soft interaction is an important consideration to determine stability constant?
(iv) Chelate effect is denied in $Ag(en)^+$
(v) Macrocyclic effect is an extension of the chelate effect

OR

- (a) State and explain the factors that affect the stability of a metal complex in a solvent. 7
(b) How stepwise formation constant can be determined spectrophotometrically? 10
3. (a) Explain why — 2×5
(i) $Cis-[Co(en)_2Cl_2]^+$ aquates at a faster rate than the trans isomer?
(ii) Anation reaction of $Cr(H_2O)_6^{3+}$ and $Cr(H_2O)_5OH^{2+}$ follow Ia and Id mechanisms with u^- as a nucleophile?

(3)

- (iii) The base hydrolysis of $\text{Co}(\text{py})_6^{3+}$ does not follow D-CB mechanism ?
- (iv) For the base hydrolysis of $\text{cis-}[\text{Co}(\text{en})_2\text{NH}_3\text{Cl}]^{2+}$ the % of cis-product and trans-product are 77.0 and 23.0 ?
- (v) The E.T rate constant of $\text{Co}(\text{NH}_3)_6^{3+}$ is smaller than that of $\text{Co}(\text{phen})_3^{3+}$ with $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ as reluctant ?
- (b) For the following mechanism determine the rate law : 5+2



of $K_{os}[\text{Red}] < 1.0$, what is the order of the reaction with respect to $[\text{Red}]$ and $[\text{ox}]$.

OR

- (a) Using Marcus Cross relationship prove that
- $$K_{AB} = (K_{AA} \times K_{BB} \times K_{AB} \times F_{AB})^{1/2}$$
- K_{AB} = Cross reaction rate constant
- $K_{AA} \times K_{BB}$ = self exchange reaction rate constants
- K_{AB} = equilibrium constant

$$F_{AB} = \frac{(Z_{AB})^2}{(Z_{AA} \times Z_{BB})} Z_{ij} = \text{Collision frequency} \quad 10$$

(4)

(b) Explain why?

2×2

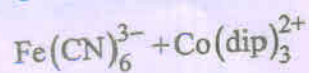
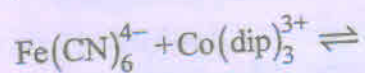
(i) E.T between $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ and $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ is much faster than between $\text{Co}(\text{NH}_3)_6^{3+}$ and $\text{Cr}(\text{H}_2\text{O})_6^{2+}$?

(ii) In O.S.E.T, $\pi - \pi^*$ and in

I.S.E.T $\sigma^* - \sigma$ E.T is favourable?

(c) Evaluate K_C for the following equilibriums process at 298 k

3



$$E^\circ (\text{R}\cdot\text{P}) \text{ for } \frac{\text{Fe}(\text{CN})_6^{3-}}{\text{Fe}(\text{CN})_6^{4-}} = +0.355\text{V}$$

$$\text{and for } \frac{\text{Co}(\text{dip})_3^{3+}}{\text{Co}(\text{dip})_3^{2+}} = +0.370\text{V}$$