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*) $S_2O_3^{2-}$

(*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*) $B_4H_6(CoCp)_2$

(*ii*) $Fe_4C(CO)_{12}^{2-}$

(*iii*) Bi_5^{3+}

(*iv*) $C_2B_4H_6\,Ni(PPh_3)_2$

(*b*) Select the species with which $\cdot CH_3$ is isolobal and explain : 2

(*i*) $Fe(CO)_5^{\oplus}$ $Cr(CO)_5$ (*ii*) $[Cr(CO)_5]^{\ominus}$ $[Mn(CO)_5]$

(*iii*) $Re(CO)_5$ $W(CO)_5$

(*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*) $BF_4^{\ominus}$ 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 $Agen^{\oplus}$

(*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–$[Co(en)_2Cl_2]^{\oplus}$ 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 ?

(*iii*) The base hydrolysis of $Co(py)_6^{3+}$ does not follow D–CB mechanism ?

(*iv*) For the base hydrolysis of cis–$[Co(en)_2NH_3Cl]^{2+}$ the % of cis-product and trans-product are 77.0 and 23.0 ?

(*v*) The E.T rate constant of $Co(NH_3)_6^{3+}$ is smaller than that of $Co(phen)_3^{3+}$ with $Cr(H_2O)_6^{2+}$ as reluctant ?

(*b*) For the following mechanism determine the rate law : 5+2

$$ox + Red \underset{}{\overset{K_{os}}{\rightleftharpoons}} [ox.....Red]$$

$$\xrightarrow{k_{ET}} product$$

of $K_{os}[Red] < 1{\cdot}0$, what is the order of the reaction with respect to [Red] and [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} = Collision frequency 10

(*b*) Explain why ? 2×2

(*i*) E.T between $Co(NH_3)_5Cl^{2+}$ and $Cr(H_2O)_6^{2+}$ is much faster than between $Co(NH_3)_6^{3+}$ and $Cr(H_2O)_6^{2+}$?

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

I . S . E . T $\overset{*}{\sigma} - \overset{*}{\sigma}$ E.T is favourable ?

(*c*) Evaluate K_C for the following equilibriums process at 298 k 3

$$Fe(CN)_6^{4-} + Co(dip)_3^{3+} \rightleftharpoons Fe(CN)_6^{3-} + Co(dip)_3^{2+}$$

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

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

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