Total number of printed pages–11

14 (CHM–2) CH 201

2019

CHEMISTRY

Paper : CH 201

(Inorganic Chemistry – 2)

Full Marks : 80

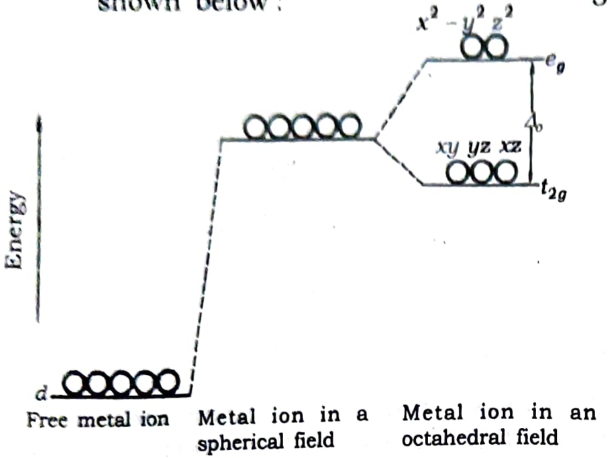
Time : Three hours

The figures in the margin indicate full marks for the questions.

1. Answer ***any four*** questions : 5×4=20

(i) Explain how valence bond theory can be applied to show the formation of six *Co-N* bonds in the complex ion $[Co(NH_3)_6]^{3+}$. Does this complex follow the EAN rule? What will be hybridization schemes to be applied to discuss the bonding in MnO_4^- and $[Ni(CN)_4]^{2-}$? 3+1+1=5

(ii) Describe the theoretical basis of the effect of crystal fields on *d*-orbitals as shown below : 5



(iii) What are various factors which determine the crystal field splitting parameter ? Is it possible to rationalize the 'spectrochemical series' using crystal field theory (CFT) ? Comment briefly on the utility of CFT in spite of its limitations. 2+1+2=5

(iv) State Jahn-Teller theorem and explain how it can affect the structure and electronic behaviour of octahedral complexes. Explain by taking Ni^{2+} and Cu^{2+} as examples why Jahn-Teller effect is generally important in octahedral complexes having odd-number occupancy of the e_g level. 3+2=5

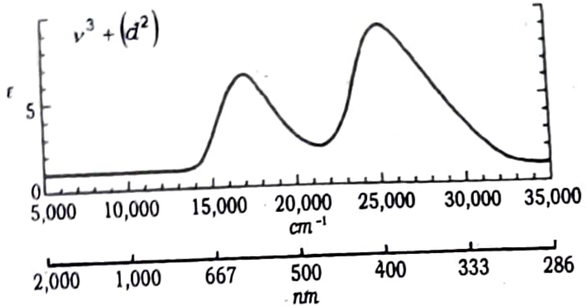
(v) Define a 'medium or strong' crystal (ligand) field and explain why it is less important to classify crystal (ligand) fields into weak and strong fields in the cases of second- and third-row transition metal complexes. Determine the ligand field ground states for the complex ions $[Fe(OH_2)_6]^{3+}$ and $[Ru(OH_2)_6]^{3+}$. 3+2=5

(vi) Highlight the aspects that make the molecular orbital theory (MOT) the best theory for taking account of metal-ligand bonding in coordination compounds. Draw the qualitative MO energy level diagram for high-spin $[CoF_6]^{3-}$ and indicate how MOT validates the idea of *d*-orbital splitting of crystal (ligand) field theory. 2+3=5

2. Answer ***(i)*** and ***any two*** from the remaining questions : 3+5×2=13

(i) What are the selection rules that govern electronic transitions occurring in transition metal complexes ? Invoke these rules to explain why charge-transfer spectra are generally more intense than ligand field spectra of transition metal complexes. 3

(ii) Study the electronic spectrum given below :



In the above electronic spectrum of $V(ClO_4)$ in aqueous $HClO_4$, in addition to the above bands occurring at ~580 *nm* and ~400 *nm* there is also a weak band that occurs in the UV region at ~260 *nm*. Interpret the spectrum in the light of ligand field theory. 5

(iii) What are Condon-Shortley and Racah parameters? What are the advantages of Racah parameters? State how Racah parameters find use in the construction of ligand field energy level diagrams for transition metal complexes.

2+2+1=5

(iv) Explain why $[FeF_6]^{3-}$ is colourless whereas $[CoF_6]^{3-}$ is coloured but exhibits only a single band in the visible region of the spectrum. 5

3. Answer *(i)* and ***any two*** from the remaining questions : 5+4×2=13

(i) Comment on various types of magnetic behaviour of transition metal complexes and briefly state how it is possible to establish experimentally that a particular type of magnetic behaviour is shown by a given species. 5

(ii) Derive the expression for magnetic moment (μ) where the multiplet width is small as compared to kT. 4

(iii) What are the conditions that can facilitate electron motion around nucleus resulting in the deviation of magnetic moments of the 3*d* transition metal complexes from the spin-only value? What do you mean by non-magnetic doublet in transition metal complexes of octahedral geometry?

4

(iv) Give brief explanations in support of ***any two*** of the following statements : 2×2=4

a. $Mn_2(CO)_{10}$ is diamagnetic.

b. Magnetic superexchange is more in $[(NH_3)_5Cr\text{-}O\text{-}Cr(NH_3)_5]^{4+}$ than $[(NH_3)_5Cr\text{-}OH\text{-}Cr(NH_3)_5]^{5+}$.

c. Magnetic moments of *Sm* (III) and *Eu* (III) complexes cannot be calculated simply using the formula,

$$\mu_j = g\beta\,[J\,(J+1)]^{1/2}$$

4. Answer ***(i)*** and ***any two*** from the remaining questions : 5+4×2=13

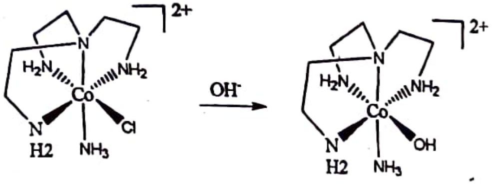
(i) Derive the rate equation for the dissociative *(D)* and associative *(A)* substitution reactions in an octahedral complex. How do you determine that a complex is undergoing substitution reaction through dissociative or associative mechanism ? 3+2=5

Or

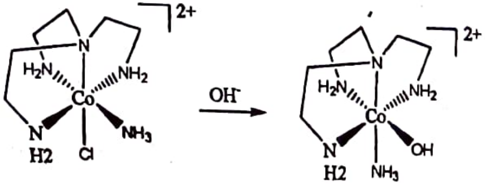
What are labile and inert complexes ? Give *one* example of each. What are the factors that affect the inertness or lability of an inorganic complex ? 2+1+2=5

(ii) Show the stereochemistry of the species involved in substitution reaction by taking a suitable octahedral complex as an example. 4

(iii) In the following base hydrolysis reactions (leaving group : Cl^-), the first reaction is 10^4 times faster than the second one. Explain. 4



(1)



(2)

85% product

Contd.

(iv) What do you mean by 'reorganization energy' in outer sphere electron transfer reactions ? How does the inner sphere reorganization energy dictate the rate of electron transfer in complexes ? Give the example of one inorganic complex showing fast electron transfer and explain the reason behind it.

1+1+2=4

5. Answer ***any two*** of the following questions :

4×2=8

(i) What are thexi and DOSENCO states as encountered while studying the photochemical behaviour of coordination compounds ? 4

(ii) Comment on the photochemical behaviour of $[Ru(bpy)_3]^{2+}$ where *bpy* stands for 2, 2'-bipyridine. Relate this behaviour of the *tris*-chelate complex with its possible utility in photocatalysis. 4

(iii) Predict major products ***(any four)*** :

1×4=4

(a) $[W(CO)_5(NH_3)]$ +

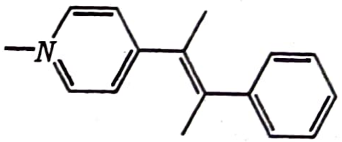
$\xrightarrow{h\nu}$

(b) $[Mo(\eta^5-C_5H_5)(CO)_3(NCS)] \xrightarrow{h\nu}$

(c) $[Rh(NH_3)_5(NCS)]^{2+} \xrightarrow{h\nu}$

(d) $[Mn(CO)_5I] \xrightarrow{h\nu}$

(e) $(CO)_5W$ —



$\xrightarrow{h\nu}$

(f) $[Fe(CO)_2(PF_3)_3] \xrightarrow[PF_3]{h\nu}$

(g) $cis-[RhCl_2(NH_3)_4]^+ \xrightarrow[H_2O]{h\nu}$

6. Answer *(i)* and ***any two*** from the remaining questions : 5+4×2=13

(i) What is the major difference between nuclear reactions and chemical reactions ? How are nuclear reactions classified ? Write what you know about nuclear spallation reactions. 1+2+2=5

Or

What is radiocarbon dating? If an old piece of wood has 25.6% as much ^{14}C as ordinary wood today has, then what is the age of the wood ? (Given : Half-life period of ^{14}C is 5760 years) 3+2=5

(ii) The half-life of the nuclide ^{220}Rn is 54.5 seconds. Find the mass of the radon nuclide which is equivalent to 1 milicurie (mCi) of radioactivity ? (Given : $1\ mCi = 3.7\times10^{7}$ disintegrations per second) 4

(iii) Explain the radioactive decay processes of ^{14}C, ^{23}Mg with the help of nuclear stability belt. 4

(iv) Explain what is neutron activation analysis and state briefly about its advantages, disadvantages and applications. 4
