MOUNTAIN TOP UNIVERSITY

E-Courseware

COLLEGE OF BASIC AND APPLIED SCIENCES

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COURSE GUIDE

COURSE TITLE: Coordination Chemistry

COURSE CODE: CHM 423

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COURSE OBJECTIVES

GENERAL INTORDUCTION AND COURSE OBJECTIVES

This course aims at explaining the concept of coordination compounds, nomenclature, ligands and isomerism in complex compounds. It will deals with the various methods of preparing complexes, theories of complexes and their various applications. It also explains the principle of thermodynamic stability of complex compounds.

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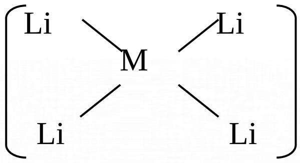
LECTURE ONE
Coordination Compounds

1.0 Introduction

Coordination compound is a complex in which a central metal atom is surrounded by molecules called ligands which acts as Lewis base while the central metal acts as Lewis acids.



A **complex** is an ion or a compound consisting of a central metal ions or atoms surrounded by and datively bonded to other ions or molecules called ligands.

Objectives

At the end of this lecture, students should be able to:

1. Define Coordination compounds;
2. Explain ligands and give examples of ligands;
3. Homoleptic and Heteroleptic Complexes;
4. Define coordination number and give examples;
5. Provide the IUPAC names of complexes, and
6. Calculate the oxidation state of the central metal atom in complexes.

Pre-Test

1. Define coordination compounds.
2. Distinguish between Homoleptic and Heteroleptic Complexes.
3. What do you understand by the term ligands?

CONTENT

A **ligand** is an ion or a molecule containing at least one atom having a lone pair of electrons which can be donated to a central cation or atom to form a dative/covalent bond. Thus, in coordination compound, metal specie acts as electron acceptor (Lewis bases) while the ligands acts as electron donor (Lewis acid).

Transition metals have high tendency to form coordination compounds/complexes and this is due to their relatively small sizes, higher ionic charges and most importantly the availability of d-orbitals for bond formation i.e. $[Pt(NH_3)Cl_2]$ is a complex in which platinum is surrounded by two ammonia molecules and two chloride ions.

Coordination number is the number of ligand donor atoms directly bonded to the central atom e.g. in the complex species $[Mo(CN_8)]^{3-}$ and $[CoCl(PR_3)_3]$, the coordination number of Mo and Co are 8 and 4 respectively. The central atom and the ligands bonded to it are enclosed in a square bracket and is collectively termed as coordination sphere. The spatial arrangement of ligands around the central atom is called coordination polyhedron.

Types of Ligands

1. **Unidentate Ligands:** These are ligands which bonds to the central metal atom through a single atom e.g. Cl^-, CN^-, H_2O and NH_3 which is bonded through Nitrogen atom.
2. **Polydentate Ligands:** These are ligands which links to the central metal atom through atoms higher than two e.g. diethylenetriamine (diamine), terpyridine (terpy) etc.

   a. Tridentates

   $H_2N – CH_2 – CH_2 – NH – CH_2 – CH_2 – NH_2$

   b. Tertradentates (four) e.g. triethylenetertramine (triene)

   $H_2N – CH_2 – CH_2 – NH – CH_2 – CH_2 – NH – CH_2 – CH_2 – NH_2$

   Here, coordination can take place through any of the four nitrogen atoms.

   c. Pendentates (five) e.g. ethylenediamineacetato

   d. Hexadentates (six) e.g. ethylenediamineteraacetato
3. **Bidentate Ligands:** These are ligands which links to the central atom through two atoms e.g. oxalate ($C_2O_4^{2-}$), ethene-1,2-diamine (en)

In many bidentate to polydentate ligands, the liagnd is bonded to the same central atom at two or more place due to which a ring structure is formed. Such a ring formed is known as a chelate. Chelate complexes are known to have higher stability as compared to ordinary complexes. Ligands which ligates to metal ions through two atoms of different elements are called ambidentate ligands e.g. NO_2^-, SCN^-.

Homoleptic and Heteroleptic Complexes

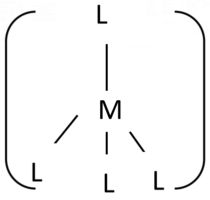
A homoleptic complex is a complex in which all the ligands which coordinate to the central metal atoms are the same e.g. $[Cr(Co)_6]$. On the other hand, heteroleptic complexes is a complex in which two or more different types of ligands coordinates to the central atom e.g. $[Co(en)_2Cl_2]^+$ etc.

Coordination Number and Structures

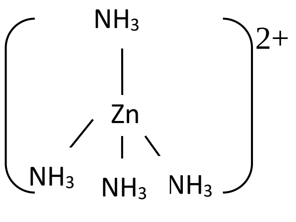
The coordination number for a metal ion in a complex is the number of ligands that are directly attached to it. Mostly, coordination number of four and six are observed and five is of considerable interest, though coordination numbers can range from 2 – 12 and beyond.

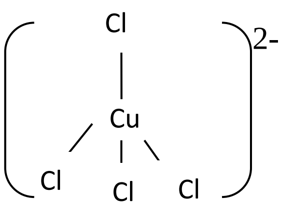
1) Coordination number 4: There are two shapes available for metal ion connected to four lone pairs

   a. Tetrahedral shapes i.e.

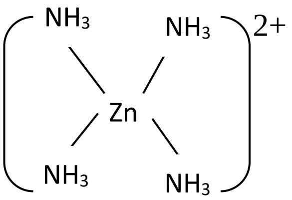


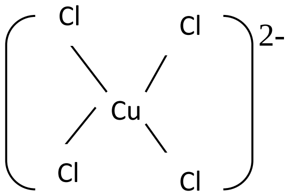
The internal bond angles are 109^0 e.g. $[Zn(NH_3)_4]^{2+}$ and $[CuCl_4]$





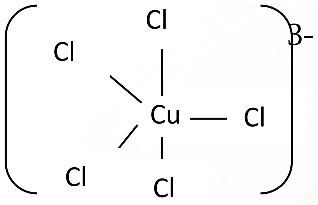
b. Square planar in which the internal bond angles are 90^0 e.g. $[Zn(NH_3)_4]^{2+}$ and $[CuCl_4]^{2-}$



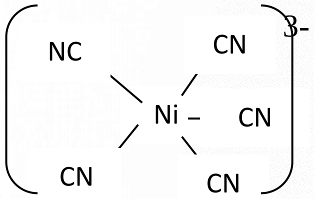


1) Coordination number 5: There are two shapes

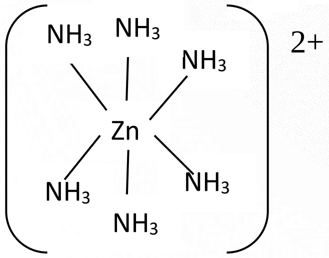
a. Trigonal bipyramid e.g. $[CuCl_5]^{3-}$



b. Square bipyramid e.g. $[Ni(CN)_5]^{3-}$



2) Coordination number 6: There is only one shape available by a metal ion surrounded by six lone pairs of electrons and the shape is octahedral e.g. $[Cu(H_2O)_6]^{2+}$



NOMENCLATURE OF COMPLEX NUMBERS

The basic rules published by IUPAC in 1989 are summarized below

i. The positive ion is named first followed by the negative ion e.g. $K_4[Fe(CN)_6]$ – Potassiumhexacyanoferrate(ii)

ii. The ligands are quoted in alphabetical order followed by the metal without any separation by hyphen.

iii. The name ligands

   a. The name of the negative ligand ends in –o

LIGAND	NAME	LIGAND	NAME
F^-	Fluoro	OH^-	Hydroxo
H^-	Hydrido	S^{2-}	Thio
Cl^-	Chloro	CN^-	Cyano

I^-	Iodo	NO^{2-}	Nitro
SO_4^{2-}	Sulfato		

b. Neutral groups have no special ending e.g.

LIGAND	**NAME**
NH_3	Amine
H_2O	Aqua
CO	Carbonyl
NO	Nitrosyl

c. Organic liagnds are usually given their normal names e.g. C_6H_5 – phenyl, CH_3 – methyl

d. Positive ligands end in –ium e.g. $NH_2 – NH_2$ hydrazinum

iv. When several ligands of the same kind occur, the prefix –di, -tri, -tetra etc. are used to show the number of ligands. An exception occurs when the name of the ligand is complex (as in organic liagnds) and in such case, bis, tris, tetrakis are used and the name of the ligand is placed in bracket e.g. $[Cr(en)_3]Cl_3$ – tris(ethenediamine)chromium(iii) chloride. Positive ion complexes and neutral molecules have no special ending but negative ion complexes end in –ate.

v. The oxidation number of the central metal is shown in Roman numeral in a bracket followed by its name.

Examples

Provide the oxidation number of the following coordination compounds and give their IUPAC names:

a. $[Co(NH_3)_6]Cl_2$

$x + (0 X 6) + (-1 X 2) = 0$

$x + 0 – 2 = 0$

$x = 2$

hexaaminecobalt(iii)chloride

b. $K_3[Fe(CN)_6]$

$(1 X 3) + x + (-1 X 6) = 0$

$3 + x – 6 = 0$

$x = 6 – 3$

$x = 3$

potassiumhexacyanoferrate(iii)

c. $[Co(NH_3)_5Cl]Cl_2$

$x + (0 X 5) + (-1) + (-1 X 2) = 0$

$x – 1 – 2 = 0$

$x = 2 + 1$

$x = 3$

pentaaminechlorocobalt(iii)chloride

Post-Test

1. Define the following: Complex, ligands and coordination number.
2. Distinguish between Homoleptic and Heteroleptic Complexes.
3. Provide the oxidation number of the following coordination compounds and give their IUPAC names:
   a. $[CrCl_3(NH_3)(OH)]Cl$
   b. $[CuCl_5]$
   c. $[Pt(CH_3)(H_2O)(NO_2)_3]Cl$

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- M.J. Winter, d-block Chemistry, Oxford Chemistry Primers, OUP, 2001.
- M.S. Silberberg, Chemistry, 3rd Ed, McGrawHill, 2003 (chapter 23).
- C.E. Housecroft, A.G. Sharpe, Inorganic Chemistry, 1st Ed, Prentice Hall, 2001
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LECTURE TWO

PREPARATIONS OF COMPLEXES AND ISOMERISM

2.0 Introduction

Several different methods can be used for the preparation of complexes which include:

i. Aqueous substitution reaction
ii. Non-aqueous substitution reaction
iii. Oxidation/reduction (REDOX) reaction
iv. Thermal dissociation of solid complexes
v. Catalysis
vi. Substitution reaction without metal-ligand bond cleavage
vii. Trans effect

Objectives

At the end of this lecture, students should be able to:

1. Mention the different methods of preparing complexes,
2. Explain the different types of isomerism in complexes and give examples,

Pre-Test

1. Mention five methods of preparing complexes.
2. Define the following: (i) Ionization isomerism (ii) linkage isomerism

CONTENT

Aqueous substitution reaction

The method involves a reaction between a metal salt in water solution and a coordinating agent (ligand). For many chemical reactions, the cations can be regarded as reacting in terms of unsolvated species $[M(H_2O)]^{n+}X^-$, the transition metal cations, the water molecule are held by more stronger bonding forces necessary for the aqueous solution reactions.

The general equation is given as

$$[M(H_2O)_{n'}]^{n+}X^- + nL \longrightarrow [MLn]X + n'H_2O$$

e.g.
$[Cu(H_2O)_6]^{2+} + 6NH_3 \longrightarrow [Cu(NH_3)_6]^{2+} + 6H_2O$

Also the synthesis of $[Cu(NH_3)_4]SO_4$ is readily prepared by the reaction between an aqueous solution of $CuSO_4.4H_2O$ and concentrated NH_3

$[Cu(H_2O)_4]SO_4 + 4NH_3 \longrightarrow [Cu(NH_3)_4] + 4H_2O$

Non aqueous substitution reaction

Substitution reactions are of course not limited to aqueous environment alone but can also be carried outside aqueous environment through many of substitution reaction e.g.

$[PtCl_4]^{2-} + C_2H_4 \longrightarrow [PtCl_3(C_2H_4)]^{-} + Cl^{-}$

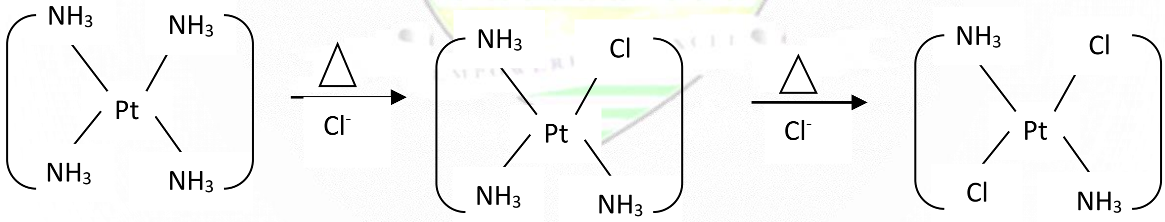
Redox reaction

Many ligands can act as reducing agents and for some metals; stabilization of high oxidation states is achieved by coordination e.g.

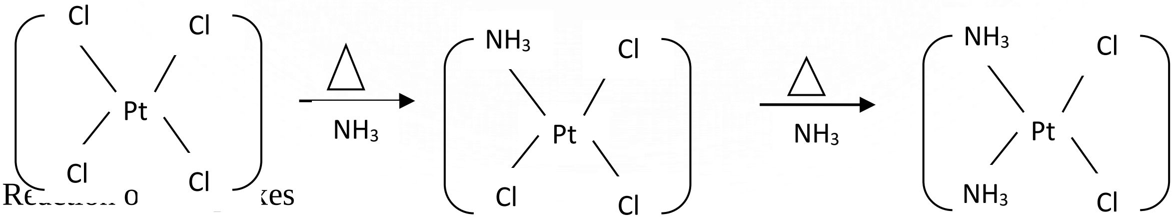
$4[Co(H_2O)_6]Cl_2 + 4NH_4Cl + 20NH_3 + 2O_2 \xrightarrow{\text{charcoal}} 4[Co(NH_3)_6]Cl_3 + 26H_2O$

Trans-effect

This is the influence in non-labile group which acts upon the rate of displacement of ligands opposite to it. The preparation of cis and trans form of complexes have been obtained through the trans-effect method. This method is relevant in the preparation of square planar complexes e.g.



The cis isomer is prepared by reaction of tetrachloro complex with ammonia (NH_3)



Re o xes

Formation processes of complexes are possible and known reactions of complexes.

Substitution reaction of complexes constitutes great part of the reactions of complexes.

Prominent reactions of complexes include:

1. Acid hydrolysis

   $[MA_5X]^{n} + H_2O \longrightarrow [MA_5(H_2O)]^{n+1} + X^{-}$

2. Acid-catalysed reaction

$[MA_5(H_2O)] + H^+ \longrightarrow [MA_5H]$

3. Anation

$[MA_5(H_2O)] + X \longrightarrow [MA_5X] + H_2O$

4. Base hydrolysis

$[MA_5X] + OH^- \longrightarrow [MA_5OH] + X^-$

ISOMERISM OF COMPLEXES

An ion or molecule has isomer if it can exist in two or more different forms with the same formula. Compounds that have the same chemical formula but different structural arrangement are called isomers.

Werner Classification

i. Ionization isomerism
ii. Hydrate isomerism
iii. Linkage isomerism
iv. Coordination isomerism
v. Geometrical/Stereoisomerism
vi. Optical isomerism

Ionization Isomerism

This type of isomerism is due to the exchange of groups between the complex ion and the ion outside it

$[Co(NH_3)_4Cl_2]NO_2 \longleftrightarrow [Co(NH_3)_4Cl(NO_2)]Cl$

$[Pt(NH_3)_4Cl_2]Br_2 \longleftrightarrow [Pt(NH_3)_4Br_2]Cl_2$

Hydrate Isomerism

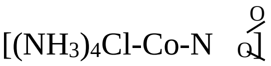
These are complexes which differ in the exchange of water molecule and ligands in the coordination sphere e.g.

$CrCl_3.6H_2O$ may have three isomers i.e.

$[Cr(H_2O)_6]Cl_3$ violet
$[Cr(H_2O)_5Cl]Cl_2.H_2O$ blue-green
$[Cr(H_2O)_4Cl_2]Cl.2H_2O$ dark green

Linkage Isomerism

These are complexes in which the donor atom have one or more coordination states e.g. SCN^-/NCS^-, NO_2/ONO^-, CN^-/NC^-, $[CoCl(NO_2)(NH_3)_4]^{2+}$ or



$[(NH_3)_4Cl\text{-}Co\text{-}N\overset{O}{\underset{O}{\rangle}}]$

Coordination Isomerism

These are complexes observed when both the positive and negative ions are complex. Isomerism may be caused by the interchange of ligand between the two complex ion e.g.

$[Co(NH_3)_6][Cr(CN)_6]$
$[Cr(NH_3)_6][Co(CN)_6]$

Post-Test

1. Discuss any three methods of preparing complexes.
2. Define the following: (i) Coordination isomerism (ii) geometric isomerism

Bibliography

- M.J. Winter, d-block Chemistry, Oxford Chemistry Primers, OUP, 2001.
- M.S. Silberberg, Chemistry, 3rd Ed, McGrawHill, 2003 (chapter 23).
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LECTURE THREE

CRYSTAL FIELD STABILIZATION ENERGY AND THEORIES OF BONDING

3.0 Introduction

CRYSTAL FIELD STABILIZATION ENERGY AND MAGNETIC PROPERTIES

This is the net effect of all the electrons i.e. the crystal field splitting. In simple terms, the d-electrons and the low complexes has a lower energy ($-0.4\ \Delta_o$) as a result of replacement of electrons in a t_2g orbitals because each electron occupying the eg orbitals of octahedral increases the energy (destabilizes by $0.6\ \Delta_o$).

Objectives

At the end of this lecture, students should be able to:

1. Define crystal field stabilization energy,
2. Explain high and low spin complexes,
3. Perform simple calculations involving crystal field stabilization energy, and
4. Explain valance bond theory and molecular bond theory.

Pre-Test

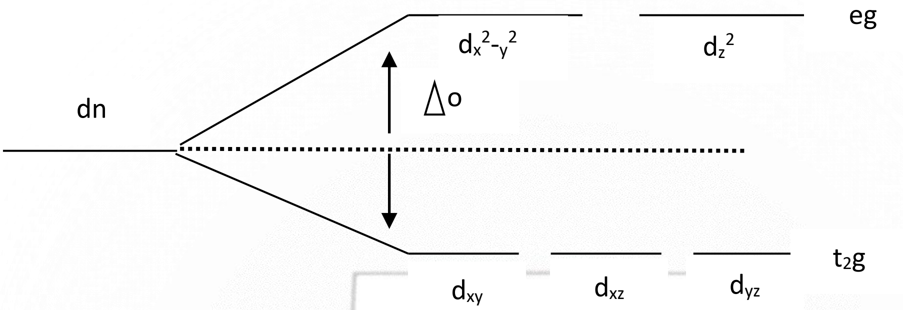
1. What is crystal field stabilization energy?
2. What do you understand by high and low spin complexes?

CONTENT

Crystal Field Theory (CFT)

This is used for interpretation of physical and chemical properties (colours, magnetic and stability properties) as well as the spectra of transition metal ions and complexes. It is the interaction of the d-orbitals of the transition metal with ligands surrounding a metal that produces crystal field effect. In crystal field theory, we imagine that the ligand acts as center of electric charge. In free (gaseous), transition metal ions, the five degenerate orbitals i.e. d_{xy}, d_{xz}, d_{yz}, d_{z^2}, $d_{x^2-y^2}$ of the d-electrons are split due to the electrostatic effects of the ligand on the central ion. As a result of the electrostatic repulsion of the ligand, the energy of the d-orbitals which lies in the direction of the ligands will be greater (e_g orbitals) while that of the orbital positions at a greater distance from the negative charge of the ligands will be smaller (t_{2g} orbitals).

In octahedral complexes, arrangement of the t_2g and eg sets of the orbitals have different energies due to the splitting being caused by the electric field of the ligands.



In a tetrahedral complex, the t_2g orbitals point more directly at the ligands than the eg orbitals and as a result in which the t_2g have higher energy than the eg orbitals.

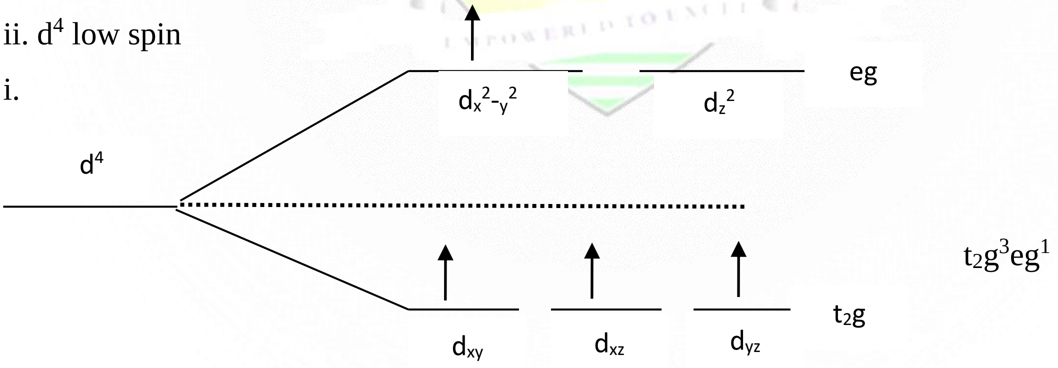
CALCULATIONS INVOLVING CRYSTAL FIELD STABILIZATION ENERGY

1. Calculate the Crystal Field Stabilization Energy (CFSE) for:

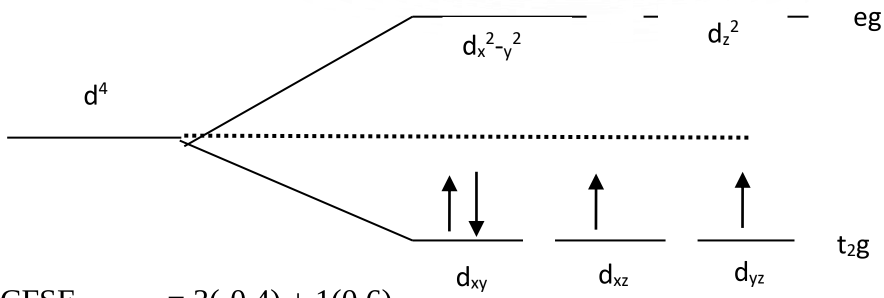
i. d^4 high spin

ii. d^4 low spin

i.



ii.



i. CFSE $= 3(-0.4) + 1(0.6)$

$= -0.6\Delta o$

ii. CFSE $= 4(-0.4)$

$= -1.6\Delta o$

2. Predict the electronic configuration of an octahedral d^5 complex with:

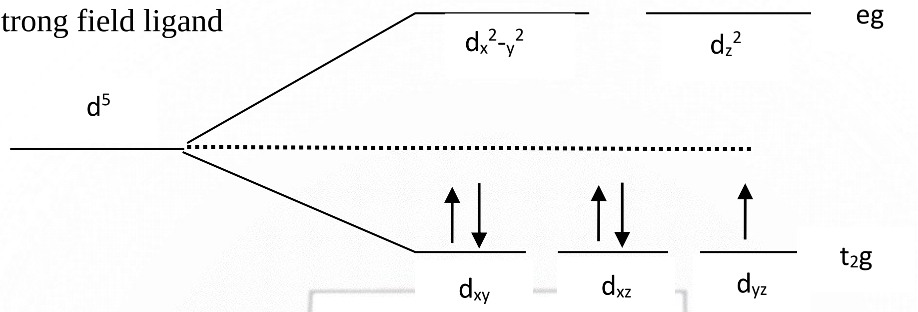
a. strong field ligand

b. weak field liand and estimate the CFSE for both cases.

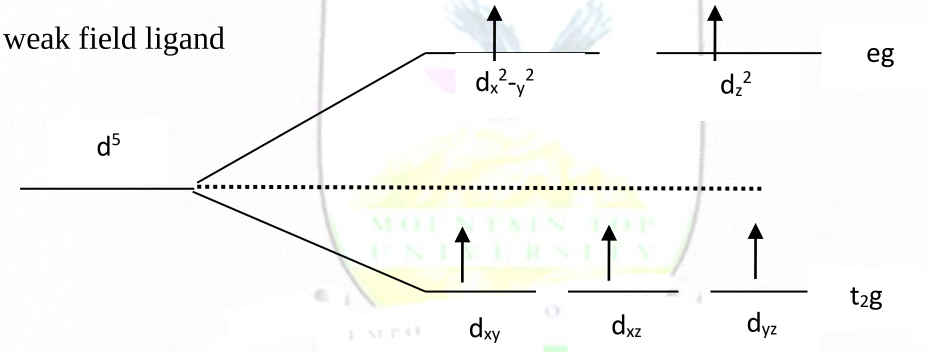
c. determine the magnetic moments and predict the magnetic property in each case.

Solution

a. strong field ligand



b. weak field ligand



a. CFSE $= 5(-0.4)$

$= -2.0\ \Delta o$

b. CFSE $= 3(-0.4) + 2(0.6)$

$= 0$

c. Magnetic moment $\mu s = \sqrt{n(n+2)}$

Where n is the number of unpaired electron(s)

i. $\mu s = \sqrt{1(1+2)}$

$= \sqrt{3}$

$= 1.73$BM

ii. $\mu s = \sqrt{5(5+2)}$

$= \sqrt{35}$

= 5.92BM

The two are paramagnetic but the weak field ligand has more magnetic properties than the strong field ligand.

The magnetic property of transition metal complexes can readily be understood in terms of crystal field theory. The magnitude of the attraction of the material to a magnet is a measure of the number of unpaired electron(s) present. Those complexes that contain unpaired electrons are paramagnetic while complexes with paired electrons are diamagnetic. Thus, a high spin complex will be more paramagnetic than a low spin complex. Some d6 complexes such as $[Co(NH_3)_6]^{3+}$ are not attracted to a magnet and as such they are known as siamagnetic but $[CoF_6]$ is paramagnetic with four unpaired electrons.

Effect of Crystal Field Splitting

In octahedral complexes, the filling of t_2g orbital decreases the energy that makes it more stable by $-0.4\Delta_o$ per electron and filling eg orbital increases the energy by $0.6\Delta_o$ per electron. The total CFSE is given by

$CFSE = 0.4nt_2g + 0.6neg$

The CFSE is zero for ions with d^0 and d^{10} in both strong and weak field ligand and also d^5 configuration in a weak field ligand.

The magnitude of CFSE depends on three factors which are:

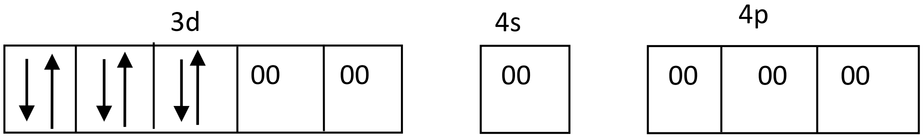
i. The nature of the ligands
ii. The charge of metal ions
iii. Whether the metal ion is 1st, 2nd or 3rd row of transition elements i.e. the magnitude of Δ_o increases as the charge on the metal ion increases. The value of Δ_o also increases on descending a group of transition elements.

Valence Bond Theory (VBT)

One of the first definite advances towards understanding why octahedral geometrics occur was made by VBT, in that empty hybrid orbitals of metals or ions having the required orientation in space accepts pairs of electrons from the ligand to for six sigma bonds. A set of six (s, p, d) orbital could be hybridized to form sp^3 and sp^2 hybridization. The orbitals are s, the 3p and the dx^2-y^2 as well as dz^2. The resulting six octahedrally oriented orbitals are called d^2sp^3 or sp^3d^2 hybrid orbitals depending on whether the principal quantum number of the d-orbital is one less than or is the same as that of the s and p orbitals.

Similarly, four equivalent hybrid orbitals directed towards a corner of a square in the xy plane can be produced from $d_{x^2-y^2}$, s, px and py. Two types of complexes could be prepared:

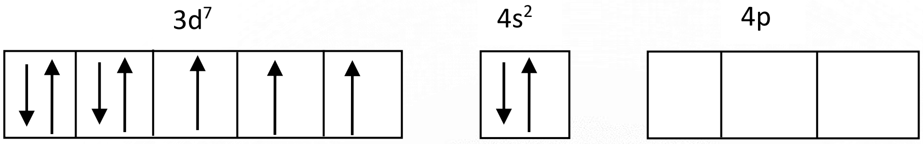
1. Outer orbital (sp^3d^2) in which the d orbital lies above the s and p orbitals.



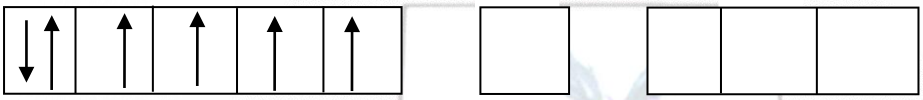
2. Inner orbital (d^2sp^3) in which the d orbital lies below the s and p orbitals

Examples: VBT explains the complexes of cobalt (ii) as follows

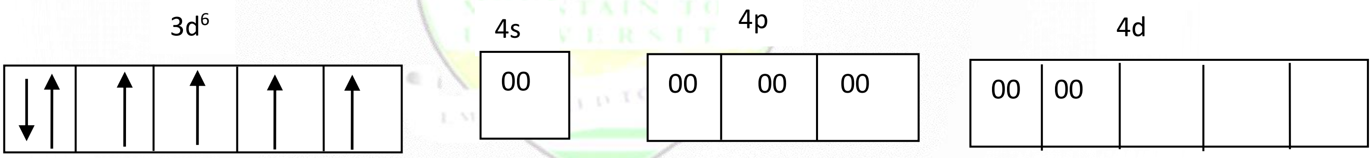
Co $1s^2$ $2s^2$ $2p^6$ $3s^2$ $4p^6$ $4s^2$ $3d^7$



Co^{3+} has six electrons which by Hund's rule will be distributed among all the 3d orbitals.

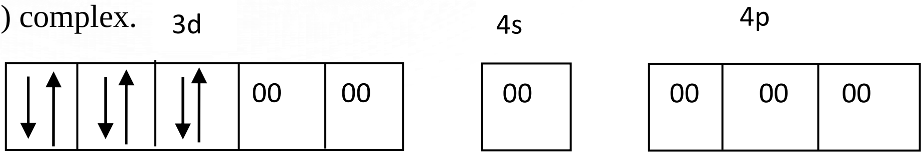


Let us assume that six ligands each with an electron pair are to form six covalent bonds with hybridized metal orbitals that are octahedrally oriented. If an outer complex is formed with 4s, 4p and 4d metal orbitals, then electrons in 3p orbitals are undisturbed.

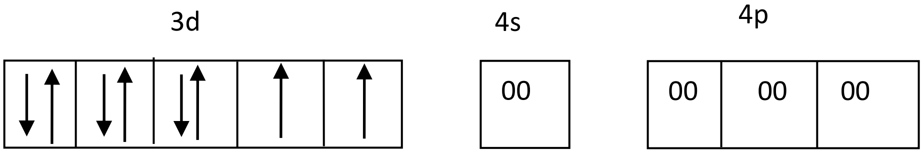


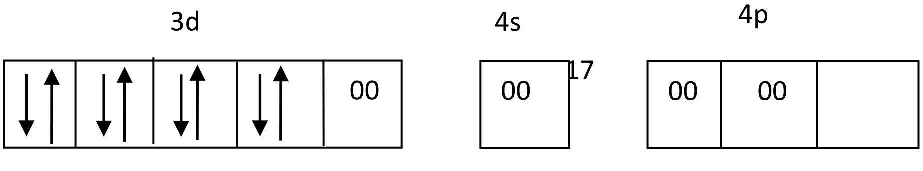
Four electrons will remain unpaired and by this theory, hexafluorocobalt (iii) ion complex $[CoF_6]^{3+}$ as an example should be paramagnetic as it is observed to be. Hexaaminecobalt (iii) ion is an inner orbital complex and it is said to be diamagnetic.

The hexafluorocobalt(iii) ion complex with high spin ligand and with the four d-orbitals form hybrid which is called outer orbital complex which is actually labile than the inner orbital complex of hexaaminecobalt (iii) complex.



VBT also account for the tetrahedral and square planar geometry of four coordinate complexes e.g. $[NiCl_4]^{2-}$ and $[Ni(CN)]^{2-}$





$[NiCl_4]^{2-}$ complex is referred to as outer sphere geometry with hybridization of sp3,which is also paramagnetic. On the other hand, $[Ni(CN)_4]^{2-}$ will form inner sphere geometry with hybridization dsp2 which is diamagnetic.

Ligand Field Theory (LFT)

It takes into account the orbitals of the ligand as they combine with d-orbitals more than near spherical charges. LFT uses the molecular orbital methods for the interpretation of the spectral of complex. It uses the concept of molecular orbital theory.

LFT describes the bonding, orbital arrangement and other characteristics of coordination complexes. It represents an application of molecular orbital theory (MOT) of transition metal complexes. A transition metal ion has nine valence atomic orbitals consisting of five and, three (n +1)p and one (n + 1)s. These orbitals are of appropriate energy to form bonding interaction with ligands.

LFT resulted from combining the principles of MOT and CFT. It uses the electrostatic principle established in CFT to describe transition metal ions in solution, and uses MOT to explain the differences in metal-ligand interactions. It was believed that the unoccupied d-orbitals of transition metals participates in bonding which influences the colour they absorb in solution.

GROUND ENERGY STATE TERMS USING RUSSEL-SANDERS SCHEME

A scheme is given as

$$^{2s+1}L_J$$

2s + 1 is spin multiplicity
L is orbital quantum number
J is the total angular momentum

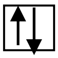
For L;
If L = 0, S-state
If L = 1, P-state
If L = 2, D-state
If L = 3, F-state

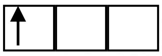
Predict the ground state term of the following
i. H ii. He iii. Al iv. Ti^{3+} v. Cr^{2+}

Answer

1. H – $1s^1$ $\boxed{\uparrow}$
   s = ½
   spin multiplicity = 2(½) + 1 = 2
   orbital quantum number = 0; S-state

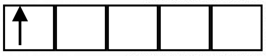
total angular momentum = L + s = 0 + ½ = ½
G.S.T. = $^2 S_{1/2}$

2. He – $1s^2$ 
   s = + ½ - ½ = 0
   spin multiplicity = 2(0) + 1 = 2
   orbital quantum number = 0; S-state
   total angular momentum = L + s = 0 + 0 = 0
   G.S.T. = $^1 S_0$

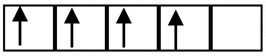
3. Al – $1s^2 2s^2 2p^6 3s^2 3p^1$
   

   s = ½
   spin multiplicity = 2(½) + 1 = 1
   orbital quantum number = 1 X (+1) = 1; P-state
   total angular momentum = L - s = 1 - ½ = ½
   G.S.T. = $^2 P_{1/2}$

4. Ti – $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$
   Ti^{3+} - $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$

   
   s = ½
   spin multiplicity = 2(½) + 1 = 1
   orbital quantum number = 1 X (+2) = 2; D-state
   total angular momentum = L - s = 2 - ½ = 3/2
   G.S.T. = $^2 D_{3/2}$

5. Cr – $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4$
   Cr^{2+} - $1s^2 2s^2 2p^6 3s^2 3p^6 3d^4$

   
   s = 4 X ½ = 2
   spin multiplicity = 2(2) + 1 = 5
   orbital quantum number = 1 X (+2) + 1 X (+1) + 1 X (0) + 1 X (-1)
   = 2 + 1 + 0 -1 = 2; D-state
   total angular momentum = L - s = 2 - 2 = 0
   G.S.T. = $^5D_0$

NEPHELAUXETIC EFFECT

The orbitals of the ligands spread out the d-electrons cloud of the central atom by changing the degree of repulsion between these electrons. This effect is called the nephelauxetic effect of ligand. The arrangement of ligands in order of increasing ability for the activity if thus F- < H_2O < (CH3)$_2$SO= CH_3CoNH_2 < urea < NH_3 < en < OX_2- < NCS- < oxide < Cl- < CN- < Br- < I- = dtp = S- <

The nephelauxetic series of ligand reflect better the degree of covalency of the complexes than how the spectrochemical series explains it. Aquo complexes and fluoride complexes are known to be least covalent by the nephelauxetic series while in the spectroxcal series, they are in the middle of the sequence. The ligands of strongly covalent complexes such as CN-, Br-, I- are at the end of the nephelauxetic series while in the spectroxcal series, they patly follow the ligand water (aquo).

Post-Test

1. Define crystal field stabilization energy.
2. Distinguish between low and high spin complexes.
3. Explain Ligand Field Theory (LFT)

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LECTURE FOUR
STEREOCHEMISTRY OF COMPLEXES

4.0 Introduction

The stereochemistry or shape of transition metal complex is determined by tendency of electron pairs to occupy positions as far away from each other as possible in exactly the same way as for the main group compounds and complexes, but the transition metals are affected by the presence of non-bonding d-electrons. If the d-electrons are symmetrically arranged with respect to an octahedral ligand field, they will repel all six ligands equally and a completely regular octahedral complexes will be formed.

Objectives

At the end of this lecture, students should be able to:

1. Explain the stability of complexes,
2. Mention the factors affecting the stability of complexes, and
3. Perform simple calculations on thermodynamic stability of complexes.

Pre-Test

1. What do you understand by symmetrical and asymmetrical complexes?
2. What are the factors affecting the stability of complexes? Contents

Contents

A symmetrical electronic configuration of d-electron

e.g.	t2g			eg		
d^0						strong/weak field ligand
d^3	↑	↑	↑			strong/weak field ligand
d^5	↑	↑	↑	↑	↑	weak field ligand
d^6	↑↓	↑↓	↑↓			strong field ligand
d^8	↑↓	↑↓	↑↓	↑	↑	weak field ligand
d^{10}	↑↓	↑↓	↑↓	↑↓	↑↓	strong/weak field ligand

An asymmetric electronic configuration of d-electron

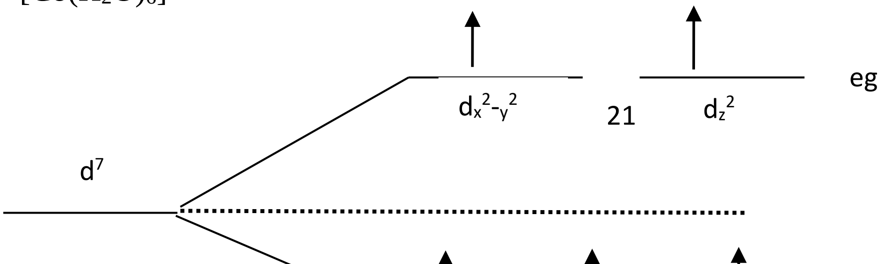
d^4	↑	↑	↑	↑		weak field ligand
d^7	↑↓	↑↓	↑↓	↑		strong field ligand
d^9	↑↓	↑↓	↑↓	↑↓	↑↓	strong/weak field ligand

Since the t2g orbitals points in between the point charges of the ligands directs assymetric filling of these orbitals.

According to Jahn-Tellar distortion theory which states that "any non-linear molecule system indegenerate electronic state will be unstable and will undergo some sort of distortion to lower its symmetry and remove the degererates". Distortion occurs in assymetric complexes where electrons are unevenly distributed.

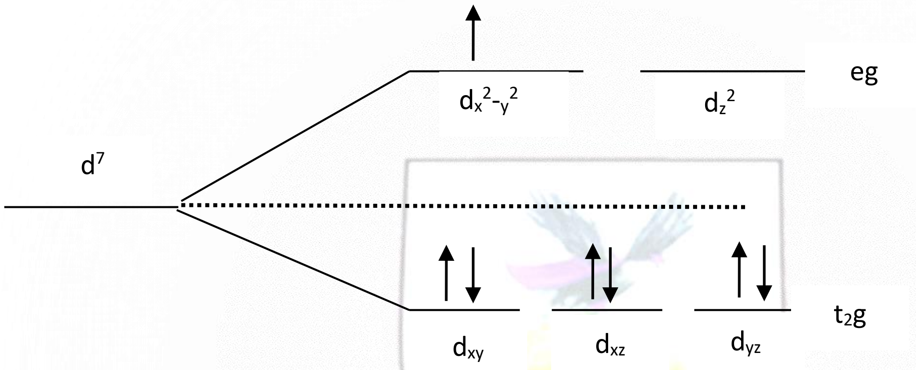
Example:

$[Co(H_2O)_6]$



Since H2O is a weak field ligand, it assumed high spin and because there is equal filling of eg orbitals, there will be no distortion.

[Co(CN)6]



Because CN is a strong field ligand and since there is unequal distortion of electron in the eg orbitals, there will be distortion.

Stability of Complexes

It is important to note that stability constant can be used to calculate concentration quantitatively only in solutions that are very dilute i.e. equilibrium measurement reveal the composition and stability present in solution. To understand the solution chemistry of metals; nature and stability of such complexes are formed in solution by step wise reaction and equilibrium constant can be written for each step

1. $M + L \longrightarrow ML$

$$k_1 = \frac{[ML]}{[M][L]}$$

2. $ML + L \longrightarrow ML_2$

$$k_2 = \frac{[ML_2]}{[ML][L]}$$

3. $ML_2 + L \longrightarrow ML_3$

$$k_3 = \frac{[ML_3]}{[ML_2][L]}$$

Generally for step wise reaction

$$ML_{n-1} + L \longrightarrow ML_n$$

$$k_n = \frac{[ML_n]}{[ML_{n-1}][L]}$$

Also, for overall reaction

$$M + {}_nL \longrightarrow ML_n$$

Besides the overall reaction could be monitored

1. $M + L \longrightarrow ML$

   $$B_1 = \frac{[ML]}{[M][L]}$$

2. $M + 2L \longrightarrow ML_2$

   $$B_2 = \frac{[ML_2]}{[M][L]^2}$$

3. $M + 3L \longrightarrow ML_3$

   $$B_3 = \frac{[ML_3]}{[M][L]^3}$$

$$B_n = \frac{[ML_n]}{[M][L]^n}$$

Consider an expression for the overall stability constant

$$B_3 = \frac{[ML_3]}{[M][L]^3}$$

It is possible to use that to relate the step wise formation thus: multiply both numerator and denominator by [ML] and [ML_2]

$$B_3 = \frac{[ML_3]}{[M][L]^3} \cdot \frac{[ML][ML_2]}{[ML][ML_2]}$$

Then rearrange

$$B_3 = \underbrace{\frac{[ML]}{[M][L]}}_{k_1} \cdot \underbrace{\frac{[ML_2]}{[ML][L]}}_{k_2} \cdot \underbrace{\frac{[ML_3]}{[ML_2][L]}}_{k_3}$$

Then

$$B_3 = k_1k_2k_3$$

Generally,

$$B_n = k_1k_2k_3 \ldots k_n$$

It is not difficult to see that this kind of relationship is perfectly generalized.

$$B_k = k_1k_2k_3 \ldots k_k = \sum_{i=1}^{i=k} ki$$

The ki's are called the stepwise formation constant or stepwise stability constant (which is the formation constant for each individual solvent replacement in the synthesis of the

complexes) and B's are called the overall formation constant or overall stability constant. Each step has its special stability constant.
The set of stepwise formation constant ki's provide particular insight into the species present as a function of concentration with only a few exception there is generally a slowly descending progression in the values of the ki's by the data for Cd^{2+} - NH_3 system where the ligands are uncharged and by the Cd^{2+} - CN^- where the ligands are charged.

$Cd^{2+} + NH_3 \longrightarrow [Cd(NH_3)]^{2+}$ $k_1 = 10^{2.65}$
$[Cd(NH_3)]^{2+} + NH_3 \longrightarrow [Cd(NH_3)_2]^{2+}$ $k_2 = 10^{2.10}$
$[Cd(NH_3)_2]^{2+} + NH_3 \longrightarrow [Cd(NH_3)_3]^{2+}$ $k_3 = 10^{1.44}$
$[Cd(NH_3)_3]^{2+} + NH_3 \longrightarrow [Cd(NH_3)_4]^{2+}$ $k_4 = 10^{0.98}$
The overall $B_4 = 10^{7.17}$

Also,
$B_4 = 10^{18.8}$
$Cd^{2+} + CN^- \longrightarrow [Cd(CN)]^+$ $k_1 = 10^{5.48}$
$[Cd(CN)]^+ + CN^- \longrightarrow [Cd(CN)_2]$ $k_2 = 10^{5.12}$
$[Cd(CN)_2] + CN^- \longrightarrow [Cd(CN)_3]^-$ $k_3 = 10^{4.63}$
$[Cd(CN)_3]^- + CN^- \longrightarrow [Cd(CN)_4]^{2-}$ $k_4 = 10^{3.35}$

This typically as the lignd is added to the solution of metl ion Mn+ first forms more rapidly than any other complexes in the series. As addition of ligand is continued, the ML2 concentration drops. Hence ML3 becomes dominant, ML and ML2 becoming unimportant and so forth until the highest complex MLn is formed to the nearly complete exclusion of all others at very high ligand concentration.

Factors that affect stability of metal complexes
The stability constant of the metal complexes depend upon
i. The metal ion
ii. The nture of the ligands
iii. The solvent to be used
iv. Chelate effects

METAL ION

The stability of metal complexes increases with decrease in size of the metal ions. Also, the charge of the metal ion affects the stability. A higher oxidation state of metal ion are more stable than lower one. The ion with high polarizability give complexes with higher stability constant. The polarizability is charge divided by size (c/s). Thus, complexes of copper (i) ion have higher polarizability over Na+ also Ga3+ > Al3+

NATURE OF THE LIGANDS

The greater the basicity [Lewis base] of the ligand, the higher the stability of the complex. Dipole moment effects and polarizability due to the greater electrostatic interaction between the metal ion and the ligand; polarity and polarizability of the ligand resule in higher stability constant (k) for the complexes. To be specific, pi-bonded complexes are more stable than the sigma bonded complexes.

NATURE OF THE SOLVENT

A donor solvent (H2O) will tend to form it own complex on the metal ion so that the incomin ligand will face competition with the solvent molecues to get attached to the metal ion. Hence, strongly donor solvent decrease the sability constant of the metal complexes.

CHELATE EFFECT

As a general way, a complex containing one or more six-membered chelate ring is more stable than a complex that is as similar as possible but lcks some or all of its chelating ring e.g

$Ni^{2+} + 6NH_3 \longrightarrow [Ni(NH_3)_6]^{2+}$ B = $10^{8.6}$
$Ni^{2+} + 3en \longrightarrow [Ni(en)_3]^{2+}$ B = $10^{18.6}$

The complex with 3-chelate ting is about 10^{10} times more stable than monodentate ligands at the same symmetry (octahedral).

Thermodynamic consieration
$[Ni(H_2O)_6]^{2+} + 6NH_3 \longrightarrow [Ni(NH_3)_6]^{2+} + 6H_2O$

$$B_n = \frac{[Ni(NH_3)_6]^{2+}}{[Ni(H_2O)_6]^{2+}\ [NH_3]^6}$$

$B_n = k_{f1} + k_{f2} + k_{f3.} + ... + k_{f6}$
$k_{fi} = k_i$ (formation constant)

the magnitude of a formation constant is a direct reflection of the sign and magnitude of Gibbs energy of formation i.e.

$\Delta G = -RT\ln K_f$

$\Delta G = \Delta H - T\Delta S$

Example

The kf for the formation of $[Ni(NH_3)_n(H_2O)_6]^{2+}$ are given below

n	**k_f**
1	186.20
2	147.90
3	45.71
4	13.2
5	4.27
6	1.1

Calculate:

i. The value of the overall formation constant (Bn)
ii. The value of Gibb’s constant at 303K for k_{f4}
iii. If the value of ΔH at 303K is -20.88kJ; find the entropy change

Answer

n	k_f	Log k_f
1	186.20	2.27
2	147.90	2.17
3	45.71	1.66
4	13.2	1.12
5	4.27	0.63
6	1.1	0.04

$\text{Log } B_n = \log k_{f1} + \log k_{f2} + \log k_{f3} \dots + \log k_{f6}$
$= 2.27 + 2.17 + 1.66 + 1.12 + 0.63 + 0.04$
$= 7.89$

i. $B_n = \text{Antilog } 7.89$
$= 77624711.66$
$= 7.7624711 \times 10^7$

ii. $\Delta G = -RT\ln K_f$
$= -8.314 \times 303 \times \ln 13.20$
$= -8.314 \times 303 \times 2.5802$
$= -6499.89 \text{kJ/mol}$

iii. $\Delta G = \Delta H - T\Delta S$
$-6499.89 = 20.88 - 303\Delta S$
$-303\Delta S = -6499.89 - 20.88$
$-303\ \Delta S = -6520.77$

$$\Delta S = \frac{-6520.77}{-303}$$
$= 21.52 K^{-1} mol^{-1}/kJ$

Post-Test

1. What do you understand by symmetrical and asymmetrical complexes?
2. What are the factors affecting the stability of complexes?

Bibliography

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