Coordination Compounds

Coordination Compounds are the backbone of modern inorganic and bio–inorganic chemistry and chemical industry.

Objectives

After studying this Unit, you will be able to

- appreciate the postulates of Werner's theory of coordination compounds;
- know the meaning of the terms: coordination entity, central atom/ion, ligand, coordination number, coordination sphere, coordination polyhedron, oxidation number, homoleptic and heteroleptic;
- learn the rules of nomenclature of coordination compounds;
- write the formulas and names of mononuclear coordination compounds;
- define different types of isomerism in coordination compounds;
- understand the nature of bonding in coordination compounds in terms of the Valence Bond and Crystal Field theories;
- learn the stability of coordination compounds;
- appreciate the importance and applications of coordination compounds in our day to day life.

In the previous Unit we learnt that the transition metals form a large number of **complex compounds** in which the metal atoms are bound to a number of anions or neutral molecules. In modern terminology such compounds are called **coordination compounds**. The chemistry of coordination compounds is an important and challenging area of modern inorganic chemistry. New concepts of chemical bonding and molecular structure have provided insights into the functioning of vital components of biological systems. Chlorophyll, haemoglobin and vitamin B_{12} are coordination compounds of magnesium, iron and cobalt respectively. Variety of metallurgical processes, industrial catalysts and analytical reagents involve the use of coordination compounds. Coordination compounds also find many applications in electroplating, textile dyeing and medicinal chemistry.

9.1 Werner's Theory of Coordination Compounds

Alfred Werner (1866-1919), a Swiss chemist was the first to formulate his ideas about the structures of coordination compounds. He prepared and characterised a large number of coordination compounds and studied their physical and chemical behaviour by simple experimental techniques. Werner proposed the concept of a **primary valence** and a **secondary valence** for a metal ion. Binary compounds such as $CrCl_3$, $CoCl_2$ or $PdCl_2$ have primary valence of 3, 2 and 2 respectively. In a series of compounds of cobalt(III) chloride with ammonia, it was found that some of the chloride ions could be precipitated as AgCl on adding excess silver nitrate solution in cold but some remained in solution.

1 mol	$CoCl_3.6NH_3$ (Yellow)	gave	3 mol AgCl
1 mol	$CoCl_3.5NH_3$ (Purple)	gave	2 mol AgCl
1 mol	$CoCl_3.4NH_3$ (Green)	gave	1 mol AgCl
1 mol	$CoCl_3.4NH_3$ (Violet)	gave	1 mol AgCl

These observations, together with the results of conductivity measurements in solution can be explained if (i) six groups in all, either chloride ions or ammonia molecules or both, remain bonded to the cobalt ion during the reaction and (ii) the compounds are formulated as shown in Table 9.1, where the atoms within the square brackets form a single entity which does not dissociate under the reaction conditions. Werner proposed the term **secondary valence** for the number of groups bound directly to the metal ion; in each of these examples the secondary valences are six.

Table 9.1: Formulation of Cobalt(III) Chloride-Ammonia Complexes

Colour	Formula	Solution conductivity corresponds to
Yellow	$[Co(NH_3)_6]^{3+}3Cl^-$	1:3 electrolyte
Purple	$[CoCl(NH_3)_5]^{2+}2Cl^-$	1:2 electrolyte
Green	$[CoCl_2(NH_3)_4]^+Cl^-$	1:1 electrolyte
Violet	$[CoCl_2(NH_3)_4]^+Cl^-$	1:1 electrolyte

Note that the last two compounds in Table 9.1 have identical empirical formula, $CoCl_3.4NH_3$, but distinct properties. Such compounds are termed as isomers. Werner in 1898, propounded his theory of coordination compounds. The main postulates are:

1. In coordination compounds metals show two types of linkages (valences)-primary and secondary.

2. The primary valences are normally ionisable and are satisfied by negative ions.

3. The secondary valences are non ionisable. These are satisfied by neutral molecules or negative ions. The secondary valence is equal to the coordination number and is fixed for a metal.

4. The ions/groups bound by the secondary linkages to the metal have characteristic spatial arrangements corresponding to different coordination numbers.

In modern formulations, such spatial arrangements are called coordination *polyhedra*. The species within the square bracket are coordination entities or complexes and the ions outside the square bracket are called counter ions.

He further postulated that octahedral, tetrahedral and square planar geometrical shapes are more common in coordination compounds of transition metals. Thus, $[Co(NH_3)_6]^{3+}$, $[CoCl(NH_3)_5]^{2+}$ and $[CoCl_2(NH_3)_4]^+$ are octahedral entities, while $[Ni(CO)_4]$ and $[PtCl_4]^{2-}$ are tetrahedral and square planar, respectively.

On the basis of the following observations made with aqueous solutions, **Example 9.1**
assign secondary valences to metals in the following compounds:

Formula	Moles of AgCl precipitated per mole of the compounds with excess $AgNO_3$
(i) $PdCl_2.4NH_3$	2
(ii) $NiCl_2.6H_2O$	2
(iii) $PtCl_4.2HCl$	0
(iv) $CoCl_3.4NH_3$	1
(v) $PtCl_2.2NH_3$	0

Solution

(i) Secondary 4   (ii) Secondary 6
(iii) Secondary 6   (iv) Secondary 6   (v) Secondary 4

Difference between a double salt and a complex

Both double salts as well as complexes are formed by the combination of two or more stable compounds in stoichiometric ratio. However, they differ in the fact that double salts such as carnallite, $KCl.MgCl_2.6H_2O$, Mohr's salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$, potash alum, $KAl(SO_4)_2.12H_2O$, etc. dissociate into simple ions completely when dissolved in water. However, complex ions such as $[Fe(CN)_6]^{4-}$ of $K_4[Fe(CN)_6]$ do not dissociate into Fe^{2+} and CN^- ions.

Werner was born on December 12, 1866, in Mülhouse, a small community in the French province of Alsace. His study of chemistry began in Karlsruhe (Germany) and continued in Zurich (Switzerland), where in his doctoral thesis in 1890, he explained the difference in properties of certain nitrogen containing organic substances on the basis of isomerism. He extended vant Hoff's theory of tetrahedral carbon atom and modified it for nitrogen. Werner showed optical and electrical differences between complex compounds based on physical measurements. In fact, Werner was the first to discover optical activity in certain coordination compounds.

1   1919

He, at the age of 29 years became a full professor at Technische Hochschule in Zurich in 1895. Alfred Werner was a chemist and educationist. His accomplishments included the development of the theory of coordination compounds. This theory, in which Werner proposed revolutionary ideas about how atoms and molecules are linked together, was formulated in a span of only three years, from 1890 to 1893. The remainder of his career was spent gathering the experimental support required to validate his new ideas. Werner became the first Swiss chemist to win the Nobel Prize in 1913 for his work on the linkage of atoms and the coordination theory.

9. **Definitions of Some important Terms Pertaining to Coordination Compounds**

(a) Coordination entity

A coordination entity constitutes a central metal atom or ion bonded to a fixed number of ions or molecules. For example, $[CoCl_3(NH_3)_3]$ is a coordination entity in which the cobalt ion is surrounded by three ammonia molecules and three chloride ions. Other examples are $[Ni(CO)_4]$, $[PtCl_2(NH_3)_2]$, $[Fe(CN)_6]^{4-}$, $[Co(NH_3)_6]^{3+}$.

(b) Central atom/ion

In a coordination entity, the atom/ion to which a fixed number of ions/groups are bound in a definite geometrical arrangement around it, is called the central atom or ion. For example, the central atom/ion in the coordination entities: $[NiCl_2(H_2O)_4]$, $[CoCl(NH_3)_5]^{2+}$ and $[Fe(CN)_6]^{3-}$ are Ni^{2+}, Co^{3+} and Fe^{3+}, respectively. These central atoms/ions are also referred to as **Lewis acids**.
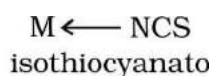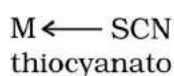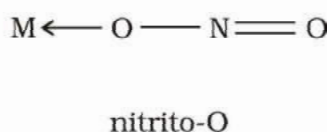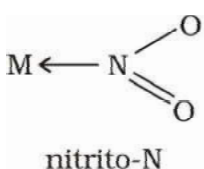
(c) Ligands

The ions or molecules bound to the central atom/ion in the coordination entity are called ligands. These may be simple ions such as Cl^-, small molecules such as H_2O or NH_3, larger molecules such as $H_2NCH_2CH_2NH_2$ or $N(CH_2CH_2NH_2)_3$ or even macromolecules, such as proteins.

When a ligand is bound to a metal ion through a single donor atom, as with Cl^-, H_2O or NH_3, the ligand is said to be **unidentate.** When a ligand can bind through two donor atoms as in $H_2NCH_2CH_2NH_2$ (ethane-1,2-diamine) or $C_2O_4^{2-}$ (oxalate), the ligand is said to be **didentate** and when several donor atoms are present in a single ligand as in $N(CH_2CH_2NH_2)_3$, the ligand is said to be **polydentate**. Ethylenediaminetetraacetate ion ($EDTA^{4-}$) is an important hexadentate ligand. It can bind through two nitrogen and four oxygen atoms to a central metal ion.
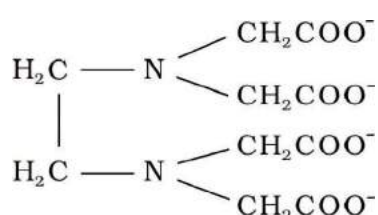
When a di- or polydentate ligand uses its two or more donor atoms to bind a single metal ion, it is said to be a **chelate** ligand. The number of such ligating groups is called the **denticity** of the ligand. Such complexes, called chelate complexes tend to be more stable than similar complexes containing unidentate ligands (for reasons see Section 9.8). Ligand which can ligate through two different atoms is called **ambidentate ligand**. Examples of such ligands are the NO_2^- and SCN^- ions. NO_2^- ion can coordinate either through nitrogen or through oxygen to a central metal atom/ion. Similarly, SCN^- ion can coordinate through the sulphur or nitrogen atom.

nitrito-N   nitrito-O

M ⟵ SCN   M ⟵ NCS
thiocyanato   isothiocyanato

(d) Coordination number

The coordination number (CN) of a metal ion in a complex can be defined as the number of ligand donor atoms to which the metal is directly bonded. For example, in the complex ions, $[PtCl_6]^{2-}$ and $[Ni(NH_3)_4]^{2+}$, the coordination number of Pt and Ni are 6 and 4 respectively. Similarly, in the complex ions, $[Fe(C_2O_4)_3]^{3-}$ and $[Co(en)_3]^{3+}$, the coordination number of both, Fe and Co, is 6 because $C_2O_4^{2-}$ and en (ethane-1,2-diamine) are didentate ligands.

It is important to note here that coordination number of the central atom/ion is determined only by the number of sigma bonds formed by the ligand with the central atom/ion. Pi bonds, if formed between the ligand and the central atom/ion, are not counted for this purpose.

(e) Coordination sphere

The central atom/ion and the ligands attached to it are enclosed in square bracket and is collectively termed as the **coordination sphere**. The ionisable groups are written outside the bracket and are called counter ions. For example, in the complex $K_4[Fe(CN)_6]$, the coordination sphere is $[Fe(CN)_6]^{4-}$ and the counter ion is K^+.

(f) Coordination polyhedron

The spatial arrangement of the ligand atoms which are directly attached to the central atom/ion defines a coordination polyhedron about the central atom. The most common coordination polyhedra are octahedral, square planar and tetrahedral. For example, $[Co(NH_3)_6]^{3+}$ is octahedral, $[Ni(CO)_4]$ is tetrahedral and $[PtCl_4]^{2-}$ is square planar. Fig. 9.1 shows the shapes of different coordination polyhedra.
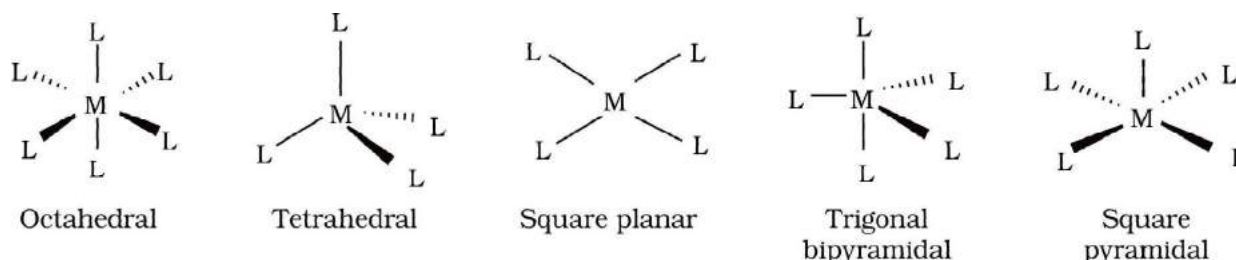

Fig. 9.1: *Shapes of different coordination polyhedra. M represents the central atom/ion and L, a unidentate ligand.*

(g) Oxidation number of central atom

The oxidation number of the central atom in a complex is defined as the charge it would carry if all the ligands are removed along with the electron pairs that are shared with the central atom. The oxidation number is represented by a Roman numeral in parenthesis following the name of the coordination entity. For example, oxidation number of copper in $[Cu(CN)_4]^{3-}$ is +1 and it is written as Cu(I).

(h) Homoleptic and heteroleptic complexes

Complexes in which a metal is bound to only one kind of donor groups, e.g., $[Co(NH_3)_6]^{3+}$, are known as homoleptic. Complexes in which a metal is bound to more than one kind of donor groups, e.g., $[Co(NH_3)_4Cl_2]^+$, are known as heteroleptic.

9. Nomenclature of Coordination Compounds

Nomenclature is important in Coordination Chemistry because of the need to have an unambiguous method of describing formulas and writing systematic names, particularly when dealing with isomers. The formulas and names adopted for coordination entities are based on the recommendations of the International Union of Pure and Applied Chemistry (IUPAC).

9.3.1 Formulas of Mononuclear Coordination Entities

The formula of a compound is a shorthand tool used to provide basic information about the constitution of the compound in a concise and convenient manner. Mononuclear coordination entities contain a single central metal atom. The following rules are applied while writing the formulas:

(i) The central atom is listed first.

(ii) The ligands are then listed in alphabetical order. The placement of a ligand in the list does not depend on its charge.

(iii) Polydentate ligands are also listed alphabetically. In case of abbreviated ligand, the first letter of the abbreviation is used to determine the position of the ligand in the alphabetical order.

(iv) The formula for the entire coordination entity, whether charged or not, is enclosed in square brackets. When ligands are polyatomic, their formulas are enclosed in parentheses. Ligand abbreviations are also enclosed in parentheses.

(v) There should be no space between the ligands and the metal within a coordination sphere.

(vi) When the formula of a charged coordination entity is to be written without that of the counter ion, the charge is indicated outside the square brackets as a right superscript with the number before the sign. For example, $[Co(CN)_6]^{3-}$, $[Cr(H_2O)_6]^{3+}$, etc.

(vii) The charge of the cation(s) is balanced by the charge of the anion(s).

9.3.2 Naming of Mononuclear Coordination Compounds

The names of coordination compounds are derived by following the principles of additive nomenclature. Thus, the groups that surround the central atom must be identified in the name. They are listed as prefixes to the name of the central atom along with any appropriate multipliers. The following rules are used when naming coordination compounds:

(i) The cation is named first in both positively and negatively charged coordination entities.

(ii) The ligands are named in an alphabetical order before the name of the central atom/ion. (This procedure is reversed from writing formula).

(iii) Names of the anionic ligands end in –o, those of neutral and cationic ligands are the same except aqua for H_2O, ammine for NH_3, carbonyl for CO and nitrosyl for NO. These are placed within enclosing marks ( ) when written in the formula of coordination entity.

(iv) Prefixes mono, di, tri, etc., are used to indicate the number of the individual ligands in the coordination entity. When the names of the ligands include a numerical prefix, then the terms, *bis*, *tris*, *tetrakis* are used, the ligand to which they refer being placed in parentheses. For example, $[NiCl_2(PPh_3)_2]$ is named as dichloridobis(triphenylphosphine)nickel(II).

(v) Oxidation state of the metal in cation, anion or neutral coordination entity is indicated by Roman numeral in parenthesis.

(vi) If the complex ion is a cation, the metal is named same as the element. For example, Co in a complex cation is called cobalt and Pt is called platinum. If the complex ion is an anion, the name of the metal ends with the suffix – ate. For example, Co in a complex anion, $\left[Co(SCN)_4\right]^{2-}$ is called cobaltate. For some metals, the Latin names are used in the complex anions, *e.g.*, ferrate for Fe.

(vii) The neutral complex molecule is named similar to that of the complex cation.

The following examples illustrate the nomenclature for coordination compounds.

1. $[Cr(NH_3)_3(H_2O)_3]Cl_3$ is named as:

triamminetriaquachromium(III) chloride

Explanation: The complex ion is inside the square bracket, which is a cation. The amine ligands are named before the aqua ligands according to alphabetical order. Since there are three chloride ions in the compound, the charge on the complex ion must be +3 (since the compound is electrically neutral). From the charge on the complex ion and the charge on the ligands, we can calculate the oxidation number of the metal. In this example, all the ligands are neutral molecules. Therefore, the oxidation number of chromium must be the same as the charge of the complex ion, +3.

2. $[Co(H_2NCH_2CH_2NH_2)_3]_2(SO_4)_3$ is named as:

tris(ethane-1,2–diamine)cobalt(III) sulphate

Explanation: The sulphate is the counter anion in this molecule. Since it takes 3 sulphates to bond with two complex cations, the charge on each complex cation must be +3. Further, ethane-1,2–diamine is a neutral molecule, so the oxidation number of cobalt in the complex ion must be +3. *Remember that you never have to indicate the number of cations and anions in the name of an ionic compound.*

3. $[Ag(NH_3)_2][Ag(CN)_2]$ is named as:

diamminesilver(I) dicyanidoargentate(I)

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ample 9. Write the formulas for the following coordination compounds:
(a) Tetraammineaquachloridocobalt(III) chloride
(b) Potassium tetrahydroxidozincate(II)
(c) Potassium trioxalatoaluminate(III)
(d) Dichloridobis(ethane-1,2-diamine)cobalt(III)
(e) Tetracarbonylnickel(0)

Solution (a) $[Co(NH_3)_4(H_2O)Cl]Cl_2$ (b) $K_2[Zn(OH)_4]$ (c) $K_3[Al(C_2O_4)_3]$
(d) $[CoCl_2(en)_2]^+$ (e) $[Ni(CO)_4]$

ample 9. Write the IUPAC names of the following coordination compounds:
(a) $[Pt(NH_3)_2Cl(NO_2)]$ (b) $K_3[Cr(C_2O_4)_3]$ (c) $[CoCl_2(en)_2]Cl$
(d) $[Co(NH_3)_5(CO_3)]Cl$ (e) $Hg[Co(SCN)_4]$

Solution (a) Diamminechloridonitrito-N-platinum(II)
(b) Potassium trioxalatochromate(III)
(c) Dichloridobis(ethane-1,2-diamine)cobalt(III) chloride
(d) Pentaamminecarbonatocobalt(III) chloride
(e) Mercury (I) tetrathiocyanatocobaltate(III)

9. Isomerism in Coordination Compounds

Isomers are two or more compounds that have the same chemical formula but a different arrangement of atoms. Because of the different arrangement of atoms, they differ in one or more physical or chemical properties. Two principal types of isomerism are known among coordination compounds. Each of which can be further subdivided.

(a) Stereoisomerism

  (i) Geometrical isomerism   (ii) Optical isomerism

(b) Structural isomerism

  (i) Linkage isomerism   (ii) Coordination isomerism
  (iii) Ionisation isomerism   (iv) Solvate isomerism

Stereoisomers have the same chemical formula and chemical bonds but they have different spatial arrangement. Structural isomers have different bonds. A detailed account of these isomers are given below.
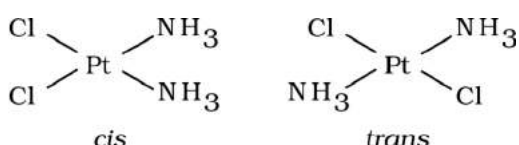
9.4.1 Geometric Isomerism

Fig. 9.2: Geometrical isomers (cis and trans) of Pt [NH₃)₂Cl₂]
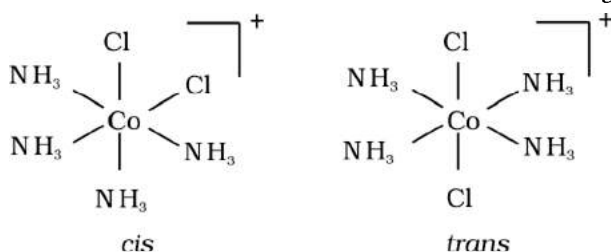
Fig. 9.3: Geometrical isomers (cis and trans) of [Co(NH₃)₄Cl₂]⁺

This type of isomerism arises in heteroleptic complexes due to different possible geometric arrangements of the ligands. Important examples of this behaviour are found with coordination numbers 4 and 6. In a square planar complex of formula $[MX_2L_2]$ (X and L are unidentate), the two ligands X may be arranged adjacent to each other in a **cis** isomer, or opposite to each other in a **trans** isomer as depicted in Fig. 9.2.

Other square planar complex of the type MABXL (where A, B, X, L are unidentates) shows three isomers-two *cis* and one *trans*. You may attempt to draw these structures. Such isomerism is not possible for a tetrahedral geometry but similar behaviour is possible in octahedral complexes of formula $[MX_2L_4]$ in which the two ligands X may be oriented **cis** or **trans** to each other (Fig. 9.3).
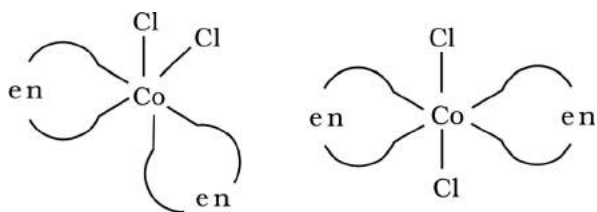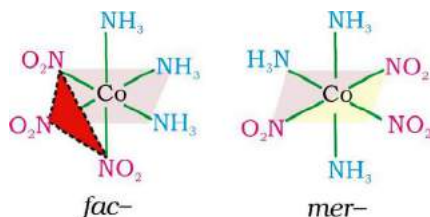
Fig. 9.4: *Geometrical isomers (cis and trans) of [CoCl$_2$(en)$_2$]*

Fig. 9.5
The facial (fac) and meridional (mer) isomers of [Co(NH$_3$)$_3$(NO$_2$)$_3$]

fac–   *mer–*

This type of isomerism also arises when didentate ligands L–L [*e.g.*, NH$_2$ CH$_2$ CH$_2$ NH$_2$ (en)] are present in complexes of formula [MX$_2$(L–L)$_2$] (Fig. 9.4).

Another type of geometrical isomerism occurs in octahedral coordination entities of the type [Ma$_3$b$_3$] like [Co(NH$_3$)$_3$(NO$_2$)$_3$]. If three donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face, we have the **facial (fac) isomer**. When the positions are around the meridian of the octahedron, we get the **meridional (mer) isomer** (Fig. 9.5).

Why is geometrical isomerism not possible in tetrahedral complexes having two different types of unidentate ligands coordinated with the central metal ion ?

Tetrahedral complexes do not show geometrical isomerism because the relative positions of the unidentate ligands attached to the central metal atom are the same with respect to each other.

9.4.2 Optical Isomerism

dextro   *mirror*   *laevo*
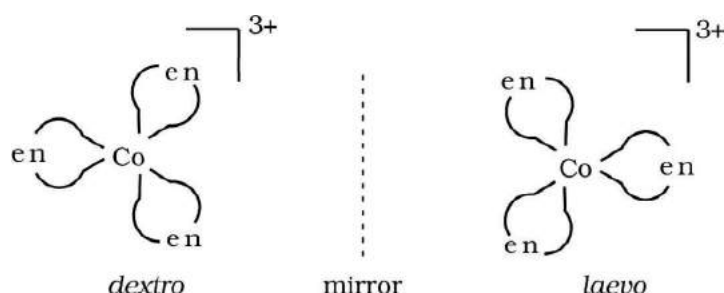
Fig.9.6: Optical isomers (d and l) of [Co(en)$_3$]$^{3+}$

Optical isomers are mirror images that cannot be superimposed on one another. These are called as *enantiomers*. The molecules or ions that cannot be superimposed are called *chiral*. The two forms are called *dextro (d)* and *laevo (l)* depending upon the direction they rotate the plane of polarised light in a polarimeter (*d* rotates to the right, *l* to the left). Optical isomerism is common in octahedral complexes involving didentate ligands (Fig. 9.6).

In a coordination entity of the type [PtCl$_2$(en)$_2$]$^{2+}$, only the *cis*-isomer shows optical activity (Fig. 9.7).

Fig.9.7
Optical isomers (d and l) of cis-[PtCl$_2$(en)$_2$]$^{2+}$

dextro   *mirror*   *laevo*
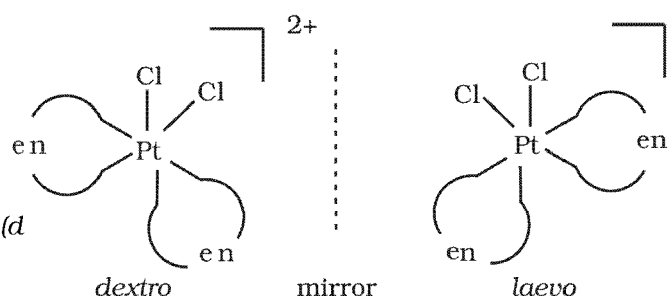
amp e 9. Draw structures of geometrical isomers of $[Fe(NH_3)_2(CN)_4]^-$

o ution

cis   *trans*

amp e 9. Out of the following two coordination entities which is chiral (optically active)?

(a) *cis*-$[CrCl_2(ox)_2]^{3-}$ (b) *trans*-$[CrCl_2(ox)_2]^{3-}$

o ution The two entities are represented as

(a) *cis* – $[CrCl_2(ox)_2]^{3-}$ (b) *trans* – $[CrCl_2(ox)_2]^{3-}$

Out of the two, (a) *cis* - $[CrCl_2(ox)_2]^{3-}$ is chiral (optically active).

9.4.3 Linkage Isomerism

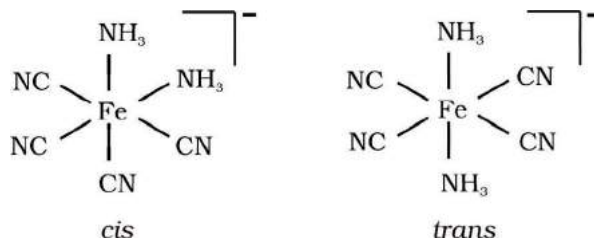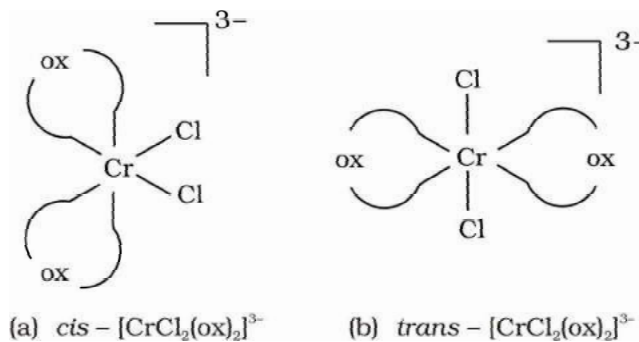Linkage isomerism arises in a coordination compound containing ambidentate ligand. A simple example is provided by complexes containing the thiocyanate ligand, NCS^-, which may bind through the nitrogen to give M–NCS or through sulphur to give M–SCN. Jørgensen discovered such behaviour in the complex $[Co(NH_3)_5(NO_2)]Cl_2$, which is obtained as the red form, in which the nitrite ligand is bound through oxygen (–ONO), and as the yellow form, in which the nitrite ligand is bound through nitrogen (–NO_2).

9.4.4 Coordination Isomerism

This type of isomerism arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex. An example is provided by $[Co(NH_3)_6][Cr(CN)_6]$, in which the NH_3 ligands are bound to Co^{3+} and the CN^- ligands to Cr^{3+}. In its coordination isomer $[Cr(NH_3)_6][Co(CN)_6]$, the NH_3 ligands are bound to Cr^{3+} and the CN^- ligands to Co^{3+}.

9.4.5 Ionisation Isomerism

This form of isomerism arises when the counter ion in a complex salt is itself a potential ligand and can displace a ligand which can then become the counter ion. An example is provided by the ionisation isomers $[Co(NH_3)_5(SO_4)]Br$ and $[Co(NH_3)_5Br]SO_4$.

9.4.6 Solvate Isomerism

This form of isomerism is known as 'hydrate isomerism' in case where water is involved as a solvent. This is similar to ionisation isomerism. Solvate isomers differ by whether or not a solvent molecule is directly bonded to the metal ion or merely present as free solvent molecules in the crystal lattice. An example is provided by the aqua complex $[Cr(H_2O)_6]Cl_3$ (violet) and its solvate isomer $[Cr(H_2O)_5Cl]Cl_2.H_2O$ (grey-green).

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9. Bonding in Coordination Compounds

Werner was the first to describe the bonding features in coordination compounds. But his theory could not answer basic questions like:

(i) Why only certain elements possess the remarkable property of forming coordination compounds?

(ii) Why the bonds in coordination compounds have directional properties?

(iii) Why coordination compounds have characteristic magnetic and optical properties?

Many approaches have been put forth to explain the nature of bonding in coordination compounds *viz.* Valence Bond Theory (VBT), Crystal Field Theory (CFT), Ligand Field Theory (LFT) and Molecular Orbital Theory (MOT). We shall focus our attention on elementary treatment of the application of VBT and CFT to coordination compounds.

9.5.1 Valence Bond Theory

According to this theory, the metal atom or ion under the influence of ligands can use its $(n-1)d$, ns, np or ns, np, nd orbitals for hybridisation to yield a set of equivalent orbitals of definite geometry such as octahedral, tetrahedral, square planar and so on (Table 9.2). These hybridised orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding. This is illustrated by the following examples.

Table 9.2: Number of Orbitals and Types of Hybridisations

Coordination number	Type of hybridisation	Distribution of hybrid orbitals in space
4	sp^3	Tetrahedral
4	dsp^2	Square planar
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral
6	d^2sp^3	Octahedral

It is usually possible to predict the geometry of a complex from the knowledge of its magnetic behaviour on the basis of the valence bond theory.
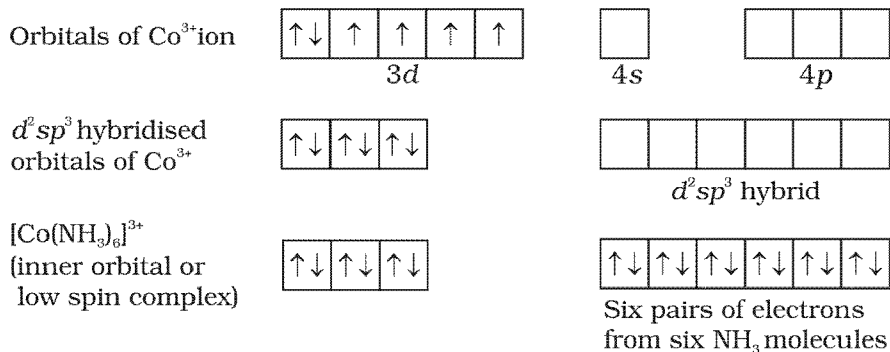
In the diamagnetic octahedral complex, $[Co(NH_3)_6]^{3+}$, the cobalt ion is in +3 oxidation state and has the electronic configuration $3d^6$. The hybridisation scheme is as shown in diagram.

Orbitals of Co^{3+}ion

d^2sp^3 hybridised orbitals of Co^{3+}

$[Co(NH_3)_6]^{3+}$ (inner orbital or low spin complex)

d^2sp^3 hybrid

Six pairs of electrons from six NH$_3$ molecules

Six pairs of electrons, one from each NH$_3$ molecule, occupy the six hybrid orbitals. Thus, the complex has octahedral geometry and is diamagnetic because of the absence of unpaired electron. In the formation of this complex, since the inner d orbital ($3d$) is used in hybridisation, the complex, $[Co(NH_3)_6]^{3+}$ is called an **inner orbital** or **low spin** or **spin paired complex**. The paramagnetic octahedral complex, $[CoF_6]^{3-}$ uses outer orbital ($4d$) in hybridisation (sp^3d^2). It is thus called **outer orbital** or **high spin** or **spin free complex**. Thus:

Orbitals of Co^{3+}ion

sp^3d^2 hybridised orbitals of Co^{3+}

$[CoF_6]^{3-}$ (outer orbital or high spin complex)

sp^3d^2 hybrid

Six pairs of electrons from six F$^-$ ions
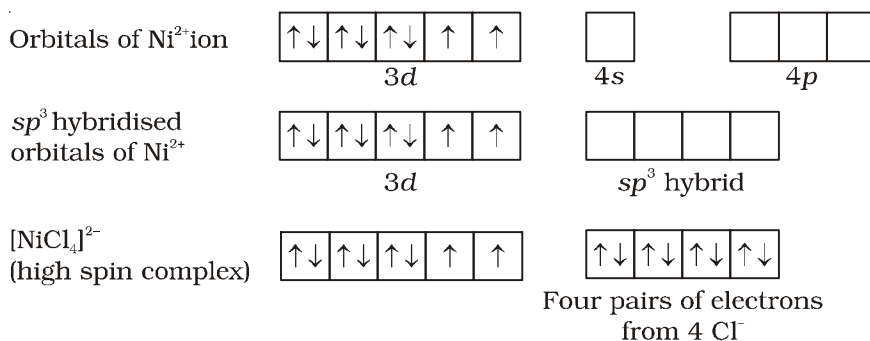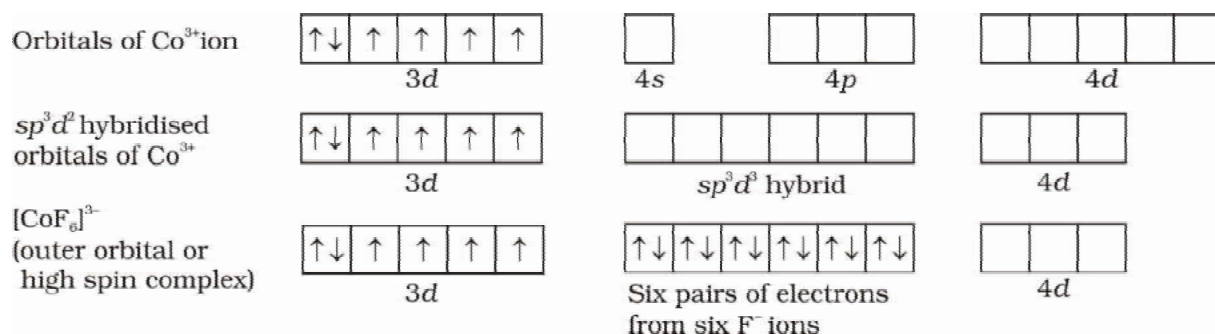
In tetrahedral complexes one s and three p orbitals are hybridised to form four equivalent orbitals oriented tetrahedrally. This is illustrated below for $[NiCl_4]^{2-}$. Here nickel is in +2 oxidation state and the ion has the electronic configuration $3d^8$. The hybridisation scheme is as shown in diagram.

Orbitals of Ni^{2+}ion

sp^3 hybridised orbitals of Ni^{2+}

$[NiCl_4]^{2-}$ (high spin complex)

sp^3 hybrid

Four pairs of electrons from 4 Cl$^-$

Each Cl$^-$ ion donates a pair of electrons. The compound is paramagnetic since it contains two unpaired electrons. Similarly, $[Ni(CO)_4]$ has tetrahedral geometry but is diamagnetic since nickel is in zero oxidation state and contains no unpaired electron.

In the square planar complexes, the hybridisation involved is dsp^2. An example is $[Ni(CN)_4]^{2-}$. Here nickel is in +2 oxidation state and has the electronic configuration $3d^8$. The hybridisation scheme is as shown in diagram:
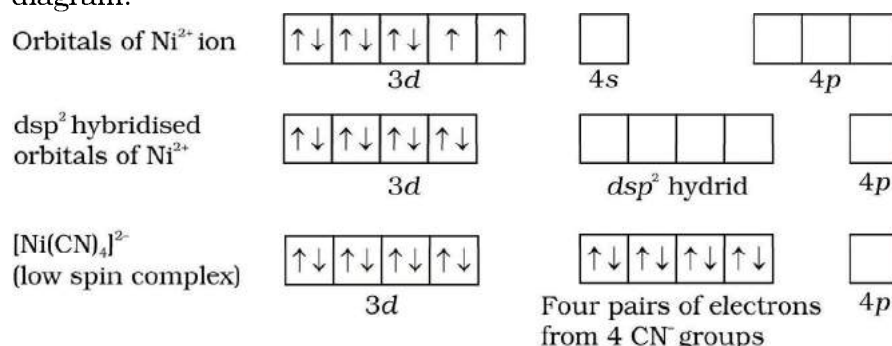

Each of the hybridised orbitals receives a pair of electrons from a cyanide ion. The compound is diamagnetic as evident from the absence of unpaired electron.

It is important to note that the hybrid orbitals do not actually exist. In fact, hybridisation is a mathematical manipulation of wave equation for the atomic orbitals involved.

9.5.2 Magnetic Properties of Coordination Compounds

The magnetic moment of coordination compounds can be measured by the magnetic susceptibility experiments. The results can be used to obtain information about the structures adopted by metal complexes.

A critical study of the magnetic data of coordination compounds of metals of the first transition series reveals some complications. For metal ions with upto three electrons in the d orbitals, like Ti^{3+} (d^1); V^{3+} (d^2); Cr^{3+} (d^3); two vacant d orbitals are available for octahedral hybridisation with $4s$ and $4p$ orbitals. The magnetic behaviour of these free ions and their coordination entities is similar. When more than three $3d$ electrons are present, the required pair of $3d$ orbitals for octahedral hybridisation is not directly available (as a consequence of Hund's rule). Thus, for d^4 (Cr^{2+}, Mn^{3+}), d^5 (Mn^{2+}, Fe^{3+}), d^6 (Fe^{2+}, Co^{3+}) cases, a vacant pair of d orbitals results only by pairing of $3d$ electrons which leaves two, one and zero unpaired electrons, respectively.

The magnetic data agree with maximum spin pairing in many cases, especially with coordination compounds containing d^6 ions. However, with species containing d^4 and d^5 ions there are complications. $[Mn(CN)_6]^{3-}$ has magnetic moment of two unpaired electrons while $[MnCl_6]^{3-}$ has a paramagnetic moment of four unpaired electrons. $[Fe(CN)_6]^{3-}$ has magnetic moment of a single unpaired electron while $[FeF_6]^{3-}$ has a paramagnetic moment of five unpaired electrons. $[CoF_6]^{3-}$ is paramagnetic with four unpaired electrons while $[Co(C_2O_4)_3]^{3-}$ is diamagnetic. This apparent anomaly is explained by valence bond theory in terms of formation of inner orbital and outer orbital coordination entities. $[Mn(CN)_6]^{3-}$, $[Fe(CN)_6]^{3-}$ and $[Co(C_2O_4)_3]^{3-}$ are inner orbital complexes involving d^2sp^3 hybridisation, the former two complexes are paramagnetic and the latter diamagnetic. On the other hand, $[MnCl_6]^{3-}$, $[FeF_6]^{3-}$ and $[CoF_6]^{3-}$ are outer orbital complexes involving sp^3d^2 hybridisation and are paramagnetic corresponding to four, five and four unpaired electrons.

9.5.3 Limitations of Valence Bond Theory

While the VB theory, to a larger extent, explains the formation, structures and magnetic behaviour of coordination compounds, it suffers from the following shortcomings:

(i) It involves a number of assumptions.

(ii) It does not give quantitative interpretation of magnetic data.

(iii) It does not explain the colour exhibited by coordination compounds.

(iv) It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.

(v) It does not make exact predictions regarding the tetrahedral and square planar structures of 4-coordinate complexes.

(vi) It does not distinguish between weak and strong ligands.

9.5.4 Crystal Field Theory

The crystal field theory (CFT) is an electrostatic model which considers the metal-ligand bond to be ionic arising purely from electrostatic interactions between the metal ion and the ligand. Ligands are treated as point charges in case of anions or dipoles in case of neutral molecules. The five d orbitals in an isolated gaseous metal atom/ion have same energy, *i.e.*, they are degenerate. This degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal atom/ion. However, when this negative field is due to ligands (either anions or the negative ends of dipolar molecules like NH_3 and H_2O) in a complex, it becomes asymmetrical and the degeneracy of the d orbitals is lifted. It results in splitting of the d orbitals. The pattern of splitting depends upon the nature of the crystal field. Let us explain this splitting in different crystal fields.

(a) Crystal field splitting in octahedral coordination entities

In an octahedral coordination entity with six ligands surrounding the metal atom/ion, there will be repulsion between the electrons in metal d orbitals and the electrons (or negative charges) of the ligands. Such a repulsion is more when the metal d orbital is directed towards the ligand than when it is away from the ligand. Thus, the $d_{x^2-y^2}$ and d_{z^2} orbitals which point towards the axes along the direction of the ligand will experience more repulsion and will be raised in energy; and the d_{xy}, d_{yz} and d_{xz} orbitals which are directed between the axes will be lowered in energy relative to the average energy in the spherical crystal field. Thus, the degeneracy of the d orbitals has been removed due to ligand electron-metal electron repulsions in the octahedral complex to yield three orbitals of lower energy, t_{2g} set and two orbitals of higher energy, e_g set. This splitting of the
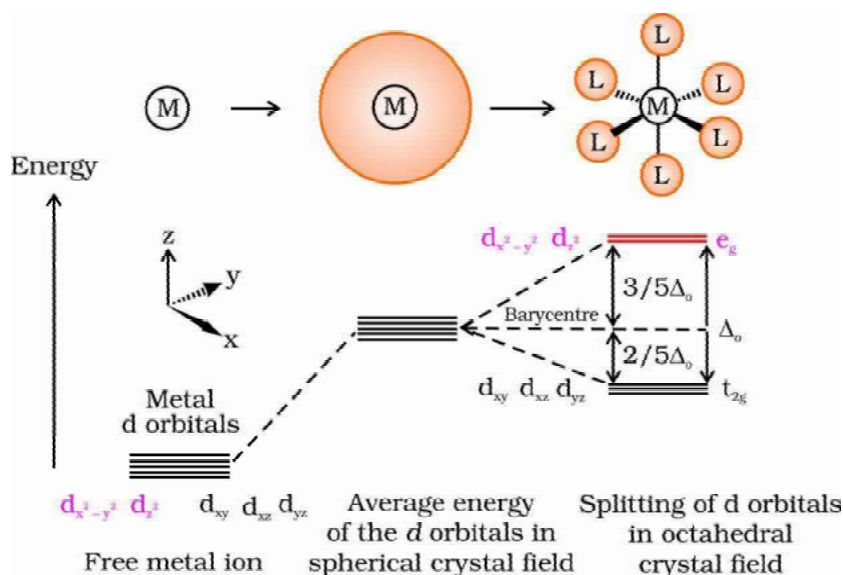
Fig.9.8: d orbital splitting in an octahedral crystal field

degenerate levels due to the presence of ligands in a definite geometry is termed as **crystal field splitting** and the energy separation is denoted by Δ_o (the subscript o is for octahedral) (Fig.9.8). Thus, the energy of the two e_g orbitals will increase by $(3/5)\,\Delta_o$ and that of the three t_{2g} will decrease by $(2/5)\Delta_o$.

The crystal field splitting, Δ_o, depends upon the field produced by the ligand and charge on the metal ion. Some ligands are able to produce strong fields in which case, the splitting will be large whereas others produce weak fields and consequently result in small splitting of d orbitals. In general, ligands can be arranged in a series in the order of increasing field strength as given below:

$$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^-$$
$$< edta^{4-} < NH_3 < en < CN^- < CO$$
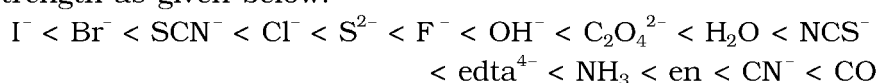
Such a series is termed as **spectrochemical series**. It is an experimentally determined series based on the absorption of light by complexes with different ligands. Let us assign electrons in the d orbitals of metal ion in octahedral coordination entities. Obviously, the single d electron occupies one of the lower energy t_{2g} orbitals. In d^2 and d^3 coordination entities, the d electrons occupy the t_{2g} orbitals singly in accordance with the Hund's rule. For d^4 ions, two possible patterns of electron distribution arise: (i) the fourth electron could either enter the t_{2g} level and pair with an existing electron, or (ii) it could avoid paying the price of the pairing energy by occupying the e_g level. Which of these possibilities occurs, depends on the relative magnitude of the crystal field splitting, Δ_o and the pairing energy, P (P represents the energy required for electron pairing in a single orbital). The two options are:

(i) If $\Delta_o < P$, the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3 e_g^1$. Ligands for which $\Delta_o < P$ are known as *weak field ligands* and form high spin complexes.

(ii) If $\Delta_o > P$, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with configuration $t_{2g}^4 e_g^0$. Ligands which produce this effect are known as *strong field ligands* and form low spin complexes.

Calculations show that d^4 to d^7 coordination entities are more stable for strong field as compared to weak field cases.

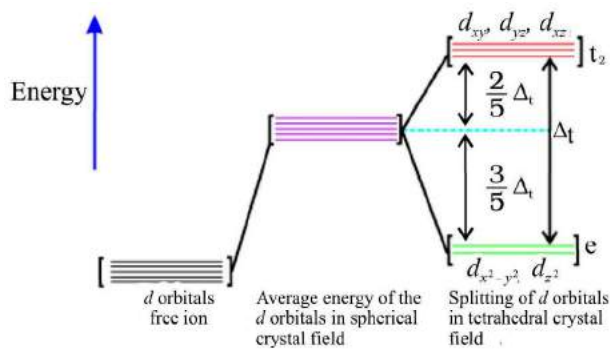### (b) Crystal field splitting in tetrahedral coordination entities

Fig.9.9: d orbital splitting in a tetrahedral crystal field.

In tetrahedral coordination entity formation, the d orbital splitting (Fig. 9.9) is inverted and is smaller as compared to the octahedral field splitting. For the same metal, the same ligands and metal-ligand distances, it can be shown that $\Delta_t = (4/9)\,\Delta_0$. Consequently, the orbital splitting energies are not sufficiently large for forcing pairing and, therefore, low spin configurations are rarely observed.

9.5.5 Colour in Coordination Compounds

In the previous Unit, we learnt that one of the most distinctive properties of transition metal complexes is their wide range of colours. This means that some of the visible spectrum is being removed from white light as it passes through the sample, so the light that emerges is no longer white. The colour of the complex is complementary to that which is absorbed. The complementary colour is the colour generated from the wavelength left over; if green light is absorbed by the complex, it appears red. Table 9.3 gives the relationship of the different wavelength absorbed and the colour observed.

Table 9.3: Relationship between the Wavelength of Light absorbed and the Colour observed in some Coordination Entities

Coordinaton entity	Wavelength of light absorbed (nm)	Colour of light absorbed	Colour of coordination entity
$[CoCl(NH_3)_5]^{2+}$	535	Yellow	Violet
$[Co(NH_3)_5(H_2O)]^{3+}$	500	Blue Green	Red
$[Co(NH_3)_6]^{3+}$	475	Blue	Yellow Orange
$[Co(CN)_6]^{3-}$	310	Ultraviolet (Not in visible region)	Pale Yellow
$[Cu(H_2O)_4]^{2+}$	600	Red	Blue
$[Ti(H_2O)_6]^{3+}$	498	Blue Green	Violet

The colour in the coordination compounds can be readily explained in terms of the crystal field theory. Consider, for example, the complex $[Ti(H_2O)_6]^{3+}$, which is violet in colour. This is an octahedral complex where the single electron (Ti^{3+} is a $3d^1$ system) in the metal d orbital is in the t_{2g} level in the ground state of the complex. The next higher state available for the electron is the empty e_g level. If light corresponding to the energy of blue-green region is absorbed by the complex, it would excite the electron from t_{2g} level to the e_g level ($t_{2g}^1 e_g^0 \rightarrow t_{2g}^0 e_g^1$). Consequently, the complex appears violet in colour (Fig. 9.10). The crystal field theory attributes the colour of the coordination compounds to d-d transition of the electron.

Fig.9.10: *Transition of an electron in [Ti(H₂O)₆]³⁺*
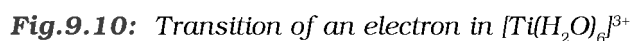
It is important to note that in the absence of ligand, crystal field splitting does not occur and hence the substance is colourless. For example, removal of water from $[Ti(H_2O)_6]Cl_3$ on heating renders it colourless. Similarly, anhydrous $CuSO_4$ is white, but $CuSO_4.5H_2O$ is blue in colour. The influence of the ligand on the colour of a complex may be illustrated by considering the $[Ni(H_2O)_6]^{2+}$ complex, which forms when nickel(II) chloride is dissolved in water. If the didentate ligand, ethane-1,2-diamine(en) is progressively added in the molar ratios en:Ni, 1:1, 2:1, 3:1, the following series of reactions and their associated colour changes occur:

$[Ni(H_2O)_6]^{2+}$ (aq)   + en (aq) = $[Ni(H_2O)_4(en)]^{2+}$(aq)   + $2H_2O$
green   pale blue

$[Ni(H_2O)_4 (en)]^{2+}$(aq) + en (aq) = $[Ni(H_2O)_2(en)_2]^{2+}$(aq) + $2H_2O$
                                                          blue/purple

$[Ni(H_2O)_2(en)_2]^{2+}$(aq) + en (aq) = $[Ni(en)_3]^{2+}$(aq)   + $2H_2O$
                                                          violet
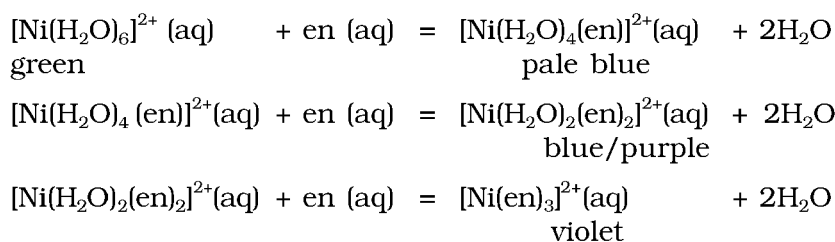
This sequence is shown in Fig. 9.11.
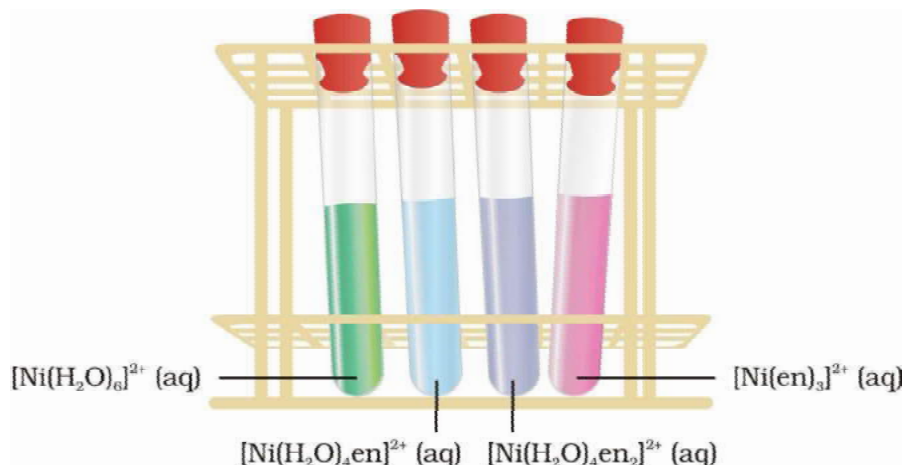
Fig.9.11
Aqueous solutions of complexes of nickel(II) with an increasing number of ethane-1, 2-diamine ligands.

$[Ni(H_2O)_6]^{2+}$ (aq) $[Ni(en)_3]^{2+}$ (aq)

$[Ni(H_2O)_4en]^{2+}$ (aq) $[Ni(H_2O)_4en_2]^{2+}$ (aq)

Colour of Some Gem Stones

The colours produced by electronic transitions within the *d* orbitals of a transition metal ion occur frequently in everyday life. Ruby [Fig.9.12(a)] is aluminium oxide (Al_2O_3) containing about 0.5-1% Cr^{3+} ions (d^3), which are randomly distributed in positions normally occupied by Al^{3+}. We may view these chromium(III) species as octahedral chromium(III) complexes incorporated into the alumina lattice; *d–d* transitions at these centres give rise to the colour.

In emerald [Fig.9.12(b)], Cr^{3+} ions occupy octahedral sites in the mineral beryl $(Be_3Al_2Si_6O_{18})$. The absorption bands seen in the ruby shift to longer wavelength, namely yellow-red and blue, causing emerald to transmit light in the green region.

Fig.9.12: *(a) Ruby: this gemstone was found in marble from Mogok, Myanmar; (b) Emerald: this gemstone was found in Muzo, Columbia.*

9.5.6 Limitations of Crystal Field Theory

The crystal field model is successful in explaining the formation, structures, colour and magnetic properties of coordination compounds to a large extent. However, from the assumptions that the ligands are point charges, it follows that anionic ligands should exert the greatest splitting effect. The anionic ligands actually are found at the low end of 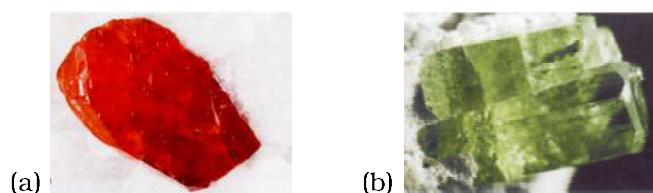the spectrochemical series. Further, it does not take into account the covalent character of bonding between the ligand and the central atom. These are some of the weaknesses of CFT, which are explained by ligand field theory (LFT) and molecular orbital theory which are beyond the scope of the present study.

Intext Questions

9.5 Explain on the basis of valence bond theory that $[Ni(CN)_4]^{2-}$ ion with square planar structure is diamagnetic and the $[NiCl_4]^{2-}$ ion with tetrahedral geometry is paramagnetic.

9.6 $[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic though both are tetrahedral. Why?

9.7 $[Fe(H_2O)_6]^{3+}$ is strongly paramagnetic whereas $[Fe(CN)_6]^{3-}$ is weakly paramagnetic. Explain.

9.8 Explain $[Co(NH_3)_6]^{3+}$ is an inner orbital complex whereas $[Ni(NH_3)_6]^{2+}$ is an outer orbital complex.

9.9 Predict the number of unpaired electrons in the square planar $[Pt(CN)_4]^{2-}$ ion.

9.10 The hexaquo manganese(II) ion contains five unpaired electrons, while the hexacyanoion contains only one unpaired electron. Explain using Crystal Field Theory.

9.6 Bonding in Metal Carbonyls

The homoleptic carbonyls (compounds containing carbonyl ligands only) are formed by most of the transition metals. These carbonyls have simple, well defined structures. Tetracarbonylnickel(0) is tetrahedral, pentacarbonyliron(0) is trigonalbipyramidal while hexacarbonyl chromium(0) is octahedral.

Decacarbonyldimanganese(0) is made up of two square pyramidal $Mn(CO)_5$ units joined by a Mn – Mn bond. Octacarbonyldicobalt(0) has a Co – Co bond bridged by two CO groups (Fig.9.13).

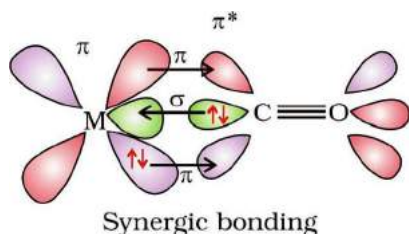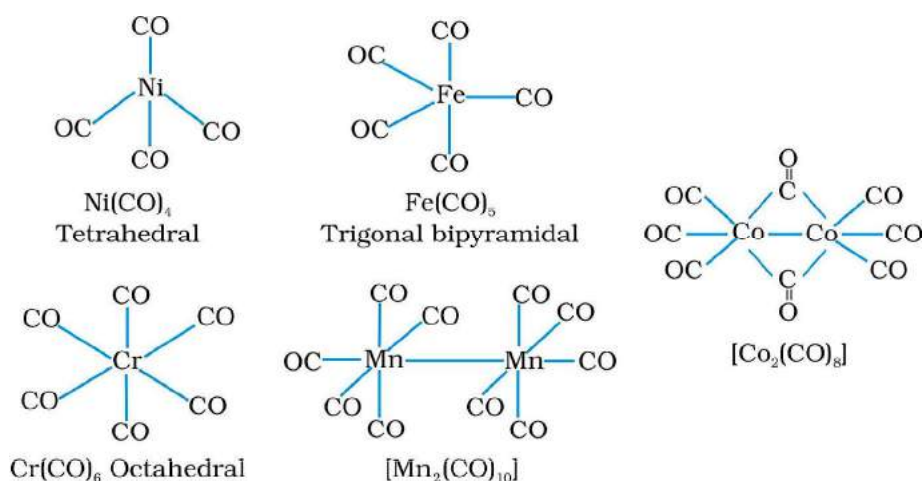**Fig. 9.13** *Structures of some representative homoleptic metal carbonyls.*

Synergic bonding

Fig. 9.14: *Example of synergic bonding interactions in a carbonyl complex.*

The metal-carbon bond in metal carbonyls possess both σ and π character. The M–C σ bond is formed by the donation of lone pair of electrons on the carbonyl carbon into a vacant orbital of the metal. The M–C π bond is formed by the donation of a pair of electrons from a filled d orbital of metal into the vacant antibonding π^* orbital of carbon monoxide. The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal (Fig.9.14).

9. Stability of Coordination Compounds

The stability of a complex in solution refers to the degree of association between the two species involved in the state of equilibrium. The magnitude of the (stability or formation) equilibrium constant for the association, quantitatively expresses the stability. Thus, if we have a reaction of the type:

$$M + 4L \rightleftharpoons ML_4$$
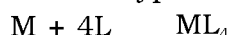
then the larger the stability constant, the higher the proportion of ML_4 that exists in solution. Free metal ions rarely exist in the solution so that M will usually be surrounded by solvent molecules which will compete with the ligand molecules, L, and be successively replaced by them. For simplicity, we generally ignore these solvent molecules and write four stability constants as follows:

M	+	L	ML	K_1	=	$[ML]/[M][L]$
ML	+	L	ML_2	K_2	=	$[ML_2]/[ML][L]$
ML_2	+	L	ML_3	K_3	=	$[ML_3]/[ML_2][L]$
ML_3	+	L	ML_4	K_4	=	$[ML_4]/[ML_3][L]$
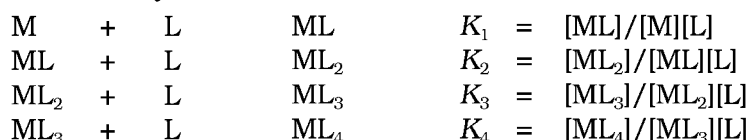
where K_1, K_2, etc., are referred to as **stepwise stability constants.** Alternatively, we can write the **overall stability constant** thus:

$$M + 4L \rightleftharpoons ML_4 \qquad \beta_4 = [ML_4]/[M][L]^4$$

The stepwise and overall stability constant are therefore related as follows:

$$\beta_4 = K_1 \times K_2 \times K_3 \times K_4 \text{ or more generally,}$$

$$\beta_n = K_1 \times K_2 \times K_3 \times K_4 \ldots\ldots K_n$$

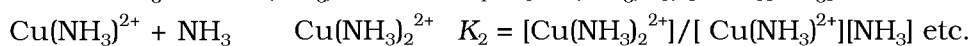If we take as an example, the steps involved in the formation of the cuprammonium ion, we have the following:

$Cu^{2+} + NH_3 \quad Cu(NH_3)^{2+} \quad K_1 = [Cu(NH_3)^{2+}]/[Cu^{2+}][NH_3]$

$Cu(NH_3)^{2+} + NH_3 \quad Cu(NH_3)_2^{2+} \quad K_2 = [Cu(NH_3)_2^{2+}]/[Cu(NH_3)^{2+}][NH_3]$ etc.

where K_1, K_2 are the stepwise stability constants and overall stability constant.

Also $\beta_4 = [Cu(NH_3)_4^{2+}]/[Cu^{2+}][NH_3]^4$

The addition of the four amine groups to copper shows a pattern found for most formation constants, in that the successive stability constants decrease. In this case, the four constants are:

$logK_1 = 4.0$, $logK_2 = 3.2$, $logK_3 = 2.7$, $logK_4 = 2.0$ or $log \beta_4 = 11.9$

The **instability constant or the dissociation constant** of coordination compounds is defined as the reciprocal of the formation constant.

Intext Question

9.11 Calculate the overall complex dissociation equilibrium constant for the $Cu(NH_3)_4^{2+}$ ion, given that β_4 for this complex is 2.1×10^{13}.

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9. Importance and Applications of Coordination Compounds

The coordination compounds are of great importance. These compounds are widely present in the mineral, plant and animal worlds and are known to play many important functions in the area of analytical chemistry, metallurgy, biological systems, industry and medicine. These are described below:

- Coordination compounds find use in many qualitative and quantitative chemical analysis. The familiar colour reactions given by metal ions with a number of ligands (especially chelating ligands), as a result of formation of coordination entities, form the basis for their detection and estimation by classical and instrumental methods of analysis. Examples of such reagents include EDTA, DMG (dimethylglyoxime), α–nitroso–β–naphthol, cupron, etc.

- Hardness of water is estimated by simple titration with Na_2EDTA. The Ca^{2+} and Mg^{2+} ions form stable complexes with EDTA. The selective estimation of these ions can be done due to difference in the stability constants of calcium and magnesium complexes.

- Some important extraction processes of metals, like those of silver and gold, make use of complex formation. Gold, for example, combines with cyanide in the presence of oxygen and water to form the coordination entity $[Au(CN)_2]^-$ in aqueous solution. Gold can be separated in metallic form from this solution by the addition of zinc (Unit 6).

- Similarly, purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds. For example, impure nickel is converted to $[Ni(CO)_4]$, which is decomposed to yield pure nickel.

- Coordination compounds are of great importance in biological systems. The pigment responsible for photosynthesis, chlorophyll, is a coordination compound of magnesium. Haemoglobin, the red pigment of blood which acts as oxygen carrier is a coordination compound of iron. Vitamin B_{12}, cyanocobalamine, the anti–pernicious anaemia factor, is a coordination compound of cobalt. Among the other compounds of biological importance with coordinated metal ions are the enzymes like, carboxypeptidase A and carbonic anhydrase (catalysts of biological systems).

- Coordination compounds are used as catalysts for many industrial processes. Examples include rhodium complex, $[(Ph_3P)_3RhCl]$, a Wilkinson catalyst, is used for the hydrogenation of alkenes.

- Articles can be electroplated with silver and gold much more smoothly and evenly from solutions of the complexes, $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$ than from a solution of simple metal ions.

- In black and white photography, the developed film is fixed by washing with hypo solution which dissolves the undecomposed AgBr to form a complex ion, $[Ag(S_2O_3)_2]^{3-}$.

- There is growing interest in the use of chelate therapy in medicinal chemistry. An example is the treatment of problems caused by the presence of metals in toxic proportions in plant/animal systems. Thus, excess of copper and iron are removed by the chelating ligands D–penicillamine and desferrioxime B via the formation of coordination compounds. EDTA is used in the treatment of lead poisoning. Some coordination compounds of platinum effectively inhibit the growth of tumours. Examples are: *cis*–platin and related compounds.

Summary

The **chemistry of coordination compounds** is an important and challenging area of modern inorganic chemistry. During the last fifty years, advances in this area, have provided development of new concepts and models of bonding and molecular structure, novel breakthroughs in **chemical industry** and vital insights into the functioning of critical components of **biological systems**.

The first systematic attempt at explaining the formation, reactions, structure and bonding of a coordination compound was made by **A. Werner**. His theory postulated the use of two types of **linkages** (**primary** and **secondary**) by a metal atom/ion in a coordination compound. In the modern language of chemistry these linkages are recognised as the ionisable (ionic) and non-ionisable (covalent) bonds, respectively. Using the property of isomerism, Werner predicted the geometrical shapes of a large number of coordination entities.

The Valence Bond Theory (VBT) explains with reasonable success, the formation, magnetic behaviour and geometrical shapes of coordination compounds. It, however, fails to provide a quantitative interpretation of magnetic behaviour and has nothing to say about the optical properties of these compounds.

The Crystal Field Theory (CFT) to coordination compounds is based on the effect of different crystal fields (provided by the ligands taken as point charges), on the degeneracy of d orbital energies of the central metal atom/ion. The splitting of the d orbitals provides different electronic arrangements in strong and weak crystal fields. The treatment provides for quantitative estimations of orbital separation energies, magnetic moments and spectral and stability

parameters. However, the assumption that ligands consititute point charges creates many theoretical difficulties.

The metal–carbon bond in **metal carbonyls** possesses both σ and π character. The ligand to metal is σ bond and metal to ligand is π bond. This unique synergic bonding provides stability to metal carbonyls.

The stability of coordination compounds is measured in terms of **stepwise stability (or formation) constant (K) or overall stability constant** (β). The stabilisation of coordination compound due to chelation is called the **chelate effect**. The stability of coordination compounds is related to Gibbs energy, enthalpy and entropy terms.

Coordination compounds are of great importance. These compounds provide critical insights into the functioning and structures of vital components of biological systems. Coordination compounds also find extensive applications in **metallurgical processes, analytical and medicinal chemistry**.

Exercises

9.1 Explain the bonding in coordination compounds in terms of Werner's postulates.

9.2 $FeSO_4$ solution mixed with $(NH_4)_2SO_4$ solution in 1:1 molar ratio gives the test of Fe^{2+} ion but $CuSO_4$ solution mixed with aqueous ammonia in 1:4 molar ratio does not give the test of Cu^{2+} ion. Explain why?

9.3 Explain with two examples each of the following: coordination entity, ligand, coordination number, coordination polyhedron, homoleptic and heteroleptic.

9.4 What is meant by unidentate, didentate and ambidentate ligands? Give two examples for each.

9.5 Specify the oxidation numbers of the metals in the following coordination entities:
   (i) $[Co(H_2O)(CN)(en)_2]^{2+}$ (iii) $[PtCl_4]^{2-}$ (v) $[Cr(NH_3)_3Cl_3]$
   (ii) $[CoBr_2(en)_2]^{+}$ (iv) $K_3[Fe(CN)_6]$

9.6 Using IUPAC norms write the formulas for the following:
   (i) Tetrahydroxidozincate(II)   (vi) Hexaamminecobalt(III) sulphate
   (ii) Potassium tetrachloridopalladate(II)   (vii) Potassium tri(oxalato)chromate(III)
   (iii) Diamminedichloridoplatinum(II)   (viii) Hexaammineplatinum(IV)
   (iv) Potassium tetracyanidonickelate(II) (ix) Tetrabromidocuprate(II)
   (v) Pentaamminenitrito-O-cobalt(III)   (x) Pentaamminenitrito-N-cobalt(III)

9.7 Using IUPAC norms write the systematic names of the following:
   (i) $[Co(NH_3)_6]Cl_3$ (iv) $[Co(NH_3)_4Cl(NO_2)]Cl$ (vii) $[Ni(NH_3)_6]Cl_2$
   (ii) $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$ (v) $[Mn(H_2O)_6]^{2+}$ (viii) $[Co(en)_3]^{3+}$
   (iii) $[Ti(H_2O)_6]^{3+}$ (vi) $[NiCl_4]^{2-}$ (ix) $[Ni(CO)_4]$

9.8 List various types of isomerism possible for coordination compounds, giving an example of each.

9.9 How many geometrical isomers are possible in the following coordination entities?
   (i) $[Cr(C_2O_4)_3]^{3-}$ (ii) $[Co(NH_3)_3Cl_3]$

9.10 Draw the structures of optical isomers of:
   (i) $[Cr(C_2O_4)_3]^{3-}$ (ii) $[PtCl_2(en)_2]^{2+}$ (iii) $[Cr(NH_3)_2Cl_2(en)]^{+}$

9.11 Draw all the isomers (geometrical and optical) of:

(i) $[CoCl_2(en)_2]^+$ (ii) $[Co(NH_3)Cl(en)_2]^{2+}$ (iii) $[Co(NH_3)_2Cl_2(en)]^+$

9.12 Write all the geometrical isomers of $[Pt(NH_3)(Br)(Cl)(py)]$ and how many of these will exhibit optical isomers?

9.13 Aqueous copper sulphate solution (blue in colour) gives:

(i) a green precipitate with aqueous potassium fluoride and

(ii) a bright green solution with aqueous potassium chloride. Explain these experimental results.

9.14 What is the coordination entity formed when excess of aqueous KCN is added to an aqueous solution of copper sulphate? Why is it that no precipitate of copper sulphide is obtained when $H_2S(g)$ is passed through this solution?

9.15 Discuss the nature of bonding in the following coordination entities on the basis of valence bond theory:

(i) $[Fe(CN)_6]^{4-}$ (ii) $[FeF_6]^{3-}$ (iii) $[Co(C_2O_4)_3]^{3-}$ (iv) $[CoF_6]^{3-}$

9.16 Draw figure to show the splitting of d orbitals in an octahedral crystal field.

9.17 What is spectrochemical series? Explain the difference between a weak field ligand and a strong field ligand.

9.18 What is crystal field splitting energy? How does the magnitude of Δ_o decide the actual configuration of d orbitals in a coordination entity?

9.19 $[Cr(NH_3)_6]^{3+}$ is paramagnetic while $[Ni(CN)_4]^{2-}$ is diamagnetic. Explain why?

9.20 A solution of $[Ni(H_2O)_6]^{2+}$ is green but a solution of $[Ni(CN)_4]^{2-}$ is colourless. Explain.

9.21 $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ are of different colours in dilute solutions. Why?

9.22 Discuss the nature of bonding in metal carbonyls.

9.23 Give the oxidation state, d orbital occupation and coordination number of the central metal ion in the following complexes:

(i) $K_3[Co(C_2O_4)_3]$ (iii) $(NH_4)_2[CoF_4]$

(ii) cis-$[CrCl_2(en)_2]Cl$ (iv) $[Mn(H_2O)_6]SO_4$

9.24 Write down the IUPAC name for each of the following complexes and indicate the oxidation state, electronic configuration and coordination number. Also give stereochemistry and magnetic moment of the complex:

(i) $K[Cr(H_2O)_2(C_2O_4)_2].3H_2O$ (iii) $[CrCl_3(py)_3]$ (v) $K_4[Mn(CN)_6]$

(ii) $[Co(NH_3)_5Cl]Cl_2$ (iv) $Cs[FeCl_4]$

9.25 What is meant by stability of a coordination compound in solution? State the factors which govern stability of complexes.

9.26 What is meant by the *chelate effect*? Give an example.

9.27 Discuss briefly giving an example in each case the role of coordination compounds in:

(i) biological systems (iii) analytical chemistry

(ii) medicinal chemistry and (iv) extraction/metallurgy of metals.

9.28 How many ions are produced from the complex $Co(NH_3)_6Cl_2$ in solution?

(i) 6 (ii) 4 (iii) 3 (iv) 2

9.29 Amongst the following ions which one has the highest magnetic moment value?

(i) $[Cr(H_2O)_6]^{3+}$ (ii) $[Fe(H_2O)_6]^{2+}$ (iii) $[Zn(H_2O)_6]^{2+}$

9.30 The oxidation number of cobalt in $K[Co(CO)_4]$ is

(i) +1 (ii) +3 (iii) −1 (iv) −3

9.31 Amongst the following, the most stable complex is

(i) $[Fe(H_2O)_6]^{3+}$ (ii) $[Fe(NH_3)_6]^{3+}$ (iii) $[Fe(C_2O_4)_3]^{3-}$ (iv) $[FeCl_6]^{3-}$

9.32 What will be the correct order for the wavelengths of absorption in the visible region for the following:

$[Ni(NO_2)_6]^{4-}$, $[Ni(NH_3)_6]^{2+}$, $[Ni(H_2O)_6]^{2+}$?

Answers to Some Intext Questions

9.1 (i) $[Co(NH_3)_4(H_2O)_2]Cl_3$ (iv) $[Pt(NH_3)BrCl(NO_2)]^-$

(ii) $K_2[Ni(CN)_4]$ (v) $[PtCl_2(en)_2](NO_3)_2$

(iii) $[Cr(en)_3]Cl_3$ (vi) $Fe_4[Fe(CN)_6]_3$

9.2 (i) Hexaamminecobalt(III) chloride

(ii) Pentaamminechloridocobalt(III) chloride

(iii) Potassium hexacyanidoferrate(III)

(iv) Potassium trioxalatoferrate(III)

(v) Potassium tetrachloridopalladate(II)

(vi) Diamminechlorido(methanamine)platinum(II) chloride

9.3 (i) Both geometrical (*cis*-, *trans*-) and optical isomers for *cis* can exist.

(ii) Two optical isomers can exist.

(iii) There are 10 possible isomers. (Hint: There are geometrical, ionisation and linkage isomers possible).

(iv) Geometrical (*cis*-, *trans*-) isomers can exist.

9.4 The ionisation isomers dissolve in water to yield different ions and thus react differently to various reagents:

$[Co(NH_3)_5Br]SO_4 + Ba^{2+} \rightarrow BaSO_4$ (s)

$[Co(NH_3)_5SO_4]Br + Ba^{2+} \rightarrow$ No reaction

$[Co(NH_3)_5Br]SO_4 + Ag^+ \rightarrow$ No reaction

$[Co(NH_3)_5SO_4]Br + Ag^+ \rightarrow AgBr$ (s)

9.6 In $Ni(CO)_4$, Ni is in zero oxidation state whereas in $NiCl_4^{2-}$, it is in +2 oxidation state. In the presence of CO ligand, the unpaired d electrons of Ni pair up but Cl^- being a weak ligand is unable to pair up the unpaired electrons.

9.7 In presence of CN^-, (a strong ligand) the $3d$ electrons pair up leaving only one unpaired electron. The hybridisation is d^2sp^3 forming inner orbital complex. In the presence of H_2O, (a weak ligand), $3d$ electrons do not pair up. The hybridisation is sp^3d^2 forming an outer orbital complex containing five unpaired electrons, it is strongly paramagnetic.

9.8 In the presence of NH_3, the $3d$ electrons pair up leaving two d orbitals empty to be involved in d^2sp^3 hybridisation forming inner orbital complex in case of $[Co(NH_3)_6]^{3+}$.

In $Ni(NH_3)_6^{2+}$, Ni is in +2 oxidation state and has d^8 configuration, the hybridisation involved is sp^3d^2 forming outer orbital complex.

9.9 For square planar shape, the hybridisation is dsp^2. Hence the unpaired electrons in $5d$ orbital pair up to make one d orbital empty for dsp^2 hybridisation. Thus there is no unpaired electron.

9.11 The overall dissociation constant is the reciprocal of overall stability constant i.e. $1/\beta_4 = 4.7 \times 10^{-14}$

Answers to Some Questions in Exercises

UNIT 1

1.11 106.57 u

1.13 143.1 pm

1.15 8.97 g cm^{-3}

1.16 Ni^{2+} = 96% and Ni^{3+} = 4%

1.24 (i) 354 pm   (ii) 2.26×10^{22} unit cells

1.25 6.02 × 10^{18} cation vacancies mol^{-1}

UNIT 2

2.4 16.23 M

2.5 0.617 m, 0.01 and 0.99, 0.67

2.6 157.8 mL

2.7 33.5%

2.8 17.95 m and 9.10 M

2.9 1.5×10^{-3}%, 1.25×10^{-4} m

2.15 40.907 g mol^{-1}

2.16 73.58 kPa

2.17 12.08 kPa

2.18 10 g

2.19 23 g mol^{-1}, 3.53 kPa

2.20 269.07 K

2.21 A = 25.58 u and B = 42.64 u

2.22 0.061 M

2.24 KCl, CH$_3$OH, CH$_3$CN, Cyclohexane

2.25 Toluene, chloroform; Phenol, Pentanol; Formic acid, ethylelne glycol

2.26 5 m

2.27 2.45×10^{-8} M

2.28 1.424%

2.29 3.2 g of water

2.30 4.575 g

2.32 0.65^0

2.33 i = 1.0753, K$_a$ = 3.07×10^{-3}

2.34 17.44 mm Hg

2.35 178×10^{-5}

2.36 280.7 torr, 32 torr

2.38 0.6 and 0.4

2.39 x (O$_2$) 4.6x10^{-5}, x (N$_2$) 9.22×10^{-5}

2.40 0.03 mol of CaCl$_2$

2.41 5.27x10^{-3} atm.

UNIT 3

3.4 (i) $E^{\ominus}$ = 0.34V, $\Delta_r G^{\ominus}$ = − 196.86 kJ mol^{-1}, K = 3.124 × 10^{34}

(ii) $E^{\ominus}$ = 0.03V, $\Delta_r G^{\ominus}$ = − 2.895 kJ mol^{-1}, K = 3.2

3.5 (i) 2.68 V, (ii) 0.53 V, (iii) 0.08 V, (iv) −1.298 V

3.6 1.56 V

3.8 124.0 S cm^2 mol^{-1}

3.9 0.219 cm^{-1}

3.11 1.85 × 10^{-5}

3.12 3F, 2F, 5F

3.13 1F, 4.44F

3.14 2F, 1F

3.15 1.8258g

3.16 14.40 min, Copper 0.427g, Zinc 0.437 g

UNIT 4

4.2 (i) 8.0×10^{-9} mol L^{-1} s^{-1}; 3.89×10^{-9} mol L^{-1} s^{-1}

4.4 $bar^{-1/2}s^{-1}$

4.6 (i) 4 times   (ii) ¼ times

4.8 (i) 4.67×10^{-3} mol $L^{-1}s^{-1}$ (ii) 1.98×10^{-2} s^{-1}

4.9 (i) rate $= k[A][B]^2$ (ii) 9 times

4.10 Orders with respect to A is 1.5 and order with respect to B is zero.

4.11 rate law $= k[A][B]^2$; rate constant $= 6.0$ $M^{-2}min^{-1}$

4.13 (i) 3.47×10^{-3} seconds   (ii) 0.35 minutes   (iii) 0.173 years

4.14 1845 years   **4.16** 4.6×10^{-2} s

4.17 0.7814 μg and 0.227 μg.   **4.19** 77.7 minutes

4.20 2.20×10^{-3} s^{-1} **4.21** 2.23×10^{-3} s^{-1}, 7.8×10^{-4} atm s^{-1}

4.23 3.9×10^{12} s^{-1} **4.24** 0.135 M

4.25 0.158 M   **4.26** 232.79 kJ mol^{-1}

4.27 239.339 kJ mol^{-1} **4.28** 24°C

4.29 $E_a = 76.750$ kJ mol^{-1}, $k = 0.9965 \times 10^{-2}$ s^{-1}

4.30 52.8 kJ mol^{-1}

UNIT 6

6.1 Zinc is highly reactive metal, it may not be possible to replace it from a solution of $ZnSO_4$ so easily.

6.2 It prevents one of the components from forming the froth by complexation.

6.3 The Gibbs energies of formation of most sulphides are greater than that for CS_2. In fact, CS_2 is an endothermic compound. Hence it is common practice to roast sulphide ores to corresponding oxides prior to reduction.

6.5 CO

6.6 Selenium, tellurium, silver, gold are the metals present in anode mud. This is because these are less reactive than copper.

6.9 Silica removes Fe_2O_3 remaining in the matte by forming silicate, $FeSiO_3$.

6.15 Cast iron is made from pig iron by melting pig iron with scrap iron and coke. It has slightly lower carbon content (» 3%) than pig iron (» 4% C)

6.17 To remove basic impurities, like Fe_2O_3

6.18 To lower the melting point of the mixture.

6.20 The reduction may require very high temperature if CO is used as a reducing agent in this case.

6.21 Yes, $2Al + \dfrac{3}{2}O_2 \rightarrow Al_2O_3$ $\Delta_r G^V = -827$ kJ mol^{-1}

$2Cr + \dfrac{3}{2}O_2 \rightarrow Cr_2O_3$ $\Delta_r G^V = -540$ kJ mol^{-1}

Hence $Cr_2O_3 + 2Al \rightarrow Al_2O_3 + 2Cr$ $-827 - (-540) = -287$ kJ mol^{-1}

6.22 Carbon is better reducing agent.

6.25 Graphite rods act as anode and get burnt away as CO and CO_2 during the process of electrolysis.

6.28 Above 1600K Al can reduce MgO.

UNIT 7

7.10 Because of inability of nitrogen to expand its covalency beyond 4.

7.20 Freons

7.22 It dissolves in rain water and produces acid rain.

7.23 Due to strong tendency to accept electrons, halogens act as strong oxidising agent.

7.24 Due to high electronegativity and small size, it cannot act as central atom in higher oxoacids.

7.25 Nitrogen has smaller size than chlorine. Smaller size favours hydrogen bonding.

7.30 Synthesis of O_2PtF_6 inspired Bartlett to prepare $XePtF_6$ as Xe and oxygen have nearly same ionisation enthalpies.

7.31 (i)   +3   (ii)   +3   (iii)   -3   (iv)   +5   (v)   +5

7.34 ClF, Yes.

7.36 (i) $I_2 < F_2 < Br_2 < Cl_2$

(ii) HF < HCl < HBr < HI

(iii) $BiH_3 \le SbH_3 < AsH_3 < PH_3 < NH_3$

7.37 (ii) NeF_2

7.38 (i) XeF_4

(ii) XeF_2

(iii) XeO_3

UNIT 8

8.2 It is because Mn^{2+} has $3d^5$ configuration which has extra stability.

8.5 Stable oxidation states.

$3d^3$ (Vanadium): (+2), +3, +4, and +5

$3d^5$ (Chromium): +3, +4, +6

$3d^5$ (Manganese): +2, +4, +6, +7

$3d^8$ (Nickel): +2, +3 (in complexes)

$3d^4$ There is no d^4 configuration in the ground state.

8.6 Vanadate VO_3^-, chromate CrO_4^{2-}, permanganate MnO_4^-

8.10 +3 is the common oxidation state of the lanthanoids

In addition to +3, oxidation states +2 and +4 are also exhibited by some of the lanthanoids.

8.13 In transition elements the oxidation states vary from +1 to any highest oxidation state by one

For example, for manganese it may vary as +2, +3, +4, +5, +6, +7. In the nontransition elements the variation is selective, always differing by 2, e.g. +2, +4, or +3, +5 or +4, +6 etc.

8.18 Except Sc^{3+}, all others will be coloured in aqueous solution because of incompletely filled $3d$-orbitals, will give rise to d-d transitions.

8.21 (i) Cr^{2+} is reducing as it involves change from d^4 to d^3, the latter is more stable configuration

(t_{2g}^3) Mn(III) to Mn(II) is from $3d^4$ to $3d^5$ again $3d^5$ is an extra stable configuration.

(ii) Due to CFSE, which more than compensates the 3rd IE.

(iii) The hydration or lattice energy more than compensates the ionisation enthalpy involved in removing electron from d^1.

8.23 Copper, because with +1 oxidation state an extra stable configuration, $3d^{10}$ results.

8.24 Unpaired electrons Mn^{3+} = 4, Cr^{3+} = 3, V^{3+} = 2, Ti^{3+} = 1. Most stable Cr^{3+}

8.28 Second part 59, 95, 102.

8.30 Lawrencium, 103, +3

8.36 $Ti^{2+} = 2$, $V^{2+} = 3$, $Cr^{3+} = 3$, $Mn^{2+} = 5$, $Fe^{2+} = 6$, $Fe^{3+} = 5$, $CO^{2+} = 7$, $Ni^{2+} = 8$, $Cu^{2+} = 9$

8.38 $M\sqrt{n(n+2)} = 2.2$, $n \approx 1$, $d^2 sp^3$, CN^- strong ligand

$= 5.3$, $n \approx 4$, sp^3, d^2, H_2O weak ligand

$= 5.9$, $n \approx 5$, sp^3, Cl^- weak ligand.

UNIT 9

9.5 (i) $+ 3$ (ii) $+3$ (iii) $+2$ (iv) $+3$ (v) $+3$

9.6 (i) $[Zn(OH)_4]^{2-}$ (ii) $K_2[PdCl_4]$ (iii) $[Pt(NH_3)_2Cl_2]$ (iv) $K_2[Ni(CN)_4]$

(v) $[Co(NH_3)_5(ONO)]^{2+}$ (vi) $[Co(NH_3)_6]_2(SO_4)_3$ (vii) $K_3[Cr(C_2O_4)_3]$ (viii) $[Pt(NH_3)_6]^{4+}$

(ix) $[CuBr_4]^{2-}$ (x) $[Co(NH_3)_5(NO_2)]^{2+}$

9.9 (i) $[Cr(C_2O_4)_3]^{3-}$ – Nil

(ii) $[Co(NH_3)_3Cl_3]$ – Two (*fac-* and *mer-*)

9.12 Three (two *cis* and one *trans*)

9.13 Aqueous $CuSO_4$ solution exists as $[Cu(H_2O)_4]SO_4$ which has blue colour due to $[Cu(H_2O)_4]^{2+}$ ions.

(i) When KF is added, the weak H_2O ligands are replaced by F^- ligands, forming $[CuF_4]^{2-}$ ions which is a green precipitate.

$[Cu(H_2O)_4]^{2+} + 4F^- \rightarrow [CuF_4]^{2-} + 4H_2O$

(ii) When KCl is added, Cl^- ligands replace the weak H_2O ligands forming $[CuCl_4]^{2-}$ ions which has bright green colour.

$[Cu(H_2O)_4]^{2+} + 4Cl^- \rightarrow [CuCl_4]^{2-} + 4H_2O$
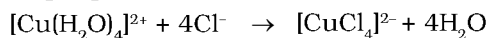
9.14 $[Cu(H_2O)_4]^{2+} + 4 CN^- \rightarrow [Cu(CN)_4]^{2-} + 4H_2O$

As CN^- is a strong ligand, it forms a highly stable complex with Cu^{2+} ion. On passing H_2S, free Cu^{2+} ions are not available to form the precipitate of CuS.

9.23 (i) OS = $+3$, CN = 6, d-orbital occupation is $t_{2g}^6 e_g^0$,

(ii) OS = $+3$, CN = 6, d^3 (t_{2g}^3),

(iii) OS = $+2$, CN = 4, d^7 ($t_{2g}^5 e_g^2$),

(iv) OS = $+2$, CN = 6, d^5 $(t_{2g}^3 e_g^2)$.

9.28 (iii)

9.29 (ii)

9.30 (iii)

9.31 (iii)

9.32 (i) The order of the ligand in the spectrochemical series :

$H_2O < NH_3 < NO_2^-$

Hence the energy of the observed light will be in the order :

$[Ni(H_2O)_6]^{2+} < [Ni(NH_3)_6]^{2+} < [Ni(NO_2)_6]^{4-}$

Thus, wavelengths absorbed ($E = hc/\lambda$) will be in the opposite order.

Elements, their Atomic Number and Molar Mass

Element	Symbol	Atomic Number	Molar mass/ (g mol^{-1})
Actinium	Ac	89	227.03
Aluminium	Al	13	26.98
Americium	Am	95	(243)
Antimony	Sb	51	121.75
Argon	Ar	18	39.95
Arsenic	As	33	74.92
Astatine	At	85	210
Barium	Ba	56	137.34
Berkelium	Bk	97	(247)
Beryllium	Be	4	9.01
Bismuth	Bi	83	208.98
Bohrium	Bh	107	(264)
Boron	B	5	10.81
Bromine	Br	35	79.91
Cadmium	Cd	48	112.40
Caesium	Cs	55	132.91
Calcium	Ca	20	40.08
Californium	Cf	98	251.08
Carbon	C	6	12.01
Cerium	Ce	58	140.12
Chlorine	Cl	17	35.45
Chromium	Cr	24	52.00
Cobalt	Co	27	58.93
Copper	Cu	29	63.54
Curium	Cm	96	247.07
Dubnium	Db	105	(263)
Dysprosium	Dy	66	162.50
Einsteinium	Es	99	(252)
Erbium	Er	68	167.26
Europium	Eu	63	151.96
Fermium	Fm	100	(257.10)
Fluorine	F	9	19.00
Francium	Fr	87	(223)
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69.72
Germanium	Ge	32	72.61
Gold	Au	79	196.97
Hafnium	Hf	72	178.49
Hassium	Hs	108	(269)
Helium	He	2	4.00
Holmium	Ho	67	164.93
Hydrogen	H	1	1.0079
Indium	In	49	114.82
Iodine	I	53	126.90
Iridium	Ir	77	192.2
Iron	Fe	26	55.85
Krypton	Kr	36	83.80
Lanthanum	La	57	138.91
Lawrencium	Lr	103	(262.1)
Lead	Pb	82	207.19
Lithium	Li	3	6.94
Lutetium	Lu	71	174.96
Magnesium	Mg	12	24.31
Manganese	Mn	25	54.94
Meitneium	Mt	109	(268)
Mendelevium	Md	101	258.10

Element	Symbol	Atomic Number	Molar mass/ (g mol^{-1})
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.94
Neodymium	Nd	60	144.24
Neon	Ne	10	20.18
Neptunium	Np	93	(237.05)
Nickel	Ni	28	58.71
Niobium	Nb	41	92.91
Nitrogen	N	7	14.0067
Nobelium	No	102	(259)
Osmium	Os	76	190.2
Oxygen	O	8	16.00
Palladium	Pd	46	106.4
Phosphorus	P	15	30.97
Platinum	Pt	78	195.09
Plutonium	Pu	94	(244)
Polonium	Po	84	210
Potassium	K	19	39.10
Praseodymium	Pr	59	140.91
Promethium	Pm	61	(145)
Protactinium	Pa	91	231.04
Radium	Ra	88	(226)
Radon	Rn	86	(222)
Rhenium	Re	75	186.2
Rhodium	Rh	45	102.91
Rubidium	Rb	37	85.47
Ruthenium	Ru	44	101.07
Rutherfordium	Rf	104	(261)
Samarium	Sm	62	150.35
Scandium	Sc	21	44.96
Seaborgium	Sg	106	(266)
Selenium	Se	34	78.96
Silicon	Si	14	28.08
Silver	Ag	47	107.87
Sodium	Na	11	22.99
Strontium	Sr	38	87.62
Sulphur	S	16	32.06
Tantalum	Ta	73	180.95
Technetium	Tc	43	(98.91)
Tellurium	Te	52	127.60
Terbium	Tb	65	158.92
Thallium	Tl	81	204.37
Thorium	Th	90	232.04
Thulium	Tm	69	168.93
Tin	Sn	50	118.69
Titanium	Ti	22	47.88
Tungsten	W	74	183.85
Ununbium	Uub	112	(277)
Ununnilium	Uun	110	(269)
Unununium	Uuu	111	(272)
Uranium	U	92	238.03
Vanadium	V	23	50.94
Xenon	Xe	54	131.30
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.91
Zinc	Zn	30	65.37
Zirconium	Zr	40	91.22

The value given in parenthesis is the molar mass of the isotope of largest known half-life.

Some Useful Conversion Factors

Common Unit of Mass and Weight
1 pound = 453.59 grams

1 pound = 453.59 grams = 0.45359 kilogram
1 kilogram = 1000 grams = 2.205 pounds
1 gram = 10 decigrams = 100 centigrams
      = 1000 milligrams
1 gram = 6.022×10^{23} atomic mass units or u
1 atomic mass unit = 1.6606×10^{-24} gram
1 metric tonne = 1000 kilograms
            = 2205 pounds

Common Unit of Volume
1 quart = 0.9463 litre
1 litre = 1.056 quarts

1 litre = 1 cubic decimetre = 1000 cubic
centimetres = 0.001 cubic metre
1 millilitre = 1 cubic centimetre = 0.001 litre
      = 1.056×10^{-3} quart
1 cubic foot = 28.316 litres = 29.902 quarts
       = 7.475 gallons

Common Units of Energy
1 joule = 1×10^7 ergs

1 thermochemical calorie**
         = 4.184 joules
         = 4.184×10^7 ergs
= 4.129×10^{-2} litre-atmospheres
= 2.612×10^{19} electron volts
1 ergs = 1×10^{-7} joule = 2.3901×10^{-8} calorie
1 electron volt = 1.6022×10^{-19} joule
        = 1.6022×10^{-12} erg
        = 96.487 kJ/mol†
1 litre-atmosphere = 24.217 calories
        = 101.32 joules
        = 1.0132×10^9 ergs
1 British thermal unit = 1055.06 joules
        = 1.05506×10^{10} ergs
        = 252.2 calories

Common Units of Length
1 inch = 2.54 centimetres (exactly)

1 mile = 5280 feet = 1.609 kilometres
1 yard = 36 inches = 0.9144 metre
1 metre = 100 centimetres = 39.37 inches
      = 3.281 feet
      = 1.094 yards
1 kilometre = 1000 metres = 1094 yards
      = 0.6215 mile
1 Angstrom = 1.0×10^{-8} centimetre
      = 0.10 nanometre
      = 1.0×10^{-10} metre
      = 3.937×10^{-9} inch

Common Units of Force* and Pressure

1 atmosphere = 760 millimetres of mercury
      = 1.013×10^5 pascals
      = 14.70 pounds per square inch
1 bar = 10^5 pascals
1 torr = 1 millimetre of mercury
1 pascal = 1 kg/ms^2 = 1 N/m^2

Temperature
SI Base Unit: Kelvin (K)

K = -273.15°C
K = °C + 273.15
°F = 1.8(°C) + 32

$$°C = \frac{°F - 32}{1.8}$$

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*   *Force: 1 newton (N) = 1 kg m/s^2, i.e.,the force that, when applied for 1 second, gives a 1-kilogram mass a velocity of 1 metre per second.*
** *The amount of heat required to raise the temperature of one gram of water from 14.5^{0}C to 15.5^{0}C.*
†   *Note that the other units are per particle and must be multiplied by 6.022 $\times 10^{23}$ to be strictly comparable.*

Standard potentials at 298 K in electrochemical order

Reduction half-reaction	$E^{\ominus}/V$	Reduction half-reaction	$E^{\ominus}/V$
$H_4XeO_6 + 2H^+ + 2e^- \longrightarrow XeO_3 + 3H_2O$	+3.0	$Cu^+ + e^- \longrightarrow Cu$	+0.52
$F_2 + 2e^- \longrightarrow 2F{-}$	+2.87	$NiOOH + H_2O + e^- \longrightarrow Ni(OH)_2 + OH^-$	+0.49
$O_3 + 2H^+ + 2e^- \longrightarrow O_2 + H_2O$	+2.07	$Ag_2CrO_4 + 2e^- \longrightarrow 2Ag + CrO_4^{2-}$	+0.45
$S_2O_8^{2-} + 2e^- \longrightarrow 2SO_4^{2-}$	+2.05	$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$	+0.40
$Ag^+ + e^- \longrightarrow Ag^+$	+1.98	$ClO_4^- + H_2O + 2e^- \longrightarrow ClO_3^- + 2OH^-$	+0.36
$Co^{3+} + e^- \longrightarrow Co^{2+}$	+1.81	$[Fe(CN)_6]^{3-} + e^- \longrightarrow [Fe(CN)_6]^{4-}$	+0.36
$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$	+1.78	$Cu^{2+} + 2e^- \longrightarrow Cu$	+0.34
$Au^+ + e^- \longrightarrow Au$	+1.69	$Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-$	+0.27
$Pb^{4+} + 2e^- \longrightarrow Pb^{2+}$	+1.67	$AgCl + e^- \longrightarrow Ag + Cl^-$	+0.27
$2HClO + 2H^+ + 2e^- \longrightarrow Cl_2 + 2H_2O$	+1.63	$Bi^{3+} + 3e^- \longrightarrow Bi$	+0.20
$Ce^{4+} + e^- \longrightarrow Ce^{3+}$	+1.61	$SO_4^{2-} + 4H^+ + 2e^- \longrightarrow H_2SO_3 + H_2O$	+0.17
$2HBrO + 2H^+ + 2e^- \longrightarrow Br_2 + 2H_2O$	+1.60	$Cu^{2+} + e^- \longrightarrow Cu^+$	+0.16
$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	+1.51	$Sn^{4+} + 2e^- \longrightarrow Sn^{2+}$	+0.15
$Mn^{3+} + e^- \longrightarrow Mn^{2+}$	+1.51	$AgBr + e^- \longrightarrow Ag + Br^-$	+0.07
$Au^{3+} + 3e^- \longrightarrow Au$	+1.40	$Ti^{4+} + e^- \longrightarrow Ti^{3+}$	0.00
$Cl_2 + 2e^- \longrightarrow 2Cl^-$	+1.36	$2H^+ + 2e- \longrightarrow H_2$	0.0 by definition
$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$	+1.33		
$O_3 + H_2O + 2e^- \longrightarrow O_2 + 2OH^-$	+1.24	$Fe^{3+} + 3e^- \longrightarrow Fe$	−0.04
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	+1.23	$O_2 + H_2O + 2e^- \longrightarrow HO_2^- + OH^-$	−0.08
$ClO_4^- + 2H^+ + 2e^- \longrightarrow ClO_3^- + 2H_2O$	+1.23	$Pb^{2+} + 2e^- \longrightarrow Pb$	−0.13
$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$	+1.23	$In^+ + e^- \longrightarrow In$	−0.14
$Pt^{2+} + 2e^- \longrightarrow Pt$	+1.20	$Sn^{2+} + 2e^- \longrightarrow Sn$	−0.14
$Br_2 + 2e^- \longrightarrow 2Br^-$	+1.09	$AgI + e^- \longrightarrow Ag + I^-$	−0.15
$Pu^{4+} + e^- \longrightarrow Pu^{3+}$	+0.97	$Ni^{2+} + 2e^- \longrightarrow Ni$	−0.23
$NO_3^- + 4H^+ + 3e^- \longrightarrow NO + 2H_2O$	+0.96	$V^{3+} + e^- \longrightarrow V^{2+}$	−0.26
$2Hg^{2+} + 2e^- \longrightarrow Hg_2^{2+}$	+0.92	$Co^{2+} + 2e^- \longrightarrow Co$	−0.28
$ClO^- + H_2O + 2e^- \longrightarrow Cl^- + 2OH^-$	+0.89	$In^{3+} + 3e^- \longrightarrow In$	−0.34
$Hg^{2+} + 2e^- \longrightarrow Hg$	+0.86	$Tl^+ + e^- \longrightarrow Tl$	−0.34
$NO_3^- + 2H^+ + e^- \longrightarrow NO_2 + H_2O$	+0.80	$PbSO_4 + 2e^- \longrightarrow Pb + SO_4^{2-}$	−0.36
$Ag^+ + e^- \longrightarrow Ag$	+0.80	$Ti^{3+} + e^- \longrightarrow Ti^{2+}$	−0.37
$Hg_2^{2+} + 2e^- \longrightarrow 2Hg$	+0.79	$Cd^{2+} + 2e^- \longrightarrow Cd$	−0.40
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	+0.77	$In^{2+} + e^- \longrightarrow In^+$	−0.40
$BrO^- + H_2O + 2e^- \longrightarrow Br^- + 2OH^-$	+0.76	$Cr^{3+} + e^- \longrightarrow Cr^{2+}$	−0.41
$Hg_2SO_4 + 2e^- \longrightarrow 2Hg + SO_4^{2-}$	+0.62	$Fe^{2+} + 2e^- \longrightarrow Fe$	−0.44
$MnO_4^{2-} + 2H_2O + 2e^- \longrightarrow MnO_2 + 4OH^-$	+0.60	$In^{3+} + 2e^- \longrightarrow In^+$	−0.44
$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$	+0.56	$S + 2e^- \longrightarrow S^{2-}$	−0.48
$I_2 + 2e^- \longrightarrow 2I^-$	+0.54	$In^{3+} + e^- \longrightarrow In^{2+}$	−0.49
$I_3^- + 2e^- \longrightarrow 3I^-$	+0.53	$U^{4+} + e^- \longrightarrow U^{3+}$	−0.61
		$Cr^{3+} + 3e^- \longrightarrow Cr$	−0.74
		$Zn^{2+} + 2e^- \longrightarrow Zn$	−0.76

(continued)

Reduction half-reaction	E^{J}/V	Reduction half-reaction	E^{J}/V
$Cd(OH)_2 + 2e^- \longrightarrow Cd + 2OH^-$	–0.81	$La^{3+} + 3e^- \longrightarrow La$	–2.52
$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$	–0.83	$Na^+ + e^- \longrightarrow Na$	–2.71
$Cr^{2+} + 2e^- \longrightarrow Cr$	–0.91	$Ca^{2+} + 2e^- \longrightarrow Ca$	–2.87
$Mn^{2+} + 2e^- \longrightarrow Mn$	–1.18	$Sr^{2+} + 2e^- \longrightarrow Sr$	–2.89
$V^{2+} + 2e^- \longrightarrow V$	–1.19	$Ba^{2+} + 2e^- \longrightarrow Ba$	–2.91
$Ti^{2+} + 2e^- \longrightarrow Ti$	–1.63	$Ra^{2+} + 2e^- \longrightarrow Ra$	–2.92
$Al^{3+} + 3e^- \longrightarrow Al$	–1.66	$Cs^+ + e^- \longrightarrow Cs$	–2.92
$U^{3+} + 3e^- \longrightarrow U$	–1.79	$Rb^+ + e^- \longrightarrow Rb$	–2.93
$Sc^{3+} + 3e^- \longrightarrow Sc$	–2.09	$K^+ + e^- \longrightarrow K$	–2.93
$Mg^{2+} + 2e^- \longrightarrow Mg$	–2.36	$Li^+ + e^- \longrightarrow Li$	–3.05
$Ce^{3+} + 3e^- \longrightarrow Ce$	–2.48		

Logarithms

Sometimes, a numerical expression may involve multiplication, division or rational powers of large numbers. For such calculations, logarithms are very useful. They help us in making difficult calculations easy. In Chemistry, logarithm values are required in solving problems of chemical kinetics, thermodynamics, electrochemistry, etc. We shall first introduce this concept, and discuss the laws, which will have to be followed in working with logarithms, and then apply this technique to a number of problems to show how it makes difficult calculations simple.

We know that

$2^3 = 8$, $3^2 = 9$, $5^3 = 125$, $7^0 = 1$

In general, for a positive real number a, and a rational number m, let $a^m = b$,

where b is a real number. In other words

the mth power of base a is b.

Another way of stating the same fact is

logarithm of b to base a is m.

If for a positive real number a, $a \neq 1$

$a^m = b$,

we say that m is the logarithm of b to the base a.

We write this as $\log_a^b = m$,

"log" being the abbreviation of the word "logarithm".

Thus, we have

$\log_2 8 = 3$,   Since $2^3 = 8$

$\log_3 9 = 2$,   Since $3^2 = 9$

$\log \dfrac{125}{5} = 3$,   Since $5^3 = 125$

$\log_7 1 = 0$,   Since $7^0 = 1$

Laws of Logarithms

In the following discussion, we shall take logarithms to any base a, (a > 0 and a ≠ 1)

First Law: $\log_a (mn) = \log_a m + \log_a n$

Proof: Suppose that $\log_a m = x$ and $\log_a n = y$

Then $a^x = m$, $a^y = n$

Hence $mn = a^x \cdot a^y = a^{x+y}$

It now follows from the definition of logarithms that

$\log_a (mn) = x + y = \log_a m - \log_a n$

Second Law: $\log_a \left(\dfrac{m}{n} \right) = \log_a m - \log_a n$

Proof: Let $\log_a m = x$, $\log_a n = y$

Then $a^x = m$, $a^y = n$

Hence $\dfrac{m}{n} = \dfrac{a^x}{a^y} = a^{x-y}$

Therefore

$$\log_a\left(\dfrac{m}{n}\right) = x - y = \log_a m - \log_a n$$

Third Law : $\log_a(m^n) = n \log_a m$

Proof : As before, if $\log_a m = x$, then $a^x = m$

Then $\quad m^n = \left(a^x\right)^n = a^{nx}$

giving $\log_a(m^n) = nx = n \log_a m$

Thus according to First Law: "the log of the product of two numbers is equal to the sum of their logs. Similarly, the Second Law says: the log of the ratio of two numbers is the difference of their logs. Thus, the use of these laws converts a problem of multiplication / division into a problem of addition/ subtraction, which are far easier to perform than multiplication/division. That is why logarithms are so useful in all numerical computations.

Logarithms to Base 10

Because number 10 is the base of writing numbers, it is very convenient to use logarithms to the base 10. Some examples are:

$\log_{10} 10 = 1$, $\qquad$ since $10^1 = 10$
$\log_{10} 100 = 2$, $\qquad$ since $10^2 = 100$
$\log_{10} 10000 = 4$, $\qquad$ since $10^4 = 10000$
$\log_{10} 0.01 = -2$, $\qquad$ since $10^{-2} = 0.01$
$\log_{10} 0.001 = -3$, $\qquad$ since $10^{-3} = 0.001$
and $\log_{10} 1 = 0$ $\qquad$ since $10^0 = 1$

The above results indicate that if n is an integral power of 10, i.e., 1 followed by several zeros or 1 preceded by several zeros immediately to the right of the decimal point, then log n can be easily found.

If n is not an integral power of 10, then it is not easy to calculate log n. But mathematicians have made tables from which we can read off approximate value of the logarithm of any positive number between 1 and 10. And these are sufficient for us to calculate the logarithm of any number expressed in decimal form. For this purpose, we always express the given decimal as the product of an integral power of 10 and a number between 1 and 10.

Standard Form of Decimal

We can express any number in decimal form, as the product of (i) an integral power of 10, and (ii) a number between 1 and 10. Here are some examples:

(i) 25.2 lies between 10 and 100

$$25.2 = \dfrac{25.2}{10} \times 10 = 2.52 \times 10^1$$

(ii) 1038.4 lies between 1000 and 10000.

$$\therefore 1038.4 = \dfrac{1038.4}{1000} \times 10^3 = 1.0384 \times 10^3$$

(iii) 0.005 lies between 0.001 and 0.01
$\quad \therefore 0.005 = (0.005 \times 1000) \times 10^{-3} = 5.0 \times 10^{-3}$

(iv) 0.00025 lies between 0.0001 and 0.001
$\quad \therefore 0.00025 = (0.00025 \times 10000) \times 10^{-4} = 2.5 \times 10^{-4}$

In each case, we divide or multiply the decimal by a power of 10, to bring one non-zero digit to the left of the decimal point, and do the reverse operation by the same power of 10, indicated separately.

Thus, any positive decimal can be written in the form

n = m × 10^p

where p is an integer (positive, zero or negative) and 1≤ m < 10. This is called the "standard form of n."

Working Rule

1. Move the decimal point to the left, or to the right, as may be necessary, to bring one non-zero digit to the left of decimal point.
2.   (i) If you move p places to the left, multiply by 10^p.
    (ii) If you move p places to the right, multiply by 10^{-p}.
    (iii) If you do not move the decimal point at all, multiply by 10^0.
    (iv) Write the new decimal obtained by the power of 10 (of step 2) to obtain the standard form of the given decimal.

Characteristic and Mantissa

Consider the standard form of n

n = m ×10^p, where 1 ≤ m < 10

Taking logarithms to the base 10 and using the laws of logarithms

log n = log m + log 10^p

     = log m + p log 10

     = p + log m

Here p is an integer and as 1 ≤ m < 10, so 0 ≤ log m < 1, i.e., m lies between 0 and 1. When log n has been expressed as p + log m, where p is an integer and 0 log m < 1, we say that p is the "characteristic" of log n and that log m is the "mantissa of log n. Note that characteristic is always an integer – positive, negative or zero, and mantissa is never negative and is always less than 1. If we can find the characteristics and the mantissa of log n, we have to just add them to get log n.

Thus to find log n, all we have to do is as follows:

1. Put n in the standard form, say

    n = m × 10^p, 1 ≤ m <10

2. Read off the characteristic p of log n from this expression (exponent of 10).
3. Look up log m from tables, which is being explained below.
4. Write log n = p + log m

If the characteristic p of a number n is say, 2 and the mantissa is .4133, then we have log n = 2 + .4133 which we can write as 2.4133. If, however, the characteristic p of a number m is say –2 and the mantissa is .4123, then we have log m = –2 + .4123. We cannot write this as –2.4123. (Why?) In order to avoid this confusion we write $\bar{2}$ for –2 and thus we write log m = $\bar{2}$.4123 .

Now let us explain how to use the table of logarithms to find mantissas. A table is appended at the end of this Appendix.

Observe that in the table, every row starts with a two digit number, 10, 11, 12,... 97, 98, 99. Every column is headed by a one-digit number, 0, 1, 2, ...9. On the right, we have the section called "Mean differences" which has 9 columns headed by 1, 2...9.

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..	..
61	7853	7860	7868	7875	7882	7889	7896	7803	7810	7817	1	1	2	3	4	4	5	6	6
62	7924	7931	7935	7945	7954	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	6	6

Now suppose we wish to find log (6.234). Then look into the row starting with 62. In this row; look

at the number in the column headed by 3. The number is 7945. This means that

log (6.230) = 0.7945*

But we want log (6.234). So our answer will be a little more than 0.7945. How much more? We look this up in the section on Mean differences. Since our fourth digit is 4, look under the column headed by 4 in the Mean difference section (in the row 62). We see the number 3 there. So add 3 to 7945. We get 7948. So we finally have

log (6.234) = 0.7948.

Take another example. To find log (8.127), we look in the row 81 under column 2, and we find 9096. We continue in the same row and see that the mean difference under 7 is 4. Adding this to 9096, and we get 9100. So, log (8.127) = 0.9100.

Finding N when log N is given

We have so far discussed the procedure for finding log n when a positive number n given. We now turn to its converse i.e., to find n when log n is given and give a method for this purpose. If log n = t, we sometimes say n = antilog t. Therefore our task is given t, find its antilog. For this, we use the ready-made antilog tables.

Suppose log n = 2.5372.

To find n, first take just the mantissa of log n. In this case it is .5372. (Make sure it is positive.) Now take up antilog of this number in the antilog table which is to be used exactly like the log table. In the antilog table, the entry under column 7 in the row .53 is 3443 and the mean difference for the last digit 2 in that row is 2, so the table gives 3445. Hence,

antilog (.5372) = 3.445

Now since log n = 2.5372, the characteristic of log n is 2. So the standard form of n is given by

$n = 3.445 \times 10^2$

or n = 344.5

Illustration 1:

If log x = 1.0712, find x.

Solution: We find that the number corresponding to 0712 is 1179. Since characteristic of log x is 1, we have

$x = 1.179 \times 10^1$

= 11.79

Illustration 2:

If log x = $\overline{2}.1352$, find x.

Solution: From antilog tables, we find that the number corresponding to 1352 is 1366. Since the characteristic is $\overline{2}$ i.e., –2, so

$x = 1.366 \times 10^{-2} = 0.01366$

Use of Logarithms in Numerical Calculations
Illustration 1:

Find 6.3 × 1.29

Solution: Let x = 6.3 × 1.29

Then log x = log (6.3 × 1.29) = log 6.3 + log 1.29

Now,

log 6.3 = 0.7993

log 1.29 = 0.1106

∴ log x = 0.9099,

Taking antilog

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* It should, however, be noted that the values given in the table are not exact. They are only approximate values, although we use the sign of equality which may give the impression that they are exact values. The same convention will be followed in respect of antilogarithm of a number.

x = 8.127

Illustration 2:

Find $\dfrac{(1.23)^{1.5}}{11.2 \times 23.5}$

Solution: Let x = $\dfrac{(1.23)^{\frac{3}{2}}}{11.2 \times 23.5}$

Then log x = log $\dfrac{(1.23)^{\frac{3}{2}}}{11.2 \times 23.5}$

$= \dfrac{3}{2}$ log 1.23 – log (11.2 × 23.5)

$= \dfrac{3}{2}$ log 1.23 – log 11.2 – 23.5

Now,

log 1.23 = 0.0899

$\dfrac{3}{2}$ log 1.23 = 0.13485

log 11.2 = 1.0492

log 23.5 = 1.3711

log x = 0.13485 – 1.0492 – 1.3711

$= \overline{3}.71455$

∴ x = 0.005183

Illustration 3:

Find $\sqrt{\dfrac{(71.24)^5 \times \sqrt{56}}{(2.3)^7 \times \sqrt{21}}}$

Solution: Let x = $\sqrt{\dfrac{(71.24)^5 \times \sqrt{56}}{(2.3)^7 \times \sqrt{21}}}$

Then log x = $\dfrac{1}{2}$ log $\left[\dfrac{(71.24)^5 \times \sqrt{56}}{(2.3)^7 \times \sqrt{21}} \right]$

$= \dfrac{1}{2}$ [log (71.24)^5 + log $\sqrt{56}$ – log (2.3)^7 – log $\sqrt{21}$]

$= \dfrac{5}{2}$ log 71.24 + $\dfrac{1}{4}$ log 56 – $\dfrac{7}{2}$ log 2.3 – $\dfrac{1}{4}$ log 21

Now, using log tables

log 71.24 = 1.8527

log 56 = 1.7482

log 2.3 = 0.3617

log 21 = 1.3222

∴ log x = $\dfrac{5}{2}$ log (1.8527) + $\dfrac{1}{4}$ (1.7482) – $\dfrac{7}{2}$ (0.3617) – $\dfrac{1}{4}$ (1.3222)

$= 3.4723$

∴ x = 2967

LOGARITHMS

TABLE I

N	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170						5	9	13	17	21	26	30	34	38
						0212	0253	0294	0334	0374	4	8	12	16	2O	24	28	32	36
11	0414	0453	0492	0531	0569						4	8	12	16	20	23	27	31	35
						0607	0645	0682	0719	0755	4	7	11	15	18	22	26	29	33
12	0792	0828	0864	0899	0934						3	7	11	14	18	21	25	28	32
						0969	1004	1038	1072	1106	3	7	10	14	17	20	24	27	31
13	1139	1173	1206	1239	1271						3	6	10	13	16	19	23	26	29
						1303	1335	1367	1399	1430	3	7	10	13	16	19	22	25	29
14	1461	1492	1523	1553	1584						3	6	9	12	15	19	22	25	28
						1614	1644	1673	1703	1732	3	6	9	12	14	17	20	23	26
15	1761	1790	1818	1847	1875						3	6	9	11	14	17	20	23	26
						1903	1931	1959	1987	2014	3	6	8	11	14	17	19	22	25
16	2041	2068	2095	2122	2148						3	6	8	11	14	16	19	22	24
						2175	2201	2227	2253	2279	3	5	8	10	13	16	18	21	23
17	2304	2330	2355	2380	2405						3	5	8	10	13	15	18	20	23
						2430	2455	2480	2504	2529	3	5	8	10	12	15	17	20	22
18	2553	2577	2601	2625	2648						2	5	7	9	12	14	17	19	21
						2672	2695	2718	2742	2765	2	4	7	9	11	14	16	18	21
19	2788	2810	2833	2856	2878						2	4	7	9	11	13	16	18	20
						2900	2923	2945	2967	2989	2	4	6	8	11	13	15	17	19
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6471	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8

LOGARITHMS

N	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9997	9996	0	1	1	2	2	3	3	3	4

ANTILOGARITHMS

TABLE II

N	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
.11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
.37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
.38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
.39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
.40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
.43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
.44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
.45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
.46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
.47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
.48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	3	4	5	6	6
.49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	3	4	5	6	6

ANTILOGARITHMS

TABLE II (*Continued*)

N	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
.50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
.51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
.52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
.53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
.54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
.55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
.56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
.57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
.58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
.59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
.60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
.61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
.62	4169	4178	4188	4198	4207	4217	4227	4236	4246	42S6	1	2	3	4	5	6	7	8	9
.63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
.64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
.65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
.66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
.67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
.68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
.69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
.70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
.71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
.72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
.73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
.74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
.75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
.76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
.77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
.78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
.79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
.80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
.81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
.82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
.83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
.84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
.85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
.86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
.87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
.88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
.89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
.90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
.91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
.92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
.93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
.94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
.95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
.96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
.97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
.98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
.99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20