كيمياء العناصر الانتقالية والمتراكبات

الفرقة الثالثة
كلية التربية عام شعبة الكيمياء
برنامج اللغة

ا.د/مصطفى ابوالوفا

الفصل الدراسى الثانى ٢٠٢٣

كيمياء المتراكبات

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COORDINATION COMPOUNDS

Contents

1. **INTRODUCTION**

You have already studied in your earlier classes that there are two types of compounds. The compounds that can easily dissociate into their constituent ions in aqueous medium are called simple salts and double salts such as NaCl, $MgCl_2$, $FeSO_4.(NH_4)_2SO_4.6H_2O$, $K_2SO_4.Al_2(SO_4)_3.24H_2O$, etc. On the other hand, the compounds which do not dissociate into their constituent ions in any solvent are known as coordination or complex compounds such as $[Cu(NH_3)_4]^{2+}$. Transition metals have an ability to form a number of coordination compounds due to their small size, high charge and presence of empty d orbitals on the metal ion. A compound formed from the union of metal ion (an electron deficient species, central metal atom/ion; Lewis acid) and electron rich species (ligand; Lewis base) which can donate one electron pair is called coordination compound or complex compound. The coordination compounds can

be represented by the general formula, $[MLn]^{\pm m}$, where M is a metal ion, L is electron rich species; n is the number of L attached to the metal atom/ion and m is the charge on complex ion.

Some metal complexes were prepared and used in the eighteenth century in the form of metal salts and vegetable extracts as paints.

In 1798, $CoCl_3.6NH_3$ was discovered. Werner gave a theory to understand the bonding in such compounds about a century later in 1893. We are studying chemistry of coordination compounds because they have many applications in analytical / environmental chemistry, metallurgy, biological systems, industries and medicine.

A salt is formed by the neutralization of an acid by a base. There are different types of salts. They are:-

a) Simple salt

b) Molecular (or) addition compounds

a) **Simple salt**

A simple salt is formed by the neutralization of an acid by a base. KOH + HCl → KCl + H2O

Normally, a simple salt ionizes in water and produces ions in solution. The solution of the simple salt exhibits the properties of its component ions.

b) **Molecular (or) addition compounds**

i**) Double salts**

These are molecular compounds which are formed by the evaporation of solution containing two (or) more salts in stoichiometric proportions. Hence the molecular compounds which dissociate in solution into its constituent ions are known as double salt. Double salts retain their properties only in solid state.

They are also called as lattice compounds.

Example

Mohr's salt

$K_2SO_4 . Al_2(SO_4)_3 . 24H_2O \rightarrow 2K^+ + 2Al^{3+} + 4SO_4^{2-} + 24H_2O$

The double salts give the test of all their constituent ions in solution.

ii) **Coordination (or complex) compounds**

Coordination compound is 'a compound formed from a Lewis acid and a Lewis base'. The molecular compounds, do not dissociate into its constituent ions in solution are called coordination compounds.

Example

$Fe(CN)_2 + 4KCN \rightarrow Fe(CN)_2 . 4KCN$ (or) $K_4[Fe(CN)_6]$

Ferrous cyanide

$Fe(CN)_2 . 4KCN \rightarrow 4K^+ + [Fe(CN)_6]^{4-}$

Complex anion

In $K_4[Fe (CN)_6]$ the individual components lose their identity.

The metal of the complex ion is not free in solution unlike metal in double salt in solution.

Nature of coordination (or) complex compounds

i) An anionic complex compound contains a complex anion and simple cation.

$K_4 [Fe(CN)_6] \rightarrow 4K^+ + [Fe (CN)_6]^{4-}$

simple cation complex anion

ii) A cationic complex contains complex cation and simple anion

$[Co(NH_3)_6] Cl_3 \rightarrow [Co(NH_3)_6]^{3+} + 3Cl^-$

Complex cation simple anion

iii) A neutral complex , In the case of a complex compound,

$[Cr (NH_3)_6] [Co(CN)_6]$, it gives both complex cation and complex anion

$[Cr(NH_3)_6] [Co(CN)_6] \rightarrow [Cr(NH_3)_6]^{3+} + [Co(CN)_6]^{3-}$

complex cation complex anion

TERMINOLOGY USED IN COORDINATION CHEMISTRY

(a) **Lewis Acid**

All electron acceptors are Lewis acids.

(b) **Lewis Base**

All electron donors are Lewis base.

(c) **Central metal ion**

In the complex ion an acceptor accepts a pair of electrons from the donor atoms. The acceptor is usually a metal / metal ion to which one (or) more of neutral molecules (or) anions are attached. The acceptor metal cation is referred to as central metal cation.

Hence, central metal cation in a complex serves as a lewis acid.

(d) **Ligand** (Latin word meaning to bind)

A ligand is an ion (or) a molecule capable of functioning as an electron donor. Therefore the neutral molecules or ions which are directly attached to the central metal ion are called as ligand (or) coordination groups. These coordination groups or ligands can donate a pair of electrons to the central metal ion (or) atom. Hence, in a complex compound ligands act as Lewis bases.

Examples:

$[Ni(NH_3)_6]^{2+}$: Ligand = NH_3 molecule and Central metal ion = Ni^{2+}

$[Co(NH_3)_5Cl]^{2+}$: Ligands = NH_3 molecule and Cl^- ion

(e) Coordination number

The total number of coordinate bonds through which the central metal ion is attached with ligand is known as coordination number. Coordination number may be two, three, four, five, six, seven, eight, nine or even higher in case of lanthanides and actinides . Coordination number depends on size, charge and electronic configuration and nature of meal/ion and ligands

For example

- large metal atoms show high CN
- bulky ligands reduce coordination number

-Lewis bases easily donate electrons to metals and metals with lesser number of electrons can easily accept electrons

Examples $K_4[Fe(CN)_6]$ the coordination number of Fe(II) is 6 and in $[Cu(NH_3)_4]SO_4$ the coordination number of Cu(II) is 4.

(f) Coordination sphere

the central metal ion and the ligands that are directly attached to it, are enclosed in a square bracket, called coordination sphere or first sphere of attraction

(g) Oxidation number or Oxidation state of central metal atom/ ion

It is the number that represent an electric charge with an atom or ion actually has or appears to have when combined with other atom

(h) Counter ions

The ions excluding the coordination sphere are called as counter ions. In $K_4[Fe(CN)_6]$ compound, K^+ is the counter ion.

Ligands and their types

The electron rich species, which may be charged species, e.g. Cl^-, CN^-, NO_2^-, etc or neutral species e.g. H_2O, NH_3, $NH_2CH_2CH_2NH_2$, CO, NO, etc., that can donate an electron pair to the metal atom/ion are called ligands.

Types of ligands

The ligands can be classified in the following ways:

Type I- Based on electron accepter/donor properties of the ligand

- σ (sigma) donor ligands are those ligands which can only donate electron pair to the meal ion, e.g. H_2O, NH_3, F^-. These ligands are also known as weak field ligands.
- σ (sigma) donor and Π (pi) accepter ligands are those ligands which can donate electron pair and also have a tendency to accept electron in their empty antibonding π molecular orbitals (MO). Such ligands can involve in

backbonding (π bond) with the metal ion. For example, CO, CN^-, NO, etc. These ligands are also known as strong field ligands.

- Π (pi) donor ligands are those ligands like benzene and ethylene, which do not have lone pair of electrons but only π electrons for donation to the metal atom/ion.

Type II- Based on the basis of number of donor atoms in the ligand

- Monodentate or unidentate ligands

The ligands that bound to a metal ion through a single donor atom are called as monodentate or unidentate ligands, e.g. Cl^-, H_2O or NH_3. These ligands can be further divided into the following subclasses on the basis of charge (Figure 1).

- Ambidentate ligands

Some ligands have two or more than two different donor atoms. These ligands can attach through any of the donor atoms. They are given different names depending upon nature of the donor atom linked to the metal atom. These ligands are known as ambidentate ligands e.g. NO_2 (donor atom may be either N or O), SCN^- (donor atom may be either S or N), CN^- (donor atom may be either C or N), $S_2O_3^{2-}$ (donor atom may be either S or N). These are also monodentate ligands.

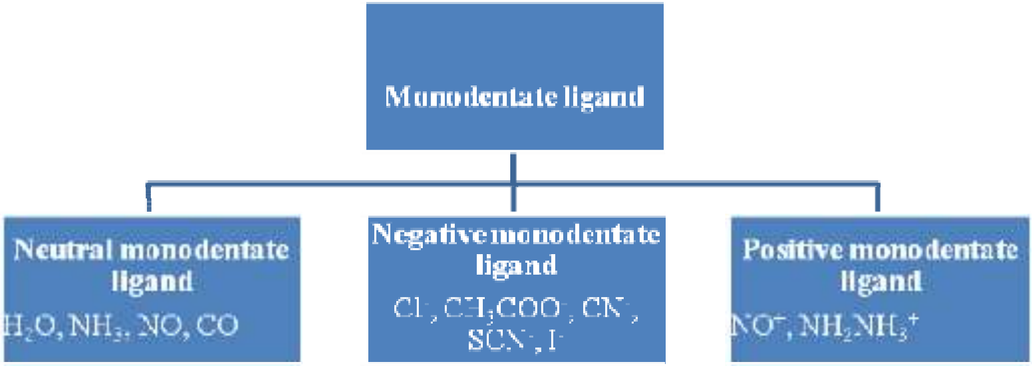


Figure1: Classification of monodentate ligands

2. WERNER’S COORDINATION THEORY AND ITS EXPERIMENTAL VERIFICATION

Alfred Werner in 1893 suggested a new theory for explaining the nature of bonding in coordination compounds known as Werner’s theory. According to this theory, there are two kinds of valences of metal atom/ion in coordination compounds: primary and secondary valences

Postulates of Werner’s theory

1) Every metal atom has two types of valencies

i) Primary valency or ionisable valency

ii) Secondary valency or non ionisable valency

2) The primary valency corresponds to the oxidation state of the metal ion. The primary valency of the metal ion is always satisfied by negative ions.

3) Secondary valency corresponds to the coordination number of the metal ion or atom. The secondary valencies may be satisfied by either negative ions or neutral molecules.

4) The molecules or ion that satisfy secondary valencies are called ligands.

5) The ligands which satisfy secondary valencies must project in definite directions in space. So the secondary valencies are directional in nature where as the primary valencies are non-directional in nature.

6) The ligands have unshared pair of electrons. These unshared pair of electrons are donated to central metal ion or atom in a compound. Such compounds are called coordination compounds.

Werner's theory can be explained on the basis of experimental evidences

- Molar conductivity measurement method

Compounds $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$, $[Co(NH_3)_4Cl_2]Cl$ and $[Co(NH_3)_3Cl_3]$ show decreasing order of conductivity due to the formation of 4 ions, 3 ions, 2 ions and no ions, respectively in solution.

$[Co(NH_3)_6]Cl_3 \longrightarrow [Co(NH_3)_6]^{3+} + 3Cl^-$ (1 complex ion + 3 chloride ions)

$[Co(NH_3)_5Cl]Cl_2 \longrightarrow [Co(NH_3)_5Cl]^{2+} + 2Cl^-$ (1complex ion +2chloride ions)

$[Co(NH_3)_4Cl_2]Cl \longrightarrow [Co(NH_3)_4Cl_2] + +Cl^-$ (1 complex ion+1chloride ion)

$[Co(NH_3)_3Cl_3] \longrightarrow [Co(NH_3)_3Cl_3]$ (No ions)

- <u>Precipitation method</u>

  When cobalt ammine chloride complexes react with $AgNO_3$, some of the Cl^- ions get precipitated with $AgNO_3$ to form AgCl. The number of Cl^- ions that are ionisable and present outside the coordination sphere can react with $AgNO_3$. Thus, coordination compounds $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$ and $[Co(NH_3)_4Cl_2]Cl$ react with 3, 2 and 1 mole of $AgNO_3$ to form 3, 2 and 1 mole of AgCl, respectively as there are 3, 2 and 1 ionisable Cl^- ions, respectively.

Defects of Werner's theory

- Although the theory describes the structure of many compounds, it can't explain the nature of bonding between metal atom/ion and ligands.
- Werner's theory was unable to explain why 4- and 6-coordination numbers are the preferred coordination numbers.

EFFECTIVE ATOMIC NUMBER CONCEPT (EAN CONCEPT)

- This rule is given by English Chemist Nevil V. Sidgwick. Effective atomic number (EAN) is the total number of electrons in metal atom/ion (atomic number) plus the electrons gained from ligands. This EAN is the atomic number of a noble gas. Therefore, EAN decides stability of coordination compound. If a coordination compound follow EAN rule, than it is stable one.
  - EAN= Atomic number of metal atom/ion + number of e- donated by ligands or 2 x number of ligands (as each ligand can donate two electrons to metal atom/ion).
  - **For $[Co(NH_3)_6]^{3+}$**
  - Atomic number of Co=27; Atomic number of Co^{3+}=24; there are six ligands hence electrons donated by 6 ligands = 6 x 2

- EAN = 24 + (6 x 2) = 36 (atomic number of Krypton; Kr)

- **For $[Ni(CO)_4]$**
- Atomic number of Ni=28; there are four ligands hence electrons donated by 4 ligands = 4 x 2
- EAN = 28 + (4 x 2) = 36 (atomic number of Krypton; Kr)

- **For $[Fe(CN)_6]^{4-}$**
- Atomic number of Fe=26; Atomic number of Fe^{2+}=24; there are six ligands hence electrons donated 6 ligands = 6 x 2
- EAN = 24 + (6 x 2) = 36 (atomic number of Krypton;

- **For $[Ag(NH_3)_4]^+$**
  - Atomic number of Ag=47; Atomic number of Ag^+=46; there are four ligands, hence electrons donated by 4 ligands = 4 x 2
  - EAN = 46 + (4 x 2) = 54 (atomic number of Xenon; Xe)

    = 54 (atomic number of Xenon; Xe)

- **For $[V(CO)_6]^-$**
  - Atomic number of V=23; Atomic number of V^- = 24; there are six ligands hence electrons donated 6 ligands = 6 x 2
  - EAN = 24 + (6 x 2)

    = 36 (atomic number of Krypton; Kr)

- **For $[Mn(CN)_4]^{2-}$**
  - Atomic number of Mn=25; Atomic number of Mn^{2+} = 23; there are four ligands hence electrons donated 4 ligands = 4 x 2

EAN = 23 + (4 x 2) = 31

Not obeying EAN rule as 31 is not the atomic number of any noble gas

NOMENCLATURE OF COORDINATION COMPOUNDS

Rules for writing formula of coordination compounds

Formula of the cation whether simple or complex must be written first followed by anion.

The coordination sphere the sequence of symbols is :

First metal name followed by anionic ligand then neutral ligand finally cationic ligand. Ligands of same type are arranged alphabetically

Polyatomic ligands are enclosed in parentheses

e.g In $Na[PtBrCl(NO^{+2})_2NH_3(NO)]$ sequence in coordination sphere is metal atom, alphabetical sequence of anionic ligand Br^-, Cl^-, NO^{2-}, followed by neutral ligand NH_3 and then cationic ligand NO^+

IUPAC nomenclature of coordination compounds

steps suggested by IUPAC (International Union of Pure and Applied Chemistry)

The rules are outlined below:

- In naming the entire complex, the name of the cation is given first and the anion second (just as for sodium chloride), no matter whether the cation or the anion is the complex species.
- Name of non-ionic or molecular complexes are written as one word without any gap.
- In the complex ion, the name of the ligand or ligands precedes that of the central metal atom (This procedure is reversed for writing formulae).
- Ligand names generally end with ‘O’ if the ligand is negative (‘chloro’ for Cl^-, ‘cyano’ for CN^-, ‘hydrido’ for H^-) and unmodified if the ligand is neutral (‘methylamine’ for $MeNH_2$). Special ligand names are ‘aqua’ for water, ‘ammine’ for ammonia, ‘carbonyl’ for CO,ni trosyl’ for NO.

- A Greek prefix (mono, di, tri, tetra, penta, hexa, etc.) indicates the number of each ligand (mono is usually omitted for a single ligand of a given type). If the name of the ligand itself contains the terms mono, di, tri, like triphenylphosphine, ligand name is enclosed in parentheses and its number is given with the alternate prefixes bis, tris, tetrakis instead.

For example, $[Ni(PPh_3)_2Cl_2]$ is named dichlorobis(triphenylphosphine)nickel(II).

- A Roman numeral or a zero in parentheses is used to indicate the oxidation state of the central metal atom.
- If the complex ion is negative, the name of the metal ends in ‘ate’ for example, ferrate, cuprate, nickelate, cobaltate etc.
- If more than one ligand is present in the species, then the ligands are named in alphabetical order regardless of the number of each.

For example, NH_3 (ammine) would be considered as ‘a’ ligand and come before Cl^-(chloro).

- Some additional notes

Some metals in anions have special names

B Borate ,Au Aurate, Ag Argentate, Fe Ferrate, Pb Plumbate, Sn Stannate, Cu Cuprate, Ni Nickelate

- Use of brackets or enclosing marks. Square brackets are used to enclose a complex ion or neutral coordination species.

Examples

$[Co(en)_3]Cl_3$ tris(ethylenediamine)cobalt(III) chloride

$[Co(NH_3)_3(NO_2)_3]$ triamminetrinitrocobalt (III)

$K_2[CoCl_4]$ potassium tetrachlorocobaltate(II)

note that it is not necessary to enclose the halogens in brackets.

Name of Negative ligands

Ligand	Name	Ligand	Name
H^-	Hydrido	HS^-	Mercapto
O^{2-}	Oxo	NH_2^-	Amido
O_2^{2-}	Peroxo	NH^{2-}	Imido
O_2H^-	Perhydroxo	NO_3^-	Nitrato
OH^-	Hydroxo	ONO^-	Nitrito
F^-	Fluoro	NO_2^-	Nitro
Cl^-	Chloro	N^{-3}	Nitride
Br^-	Bromo	P^{3-}	Phosphido
I^-	Iodo	N_3^-	Azido
CO_3^-	Carbonato	CNO^-	Cyanato
$C_2O_4^-$	Oxalate	NCO^-	Cyanato
$CH_3CO_2^-$	Acetate	SCN^-	Thiocyanato
SO_4^{2-}	Sulphato	HCO_3^-	Hydrogencarbonato
SO_3^{2-}	Sulphito	$S_4O_6^{2-}$	Tetrathionato
S^{2-}	Sulphido	HSO_3^-	Hydrogensulphito
$NH_2CH_2CO_2^-$	glycinato	$C_5H_5^-$	Cyclopentadienyl
$(OCCH_2)_2NCH_2CH_2CH_2$ $N\ (CH_2CO_2^-)_2$	Ethylenediammine tetraacetato (EDTA)	$S_2O_3^{2-}$	Thiosulpahato

Name of neutral ligands

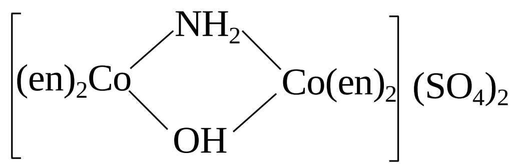
Ligand	Name	Ligand	Name
C_5H_5N (py)	pyridine	$NH_2(CH_2)_2NH_2$ (en)	ethlenediammine
NH_3	Ammine	CH_3NH_2	Methylamine
H_2O	Aqua/aquo	CO	Carbonyl
C_6H_6	Benzene	NO	Nitrosyl
N_2	Dinitrogen	CS	Thiocarbonyl
O_2	Dioxygen	NS	Thionitrosyl
Ph_3P	Triphenylphosphine	CH_3COCH_3	Acetone

Name of Positive ligands

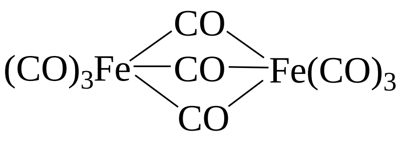
Ligand	Name
NO^+	Nitosonium
NO_2^+	Nitronium
$NH_2NH_3^+$	hydrazinium

These rules are illustrated by the following examples:

COMPOUNDS	SYSTEMATIC NAMES
$[Co(NH_3)_6]Cl_3$	Hexaamminecobalt(II) chloride
$[Co(NH_3)_5Cl]^{2+}$	Chloropentamminecobalt(III) ion
$[Co(NH_3)_4SO_4]NO_3$	Sulphatotetramminecobalt(III) nitrate
$[Co(NH_3)_3(NO_2)_3]$	Trinitrotriamminecobalt(III)
$[Co(NH_3)_3NO_2.Cl.CN]$	Chlorocyanonitrotriamminecobalt(III)
$[Cr(en)_3]Cl_3$	Tris(ethylenediamine)chromium(III) chloride
$K_4[Fe(CN)_6]$	Potassium hexacyanoferrate(II)
$[Pt(py)_4][PtCl_4]$	Tetrapyridineplatinum(II)tetrachloroplatinate(II)
$[(NH_3)_5Co.NH.Co(NH_3)_5](NO_3)_5$	Decammine-μ-amidodicobalt(III) nitrate



Tetrakis(ethylenediamine)-μ-amido-μ-hydroxo-dicobalt(III) sulphate

	Tri-μ-carbonylbis(tricarbonyliron(III)) OR Hexacarbonyltri-m-carbonyl-diiron(III)
$AlCl_3.(EtOH)_4$	Aluminum(III)chloride-4-ethanol.

Name the following complexes:

(a) $[Cu(NH_3)_4]SO_4$; (b) $K_2[CoCl_4]$;

(c) $Co(phen)_2Cl_2$; (d) $[Co(en)_2(H_2O)Cl]Cl_2$

ISOMERISM OF COORDINATION COMPOUNDS

INTRODUCTION

The objectives of this unit are to familiarize you with the isomerism in coordination compounds and its types. The coordination compounds which have the same chemical formula but different ways of attachment of ligands are called as isomers. These isomers have different physical and chemical properties. The phenomenon that gives rise to the isomers is known as isomerism. There are two main types of isomerism in coordination compounds; structural and stereo- isomerism. Our focus will be on both structural isomerism and stereoisomerism. Structural isomerism is due to the different bond arrangement of atoms in coordination compound around the central metal atom/ ion while stereoisomerism arises due to different three-dimensional arrangement of atoms in space.

Isomerism in coordination compounds

The coordination compounds having the same molecular formula but different arrangement of atoms/ groups around the central metal/ ion are called isomers and the phenomenon which gives rise to isomers is called as isomerism. The isomers have different physical and chemical properties.

Coordination compounds exhibit two major types of isomerism, namely

(A) structural isomerism and (B) stereoisomerism (space isomerism). Each of these is further classified as shown below.

A) Structural isomerism

i) Coordination isomerism ii) Ionization isomerism

iii) Hydrate or Solvate isomerism iv) Linkage isomerism

B) Stereoisomerism

i) Geometrical isomerism ii) Optical isomerism

A) Structural isomerism

Structural isomerism is also known as constitutional isomerism. The molecules have same number of atoms which differ in their structure or bonding. The different chemical formulae of structural isomers are either due to difference in ligands that are bonded to the central atoms or the mode of bonding of individual ligand (which atom of the ligand is bonded to the central atom). Now we will discuss the various types of structural isomerism one by one in brief.

i) Coordination isomerism

In a bimetallic complex, both complex cation and complex anion may be present. In such a case the distribution of ligands between the two coordination spheres can vary, giving rise to isomers called the coordination isomers. This phenomenon is called coordination isomerism. This isomerism is illustrated by the following pairs of complexes where the complex cation and anion contain different metal centers.

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

$[Pt^{II}(NH_3)_4]\ [CuCl_4]$ and $[Cu(NH_3)_4]\ [PtCl_4]$

$[Zn(NH_3)_4][CuCl_4]$ and $[Cu(NH_3)_4][ZnCl_4]$.

In a bimetallic complex, both complex cation and complex anion may be present. In such a case the distribution of ligands between the two coordination spheres can vary, giving rise to isomers called the coordination isomers. This phenomenon is called coordination isomerism. This isomerism is illustrated by the following pairs of complexes where the complex cation and anion contain different metal centers.

The coordination compounds in which both the cationic and anionic species are complex ions, show coordination isomerism. This isomerism occurs by the interchange of ligands in between the cationic part and the anionic part. In another words, you can define the coordination isomers as the isomers in which the complex anion and complex cation of a coordination compound exchange one or more ligands

ii) **Ionization Isomerism**

This is the phenomenon by which ligands present inside the coordination sphere and anion or neutral molecule present outside the coordination sphere can exchange their place. The central metal / ion and the other ligands except one that is exchangeable are similar in both the isomers. Thus, ionization isomerism is the exchange of ions between coordination sphere and ionization sphere. The physical and chemical properties of the two isomers are entirely different as they give different ions on dissolving in suitable solvent. Two octahedral ionization isomers will have five identical ligands while the sixth ligand will be different. In case of tetra coordinated isomers, three ligands will be identical and the fourth one will be the different one. The different ligand in one isomer may be outside of the coordination sphere in the other isomer. The oxidation state of the central ion would not be changed in the two isomers

Coordination compounds having the same molecular formula but forming different ions in solution are called ionization isomers. This property is known as ionization isomerism.

An example of this type of isomerism is furnished by the red-violet, $[Co(NH_3)_5Br]SO_4$ $[Co(NH_3)_5SO_4]Br$

The red-violet isomer yields sulphate ion and the red isomer furnishes bromide ion in solution.

$[Co(NH_3)_4Cl_2]NO_2$ and $[Co(NH_3)_4NO_2Cl]Cl$

$[Co(NH_3)_5NO_3]SO_4$ and $[Co(NH_3)_5SO_4]NO_3$

iii) Hydrate isomerism

In hydrate isomerism, there is exchange between water molecule inside the coordination sphere and ions present in the ionization sphere. Composition of hydrate isomers is the same but the number of water molecules inside the coordination sphere is different . For example, $CrCl_3.6H_2O$ has the following three hydrate isomers:

A. $[Cr(H_2O)_6]Cl_3$ (violet)
B. $[Cr(H_2O)_5Cl]Cl_2.H_2O$ (blue green)
C. $[Cr(H_2O)_4Cl_2]Cl.2H_2O$ (green)

These isomers have very different chemical properties and on reaction with $AgNO_3$ to test for Cl^- ions, would find 3,2, and 1 Cl^- ions in solution respectively.

iv) Linkage Isomerism

Complexes having ambidentate ligands like SCN^- / NCS^-, CN^-/NC^- and NO_2^-/ ONO^- (capable of coordinating in more than one way) show linkage isomerism. The two isomers differ from each other by the linkage atom attachment to the central atom/ ion. The ligand can have more than two donor atoms but should be joined to the central atom/ ion via only one atom (unidentate ligand). The formula of the compound is same but their properties are entirely different. The name of the ligands is also changed according to their donor atom. When donor atom is N, NO_2^- is called as nitro, while it is called nitrito if the donor atom is O atom.

For example

$[Co(NH_3)_5ONO]Cl_2$ the nitrito isomer -

red colour - O attached

$[Co(NH_3)_5NO_2]Cl_2$ the nitro isomer -

yellow colour - N attached

B) Stereoisomerism (space isomerism)

Consider two compounds containing the same ligands attached to the same central metal ion, but the arrangement of ligands in space about the central metal ion are different, then these two compounds are said to be stereoisomers and this phenomenon is known as stereoisomerism.

Compounds which have the same atoms/groups, same position of atoms/groups and same sets of bonds, but differ in their spatial arrangement around the central atom/ ion are called as stereoisomers and the phenomenon is known as stereoisomers

There are two different types of stereoisomerism.

i) Geometrical isomerism or ii) Optical isomerism.

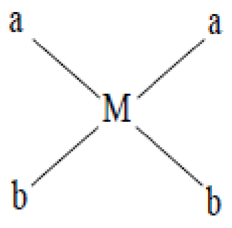
i) Geometrical isomerism (or) cis-trans isomerism

The compounds with differences in geometrical arrangement of the ligands around the central atom/ ion are known as geometrical isomers and the phenomenon as geometrical isomerism. This is also called as cis-trans isomerism. The geometrical isomers have the same empirical formula but different physical and chemical properties due to different arrangement of the ligands in space. The geometrical isomers can be easily separated from each other. When similar atoms/ groups (ligands) are adjacent to each other, the isomer is called cis-isomer (Latin, cis= same). In trans-isomer, the similar ligands are present diagonally opposite to each other (Latin, trans = across). It is common in di-substituted square planar and octahedral complexes with co-ordination number of 4 and 6, respectively. Tetrahedral (coordination number 4) complexes do not show geometrical isomerism because in this geometry, all the ligands are present in cis- position (adjacent) with respect to each other (all bond angles are same).

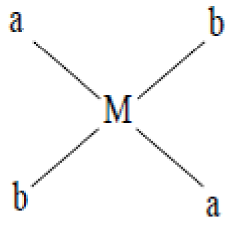
Geometrical isomerism is due to ligands occupying different position around the central ion. The ligands occupy position either adjacent to one another or opposite to one another. These are referred to as cis-form respectively. This type of isomerism is, therefore, also referred to as cis-trans isomerism. Geometric isomers are possible for both square planar and octahedral complexes, but not tetrahedral

Geometrial isomerism in 4-coordinate complex

(1) **[Ma2b2] type complexes Square planar**



cis-isomer



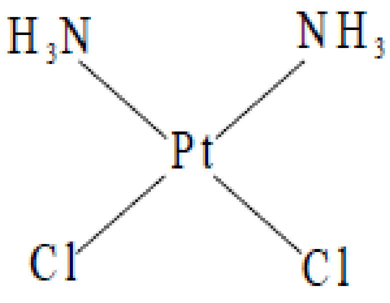
trans-isomer

In a cis-isomer two identical (or) similar groups are adjacent to each other whereas in a trans-isomer they are diametrically opposite to each other.

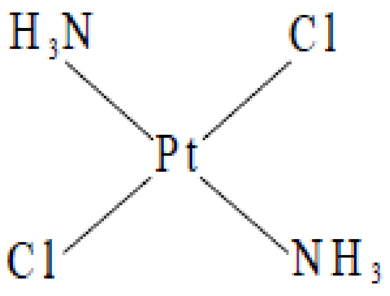
Square planar complexes of the type [Ma2b2]n+ where a and b are monodentate ligands, exist as cis and trans-isomers as shown

Example of this type of complexes are

$[Pt (NH_3)_2Cl_2]$ and $[Pd(NH_3)_2(NO_2)_2]$



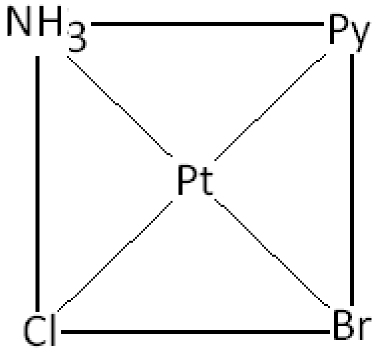
cis-isomer

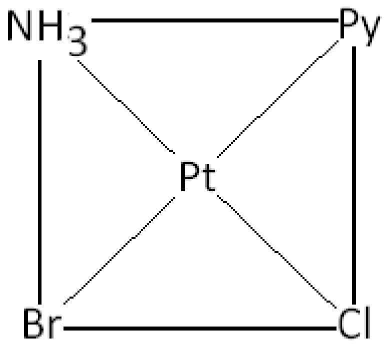


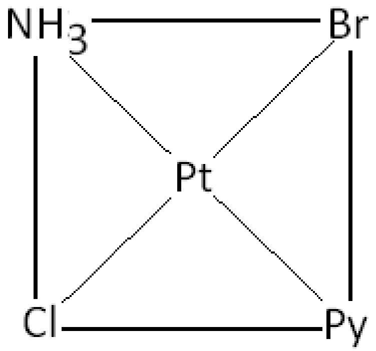
trans-isomer

(2) [Mabcd] type complexs

Square planar complex of this type exist in three isomeric forms for example [Pt(NH_3)(Py)(Cl)(Br)] exist in the following structures

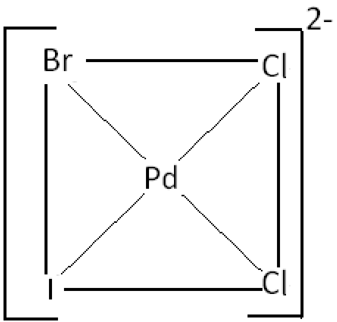




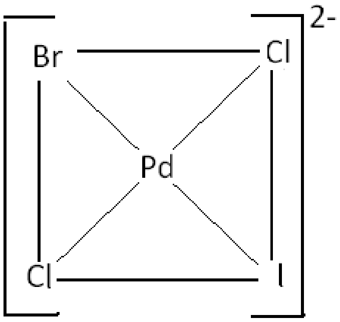


(3) [Ma2bc] type complexes

Square planar complexes of this type also shows cis-trans isomerism. For example [Pd $(Cl)_2BrI]^{2-}$ exists in the following cis-trans



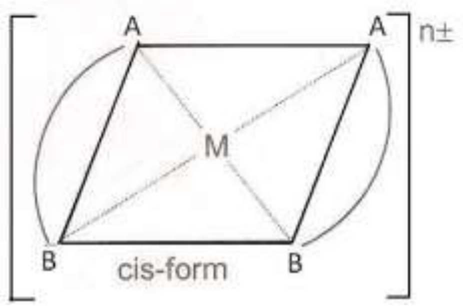
cis-isomer

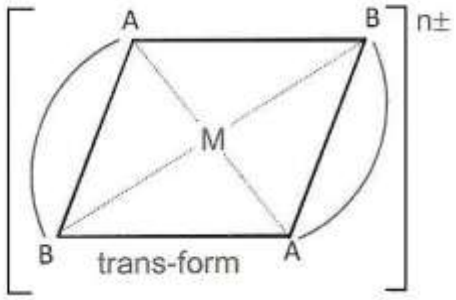


trans-isomer

(4) [M(AB)2]n± type complex

Here m is the central metal ion and (AB) represents an unsymmetrical bidentate ligand(A) and (B) arethe two ends (i.e. coordinating atoms) of the bidentates ligands such type of complexes also show trans and cis isomerism

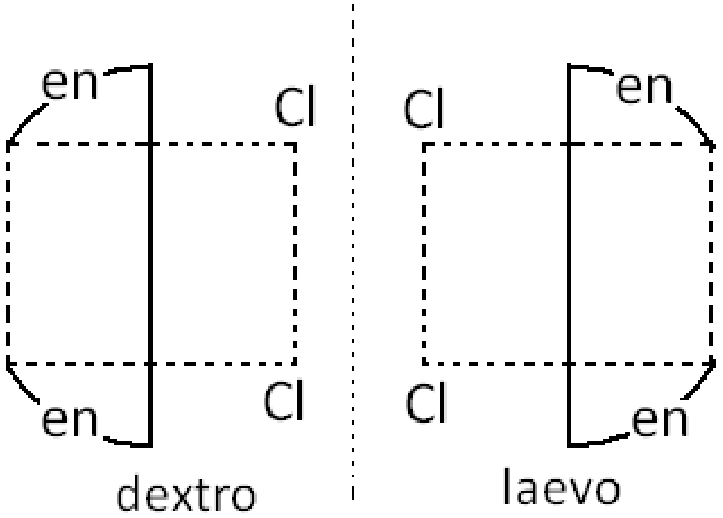




a) Optical Isomerism

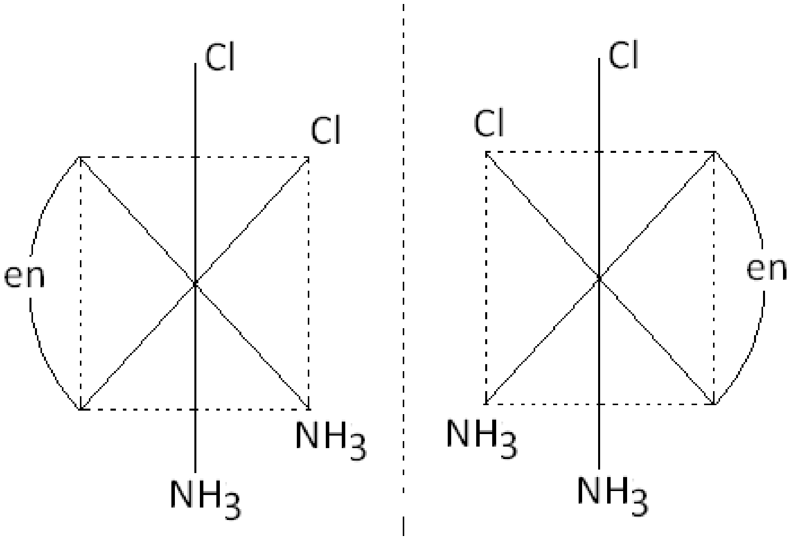
This is a phenomenon in which certain organic or inorganic compounds have the property of rotating plane polarized light. The compounds which exhibit this property are called optical isomers. The optical isomers of a compound have identical physical and chemical properties. The only distinguishing property is that the isomers rotate the plane of polarized light either to the left or right. If the rotation is on the left side, then that isomer is levo and if on right side, then isomer is dextro. The equal proportion of levo and dextro mixture is called racemic mixture

It is generally found octahedral chelate ions. The two isomers of this type of complex are mirror image of each other and cannot super impose on each other, hence they possess chirality character.



coordination compound of type $[PtCl_2(en)_2]^{2+}$ two geometrical isomers are possible. They are cis and trans. Among these two isomers, cis isomer shows optical activity because the whole molecule is asymmetric.

The optical isomers of $[CoCl_2(en)(NH_3)_2]^+$ are as follows



Importance and applications of Coordination Compounds

Coordination 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

- 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 B12, 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 un decomposed 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.

List of References:

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E.S. Gilreath

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S. F. A. Kettle

3- Advanced Inorganic Chemistry: A Comprehensive Text

Cotton and Wilkinson

كيمياء العناصر الانتقالية

الفرقة الثالثة
كلية التربية عام شعبة الكيمياء

ا.د/مصطفى ابوالوفا

الفصل الدراسى الثانى ٢٠٢٣

Inorganic Chemistry

WHAT IS INORGANIC CHEMISTRY?

If organic chemistry is defined as the chemistry of hydrocarbon compounds and their derivatives, inorganic chemistry can be described broadly as the chemistry of "every-thing else." This includes all the remaining elements in the periodic table, as well as carbon, which plays a major role in many inorganic compounds. Organometallic chemistry, a very large and rapidly growing field, bridges both areas by considering compounds containing direct metal-carbon bonds, and includes catalysis of many organic reactions. Bioinorganic chemistry bridges biochemistry and inorganic chemistry, and environmental chemistry includes the study of both inorganic and organic compounds. As can be imagined, the inorganic realm is extremely broad, providing essentially limitless areas for investigation.

A generally-accepted definition of Inorganic Chemistry is the study of non-carbon molecules, or all the elements on the periodic table except carbon. But, this definition is not completely correct because the field of Inorganic Chemistry also includes organometallic compounds and the study of some carbon-based molecules that have properties that are familiar to metals (like conduction of electricity).

This makes the field of inorganic chemistry very broad, and practically limitless.

Inorganic chemistry deals with synthesis and behavior of inorganic and organometallic compounds. This field covers chemical compounds that are not carbon-based, which are the subjects of organic chemistry. The distinction between the two disciplines is far from absolute, as there is much overlap in the sub discipline of organometallic chemistry. It has applications in every aspect of the chemical industry, including catalysis, materials science, pigments, surfactants, coatings, medications, fuels, and agriculture.

Many inorganic compounds are ionic compounds, consisting of cations and anions joined by ionic bonding. Examples of salts (which are ionic compounds) are magnesium chloride $MgCl_2$, which consists of magnesium cations Mg^{2+} and chloride anions Cl^{-}; or sodium oxide Na_2O, which consists of sodium cations Na^{+} and oxide anions O^{2-}. In any salt, the proportions of the ions are such that the electric charges cancel out, so that the bulk compound is electrically neutral. The ions are described by their oxidation state and their ease of formation can be inferred from the ionization potential (for cations) or from the electron affinity (anions) of the parent elements.

Important classes of inorganic compounds are the oxides, the carbonates, the sulfates, and the halides. Many inorganic compounds are characterized by high melting points. Inorganic salts typically are poor conductors in the solid state. Other important features include their high melting point and ease of crystallization. Where some salts (e.g., NaCl) are very soluble in water, others (e.g., FeS) are not.

The simplest inorganic reaction is double displacement when in mixing of two salts the ions are swapped without a change in oxidation state. In redox reactions one reactant, the oxidant, lowers its oxidation state and another reactant, the reductant, has its oxidation state increased. The net result is an exchange of electrons. Electron exchange can occur indirectly as well, e.g., in batteries, a key concept in electrochemistry.

When one reactant contains hydrogen atoms, a reaction can take place by exchanging protons in acid-base chemistry. In a more general definition, any chemical species capable of binding to electron pairs is called a Lewis acid; conversely any molecule that tends to donate an electron pair is referred to as a Lewis base. As a refinement of acid-base interactions, the HSAB theory takes into account polarizability and size of ions.

Industrial inorganic chemistry

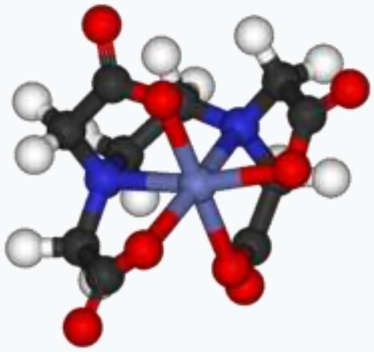
Inorganic chemistry is a highly practical area of science. Traditionally, the scale of a nation's economy could be evaluated by their productivity of sulfuric acid. The manufacturing of fertilizers, which often begins with the Haber-Bosch process, is another practical application of industrial inorganic chemistry.

Coordination compounds

Classical coordination compounds feature metals bound to "lone pairs" of electrons residing on the main group atoms of ligands such as H_2O, NH_3, Cl^-, and CN^-. In modern coordination compounds almost all organic and inorganic compounds can be used as ligands. The "metal" usually is a metal from the groups 3-13, as well as the trans-lanthanides and trans-actinides, but from a certain perspective, all chemical compounds can be described as coordination complexes.

The stereochemistry of coordination complexes can be quite rich, as hinted at by Werner's separation of two enantiomers of $[Co((OH)_2Co(NH_3)_4)_3]^{6+}$, an early demonstration that chirality is not inherent to organic compounds. A topical theme within this specialization is supramolecular coordination chemistry.

Examples: $[Co(EDTA)]^-$, $[Co(NH_3)_6]^{3+}$, $TiCl_4(THF)_2$.



EDTA chelates an octahedrally coordinated Co^{3+} ion in $[Co(EDTA)]^-$

Transition metal compounds

Compounds containing metals from group 4 to 11 are considered transition metal compounds. Compounds with a metal from group 3 or 12 are sometimes also incorporated into this group, but also often classified as main group compounds.

Transition metal compounds show a rich coordination chemistry, varying from tetrahedral for titanium (e.g., $TiCl_4$) to square planar for some nickel complexes to octahedral for coordination complexes of cobalt. A range of transition metals can be found in biologically important compounds, such as iron in hemoglobin.

- Examples: iron pentacarbonyl, titanium tetrachloride, cisplatin

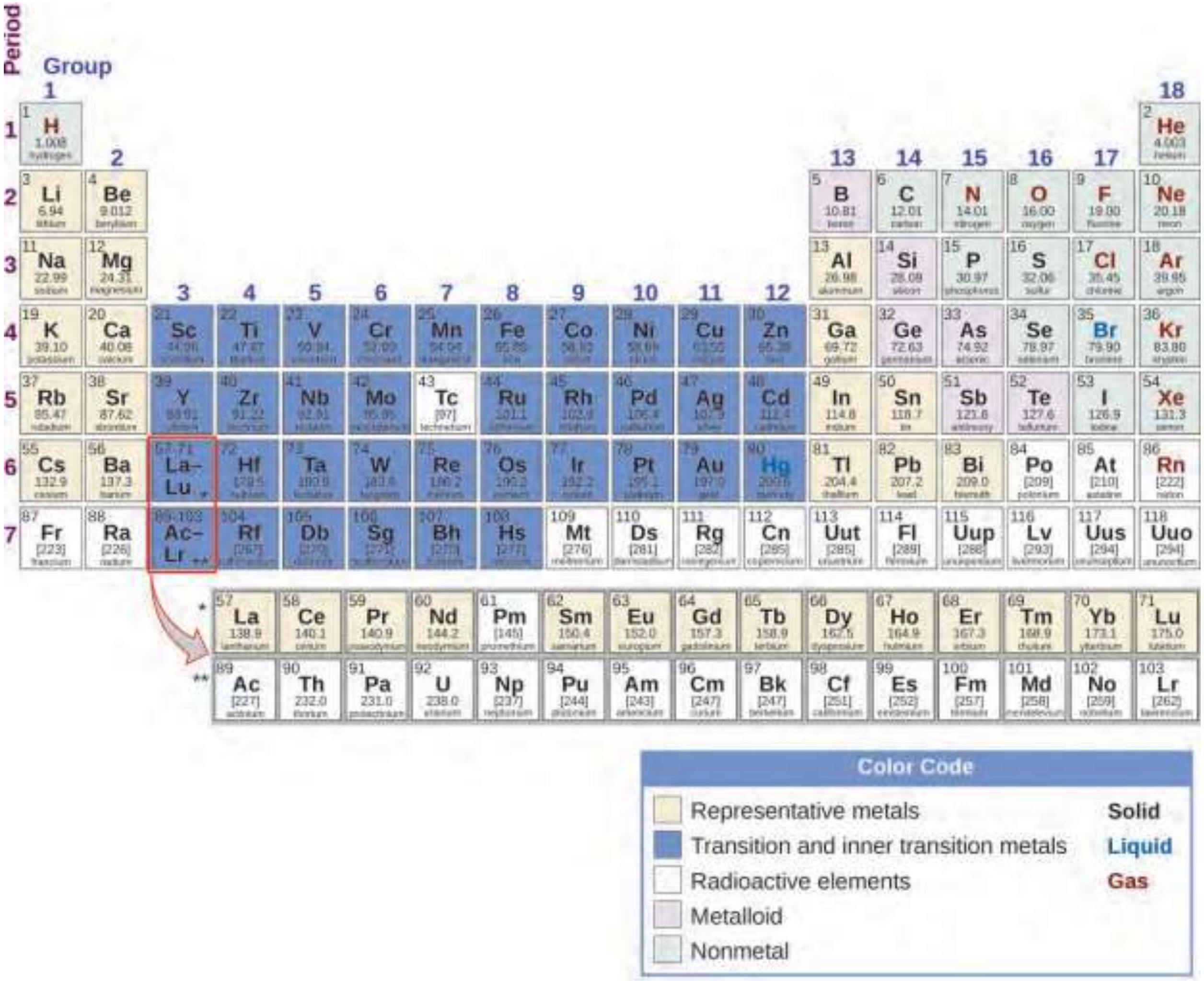
Periodicity

We begin this section by examining the behaviors of representative metals in relation to their positions in the periodic table. The primary focus of this section will be the application of periodicity to the representative metals.

It is possible to divide elements into groups according to their electron configurations. The representative elements are elements where the s and p orbitals are filling. The transition elements are elements where the d orbitals (groups 3–11 on the periodic table) are filling, and the inner transition metals are the elements where the f orbitals are filling. The d orbitals fill with the elements in group 11; therefore, the elements in group 12 qualify as representative elements because the last electron enters an s orbital. Metals among the representative elements are the representative metals. Metallic character results from an element’s ability to lose its outer valence electrons and results in high thermal and electrical conductivity, among other physical and chemical properties. There are 20 nonradioactive representative metals in groups 1, 2, 3, 12, 13, 14, and 15 of the periodic table (in Figure 1). The radioactive elements copernicium, flerovium, polonium, and livermorium are also metals but are beyond the scope of this chapter.

In addition to the representative metals, some of the representative elements are metalloids. A metalloid is an element that has properties that are between those of metals and nonmetals; these elements are typically semiconductors.

The remaining representative elements are nonmetals. Unlike metals, which typically form cations and ionic compounds (containing ionic bonds), nonmetals tend to form anions or molecular compounds. In general, the combination of a metal and a nonmetal produces a salt. A salt is an ionic compound consisting of cations and anions.



The alkali metals lithium, sodium, potassium, rubidium, cesium, and francium constitute group 1 of the periodic table. Although hydrogen is in group 1 (and also in group 17), it is a nonmetal and deserves separate consideration later in this chapter. The name alkali metal is in reference to the fact that these metals and their oxides react with water to form very basic (alkaline) solutions.

Group 2: The Alkaline Earth Metals

The alkaline earth metals (beryllium, magnesium, calcium, strontium, barium, and radium) constitute group 2 of the periodic table. The name alkaline metal comes from the fact that the oxides of the heavier members of the group react with water to form alkaline solutions. The nuclear charge increases when going from group 1 to group 2. Because of this charge increase, the atoms of the alkaline earth metals are smaller and have higher first ionization energies than the alkali metals within the same period. The higher ionization energy makes the alkaline earth metals less reactive than the alkali metals; however, they are still very reactive elements. Their reactivity increases, as expected, with increasing size and decreasing ionization energy. In chemical reactions, these metals readily lose both valence electrons to form compounds in which they exhibit an oxidation state of 2+. Due to their high reactivity, it is common to produce the alkaline earth metals, like the alkali metals, by electrolysis. Even though the ionization energies are low, the two metals with the highest ionization energies (beryllium and magnesium) do form compounds that exhibit some covalent characters. Like the alkali metals, the heavier alkaline earth metals impart color to a flame. As in the case of the alkali metals, this is part of the emission spectrum of these elements.

Calcium and strontium produce shades of red, whereas barium produces a green color.

Transition Metals

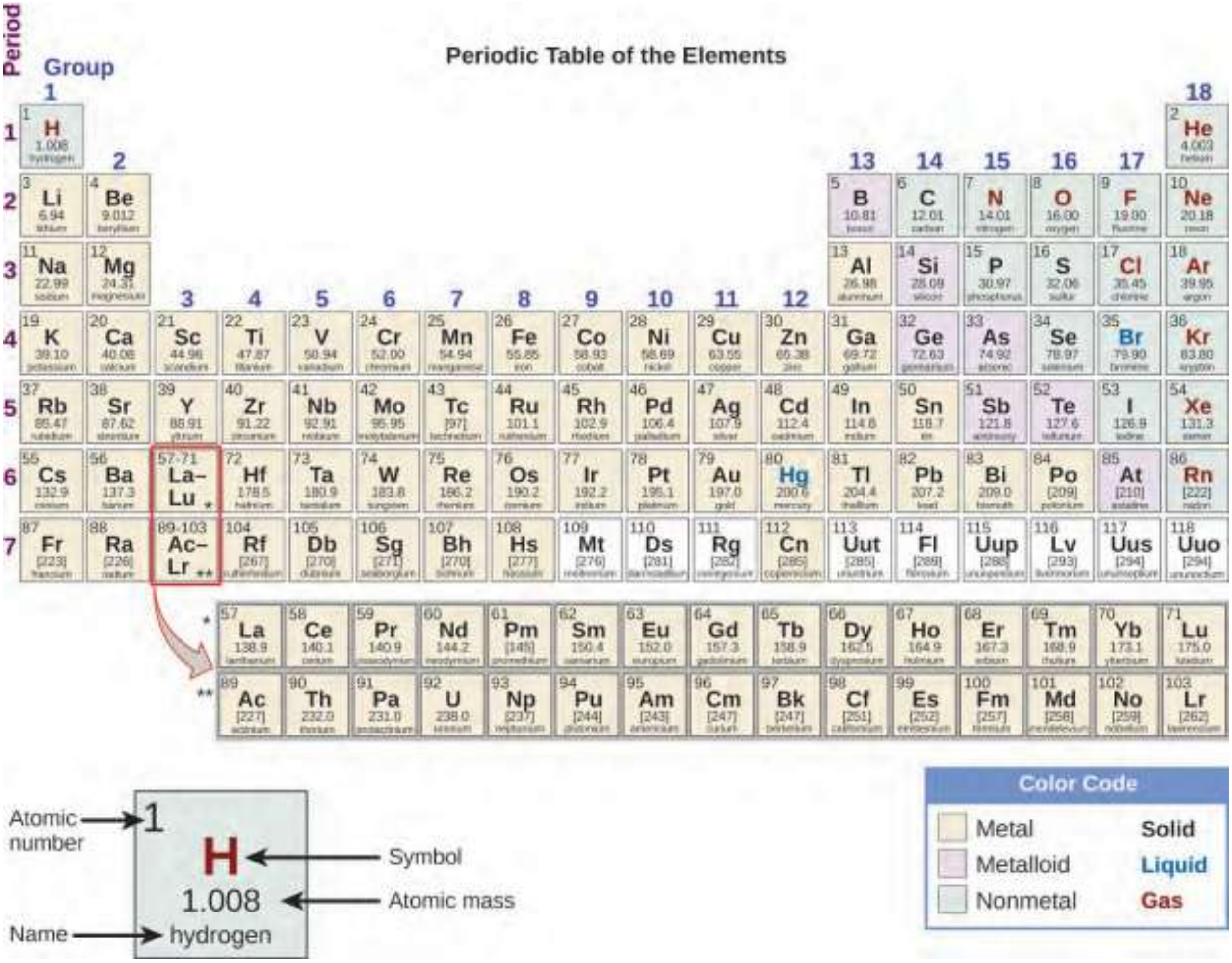
Introduction

We have daily contact with many transition metals. Iron occurs everywhere—from the rings in your spiral notebook and the cutlery in your kitchen to automobiles, ships, buildings, and in the hemoglobin in your blood. Titanium is useful in the manufacture of lightweight, durable products such as bicycle frames, artificial hips, and jewelry. Chromium is useful as a protective plating on plumbing fixtures and automotive detailing.

In addition to being used in their pure elemental forms, many compounds containing transition metals have numerous other applications. Silver nitrate is used to create mirrors, zirconium silicate provides friction in automotive brakes, and many important cancer-fighting agents, like the drug cisplatin and related species, are platinum compounds.

The variety of properties exhibited by transition metals is due to their complex valence shells. Unlike most main group metals where one oxidation state is normally observed, the valence shell structure of transition metals means that they usually occur in several different stable oxidation states. In addition, electron transitions in these elements can correspond with absorption of photons in the visible electromagnetic spectrum, leading to colored compounds. Because of these behaviors, transition metals exhibit a rich and fascinating chemistry.

Transition metals are defined as those elements that have (or readily form) partially filled d orbitals. As shown in Figure 2, the d-block elements in groups 3–11 are transition elements. The f-block elements, also called inner transition metals (the lanthanides and actinides), also meet this criterion because the d orbital is partially occupied before the f orbitals. The d orbitals fill with the copper family (group 11); for this reason, the next family (group 12) are technically not transition elements. However, the group 12 elements do display some of the same chemical properties and are commonly included in discussions of transition metals. Some chemists do treat the group 12 elements as transition metals.



Periodic Table of the Elements

Period	Group 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H 1.008																	2 He 4.003
2	3 Li 6.94	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.63	33 As 74.92	34 Se 78.97	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc [97]	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	57-71 La–Lu *	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po [209]	85 At [210]	86 Rn [222]
7	87 Fr [223]	88 Ra [226]	89-103 Ac–Lr **	104 Rf [267]	105 Db [270]	106 Sg [271]	107 Bh [270]	108 Hs [277]	109 Mt [276]	110 Ds [281]	111 Rg [282]	112 Cn [285]	113 Uut [285]	114 Fl [289]	115 Uup [288]	116 Lv [293]	117 Uus [294]	118 Uuo [294]

*	57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm [145]	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.1	71 Lu 175.0
**	89 Ac [227]	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np [237]	94 Pu [244]	95 Am [243]	96 Cm [247]	97 Bk [247]	98 Cf [251]	99 Es [252]	100 Fm [257]	101 Md [258]	102 No [259]	103 Lr [262]

Figure 2: The transition metals are located in groups 3–11 of the periodic table. The inner transition metals are in the two rows below the body of the table.

The **f-block elements** are the elements Ce through Lu, which constitute the lanthanide series (or lanthanoid series), and the elements Th through Lr, which constitute the actinide series (or actinoid series). Because lanthanum behaves very much like the lanthanide elements, it is considered a lanthanide element, even though its electron configuration makes it the first member of the third transition series. Similarly, the behavior of actinium means it is part of the actinide series, although its electron configuration makes it the first member of the fourth transition series.

The **d-block elements** have been defined as “the elements whose atoms receive the last electron in the d-subshell belonging to the penultimate or (n-1)th shell”. The d-block elements are also called the transition elements or metals. This is because they exhibit gradual transitional behaviour between highly reactive s-block (electropositive) and p-block (electronegative) elements, i.e. their properties have been found to be intermediate between those of the s-block and p-block elements. Thus these elements are located in the middle of the periodic table and are the members of the Groups 3 to 12 (IIIB to VIII to II B) in the modern periodic table.

According to IUPAC definiton, “a transition element is an element which has an incomplete d-subshell in either neutral atom or in ions in chemically significant (or common) oxidation state”. According to this definition zinc (Zn), cadmium (Cd) and mercury (Hg) are excluded from the list of transition elements as they neither have partly filled d-subshell in their atoms or ions nor they show the usual properties of transition elements to an appreciable extent. Still in order to rationalize the classification of elements, they are studied along with other d-block elements.

Now according to IUPAC, transition metals are defined as metals which have incomplete d subshell either in neutral atom or in their ions. Zinc, cadmium and mercury of group 12 have full d10 configuration in their ground state as well as in their common oxidation states and hence, are not regarded as transition metals.

However, being the end members of the 3d, 4d and 5d transition series, respectively, their chemistry is studied along with the chemistry of the transition metals.

The presence of partly filled d or f orbitals in their atoms makes transition elements different from that of the non-transition elements. Hence, transition elements and their compounds are studied separately. However, the usual theory of valence as applicable to the non- transition elements can be applied successfully to the transition elements also.

Various precious metals such as silver, gold and platinum and industrially important metals like iron, copper and titanium belong to the transition metals series.

We shall first deal with the electronic configuration, occurrence and general characteristics of transition elements with special emphasis on the trends in the properties of the first row (3d) transition metals along with the preparation and properties of some important compounds. This will be followed by consideration of certain general aspects such as electronic configurations, oxidation states and chemical reactivity of the inner transition metals.

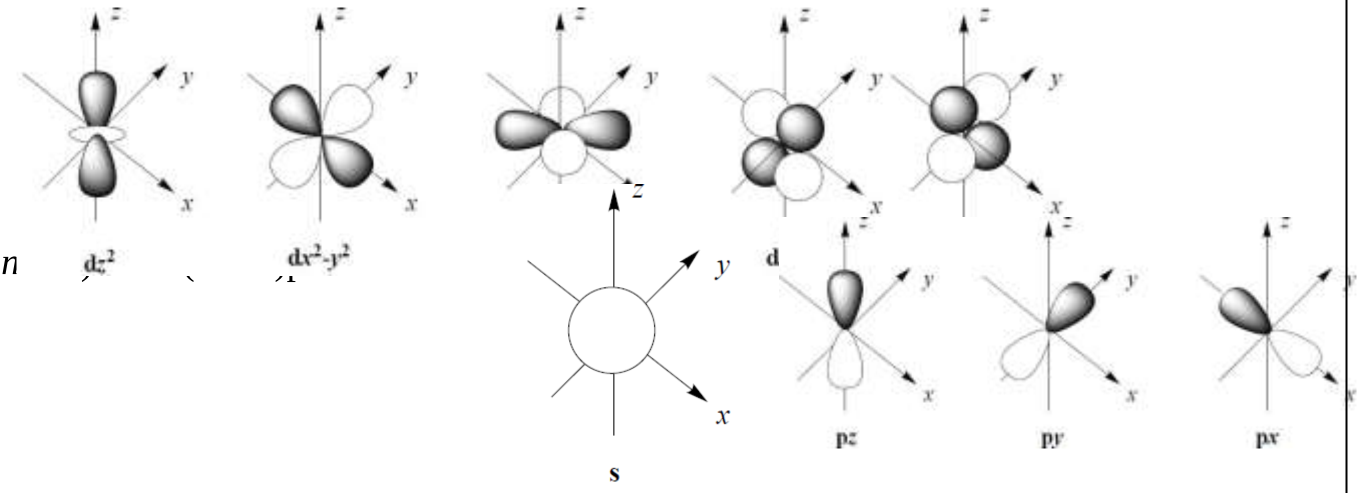
The d-block elements are divided into the **first transition series** (the elements Sc through Cu), **the second transition series** (the elements Y through Ag), and the **third transition series** (the element La and the elements Hf through Au). Actinium, Ac, is the first member of the **fourth transition series**, which also includes Rf through Rg.

There are four series of elements which constitute the d-block elements. Each series comprises ten elements as given below:

1. **Elements of the First Transition series or 3d-Transition series**: The elements from scandium (Sc, Z = 21) to Zinc (Zn, Z = 30) form the 3d-series.
2. **Elements of the Second Transition series or 4d-Transition series**: This series consists of the elements from yttrium (Y, Z = 39) to cadmium (Cd, Z = 48).
3. **Elements of the Third Transition series or 5d-Transition series**: The elements lanthanum (La, Z= 57) and hafnium (Hf, Z= 72) to mercury (Hg, Z = 80) constitute the 5d-Transition series.
4. **Elements of the Fourth Transition series or 6d-Transition series**: The elements actinium (Ac, Z = 89) and rutherfordium (Rf, Z = 104) to copernicum (Cn, Z = 112) are the members of this series. All these elements are radioactive and do not occur in nature. These have been artificially made in the laboratory.

Transition Metal Valence Orbitals

- *n*d orbitals



- (*n*

- dx²-dy² and dz² (e$_g$) lobes located on the axes
- dxy, dxz, dyz lobes (t$_{2g}$) located between axes

CHARACTERISTIC PROPERTIES OF D-BLOCK ELEMENTS

The transition elements have several characteristic properties.

- All are metals with high tensile strength and good conductor of heat and electricity.
- All, except mercury (which is liquid at room temperature), appear as high melting point and boiling point lustrous solids. The high melting points are attributed to the involvement of greater number of electrons from (n-1) d orbitals in addition to the ns electrons in the interatomic metallic bonding. In a particular row, in general, the melting points rise to a maximum at d5, except for anomalous values of Mn and Tc, and fall regularly as the atomic number increases .
- All have high enthalpy of atomization. The higher enthalpy values of atomization for the second and third series account for the occurrence of much more frequent metal – metal bonding in compounds of the heavy transition series.
- All form alloys with one another, and with metallic main group elements.

- Many of them are sufficiently electropositive to react with mineral acids to form salts, though some of them are rather inert in this respect.
- Most of them show more than one oxidation state (variable valence).
- Because of partly filled d orbitals some transition metal ions containing odd number of electrons form paramagnetic compounds.
- They have unparallel tendency to form coordination compounds with Lewis bases because of their small size, high charge and availability of low energy orbitals.
- Many form coloured compounds in one if not in all oxidation states; the absorption of visible light being associated with the presence of partly filled d orbitals.
- The redox behavior, magnetic and optical properties of the transition elements are important features underlying their use in innumerable applications.

Atomic Structures and Properties

- **Electronic Configuration and Variable Oxidation States**

- **Electronic configurations**
- The electronic configurations of the valence shells of the d-block elements can be given as
- $(n-1)d^{1-10}\,ns^{1-2}$, where (n-1) stands for the inner d orbitals (Table 1). It is observed that the electron first enters in higher principal quantum number orbital (n) rather than in unoccupied (n-1)d orbital. The reason for the preferential filling up of 4s in comparison to 3d can be understood in terms of the shielding effect and the effective nuclear charge. In fact, the relative energies of the atomic orbitals varies with increase in atomic number as shown in figure 2. In building up the elements from hydrogen (Z=1) to calcium (Z=20), the unoccupied 3d orbitals are effectively shielded from the increasing nuclear charge by the electrons of (Ar) core. As a consequence, the energy of 3d orbitals remains fairly constant.

- In contrast, the energies of the 4s and 4p orbitals are declining as they penetrate the (Ar) core more. However, the 3d orbitals penetrate the 4s and 4p orbitals so that after Ca a 3d electron is not fully shielded from the increasing nuclear charge by the 4s electrons. Thus, by the time Sc (Z=21) is reached the energy of 3d orbitals fall below the level of 4p orbitals and close to that of 4s orbital. The next electron therefore enters the 3d orbital. Since the d electrons shield one another rather poorly from the nuclear charge, the energy of 3d orbitals continues to fall as Zeff increases. Thus, by the time Ga (Z=31) is reached, the new filled d orbitals have fallen well below the
- 4s and 4p orbitals in energy and are no longer part of the valence shell, but become a core. The same sequence of events follow in the case of the heavier transition metal series.

Table 1: Electronic Configurations of outer orbitals of the Transition Elements(ground state)

1st Series

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Z	21	22	23	24	25	26	27	28	29	30
4*s*	2	2	2	1	2	2	2	2	1	2
3*d*	1	2	3	5	5	6	7	8	10	10

2nd Series

	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Z	39	40	41	42	43	44	45	46	47	48
5*s*	2	2	1	1	1	1	1	0	1	2
4*d*	1	2	4	5	6	7	8	10	10	10

3rd Series

	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Z	57	72	73	74	75	76	77	78	79	80
6*s*	2	2	2	2	2	2	2	1	1	2
5*d*	1	2	3	4	5	6	7	9	10	10

4th Series

	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn
Z	89	104	105	106	107	108	109	110	111	112
7*s*	2	2	2	2	2	2	2	2	1	2
6*d*	1	2	3	4	5	6	7	8	10	10

Transition Elements	Atomic Number	Electronic Configuration
Sc	21	[Ar] $3d^1$ $4s^2$
Ti	22	[Ar] $3d^2$ $4s^2$
V	23	[Ar] $3d^3$ $4s^2$
Cr	24	[Ar] $3d^5$ $4s^1$
Mn	25	[Ar] $3d^5$ $4s^2$
Fe	26	[Ar] $3d^6$ $4s^2$
Co	27	[Ar] $3d^7$ $4s^2$
Ni	28	[Ar] $3d^8$ $4s^2$
Cu	29	[Ar] $3d^{10}$ $4s^1$
Zn	30	[Ar] $3d^{10}$ $4s^2$
Y	39	[Kr] $4d^1$ $5s^2$
Zr	40	[Kr] $4d^2$ $5s^2$
Nb	41	[Kr] $4d^4$ $5s^1$
Mo	42	[Kr] $4d^5$ $5s^1$
Tc	43	[Kr] $4d^5$ $5s^2$
Ru	44	[Kr] $4d^7$ $5s^1$
Rh	45	[Kr] $4d^8$ $5s^1$
Pd	46	[Kr] $4d^{10}$
Ag	47	[Kr] $4d^{10}$ $5s^1$
Cd	48	[Kr] $4d^{10}$ $5s^2$

- **Radii of atoms and ions**

In general, atomic radii (Table 1) of the elements show progressive decrease with increasing atomic number across a row in the transition series. This is because as the new electron enters a d orbital, each time the nuclear charge increases by unity. Since the shielding effect of a d electron is not that effective, the net electrostatic attraction between the nuclear charge and the outermost electron increases and hence a contraction in size. The same trend is observed in the ionic radii of a given series. However, the variation within a series is quite small. It may be attributed to the two opposing factors : one the increasing nuclear charge tending to decrease the size and the other electron-electron repulsion, because of addition of electrons in the same penultimate d shell, tending to increase the size.

An interesting feature emerges when atomic sizes of one series are compared with those of the corresponding elements in the other series. The data in Figure 3 show an increase from the first (3d) to the second (4d) series of the elements but the radii of the third (5d) series are virtually the same as those of the corresponding members of the second series. This phenomenon is associated with the intervention of the 4f orbitals which must be filled before the 5d series of elements begin. The filling of 4f before 5d orbital results in a regular decrease in atomic radii called Lanthanoid contraction which essentially compensates for the expected increase in atomic size with increasing atomic number. The net result of the lanthanoid contraction is that the second and the third d series exhibit similar radii (e.g. Zr 160 pm, Hf 159 pm) and have very similar physical and chemical properties much more than that expected on the basis of usual family relationship.

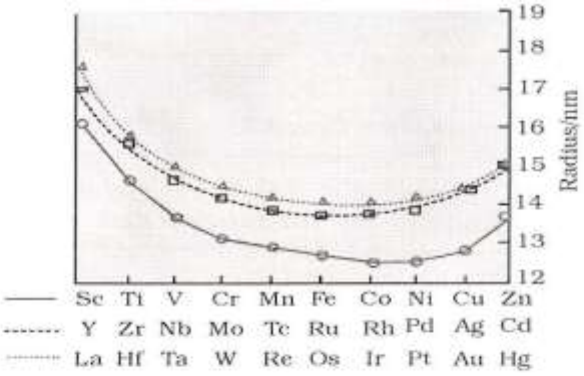


Figure3 : The variation in atomic radii of transition metals across the series

The decrease in metallic radius coupled with increase in atomic mass results in a general increase in the density of these elements. Thus from titanium (Z=22) to copper (Z=29) the increase in the density is significant.

- **Ionization enthalpies**

With increasing nuclear charge, which accompanies the filling of the inner d orbitals, there is an increase in magnitude of ionization enthalpy along each series of the transition elements from left to right. However, many small variations occur. Table 1 gives the values for the first three ionization enthalpies corresponding to successive removal of electrons from outermost s orbital and d orbital of the first row elements.

These values show that the successive enthalpies of these elements do not increase as steeply as in the main group elements. Although the first ionization enthalpy (removal of electron from s orbital), in general, increase, the increase in the second and third ionization enthalpies for the successive elements are not of the same magnitude. However, the trend is similar for the second ionization enthalpies, which for the most part increase smoothly as the atomic number increases; the exceptions are
chromium and copper for which these values are notably larger than those of their neighbors.

The irregular trend in the first ionization enthalpy of the 3d metals, though of little chemical significance, can be accounted for by considering that the removal of one electron alters the relative energies of 4s and 3d orbitals. There is thus a reorganization energy accompanying ionization with some gain in exchange energy as the number of electrons increases.

In general, there is an expected increasing trend in the values as the effective nuclear charge increases with the value of Cr being lower because of the absence of any change in the d configuration and the value of Zn being relatively high because of ionization from the filled 4s level. The lowest common oxidation state of these metals is +2. To form the M^{2+} ions from the gaseous atoms, the sum of the first and second ionization energies is required in addition to the enthalpy of atomization for each element. The dominant term is the second ionization enthalpy which shows unusually high values for Cr and Cu where the d5 and d10 configurations of the M^{+} ions are disrupted, with considerable loss of exchange energy. The value for Zn is correspondingly low as the ionization leads to the production of the stable d^{10} configuration. The trend in the third ionization enthalpies is not complicated by the 4s orbital factor and shows the greater difficulty of removing an electron from the $d^{5}(Mn^{2+})$ and $d^{10}(Zn^{2+})$ ions superimposed upon the general increasing trend. In general, the third ionization enthalpies are quite high and there is a marked break between the values for Mn^{2+} and Fe^{2+}.

Also the high values for copper, nickel and zinc indicate difficulty in obtaining oxidation state greater than two for these elements.

Although ionization enthalpies give some guidance concerning the relative stabilities of oxidation states, this problem is complicated by differing salvation (hydration) energies of different ions and, therefore not easily amenable for broad generalization .

- **Oxidation states**

The oxidation states (or number) exhibited by the transition elements . The most common and important ones are shown in bold type. It is obvious that the transition metals exhibit a great variety of oxidation states. The elements which give the greatest number of oxidation states occur in or near the middle of the series. Manganese, for example, exhibits all the oxidation states from +2 to +7. Ruthenium and Osmium commonly form compounds in +8 oxidation state, which is among the highest for isolable compounds. The lesser number of oxidation states at the extreme ends stems from either too few electrons to lose or share (Sc, Ti) or too many d electrons (hence fewer orbitals available for sharing electrons with others) for higher valence (Cu, Zn.). Thus, early in the series scandium(II) is virtually unknown and titanium(IV) is more stable than Ti(III) or Ti(II). At the other end, the only oxidation state of zinc is +2 (no d electrons are involved).

The maximum oxidation states of reasonable stability correspond to the sum of the s and d electrons upto manganese (TiO_2, VO^{2+}, CrO_4^{2-}, MnO_4^-) followed by a rather abrupt decrease in stability of higher oxidation states, so that the typical species to follow are Fe II, III, Co II,III, Ni II, Cu I,II, Zn II. It is mainly because the latter transition metals require more energy to remove the electrons.

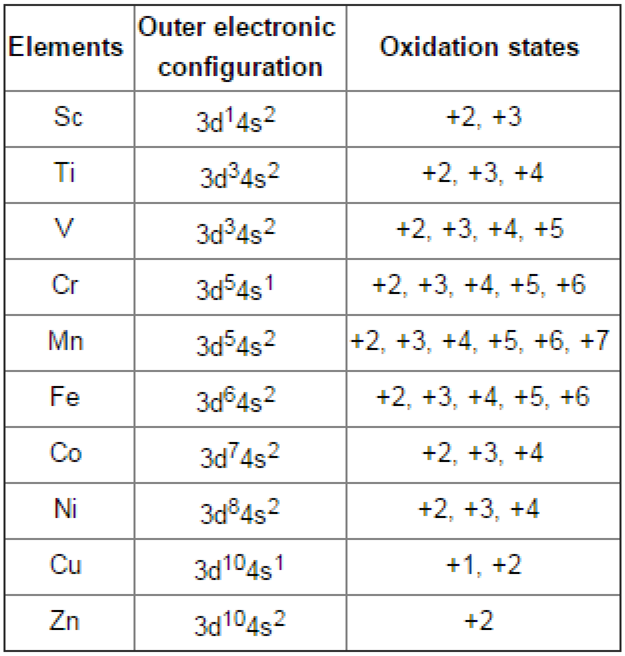
Most of the d-block elements show several oxidation states (variable) in their compounds due to the availability of d-electrons in the valence shell which comprises of the two subshells, viz., (n-1)d and ns whose orbitals are quite close together in energy and hence the electrons can be used from both the subshells for bonding and under different conditions different number of electrons can be used by them. The variability in the oxidation states increases towards the middle of the series from both ends, i.e. left → middle ← right. It has been observed that the d-block elements can form ionic bonds in their lower oxidation states and the ionic character of the bond decreases as well as the covalent character increases with increasing oxidation state.

As a result, with decreasing ionic character the acidic character of the oxides and chlorides increases.

The variability of oxidation states, a characteristic of transition elements, arises out of incomplete filling of d orbitals in such a way that their oxidation states differ from each other by unity, e.g. VII, VIII, VIV, Vv. This is in contrast with the variability of oxidation states of non-transition elements where oxidation states normally differ by units of two.

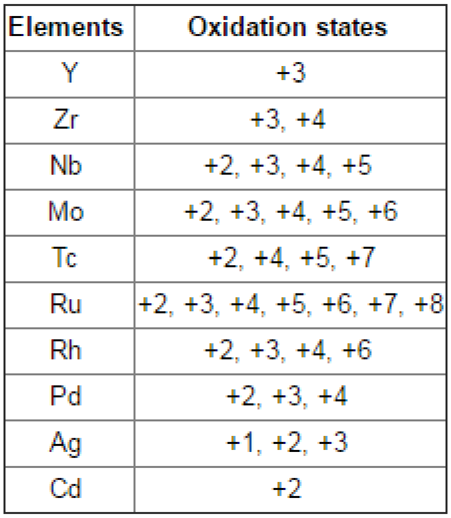
Low oxidation states are found when a complex compound has ligands capable of π–acceptor character in addition to the σ- bonding. For example in $Ni(CO)_4$ and $Fe(CO)_5$ the oxidation state of nickel and iron is zero.

Oxidation States of 3d Series



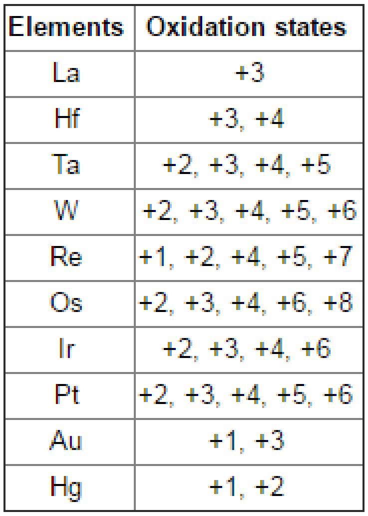
Elements	Outer electronic configuration	Oxidation states
Sc	$3d^1 4s^2$	+2, +3
Ti	$3d^3 4s^2$	+2, +3, +4
V	$3d^3 4s^2$	+2, +3, +4, +5
Cr	$3d^5 4s^1$	+2, +3, +4, +5, +6
Mn	$3d^5 4s^2$	+2, +3, +4, +5, +6, +7
Fe	$3d^6 4s^2$	+2, +3, +4, +5, +6
Co	$3d^7 4s^2$	+2, +3, +4
Ni	$3d^8 4s^2$	+2, +3, +4
Cu	$3d^{10} 4s^1$	+1, +2
Zn	$3d^{10} 4s^2$	+2

Oxidation state of 4d series



Elements	Oxidation states
Y	+3
Zr	+3, +4
Nb	+2, +3, +4, +5
Mo	+2, +3, +4, +5, +6
Tc	+2, +4, +5, +7
Ru	+2, +3, +4, +5, +6, +7, +8
Rh	+2, +3, +4, +6
Pd	+2, +3, +4
Ag	+1, +2, +3
Cd	+2

Oxidation State of 5d Series



Elements	Oxidation states
La	+3
Hf	+3, +4
Ta	+2, +3, +4, +5
W	+2, +3, +4, +5, +6
Re	+1, +2, +4, +5, +7
Os	+2, +3, +4, +6, +8
Ir	+2, +3, +4, +6
Pt	+2, +3, +4, +5, +6
Au	+1, +3
Hg	+1, +2

Cause for Variable Oxidation States

The valence electrons of the transition elements are in (n-1) d and ns orbitals which have a little distinction in energies. Both energy levels can be utilized as a part of bond development.

They demonstrate the +2 oxidation state because of the 2 electrons in ns

orbitals when the electrons of (n-1) d stay unaffected.

The higher oxidation state from +3 to +7 is because of the utilization of all 4s and 3d electrons in the transition series of elements. In the excited state, the (n-1) d electrons get to be bonding and give the variable states to the iota. Subsequently, the variable

oxidation state is because of the support of both ns and (n-1) d orbitals in bonding.

- **Magnetic Properties:**

The magnetic properties of D-Block Elements are dictated by the number of unpaired electrons in it.

There are two fundamental sorts of substances.

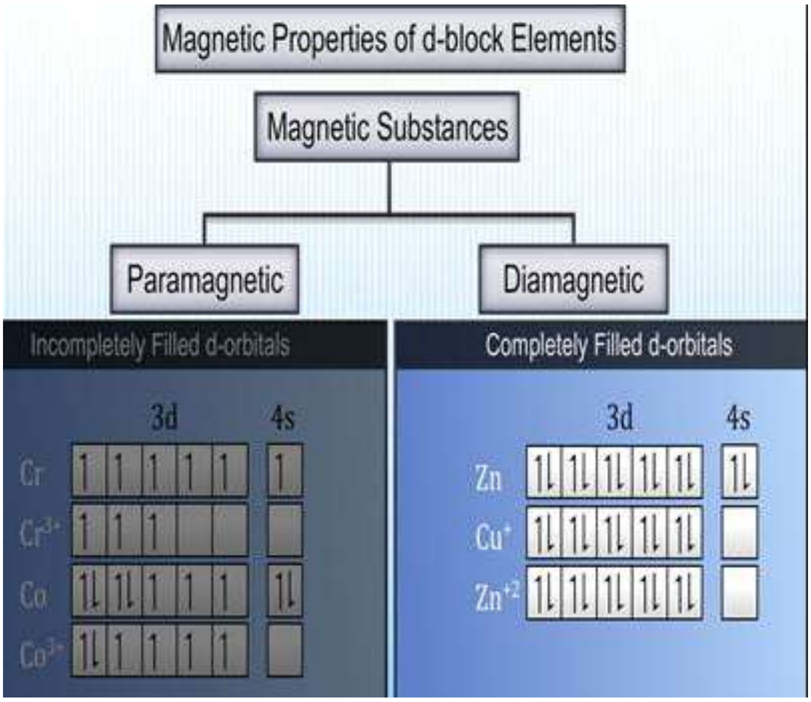
(i) Paramagnetic substances

The paramagnetic character emerges in view of the nearness of unpaired electrons. Paramagnetic substances are the substances which are pulled in by the magnetic field.

(ii) Diamagnetic Substances

Diamagnetic character emerges as a result of the nonappearance of unpaired electrons. Diamagnetic substances are the substances which are repulsed by the magnetic field.

A large portion of the transition elements and their compounds are paramagnetic and are pulled in by the magnetic field. More prominent the number of unpaired electrons in the substance more noteworthy is the paramagnetic character


Magnetic Properties of d-block Elements
Magnetic Substances
Paramagnetic
Diamagnetic
Incompletely Filled d-orbitals
Completely Filled d-orbitals
3d
4s
Cr
Cr3+
Co
Co3+
3d
4s
Zn
Cu+
Zn+2

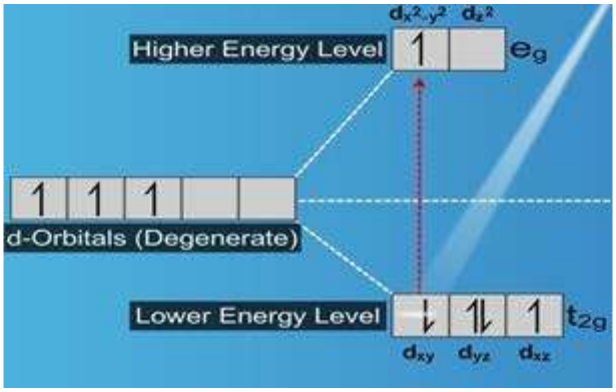
- **Formation of colored compounds:**

Most d-block metal compounds are coloured in their solid or liquid states.

In the case of transition metal ions, under the influence of ligands, the degeneracy of the 5 d-orbitals is lost and they separate into two distinct energy levels.

eg set: d x^2- y^2 and dz^2 orbitals

t_2g set: dxy, dxz and dyz orbitals



When white light is incident on a transition metal ion, the electron in the lower energy d-orbital set absorbs certain radiations and gets promoted to a d-orbital set of higher energy. The transmitted radiation devoid of the absorbed radiations is the complementary colour of the absorbed light. This complementary colour is the colour of the substance.

Colour in transition-series metal compounds is generally due to electronic transitions of two principal types.

- charge transfer transitions. An electron may jump from a predominantly ligand orbital to a predominantly metal orbital, giving rise to a ligand-to-metal charge-transfer (LMCT) transition. These can most easily occur when the metal is in a high oxidation state. For example, the colour of chromate, dichromate and permanganate ions is due to LMCT transitions. Another example is that mercuric iodide, HgI_2, is red because of a LMCT transition.

A metal-to-ligand charge transfer (MLCT) transition will be most likely when the metal is in a low oxidation state and the ligand is easily reduced.

In general charge transfer transitions result in more intense colours than d-d transitions.

- d-d transitions. An electron jumps from one d-orbital to another. In complexes of the transition metals the d orbitals do not all have the same energy. The pattern of splitting of the d orbitals can be calculated using crystal field theory. The extent of the splitting depends on the particular metal, its oxidation state and the nature of the ligands. The actual energy levels are shown on Tanabe–Sugano diagrams.

- **Catalytic Activity**

Transition metals and their compounds are often good catalysts. A few of the more obvious cases are mentioned below, but you will find catalysis explored in detail elsewhere on the site (follow the link after the examples). Transition metals and their compounds function as catalysts either because of their ability to change oxidation state or, in the case of the metals, to adsorb other substances on to their surface and activate them in the process. All this is explored in the main catalysis section.

Iron in the Haber Process

The Haber Process combines hydrogen and nitrogen to make ammonia using an iron catalyst.

Nickel in the hydrogenation of C=C bonds

This reaction is at the heart of the manufacture of margarine from vegetable oils. However, the simplest example is the reaction between ethene and hydrogen in the presence of a nickel catalyst.

Vanadium(V) oxide in the Contact Process

At the heart of the Contact Process is a reaction which converts Sulfur dioxide into Sulfur trioxide. Sulfur dioxide gas is passed together with air (as a source of oxygen) over a solid vanadium(V) oxide catalyst.

Iron ions in the reaction between persulfate ions and iodide ions

Persulphate ions (peroxodisulphate ions), $S_2O_8^{2-}$, are very powerful oxidizing agents. Iodide ions are very easily oxidized to iodine. And yet the reaction between them in solution in water is very slow. The reaction is catalyzed by the presence of either iron(II) or iron(III) ions.

$S_2O_8^{2-}+2I^{-}\rightarrow 2SO_4^{2-}+I_2$ (1)

- **Alloy formation**

The transition metals readily form alloys with each other because of similar radii. The alloys so formed are hard and have often high melting points. The best known are ferrous alloys; vanadium, chromium, molybdenum, tungsten and manganese are used for the production of variety of steels and stainless steel.

Industrially important alloys of transition metals with non-transition metals are brass (copper-zinc), bronze (copper-tin) etc.

- **Coordination Compounds**

The transition metals and their ions have much higher tendency to from coordination compounds as compared to the s- and p- block elements. It is because of their relatively smaller sizes, higher ionic charges and the availability of d orbitals for bond formation. Coordination compounds, unlike normal compounds, retain their identity even when dissolved in water or any other suitable solvent. The properties of these compounds are totally different from those of their constituents.

Alfred Werner can be considered to be the pioneer in the field of coordination chemistry and he received Nobel Prize in 1913 in recognition of his efforts. He showed that neutral molecules were bound directly to the metal so that complex salt such as $CoCl_3.6NH_3$ is correctly formulated as $[Co(NH_3)_6]^{3+}(Cl^-)_3$.

G.N. Lewis and N.V. Sidgwick proposed that a chemical bond required the sharing of an electron pair. This led to the idea that a neutral molecule with an electron pair can donate these electrons to a metal ion or other electron acceptor.

Thus, in a coordination compound, the metal species acts as electron acceptor (Lewis acid) and neutral molecule with lone pair of electrons or anion as electron donor (Lewis bases). A metal atom or ion when bonded directly to a fixed number of anions or molecules constitutes a coordination entity. For example, $[Pt(NH_3)_2Cl_2]$ is a coordination entity in which platinum(II) is surrounded by two ammonia molecules and two chloride ions. Other examples are $[Fe(CN)_6]^{4-}$, $[Co(NH_3)_5Cl]^{2+}$, $[Ni(CO)_4]$ etc. 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 in $[Ni(NH_3)_6]^{2+}$ is Ni(II), in $[Mo(CN)_8]^{3-}$, Mo(V), and in $[Co(PR_3)_3Cl]$, Co(I). The charged ions or neutral molecules bound to the central atom in the coordination entitiy are called ligands. For example, PR_3 and Cl- are ligands in $[CoCl(PR_3)_3]$.

The number of ligand donor atoms directly bonded to the central atom is defined as the coordination number. For example, in the complex species $[Mo(CN)_8]^{3-}$ and $[CoCl(PR_3)_3]$, the coordination number of Mo and Co are 8 and 4, respectively. The central atom and the ligands bonded to it are enclosed in square bracket and is collectively termed as the coordination sphere. For example in the complex $[Ni(NH_3)_6]Cl_2$, the coordination sphere is $[Ni(NH_3)_6]^{2+}$. The spatial arrangement of the ligands around the central atom is termed as coordination polyhedron. The most common coordination polyhedra are octahedral, tetrahedral and square planar.

- **Melting and Boiling Points**

The melting and boiling points of these elements are generally very high showing that they are held by strong forces. The melting and boiling points have the highest values in the middle of the series because, perhaps these elements have the maximum number of unpaired d-electrons available for bonding, detailed account of which will be given ahead for every series.

Scandium

Definition

Scandium is a transition element in Group 3 (IIIB) and Period 4 with an atomic number of 21.

Chemical Properties of Scandium

Scandium is the lightest Group 3 (IIIB) element and is the lightest of the transition metals. Its atomic number (proton number) is 21, has only one long-lived isotope, and has an atomic mass of 44.95591 a.m.u. Scandium's electronic configuration is $[Ar]4s^2 3d^1$, and only occurs in the trivalent state (Sc^{3+}) in nature. Thus, unlike most other period 4 transition metals, the geochemical behavior of scandium is not affected by redox conditions, and shows lithophile behaviour. The effective ionic radii in six- and eight-fold coordination are 74.5 and 87 pm, respectively (Shannon 1976) and its Pauling electronegativity is 1.36. Pure scandium metal has a melting point of 1541 ℃ at 1 atm. The International Union of Pure and Applied Chemistry consider Sc to be a rare earth element (REE) (Damhus et al. 2005), however, the ionic radius and electronic configuration of Sc are sufficiently different from yttrium and the lanthanides that it is generally excluded from discussions of the REE.

Scandium was “discovered” by Lars Fredrik Nilson in 1879 by separation from rare earth mixtures from euxenite and gadolinite, and is named for Scandinavia.

Sources and Uses

Global production of Sc is small (~10 tonnes per year) as a by-product from mining of ores of titanium, rare earths, apatite, and uranium. Bauxites are another potential source of Sc, as it gets concentrated, along with other elements, in the “red mud” residue that results from Al processing (Deady et al. 2014). The principal uses of Sc are in Sc-Al alloys and in solid oxide fuel cells. Minor amounts of Sc are also used in variety of other applications including electronics, lasers, and lighting.

Titanium

Chemistry of Titanium

Discovered independently by William Gregor and Martin Klaproth in 1795, titanium (named for the mythological Greek Titans) was first isolated in 1910. Gregor, a Cornish vicar and amateur chemist isolated an impure oxide from ilmenite ($FeTiO_3$) by treatment with HCl and H_2SO_4 .Titanium is the second most abundant transition metal on Earth (6320 ppm) and plays a vital role as a material of construction .

For example, when it's alloyed with 6% aluminum and 4% vanadium, titanium has half the weight of steel and up to four times the strength.

Uses of titanium

Titanium is a highly corrosion-resistant metal with great tensile strength. It is ninth in abundance for elements in the earth's crust. It has a relatively low density (about 60% that of iron). It is also the tenth most commonly occurring element in the Earth's crust. That all means that titanium should be a really important metal for all sorts of engineering applications. In fact, it is very expensive and only used for rather specialized purposes.

Titanium is very expensive because it is awkward to extract from its ores - for example, from rutile, T iO_2. Whilst a biological function in man is not known, it has excellent biocompatibility--that is the ability to be ignored by the human body's immune system--and an extreme resistance to corrosion. Titanium is now the metal of choice for hip and knee replacements

Titanium Extraction

Titanium cannot be extracted by reducing the ore using carbon as a cheap reducing agent, like with iron. The problem is that titanium forms a carbide, TiC, if it is heated with carbon, so you don't get the pure metal that you need. The presence of the carbide makes the metal very brittle. That means that you have to use an alternative reducing agent. In the case of titanium, the reducing agent is either sodium or magnesium. Both of these would, of course, first have to be extracted from their ores by expensive processes.

The titanium is produced by reacting titanium(IV) chloride, $TiCl_4$ - NOT the oxide - with either sodium or magnesium. That means that you first have to convert the oxide into the chloride. That in turn means that you have the expense of the chlorine as well as the energy costs of the conversion. High temperatures are needed in both stages of the reaction.

Titanium is made by a batch process. In the production of iron, for example, there is a continuous flow through the Blast Furnace. Iron ore and coke and limestone are added to the top, and iron and slag removed from the bottom. This is a very efficient way of making something. With titanium, however, you make it one batch at a time. Titanium(IV) chloride is heated with sodium or magnesium to produce titanium. The titanium is then separated from the waste products, and an entirely new reaction is set up in the same reactor. This is a slow and inefficient way of doing things. Traces of oxygen or nitrogen in the titanium tend to make the metal brittle. The reduction has to be carried out in an inert argon atmosphere rather than in air; that also adds to costs.

Wilhelm J. Kroll developed the process in Luxemburg around the mid 1930's and then after moving to the USA extended it to enable the extraction of Zirconium as well. Titanium ores, mainly rutile (TiO_2) and ilmentite ($FeTiO_3$), are treated with carbon and chlorine gas to produce titanium tetrachloride.

$$TiO_2 + Cl_2 \rightarrow TiCl_4 + CO_2$$

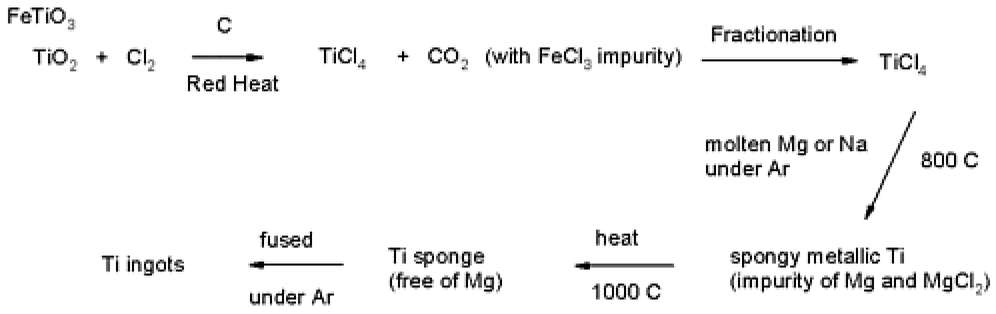
Fractionation

Titanium tetrachloride is purified by distillation (Boiling point of 136.4) to remove iron chloride.

Reduction

Purified titanium tetrachloride is reacted with molten magnesium under argon to produce a porous “titanium sponge”.

$$\mathrm{TiCl_4 + 2\ Mg \rightarrow Ti + 2\ MgCl_2}$$



Kroll process

Titanium Halides

- Titanium(Halides IV) TiX_4

Preparations

They can all be prepared by direct reaction of Ti with halogen gas (X_2). All are readily hydrolyzed. They are all expected to be diamagnetic.

- Titanium(III) halides TiX_3

Preparations

They can be prepared by reduction of TiX4 with H2. Titanium Oxides and Aqueous Chemistry

Titanium oxides

Preparations

obtained from hydrolysis of TiX_4 or Ti(III) salts. TiO_2 reacts with acids and bases.

In Acid: $TiOSO_4$ formed in H_2SO_4 (Titanyl sulfate)

In Base: $MTiO_3$ metatitanates (eg Perovskite, $CaTiO_3$ and ilmenite, $FeTiO_3$) M_2TiO_4 ortho titanates. Peroxides are highly colored and can be used for Colorimetric analysis.

$TiCl_4$ is a good Lewis acid and forms adducts on reaction with Lewis bases

$TiCl_3$ has less Lewis acid strength but can form adducts

Conversion of titanium oxide into titanium chloride

The ore rutile (impure titanium(IV) oxide) is heated with chlorine and coke at a temperature of about 900°C.

$$TiO_2 + 2Cl_2 + 2C \rightarrow TiCl_4 + 2CO$$

Other metal chlorides are formed as well because of other metal compounds in the ore. Very pure liquid titanium(IV) chloride can be separated from the other chlorides by fractional distillation under an argon or nitrogen atmosphere. Titanium(IV) chloride reacts violently with water. Handling it therefore needs care and is stored in totally dry tanks.

Reduction of the titanium chloride

Reduction by sodium: The titanium(IV) chloride is added to a reactor in which very pure sodium has been heated to about 550°C - everything being under an inert argon atmosphere. During the reaction, the temperature increases to about 1000°C.

$$TiCl_4 + 4\ Na \rightarrow Ti + 4\ NaCl \qquad (4)$$

After the reaction is complete, and everything has cooled (several days in total - an obvious inefficiency of the batch process), the mixture is crushed and washed with dilute hydrochloric acid to remove the sodium chloride.

Reduction by magnesium

This is the method used in the rest of the world. The method is similar to using sodium, but this time the reaction is:

$TiCl_4 + 4\ Mg \rightarrow Ti + 2\ MgCl_2$ (5)

The magnesium chloride is removed from the titanium by distillation under very low pressure at a high temperature.

Vanadium

Chemistry of Vanadium

Vanadium takes its name from the Scandinavian goddess Vanadis and was discovered in 1801 by Andrés Manuel del Rio. It was isolated in 1867 by Henry Roscoe as a silvery-white metal that is somewhat heavier than aluminum but lighter than iron. It has excellent corrosion resistance at room temperature.

The history of its discovery is an interesting tale. del Rio sent his brown ore samples, containing what he thought was a new element to Paris for analysis and confirmation, along with a brief explanation that was ambiguous. The complete analysis and description of his work were lost in a shipwreck so the Paris lab saw nothing but brown powder and a brief confusing note. A second sample sent to Berlin was mislabeled lead chromate when it arrived. del Rio gave up, losing confidence in his discovery. The element was rediscovered in 1867 by Nils Sefstrôm.

Vanadium has an unusually large number of stable oxidation states (+2, +3, +4, +5)each of which is characterized by a unique color in solution. The metal is used as an alloying agent for steel. It combines with nearly all non-metals in compounds.

Vanadium(V) oxide as a Catalyst

During the Contact Process for manufacturing sulfuric acid, sulfur dioxide has to be converted into sulfur trioxide, which is done by passing sulfur dioxide and oxygen over a solid vanadium(V) oxide catalyst.

This is a good example of the ability of transition metals and their compounds to act as catalysts because of their ability to change their oxidation state (oxidation number). The sulfur dioxide is oxidized to sulfur trioxide by the vanadium(V) oxide. In the process, the vanadium(V) oxide is reduced to vanadium(IV) oxide.

$$SO_2 + V_2O_5 \rightarrow SO_3 + V_2O_4$$

The vanadium(IV) oxide is then re-oxidized by the oxygen.

$$V_2O_4 + 1/2\ O_2 \rightarrow V_2O_5$$

Although the catalyst has been temporarily changed during the reaction, at the end it is chemically the same as it started.

Vanadium's oxidation states

Vanadium has oxidation states in its compounds of +5, +4, +3 and +2. This section looks at ways of changing between them. It starts with a bit of description, and then goes on to look at the reactions in terms of standard redox potentials (standard electrode potentials).

Chromium

Chromium Chemistry

History

Discovered in 1797 by the French chemist Louis Nicolas Vauquelin, it was named chromium (Greek chroma, "colour") because of the many different colours characteristic of its compounds.

Occurrence

Chromium is the earth's 21st most abundant element (about 122 ppm) and the 6th most abundant transition metal.

The principal and commercially viable ore is chromite, $FeCr_2O_4$, which is found mainly in southern Africa (with 96% of the worlds reserves), the former U.S.S.R and the Philippines. Less common sources include crocoite, $PbCrO_4$, and chrome ochre, Cr_2O_3, while the gemstones emerald and ruby owe their colours to traces of chromium.

See the International Chromium Development Association web site for more details.

Extraction

Chromite, $FeCr_2O_4$, is the most commercially useful ore, and is extensively used for extraction of chromium. Chromium is produced in two forms

Ferrochrome by the reduction of chromite with coke in an electric arc furnace. A low-carbon ferrochrome can be produced by using ferrosilicon instead of coke as the reductant. This iron/chromium alloy is used directly as an additive to produce chromium-steels which are "stainless" and hard.

Chromium metal by the reduction of Cr_2O_3. This is obtained by aerial oxidation of chromite in molten alkali to give sodium chromate, Na_2CrO_4, which is leached out with water, precipitated and then reduced to the Cr(III) oxide by carbon. The oxide can be reduced by aluminium (aluminothermic process) or silicon:

$Cr_2O_3 + 2Al \rightarrow 2Cr + Al_2O_3$ $2Cr_2O_3 + 3Si \rightarrow 4Cr + 3SiO_2$

The main use of the chromium metal so produced is in the production of nonferrous alloys, the use of pure chromium being limited because of its low ductility at ordinary temperatures. Alternatively, the Cr_2O_3 can be dissolved in sulphuric acid to give the electrolyte used to produce the ubiquitous chromium-plating which is at once both protective and decorative. The sodium chromate produced in the isolation of chromium is itself the basis for the manufacture of all industrially important chromium chemicals. World production of chromite ores approached 12 million tonnes in 1995.

Chromium Compounds

Most compounds of chromium are coloured , the most important are the chromates and dichromates of sodium and potassium and the potassium and ammonium

Preparations:

Reduction of CrX_3 with H_2/HX gives CrX_2.

$$Cr + Cl_2 \rightarrow CrCl_3$$

$$Cr_2O_3 + C + Cl_2 \rightarrow CrCl_3$$

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