

SYNOPSIS

(INORGANIC CHEMISTRY)

Introduction

Inorganic chemistry deals with the properties of over one hundred twenty elements and their compounds. These elements range from highly reactive metals of the s-block to noble metals in the d-block (such as gold, platinum). The elements also include highly reactive non-metals of group 17 to unreactive noble gases of group 18 in the p-block.

Inorganic compounds vary from ionic solids such as NaCl, $MgCl_2$ to covalent compounds such as silica, and metallic compounds.

In order to study and understand inorganic chemistry, the students should have a very strong grasp of the electronic configuration, periodic properties, chemical bonding, acid-base concepts and redox reactions.

Inorganic chemistry is essential to the formulation and improvement of modern materials such as catalysts, semiconductors, non-linear optical devices, super conductors and advanced ceramic materials.

Many coordination compounds found application in medicine, biological system etc. In this inorganic chemistry part, we are discussing about the following chapter in detail using the basic fundamental and principles of chemistry.

These are

- (i) General processes and principles of extraction of metals.
- (ii) Chemistry of p-block elements (group 15 to group 18)
- (iii) d and f block elements
- (iv) Coordination compounds

General principles and process of Isolation of Elements

Metals exists in the earth crust either in the combined state or in the native form but along with some unwanted impurities. Although some metals exists in sea water also.

The inorganic substance containing metal in the combined state or in the native state along with unwanted impurities is called **mineral**.

The minerals from which the metal can be extracted profitably and conveniently are called **Ores**. The unwanted impurities present in the ore are called **gangue or matrix**.

There are number of steps involved in the extraction of metal in the pure form.

1. **Concentration or enrichment of ore** to remove the unwanted impurities. Number of different methods are used depending on the nature of the impurities.

(i) **Hydraulic washing or Gravity separation**

(ii) **Magnetic separation**

(iii) **Froth floatation method** which depends on the difference in the wettability of the ore and the gangue particles. This method is mainly used for sulphide ores.

Sometimes we use chemical treatment of the ore to remove unwanted impurities.

The chemical treatment of the ore is called **leaching**

Leaching is used for

(i) the purification of bauxite ore (**Baeyer's process**)

(ii) extraction of silver and gold by **Mac-Arther's cyanide process**.

2. **Roasting and calcination** are used to convert the ore into metal oxide.

Roasting is heating the ore strongly in the presence of oxygen. It is mainly used for the sulphide ores like galena, copper pyrites.

Calcination is heating the ore strongly in the absence of oxygen. It is used for carbonate ores, hydrated ores like limestone.

3. **Reduction of metal oxides** to metal using reducing agent.

The metals which are highly reactive (Na, Mg and Al) and present at the top of the activity series are extracted by **electrolytic reduction**.

Aluminum is obtained from molten alumina using **Hall-Herault's process** and sodium is obtained from molten NaCl using Down's cell process.

Metals in the middle of the activity series like Fe, Zn, Cu are extracted by using carbon reduction, reduction with carbon monoxide, reduction with aluminum and also auto or self reduction.

4. **Refining of metals** once the metal is obtained, we use variety of methods to purify the metal depending upon the impurities. The various method used are

(i) Distillation

- (ii) Liquation
- (iii) Vapour phase refining
- (iv) Zone refining
- (v) Electrolytic refining
- (vi) Chromatography

Thermodynamics of Metallurgy

The metal oxide reacts with reducing agent, the oxide is reduced to the metal and the reducing agent is oxidized. In the two reaction, the net Gibbs energy change is negative, which becomes more negative on raising the temperature. Also conversion of the physical states from solid to liquid or to gas and formation of gaseous states favours decrease in the Gibbs energy for the entire system. This concept is displaced graphically by plotting ΔG° vs temperature (Ellingham diagram) for such oxidation and reduction reactions at different temperatures.

We will also be discussing in detail

- (i) Extraction of aluminum by leaching bauxite with NaOH to form sodium aluminate which is then separated and neutralized to give back the pure hydrated oxide. This hydrated oxide on electrolysis gives aluminum.
- (ii) Extraction of iron is done by reduction of its oxide ore in blast furnace.
- (iii) Copper is extracted by smelting and heating in a reverberatory furnace.
- (iii) Zinc is extracted from zinc oxide using coke. Metals are in general, widely used as alloys and have contributed significantly in the development of variety of industries.

The p-Block Elements

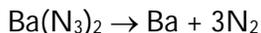
The p-block of the periodic table consists of group 13 to group 18. Their valence shell electronic configuration is $ns^2 np^{1-6}$, the p-subshell can accommodate maximum of six electrons hence, there are six groups in the p-block.

The group 15 includes nitrogen, phosphorus, arsenic, antimony and bismuth, which have general electronic configuration of $ns^2 np^3$ and p-subshell is half filled. 78% by volume of nitrogen is present in the air.

Nitrogen is the most electronegative element in the group 15 and shows anomalous behavior due to its small size, absence of d-orbitals and ability to form $p\pi-p\pi$ bond formation.

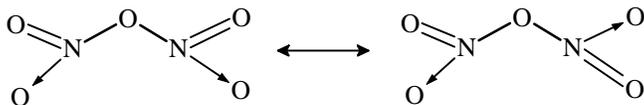
There is a transition from non-metallic nitrogen to metallic character (bismuth) for the elements in the group. They exhibit two important oxidation states, +3 and +5 but +3 oxidation state is favoured by heavier elements due to **inert pair effect**.

Dinitrogen can be prepared in the laboratory as well as on the industrial scale. Pure N_2 can be obtained by the decomposition of sodium azide or barium azide.



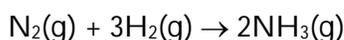
Nitrogen forms number of oxides from +1 oxidation state in N_2O to +5 oxidation state in N_2O_5 .

All these oxides have a resonating structure and contains multiple $p\pi-p\pi$ bonds.



NO and NO_2 are odd electron molecules and are paramagnetic in nature.

Ammonia, NH_3 is an important compound of nitrogen and is obtained commercially by Haber's process.



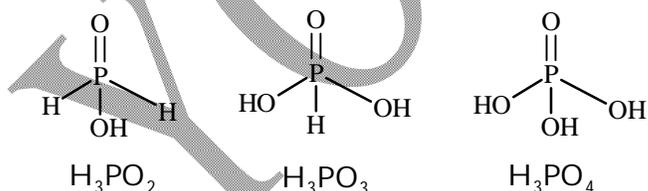
Nitric acid, HNO_3 is prepared commercially by Ostwald's process. HNO_3 is a strong oxidizing agent and its oxidizing action depends on the concentration of HNO_3 and the E° value of the reducing agent.

Metals and non-metals reacts with HNO_3 to give NO or NO_2 .

Phosphorus shows allotropy and mainly exists in red, black and yellow phosphorus. Phosphorus form hydride called phosphine, PH_3 which is used as a reducing agent and is poisonous.

Nitrogen and phosphorus both form halides MX_3 but phosphorus also form pentahalides, PX_5 ($X = Cl, Br$).

Phosphorus also form number of oxoacids containing atleast one $P = O$ and OH groups directly attached to phosphorus.

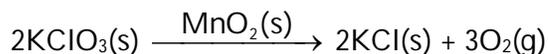


The oxoacids containing $P - H$ bonds are reducing agents. The basicity of oxoacids depends on the number of OH groups directly bonded to phosphorus.

Group 16 elements are oxygen, sulphur, selenium, tellurium and polonium. Polonium is a radioactive element.

Their electronic configuration in the valence shell is $ns^2 np^4$. Oxygen is the second most electronegative element. The anomalous behavior of oxygen is due to its small size, high

electronegative, tendency to form $p\pi-p\pi$ bonds and non-availability of d-orbitals. Oxygen is prepared in the laboratory by the decomposition of KClO_3 in the presence of MnO_2 as a catalyst.



Oxygen form mainly four types of oxides:

1. Neutral oxides, NO , N_2O , CO
2. Amphoteric oxides, ZnO , Al_2O_3
3. Basic oxides MgO , Na_2O
4. Acidic oxides SO_2 , CO_2

Ozone, O_3 is an allotrope of O_2 . Ozone is a powerful oxidizing agent and is used in organic chemistry to determine the position of the double bond in alkenes.

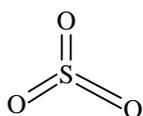
Sulphur exists in number of allotropic form, rhombic, monoclinic, etc.

Two main oxides of sulphur are SO_2 and SO_3 .

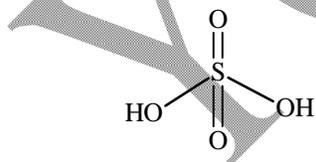
SO_2



SO_3



Sulphur form large number of oxoacids and they exists as free acids, salts or in the form of their solutions. Sulphuric acid, H_2SO_4 is the most important oxoacid of sulphur, manufactured by **contact process**.



H_2SO_4 is used as a/an

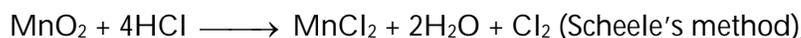
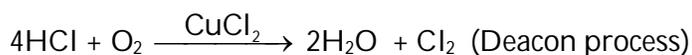
- (i) dehydrating agent
- (ii) oxidizing agent
- (iii) a reagent to prepare volatile acids like HCl , HF , HNO_3 .

Group 17 elements are collectively called halogens means salt forming elements. These elements are fluorine, chlorine, bromine, iodine and astatine. Their valence shell electronic configuration is ns^2np^5 .

They are short of one electron to attain the nearest noble gas electronic configuration. Their common oxidation state is -1 .

Fluorine always show -1 , other halogen shows $+1$, $+3$, $+5$ and $+7$ due to the availability of d-orbitals.

Chlorine is prepared by number of methods.



Chlorine is a powerful oxidizing agent, react with NH_3 , alkali, with metal and non-metal and used as a bleaching agent.

Hydrogen chloride is an important hydrogen halide, used in the preparation of aqua regia HCl reacts with metals, neutralizes bases and salts.

Halogen form interhalogens XX'_n ($n = 1, 3, 5, 7$) in which X' is more electronegative and smaller in size than X .

Interhalogens are more reactive and more oxidizing than halogen.

Halogen form four types of oxoacids which are

Hypohalous acid, $\overset{+1}{\text{HOX}}$

Halous acid, $\overset{+3}{\text{HOXO}}$

Halic acid, $\overset{+5}{\text{HOXO}_2}$

Perhalic acid $\overset{+7}{\text{HOXO}_3}$

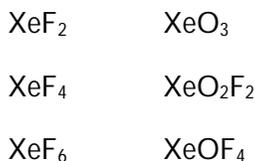
In the hydrides of groups 15, 16, 17

- (i) the thermal stability decreases down the group
- (ii) reducing power increases down the group
- (iii) acidic strength increases down the group
- (iv) boiling point increases down the group but H_2O , NH_3 and HF have exceptionally high boiling points due to intermolecular hydrogen bonding.

Group-18 elements are called noble gases. They have fully filled valence shell of $ns^2 np^6$, except helium, $1s^2$

Due to complete octet of outermost shell, positive electron gain enthalpy and very high ionization enthalpy, noble gases have a very low chemical reactivity.

In group 18, Xenon form number of compounds with two most electronegative element of the periodic table: F and O. The compounds of xenon were first prepared by Neil Bartlett. These are



The d-and f-Block Elements

The d-block elements are those elements in which the filling of electrons takes place in the penultimate d-subshell. The d-block elements are present at the middle of the periodic table. d-subshell can accommodate maximum of 10 electrons. As a result, we have 10 groups in the d-block of the periodic table from group 3 to group-12. The d-block elements having incompletely filled d-subshell in the ground state or in one of the stable oxidation state are called **transition elements**. All d-block elements are metals, hence these elements are called **transition metals** and show typical metallic properties such as

- High tensile strength
- High melting and boiling point
- Ductility and malleability
- Thermal and electrical conductivity

There are three complete rows in the d-block, each consists of 10 elements.

First row is called 3d series [Ar] 3d¹⁻¹⁰ 4s¹⁻²

Second row is called 4d series [Kr] 4d¹⁻¹⁰ 5s¹⁻²

Third row is called 5d series [Xe] 4f¹⁴ 5d¹⁻¹⁰ 6s¹⁻²

The high melting and boiling points are due to strong interatomic forces of attraction arising due to the involvement of (n-1)d and ns electron in the metallic bond formation. Mn has an exceptionally low melting point. In the 3d series, Zn has lowest melting point due to the presence of fully filled 3d¹⁰ and 4s² subshells.

Because of the strong interatomic forces of attraction involving (n-1)d and ns electrons, the transition elements have **high enthalpy of atomization**. Again, in the 3d series, zinc has lowest enthalpy of atomization.

The d-block elements and their compounds show colour as well as **paramagnetism**. This is due to the presence of one or more unpaired electrons. The colour is due to the excitation of electron from one d-

orbital to another d-orbital (d-d transition). The degree of paramagnetism is expressed in terms of magnetic moment.

The spin only magnetic moment, μ is given by

$$\mu = \sqrt{n(n+2)} \text{ Bohr magneton}$$

Where n = number of unpaired electrons.

Due to comparable energy of $(n-1)d$ and ns , the d-block elements show variable oxidation states. The common oxidation state of 3d series elements is +2 although Mn shows highest oxidation state of +7 in KMnO_4 . The stability of +2 oxidation state is more in the second half of the 3d series.

Higher oxidation states are oxidizing and lower oxidation states are reducing. The d-block elements and their compounds are used as catalyst. The d-block elements are used in the formation of alloys (Brass, bronze, stainless steel) and the interstitial compounds (tungsten carbide).

The **atomic size** decreases from left to right in a given series but the decrease in size is not very large. Also, near the end of the series, the size slightly increases due to inter electronic repulsions. The 5d series elements have an atomic size comparable to 4d series due to presence of fully filled $4f^{14}$ subshell and ineffective shielding of 4f electrons.

The **ionisation enthalpy** increases from left to right in a given series.

The successive ionization enthalpies do not increase as steeply as in the s- and p-block elements with increasing atomic number. Hence, the loss of variable number of electrons from $(n-1)d$ orbitals is not energetically unfavourable.

The transition elements vary widely in their chemical behavior. Many of them are sufficiently electropositive to dissolve in mineral acids, although few are noble metals like gold, platinum. In the first 3d series with the exception of copper, all the metals are relatively reactive.

The transition metals react with a number of non-metals like oxygen, nitrogen and halogen to form binary compounds.

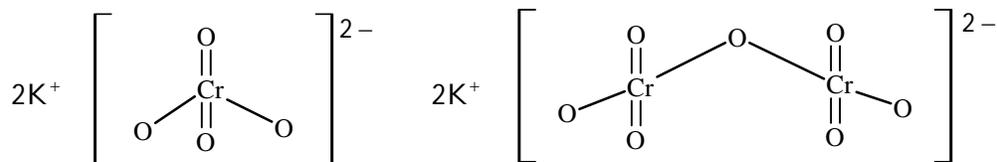
The oxides of d-block elements dissolve in acids and bases to form **oxometallic salts**. The d-block elements show their highest oxidation states in oxometal anion like CrO_4^{2-} , MnO_4^- , etc. Potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$ and potassium permanganate, KMnO_4 are the two important oxometallic salts.

$\text{K}_2\text{Cr}_2\text{O}_7$ is prepared from the chromite ore,

FeCr_2O_4 by fusion with Na_2CO_3 and air followed by acidification.

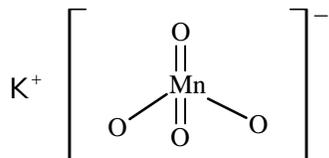
$\text{K}_2\text{Cr}_2\text{O}_7$ is a stronger oxidizing agent than K_2CrO_4 .

Their structures are



$\text{K}_2\text{Cr}_2\text{O}_7$ is used as an oxidising agent in acidic medium.

KMnO_4 is prepared by fusion of pyrolusite ore, MnO_2 with KOH and air followed by acidification
 KMnO_4 structure is



KMnO_4 act as an oxidizing agent in

- (i) acidic medium
- (ii) basic medium
- (iii) neutral medium

KMnO_4 on heating gives K_2MnO_4 , MnO_2 and O_2



$\text{K}_2\text{Cr}_2\text{O}_7$ and KMnO_4 both are coloured due to charge transfer spectra.

The two series of inner transition elements, **lanthanoids and actinoids** constitute the f-block of the periodic table and placed outside at the bottom of the periodic table in which 4f and 5f orbitals are progressively filled.

With the successive filling of the inner orbitals, 4f there is a gradual decrease in the atomic and ionic sizes of the lanthanoids along the series. This regular decrease in size as atomic number increases is called **Lanthanoid contraction**.

Due to lanthanoid contraction, (i) 5d series elements have a comparable size as 4d series elements (ii) 5d series elements have a higher ionization enthalpy than 3d or 4d series elements.

The common oxidation states of lanthanoids is +3 although +4 (Ce^{4+}) and +2 (Eu^{2+} , Yb^{2+}) oxidation states are also exhibited by some lanthanoids. All the lanthanoids are soft white metals; react easily with water to give solutions with +3 ions. The chemistry of actinoids is more complex in view of their ability to show variable oxidation states and their radioactive nature.

There is also a regular decrease in atomic size amongst actinoids as atomic number increases. This is called **actinoid contraction**. The actinoids with atomic number greater than 92 are all artificially produced and are called **transuranic elements**.

Coordination compounds

Transition metals possess a characteristic property of formation of metal complexes or metal coordination compounds. A coordination compound contains a central metal atoms/ion, surrounded by number of charged ions or neutral molecules called **ligands**.

Ligands are Lewis bases having atleast one lone pair of electrons. Ligands may be

- (i) anionic or negative, e.g., Cl^- , OH^- , CO_3^{2-} , etc.
- (ii) neutral $:\text{NH}_3$, $\text{H}_2\ddot{\text{O}}:$, $\text{H}_2\ddot{\text{N}}-\text{CH}_2-\text{CH}_2-\ddot{\text{N}}\text{H}_2$ etc.
- (iii) cationic or positive, e.g., NO_2^+ , NO^+

Ligands may be

- (i) monodentate having only one donor atom like NH_3 , Cl^- , CH_3COO^- , etc
- (ii) didentate which can donate two lone pair of electrons from two different donor atoms simultaneously e.g., $\text{H}_2\ddot{\text{N}}-\text{CH}_2-\text{CH}_2-\ddot{\text{N}}\text{H}_2$, $\text{C}_2\text{O}_4^{2-}$, etc
- (iii) **polydentate** having more than two donor atoms which can donate the lone pair of electron simultaneously to the metal atom, e.g, EDTA. The number of ligands which are directly bonded to central atom/ion in a complex is known as **coordination number**. The coordination number of the metal ion depends on change on the metal ions, charge on the ligand, relative sizes of ligand and metal ion, etc. Coordination number determines the geometry of a complex.

If the coordination number = 6, the geometry is octahedral and if the coordination number is equal to 4, the geometry is either tetrahedral or square planar.

If the complex is attached to only one kind of ligands then complex is called homoleptic complex $[\text{Fe}(\text{CN})_6]^{4-}$ and if more than one type of ligands present, then the complex is called heteroleptic complex $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$.

IUPAC nomenclature system is used to name the complexes. Cation complex is written first while the name of anionic complex is mentioned at the end in its nomenclature. The ligands are named first using a prefix di, tri, tetra, etc, to indicates the number of ligands present followed by name of the metal along with its oxidation state in Roman numerals.

The complex having the ring structure is called **chelate**, get attached to the central atom by two or more of its donor atoms.

The coordination compounds show two different type of isomerism.

1. Structural isomerism. This is further divided into

(i) linkage	(ii) ionisation
(iii) coordination	(iv) hydration isomerism
2. Stereoisomerism. This is further divided into geometrical isomerism and optical isomerism. The geometrical isomerism is due to different spatial arrangements of groups around to central metal atoms, results in cis and trans isomerism Tetrahedral complex, however do not show geometrical isomerism. Octahedral complexes of the type MA_6 , MA_5B , MAB_5 do not show geometrical isomerism. In MA_4B_2 exhibits geometrical isomerism cis isomer when ligands B occupy adjacent positions and trans isomer when ligands B are opposite to each other. In MA_3B_3 type complexes due to similar ligands in facial and meridional positions exhibit the geometrical isomerism. The complex of the type MA'_2B_2 where A' is a didentate ligand also exhibit cis and trans isomerism.

The complexes, where molecules are asymmetric, exhibit optical isomerism. Generally, optical isomerism, is not common in tetrahedral complexes as well as in square planar complexes. In square planar complexes there is axis of symmetry, hence they are optically inactive. The optical isomerism is more common in six coordinate octahedral complexes. However, d and l form are not resolvable. When the octahedral complex contains one or more didentate ligands, then it is possible to resolve it into its optically active form. The complexes MA'_2B_2 exhibits with geometrical as well as optical isomerism MA'_3 only exhibits optical isomerism.

There are numbers of theories which explain the nature of bonding as well as various properties of coordination compounds. According to Werner's theory, the metallic element possess primary and secondary valencies. The primary valencies are ionisable, variable and satisfied by anions.

The secondary valencies are fixed, determines the coordination number of metal and are satisfied by the ligands.

The **valence bond** theory helps to predict the shape of the complexes and their magnetic properties. The complexes having unpaired electron are paramagnetic and those having all electron paired are diamagnetic. The metal using $(n-1)d$ orbitals in bonding are called **inner orbital complexes** and complexes in which the metal is using all orbital from the outer shell in bonding are called outer orbital complexes.

The colour of the complexes can be explained on the basis of **crystal field theory** in which the ligands are considered as point charges and there exists an electrostatic force of attraction between the metal and the ligand. In the presence of ligand octahedral or tetrahedral field, d-orbitals split into two sets t_{2g} and e_g orbitals. The colour is due to the excitation of electron from one d-orbital to another d-orbital. This is called d-d transition. The energy of the incoming photon is equal to the crystal field splitting of d-d orbitals. From the absorption at a particular wavelength it is easy to calculate crystal field splitting. The concept of back bonding is used in metal carbonyls.

The stability of coordination compounds in solution is determined by knowing the value of stability constant. Higher the value of the stability constant, more the stability of coordination compound.

The factors affecting the stability of complexes are

- (i) charge density on central metal ion
- (ii) nature of the ligands (weak field ligands or strong field ligands)

According to Sidgwick's concept, the ligands donate electron pair(s) to the central metal ion and form a number of coordinate bonds. The **effective atomic number** (EAN) is the total number of electrons around the central metal ion in a complex. It is calculated as sum of the electron on the metal ion and the number of electrons donated by the ligands.

$$\text{EAN} = Z - X + Y$$

Z = atomic number of metal

X = number of electrons lost while forming metal ion

Y = number of electrons donated by ligands.

The coordination compounds have variety of applications in

- (i) Analytical chemistry
- (ii) Qualitative analysis
- (iii) Metallurgy
- (iv) Biological systems
- (v) Medicine
- (vi) Catalysis