GOVERNMENT OF TAMIL NADU

HIGHER SECONDARY SECOND YEAR

CHEMISTRY

VOLUME - I

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Department of School Education

Untouchability is Inhuman and a Crime

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	Scope of Chemistry	Awareness about higher education avenues in the field of Chemistry	
	Learning objectives	Describe the specific competency / performance capability acquired by the learner	
	Do you know	Additional information provided to relate the content to day-to-day life / development in the field	DO YOU KNOW?
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RESEARCH AREAS AND WEBSITES ARE SUMMARIZED BELOW.

INSTITUTE	RESEARCH AREAS	WEBSITE
Indian institute of STcience (IISC) *Bangalore, Karnataka*	❖ Peptides and peptidomimetics: Sugar amino acids ❖ Delivery of therapeutic oligonucleotides ❖ Carbohydrate-protein interactions ❖ Functional soft and hybrid materials ❖ Studies of dendrimers and liquid crystals ❖ Inorganicand organic semiconductors	www.iisc.ac.in
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Central Electrochemical Research Institute (CECRI) *Karaikudi, Tamil Nadu.*	❖ Li Batteries ❖ Corrosion ❖ Bio-Sensors ❖ Materials Electrochemistry ❖ Electro catalysis and Fuel Cells	www.cecri.res.in

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LIST OF ENTRANCE EXAMINATIONS AFTER HSC

NAME OF THE EXAM	MODE OF SELECTION	COURSE	WEBSITE
NEET (National Eligibility cum Entrance test	Written test	MBBS., BDS.,	www.cbscneet.nic.in
AIIMS (All India Institute of Medical Sciences)	Written test	MBBS.,	www.aiimsexams.org
JIPMER (Jawaharlal Institute Of Postgraduate Medical Education & Research)	Computer based test	MBBS.,	www.jipmer.edu.in
AFMC (Armed Forces Medical College Entrance Exam	Written test	M.B.B.S., (Should Serve 7 Years in Armed Forces)	www.afmc.nic.in
IIT – JEE (IIT- Joint Entrance Exam)	Written test	B.E., B.Tech., B.Arch.,	www.jeemain.nic.in
CUCET (Central Universities Common Entrance Test)	Written test	Integrated M.Tech., B.Tech., Integrated B.Sc., B.Ed., Integrated M.Sc., Integrated M.A., B.Des., (craft and design)	www.cucet.co.in
NISER (National Institute of Science Education and Research	Written test	Integrated M Sc., (Biology, Chemistry, Mathematics and Physics)	www.niser.ac.in
IISC (Indian Institute of Science Bangalore)	Written test	B.Sc., (4 years)	www.iisc.ernet.in

NAME OF THE EXAM	MODE OF SELECTION	COURSE	WEBSITE
IISER (Indian Institutes of Science Education and Research)	Written test	5-year BS-MS dual degree (Biology, Chemistry, Mathematics and Physics) **IISER Kolkata offers major in Earth Sciences	www.iiserpune.ac.in
NATA (National Aptitude Test in Architecture)	Computer Based Test	B.Arch.,	www.nata.in
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NCHMCT (National Council for Hotel Management Catering Technology Joint Entrance Exam)	Written test	B.Sc., (Hospitality and Hotel Administration)	www.nchm.nic.in
NDA and NA (National Defence Academy and Naval Academy)	Written Exam	3 Years Training for entry into ARMY/ NAVY/AIRFORCE	www.nda.nic.in
AIMNET (All India Merchant Navy Entrance Test)	Written Exam	B.Tech., Marine Engineering B.Sc., Nautical Science B.Tech.,Navel Architecture and Ship Building	www.aim.net.co.in

VARIOUS SCHOLARSHIP SCHEME OFFERED AFTER HSC

CENTRAL GOVERNMENT SCHOLARSHIPS OFFERED	OFFERED BY	APPLICATION PERIOD
Central Sector Scheme of Scholarship for College and University Students	Ministry of Human Resource Development, Government of India	July to October
Kishore Vaigyanik Protsahan Yojana (KVPY)	Department of Science and Technology (DST), Government of India	June to August
Inspire Scholarship	Department of Science and Technology (DST), Government of India	October to December
ONGC scholarship (Applicable for SC/ST Students)	Oil and Natural Gas Corporation Limited	January to March
National Fellowship and Scholarship for Higher Education of ST Students	Ministry of Tribal Affairs, Government of India	July to October
MOMA scholarship (applicable only for Minority students)	Ministry of Minority Affairs, Government of India	July to September
Scholarships for Top Class Education for Students with Disabilities	Ministry of Social Justice and Empowerment, Government of India	July to October
Saksham Scholarship (Applicable for Disable students)	AICTE	September to November
AICTE Pragati scholarship for Girls	AICTE	September to November

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- Once the camera detects the QR code, a url appears in the screen.Click the url and goto the content page.

UNIT 1

METALLURGY

Harold Johann Thomas Ellingham
(1897–1975)

Ellingham was a British physical chemist, best known for his Ellingham diagrams. Ellingham diagram summarizes a large amount of information about extractive metallurgy, and are useful in predicting the favourable thermodynamic conditions under which an ore will be reduced to its metal. Ellingham was able to compare the temperature stability of many different oxides. The phenomenon of reduction of metal oxides into free metal by carbon or carbon monoxide was known before Ellingham's time, but Ellingham demonstrated it in a scientific manner.

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Learning Objectives

After studying this unit, students will be able to

- describe various methods of concentrating ores
- explain various methods of extraction of crude metals
- apply thermodynamic principles to metallurgical processes
- predict the favourable conditions for the reduction process using Ellingham diagram
- describe the electrochemical principles of metallurgy
- apply the electrochemical principles in the extraction of metals
- explain the electrode reactions in electrolytic refining.
- list the uses of Al, Zn, Fe, Cu and Au

INTRODUCTION

Metallurgy relate to the science and technology of metals. In nature, only a few metals occur in their native state, all other metals occur in a combined state as their oxides, sulphides, silicates etc... The extraction of pure metals from their natural sources, is linked to the history of human civilisation. Ancient people used the available materials in their environment which includes fire and metals, and they were limited to the metals available on the earth's surface. In the modern world, we use a wide range of metals in our daily life, which is the result of the development of metallurgical knowledge over thousands of years. Our need for the materials with specific properties have led to production of many metal alloys. It is essential to design an eco-friendly metallurgical process that would minimize waste, maximize energy efficiency. Such advances in metallurgy is vital for the economic and technical progress in the current era. In this unit we will study the various steps involved in the extraction of metals and the chemical principles behind these processes.

1.1 Occurrence of metals

In general, pure metals are shiny and malleable, however, most of them are found in nature as compounds with different properties. Metals having least chemical reactivity such as copper, silver, gold and platinum occur in significant amounts as native elements. Reactive metals such as alkali metals usually occurs in their combined state and are extracted using suitable metallurgical process.

1.1.1 Mineral and ore

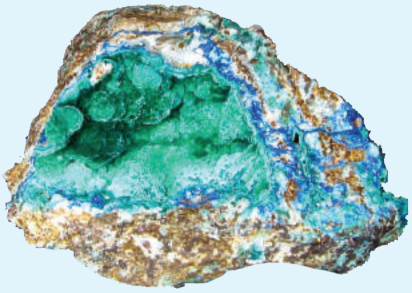
A naturally occurring substance obtained by mining which contains the metal in free state or in the form of compounds like oxides, sulphides etc... is called a **mineral**. In most of the minerals, the metal of interest is present only in small amounts and some of them contains a reasonable percentage of metal. For example iron is present in around 800 minerals. However, some of them such as hematite magnetite etc., containing high percentage of iron are commonly used for the extraction of iron. Such minerals that contains a high percentage of metal, from which it can be extracted conveniently and economically are called **ores**. Hence all ores are minerals but all minerals are not ores. Let us consider another example, bauxite and china clay ($Al_2O_3.SiO_2.2H_2O$). Both are minerals of aluminium. However, aluminium can be commercially extracted from bauxite while extraction from china clay is not a profitable one. Hence the mineral, bauxite is an ore of aluminium while china clay is not.

The extraction of a metal of interest from its ore consists of the following metallurgical processes.

(i) concentration of the ore

(ii) extraction of crude metal

(iii) refining of crude metal



Malachite – copper mineral

Table 1.1 List of some metals and their common ores with their chemical formula

Metal	Ore	Composition	Metal	Ore	Composition
Aluminum	Bauxite	$Al_2O_3.nH_2O$	Zinc	Zinc blende or Sphalerite	ZnS
	Diaspore	$Al_2O_3.H_2O$		Calamine	$ZnCO_3$
	Kaolinite	$Al_2Si_2O_5(OH)_4$		Zincite	ZnO
Iron	Haematite	Fe_2O_3	Lead	Galena	PbS
	Magnetite	Fe_3O_4		Anglesite	$PbSO_4$
	Siderite	$FeCO_3$		Cerrusite	$PbCO_3$
	Iron pyrite	FeS_2	Tin	Cassiterite (Tin stone)	SnO_2
	Limonite	$Fe_2O_3.3H_2O$	Silver	Silver glance (Argentite)	Ag_2S
Copper	Copper pyrite	$CuFeS_2$		Pyrargyrite (Ruby silver)	Ag_3SbS_3
	Copper glance	Cu_2S		Chlorargyrite (Horn Silver)	$AgCl$
	Cuprite	Cu_2O		Stefinite	Ag_2SbS_4
	Malachite	$CuCO_3.Cu(OH)_2$		Prousitite	Ag_2AsS_3
	Azurite	$2CuCO_3.Cu(OH)_2$			

1.2 Concentration of ores

Generally, the ores are associated with nonmetallic impurities, rocky materials and siliceous matter which are collectively known as gangue. The preliminary step in metallurgical process is removal of these impurities. This removal process is known as concentration of ore. It increases the concentration of the metal of interest or its compound in the ore. Several methods are available for this process and the choice of method will depend on the nature of the ore, type of impurity and environmental factors. Some of the common methods of ore concentration are discussed below.

1.2.1 Gravity separation or Hydraulic wash

In this method, the ore having high specific gravity is separated from the gangue that has low specific gravity by simply washing with running water. Ore is crushed to a finely powdered form and treated with rapidly flowing current of water. During this process the lighter gangue particles are washed away by the running water. This method is generally applied to concentrate the native ore such as gold and oxide ores such as haematite (Fe_2O_3), tin stone (SnO_2) etc.

1.2.2 Froth flotation

This method is commonly used to concentrate sulphide ores such as galena (PbS), zinc blende (ZnS) etc... In this method, the metallic ore particles which are preferentially wetted by oil can be separated from gangue.

In this method, the crushed ore is suspended in water and mixed with frothing agent such as pine oil, eucalyptus oil etc. A small quantity of sodium ethyl xanthate which acts as a collector is also added. A froth is generated by blowing air through this mixture. The collector molecules attach to the ore particle and make them water repellent. As a result, ore particles, wetted by the oil, rise to the surface along with the froth. The froth is skimmed off and dried to recover the concentrated ore. The gangue particles that are preferentially wetted by water settle at the bottom.

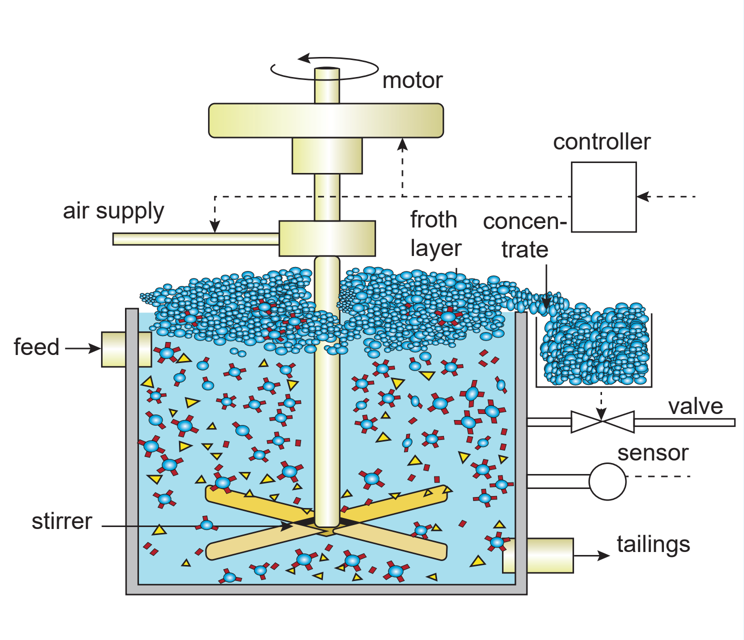


Figure 1.1 Froth Flotation

When a sulphide ore of a metal of interest contains other metal sulphides as impurities, depressing agents such as sodium cyanide, sodium carbonate etc are used to selectively prevent other metal sulphides from coming to the froth. For example, when impurities such as ZnS is present in galena (PbS), sodium cyanide (NaCN) is added to depresses the flotation property of ZnS by forming a layer of zinc complex $Na_2[Zn(CN)_4]$ on the surface of zinc sulphide.

1.2.3 Leaching

This method is based on the solubility of the ore in a suitable solvent and the reactions in aqueous solution. In this method, the crushed ore is allowed to dissolve in a suitable solvent, the metal present in the ore is converted to its soluble salt or complex while the gangue remains insoluble. The following examples illustrate the leaching processes.

Cyanide leaching

Let us consider the concentration of gold ore as an example. The crushed ore of gold is leached with aerated dilute solution of sodium cyanide. Gold is converted into a soluble cyanide complex. The gangue, aluminosilicate remains insoluble.

$$4Au\ (s) + 8CN^-\ (aq) + O_2\ (g) + 2H_2O\ (l) \longrightarrow 4[Au(CN)_2]^-\ (aq) + 4OH^-(aq)$$

Recovery of metal of interest from the complex by reduction:

Gold can be recovered by reacting the deoxygenated leached solution with zinc. In this process the gold is reduced to its elemental state (zero oxidation sate) and the process is called **cementation**.

$$Zn\ (s) + 2[Au(CN)_2]^-\ (aq) \longrightarrow [Zn(CN)_4]_2^-(aq) + 2Au\ (s)$$

Ammonia leaching

When a crushed ore containing nickel, copper and cobalt is treated with aqueous ammonia under suitable pressure, ammonia selectively leaches these metals by forming their soluble complexes viz. $[Ni(NH_3)_6]^{2+}$, $[Cu(NH_3)_4]^{2+}$, and $[Co(NH_3)_5H_2O]^{3+}$ respectively from the ore leaving behind the gangue, iron(III) oxides/hydroxides and aluminosilicate.

Alkali leaching

In this method, the ore is treated with aqueous alkali to form a soluble complex. For example, bauxite, an important ore of aluminum is heated with a solution of sodium hydroxde or sodium carbonate in the temperature range 470 - 520 K at 35 atm to form soluble sodium meta-aluminate leaving behind the impurities, iron oxide and titanium oxide.

$$Al_2O_3\ (s) + 2NaOH\ (aq) + 3H_2O\ (l) \longrightarrow 2Na[Al(OH)_4]\ (aq)$$

The hot solution is decanted, cooled, and diluted. This solution is neutralised by passing CO_2 gas, to the form hydrated Al_2O_3 precipitate.

$$2Na[Al(OH)_4]\ (aq) + CO_2\ (g) \longrightarrow Al_2O_3.xH_2O\ (s) + 2NaHCO_3\ (aq)$$

The precipitate is filtered off and heated around 1670 K to get pure alumina $Al_2O_{3.}$

Acid leaching

Leaching of sulphide ores such as ZnS, PbS etc., can be done by treating them with hot aqueous sulphuric acid.

$$2ZnS\ (s) + 2H_2SO_4\ (aq) + O_2(g) \longrightarrow 2ZnSO_4\ (aq) + 2S\ (s) + H_2O$$

In this process the insoluble sulphide is converted into soluble sulphate and elemental sulphur.

Evaluate yourself 1

1. Write the equation for the extraction of silver by leaching with sodium cyanide and show that the leaching process is a redox reaction.

1.2.4 Magnetic separation

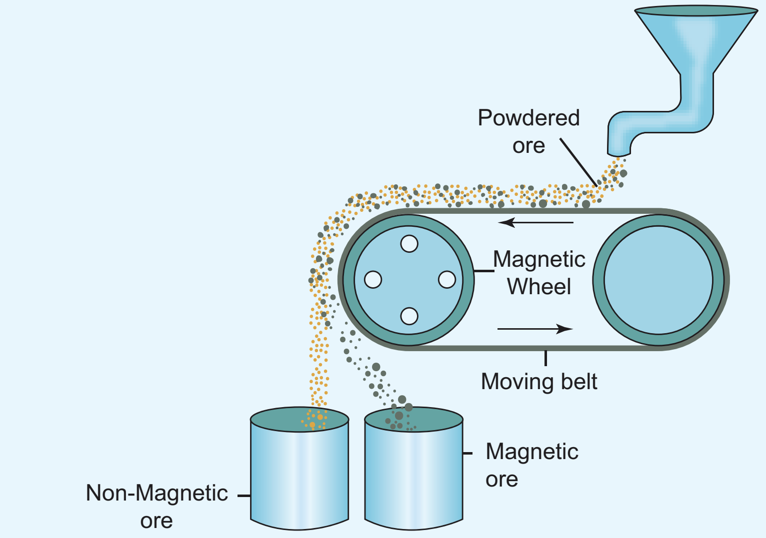


Figure 1.2 Magnetic separation

This method is applicable to ferromagnetic ores and it is based on the difference in the magnetic properties of the ore and the impurities. For example tin stone can be separated from the wolframite impurities which is magnetic. Similarly, ores such as chromite, pyrolusite having magnetic property can be removed from the non magnetic siliceous impurities. The crushed ore is poured on to an electromagnetic separator consisting of a belt moving over two rollers of which one is magnetic. The magnetic part of the ore is attracted towards the magnet and falls as a heap close to the magnetic region while the nonmagnetic part falls away from it as shown in the figure 1.2.

1.3 Extraction of crude metal

The extraction of crude metals from the concentrated ores is carried out in two steps namely, (i) conversion of the ore into oxides of the metal of interest and (ii) reduction of the metal oxides to elemental metals. In the concentrated ore, the metal exists in positive oxidation state and hence it is to be reduced to its elemental state. We can infer from the principles of thermodynamics, that the reduction of oxide is easier when compared to reduction of other compounds of metal and hence, before reduction, the ore is first converted into the oxide of metal of interest.

Let us discuss some of the common methods used to convert the concentrated ore into the oxides of the metal of interest.

1.3.1 Conversion of ores into oxides

Roasting

Roasting is the method, usually applied for the conversion of sulphide ores into their oxides. In this method, the concentrated ore is oxidised by heating it with excess of oxygen in a suitable furnace below the melting point of the metal.

$$2PbS + 3O_2 \xrightarrow{\Delta} 2PbO + 2SO_2\uparrow$$

$$2ZnS + 3O_2 \xrightarrow{\Delta} 2ZnO + 2SO_2\uparrow$$

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2\uparrow$$

Roasting also removes impurities such as arsenic, sulphur, phosphorous by converting them into their volatile oxides.

For example

$$4As + 3O_2 \longrightarrow 2As_2O_3\uparrow$$

$$S_8 + 8O_2 \longrightarrow 8SO_2\uparrow$$

$$P_4 + 5O_2 \longrightarrow P_4O_{10}\uparrow$$

DO YOU KNOW?

The sulphur dioxide produced during roasting process is harmful to the environment. In modern metallurgical factories, this by product is trapped and converted into sulphuric acid to avoid air pollution.

Calcination

Calcination is the process in which the concentrated ore is strongly heated in the absence of air. During this process, the water of crystallisation present in the hydrated oxide escapes as moisture. Any organic matter (if present) also get expelled leaving behind a porous ore. This method can also be carried out with a limited supply of air.

For examples,

During calcination of carbonate ore, carbon dioxide is expelled

$$PbCO_3 \xrightarrow{\Delta} PbO + CO_2\uparrow$$

$$CaCO_3 \longrightarrow CaO + CO_2\uparrow$$

$$ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2\uparrow$$

$$MgCO_3.CaCO_3 \xrightarrow{\Delta} MgO + CaO + 2CO_2\uparrow$$

During calcination of hydrated ore, the water of hydration is expelled as vapour

$$Fe_2O_3.3H_2O \xrightarrow{\Delta} Fe_2O_3\,(s) + 3H_2O\,(g)\uparrow$$

$$Al_2O_3.2H_2O \xrightarrow{\Delta} Al_2O_3\,(s) + 2H_2O\,(g)\uparrow$$

Evaluate yourself 2

2. Magnesite (Magnesium carbonate) is calcined to obtain magnesia, which is used to make refractory bricks. Write the decomposition reaction.

1.3.2 Reduction of metal oxides

Metal oxide can be reduced to crude metal by using a suitable reducing agent like carbon, carbon monoxide, hydrogen, aluminium and other reactive metals such as sodium etc...The choice of reducing agent depends on the nature of the metal. For example, carbon cannot be used as a reducing agent for the reactive metals such as sodium, potassium, aluminium etc...Similarly CO cannot be used to reduce oxides such as ZnO, Al_2O_3. Later in this,we study selection of suitable reducing agents by applying Ellingham diagram.

Smelting

In this method, a flux (a chemical substance that forms an easily fusible slag with gangue) and a reducing agent such as carbon, carbon monoxide (or) aluminium is added to the concentrated ore and the mixture is melted by heating at an elevated temperature (above the melting point of the metal) in a smelting furnace. For example the oxide of iron can be reduced by carbon monoxide as follows.

$$Fe_2O_3\,(s) + 3CO\,(g) \longrightarrow 2Fe\,(s) + 3CO_2\,(g)\uparrow$$

In this extraction, a basic flux, limestone (CaO) is used. Since the silica gangue present in the ore is acidic in nature, the limestone combines with it to form calcium silicate (slag).

$$\underset{\text{Flux}}{CaO\,(s)} + \underset{\text{Gangue}}{SiO_2\,(s)} \longrightarrow \underset{\text{Slag}}{CaSiO_3\,(s)}$$

In the extraction of copper from copper pyrites, the concentrated ore is heated in a reverberatory furnace after mixing with silica, an acidic flux. The ferrous oxide formed due to melting is basic in nature and it combines with silica to form ferrous silicate (slag). The remaining metal sulphides Cu_2S and FeS are mutually soluble and form a copper matte.

$$2CuFeS_2\,(s) + O_2\,(g) \longrightarrow 2FeS\,(l) + Cu_2S\,(l) + SO_2\,(g)$$

$$2FeS\,(l) + 3O_2\,(g) \longrightarrow 2FeO\,(l) + 2SO_2\,(g)$$

$$\underset{\text{Flux}}{FeO\,(s)} + \underset{\text{Gangue}}{SiO_2\,(s)} \longrightarrow \underset{\text{Slag}}{FeSiO_3\,(s)}$$

The matte is separated from the slag and fed to the converting furnace. During conversion, the FeS present in the matte is first oxidised to FeO. This is removed by slag formation with silica. The remaining copper sulphide is further oxidised to its oxide which is subsequently converted to metallic copper as shown below.

$$2Cu_2S\ (l,s) + 3O_2\ (g) \longrightarrow 2Cu_2O\ (l,s) + 2SO_2\ (g)$$

$$2Cu_2O\ (l) + Cu_2S\ (l) \longrightarrow 6Cu\ (l) + SO_2\ (g)$$

The metallic copper is solidified and it has blistered appearance due to evolution of SO_2 gas formed in this process. This copper is called blistered copper.

Reduction by carbon:

In this method the oxide ore of the metal is mixed with coal (coke) and heated strongly in a furnace (usually in a blast furnace). This process can be applied to the metals which do not form carbides with carbon at the reduction temperature.

Examples:

$$ZnO\ (s) + C\ (s) \longrightarrow Zn\ (s) + CO\ (g)\uparrow$$

$$Mn_3O_4\ (s) + 4C\ (s) \longrightarrow 3Mn\ (s) + 4CO\ (g)\uparrow$$

$$Cr_2O_3\ (s) + 3C\ (s) \longrightarrow 2Cr\ (s) + 3CO\ (g)\uparrow$$

Reduction by hydrogen:

This method can be applied to the oxides of the metals (Fe, Pb, Cu) having less electropositive character than hydrogen.

$$Ag_2O\ (s) + H_2\ (g) \longrightarrow 2Ag\ (s) + H_2O\ (l)$$

$$Fe_3O_4\ (s) + 4H_2\ (g) \longrightarrow 3Fe\ (s) + 4H_2O\ (l)$$

Nickel oxide can be reduced to nickel by using a mixture of hydrogen and carbon monoxide (water gas)

$$2NiO\ (s) + CO\ (g) + H_2\ (g) \longrightarrow 2Ni\ (s) + CO_2\ (g) + H_2O\ (l)$$

Reduction by metal:

Metallic oxides such as Cr_2O_3 can be reduced by an aluminothermite process. In this process, the metal oxide is mixed with aluminium powder and placed in a fire clay crucible. To initiate the reduction process, an ignition mixture (usually magneisium and barium peroxide) is used.

$$BaO_2 + Mg \longrightarrow BaO + MgO$$

During the above reaction a large amount of heat is evolved (temperature up to 2400°C, is generated and the reaction enthalpy is : 852 kJ mol^{-1}) which facilitates the reduction of Cr_2O_3 by aluminium power.

$$Cr_2O_3 + 2Al \xrightarrow{\Delta} 2Cr + Al_2O_3$$

Active metals such as sodium, potassium and calcium can also be used to reduce the metal oxide

$$B_2O_3 + 6Na \longrightarrow 2B + 3Na_2O$$

$$Rb_2O_3 + 3Mg \longrightarrow 2Rb + 3MgO$$

$$TiO_2 + 2Mg \longrightarrow Ti + 2MgO$$

$$ThO_2 + 2Ca \xrightarrow{1250\ K} Th + 3CaO$$

Auto-reduction:

Simple roasting of some of the ores give the crude metal. In such cases, the use of reducing agents is not necessary. For example, mercury is obtained by roasting of its ore cinnabar (HgS)

$$HgS\ (s) + O_2\ (g) \longrightarrow Hg\ (l) + SO_2 \uparrow$$

1.4 Thermodynamic principle of metallurgy

As we discussed, the extraction of metals from their oxides can be carried out by using different reducing agents. For example, consider the reduction of a metal oxide M_xO_y.

$$\tfrac{2}{y}M_xO_y\ (s) \longrightarrow \tfrac{2x}{y}M\ (s) + O_2\ (g)\ \text{------}\ (1)$$

The above reduction may be carried out with carbon. In this case, the reducing agent carbon may be oxidised to either CO or CO_2.

$$C + O_2 \longrightarrow CO_2\ (g)\ \text{------}\ (2)$$

$$2C + O_2 \longrightarrow 2CO\ (g)\ \text{------}\ (3)$$

If carbon monoxide is used as a reducing agent, it is oxidised to CO_2 as follows,

$$2CO + O_2 \longrightarrow 2CO_2\ (g)\ \text{------}\ (4)$$

A suitable reducing agent is selected based on the thermodynamic considerations. We know that for a spontaneous reaction, the change in free energy (ΔG) should be negative. Therefore, thermodynamically, the reduction of metal oxide [equation (1)] with a given reducing agent [Equation (2), (3) or (4)] can occur if the free energy change for the coupled reaction. [Equations (1) & (2), (1) & (3) or (1) & (4)] is negative. Hence, the reducing agent is selected in such a way that it provides a large negative ΔG value for the coupled reaction.

1.4.1 Ellingham diagram

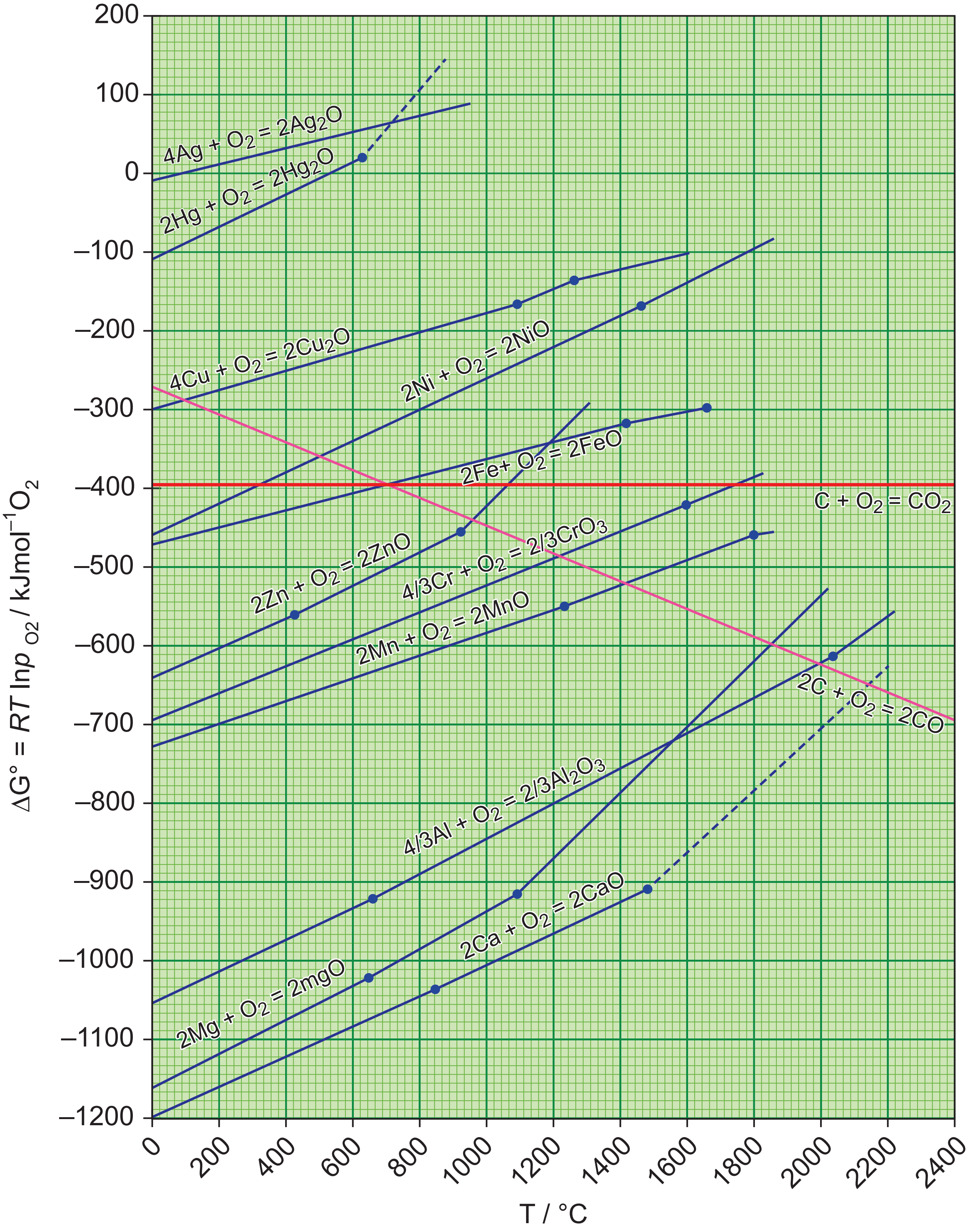


Figure 1.4 Ellingham diagram

The change in Gibbs free energy (ΔG) for a reaction is given by the expression.

$$\Delta G = \Delta H - T\Delta S \text{ ------ } (1)$$

where, ΔH is the enthalpy change , T the temperature in kelvin and ΔS the entropy change. For an equilibrium process, ΔG^0 can be calculated using the equilibrium constant by the following expression

$$\Delta G^0 = -RT \ln K_p$$

Harold Ellingham used the above relationship to calculate the ΔG^0 values at various temperatures for the reduction of metal oxides by treating the reduction as an equilibrium process.

He has drawn a plot by considering the temperature in the x-axis and the standard free energy change for the formation of metal oxide in y-axis. The resultant plot is a straight line with ΔS as slope and ΔH as y-intercept. The graphical representation of variation of the standard Gibbs free energy of reaction for the formation of various metal oxides with temperature is called Ellingham diagram

Observations from the Ellingham diagram.

1. For most of the metal oxide formation, the slope is positive. It can be explained as follows. Oxygen gas is consumed during the formation of metal oxides which results in the decrease in randomness. Hence, ΔS becomes negative and it makes the term, TΔS positive in the straight line equation.
2. The graph for the formation of carbon monoxide is a straight line with negative slope. In this case ΔS is positive as 2 moles of CO gas is formed by the consumption of one mole of oxygen gas. It indicates that CO is more stable at higher temperature.
3. As the temperature increases, generally ΔG value for the formation of the metal oxide become less negative and becomes zero at a particular temperature. Below this temperature, ΔG is negative and the oxide is stable and above this temperature ΔG is positive. This general trend suggests that metal oxides become less stable at higher temperature and their decomposition becomes easier.
4. There is a sudden change in the slope at a particular temperature for some metal oxides like MgO, HgO. This is due to the phase transition (melting or evaporation).

1.4.2 Applications of the Ellingham diagram:

Ellingham diagram helps us to select a suitable reducing agent and appropriate temperature range for reduction. The reduction of a metal oxide to its metal can be considered as a competition between the element used for reduction and the metal to combine with oxygen. If the metal oxide is more stable, then oxygen remains with the metal and if the oxide of element used for reduction is more stable, then the oxygen from the metal oxide combines with elements used for the reduction. From the Ellingham diagram, we can infer the relative stability of different metal oxides at a given temperature.

1. Ellingham diagram for the formation of Ag_2O and HgO is at upper part of the diagram and their decomposition temperatures are 600 and 700 K respectively. It indicates that these oxides are unstable at moderate temperatures and will decompose on heating even in the absence of a reducing agent.
2. Ellingham diagram is used to predict thermodynamic feasibility of reduction of oxides of one metal by another metal. Any metal can reduce the oxides of other metals that are located above it in the diagram. For example, in the Ellignham diagram, for the formation of chromium oxide lies above that of the aluminium, meaning that Al_2O_3 is more stable than Cr_2O_3. Hence aluminium can be used as a reducing agent for the reduction of chromic oxide. However, it cannot be used to reduce the oxides of magnesium and calcium which occupy lower position than aluminium oxide.
3. The carbon line cuts across the lines of many metal oxides and hence it can reduce all those metal oxides at sufficiently high temperature. Let us analyse the thermodynamically favourable conditions for the reduction of iron oxide by carbon. Ellingham diagram for the formation of FeO and CO intersects around 1000 K. Below this temperature the carbon line lies above the iron line which indicates that FeO is more stable than CO and hence at this temperature range, the reduction is not thermodynamically feasible. However, above 1000 K carbon line lies below the iron line and hence, we can use coke as reducing agent above this temperature. The following free energy calculation also confirm that the reduction is thermodynamically favoured.

From the Ellingham Diagram at 1500 K,

$$2Fe\ (s) + O_2\ (g) \longrightarrow 2FeO\ (g) \qquad \Delta G_1 = -350\ kJ\ mol^{-1}\ \text{------}\ (5)$$

$$2C\ (s) + O_2\ (g) \longrightarrow 2CO\ (g) \qquad \Delta G_2 = -480\ kJ\ mol^{-1}\ \text{------}\ (6)$$

Reverse the reaction (1)

$$2FeO\ (s) \longrightarrow 2Fe\ (s) + O_2\ (g) \quad -\Delta G_1 = +350\ kJ\ mol^{-1}\ \text{------}\ (5)$$

Now couple the reactions (2) and (3)

$$2FeO\ (s) + 2C \longrightarrow 2Fe\ (l,s) + 2CO\ (g) \qquad \Delta G_3 = -130\ kJ\ mol^{-1}\ \text{------}\ (8)$$

The standard free energy change for the reduction of one mole of FeO is, $\Delta G_3/2 = -65\ kJ\ mol^{-1}$

Limitations of Ellingham diagram

1. Ellingham diagram is constructed based only on thermodynamic considerations. It gives information about the thermodynamic feasibility of a reaction. It does not tell anything about the rate of the reaction. More over, it does not give any idea about the possibility of other reactions that might be taking place.
2. The interpretation of ΔG is based on the assumption that the reactants are in equilibrium with the products which is not always true.

Evaluate yourself 3

3. Using Ellingham diagram (fig 1.4) indicate the lowest temperature at which ZnO can be reduced to Zinc metal by carbon. Write the overall reduction reaction at this temperature.

1.5 Electrochemical principle of metallurgy

Similar to thermodynamic principles, electrochemical principles also find applications in metallurgical process. The reduction of oxides of active metals such as sodium, potassium etc., by carbon is thermodynamically not feasible. Such metals are extracted from their ores by using electrochemical methods. In this technique, the metal salts are taken in a fused form or in solution form. The metal ion present can be reduced by treating it with some suitable reducing agent or by electrolysis.

Gibbs free energy change for the electrolysis process is given by the following expression

$$\Delta G^\circ = -nFE^\circ$$

Where n is number of electrons involved in the reduction process, F is the Faraday and E^0 is the electrode potential of the redox couple.

If E^0 is positive then the ΔG is negative and the reduction is spontaneous and hence a redox reaction is planned in such a way that the e.m.f of the net redox reaction is positive. When a more reactive metal is added to the solution containing the relatively less reactive metal ions, the more reactive metal will go into the solution. For example,

$$Cu\,(s) + 2Ag^+\,(s) \longrightarrow Cu^{2+}\,(aq) + 2Ag\,(s)$$

$$Cu^{2+}\,(aq) + Zn\,(s) \longrightarrow Cu\,(s) + Zn^{2+}\,(aq)$$

1.5.1 Electrochemial extraction of aluminium - Hall-Herold process:

In this method, electrolysis is carried out in an iron tank lined with carbon which acts as a cathode. The carbon blocks immersed in the electrolyte act as a anode. A 20% solution of alumina, obtained from the bauxite ore is mixed with molten cyrolite and is taken in the electrolysis chamber. About 10% calcium chloride is also added to the solution. Here calcium chloride helps to lower the melting point of the mixture. The fused mixture is maintained at a temperature of above 1270 K. The chemical reactions involved in this process are as follows.

Ionisaiton of alumina $Al_2O_3 \longrightarrow 2Al^{3+} + 3O^{2-}$

Reaction at cathode $2Al^{3+}\,(melt) + 6e^- \longrightarrow 2Al\,(l)$

Reaction at anode $6O^{2-}\,(melt) \longrightarrow 3O_2 + 12e^-$

Since carbon acts as anode the following reaction also takes place on it.

$$C\ (s) + O^{2-}\ (melt) \longrightarrow CO + 2e^-$$

$$C\ (s) + 2O^{2-}\ (melt) \longrightarrow CO_2 + 4e^-$$

Due to the above two reactions, anodes are slowly consumed during the electrolysis. The pure aluminium is formed at the cathode and settles at the bottom. The net electrolysis reaction can be written as follows.

$$4Al^{3+}\ (melt) + 6O^{2-}\ (melt) + 3C\ (s) \longrightarrow 4Al\ (l) + 3CO_2\ (g)$$

Evaluate yourself 4

4. Metallic sodium is extracted by the electrolysis of brine (aq. NaCl). After electrolysis the electrolytic solution becomes basic in nature. Write the possible electrode reactions.

1.6 Refining process

Generally the metal extracted from its ore contains some impurities such as unreacted oxide ore, other metals, nonmetals etc...Removal of such impurities associated with the isolated crude metal is called refining process. In this section, let us discuss some of the common refining methods.

1.6.1 Distillation

This method is employed for low boiling volatile metals like zinc (boiling point 1180 K) and mercury (630 K). In this method, the impure metal is heated to evaporate and the vapours are condensed to get pure metal.

1.6.2 Liquation

This method, is employed to remove the impurities with high melting points from metals having relatively low melting points such as tin (Sb; mp= 904 K), lead (Pb; mp=600 K), mercury (Hg; mp=234 K), and bismuth (Bi; mp=545 K). In this process, the crude metal is heated to form fusible liquid and allowed to flow on a sloping surface. The impure metal is placed on sloping hearth of a reverberatory furnace and it is heated just above the melting point of the metal in the absence of air, the molten pure metal flows down and the impurities are left behind. The molten metal is collected and solidified.

1.6.3 Electrolytic refining:

The crude metal is refined by electrolysis. It is carried out in an electrolytic cell containing aqueous solution of the salts of the metal of interest. The rods of impure metal are used as anode and thin strips of pure metal are used as cathode. The metal of interest dissolves from the anode, pass into the solution while the same amount of metal ions from the solution will be deposited at the cathode. During electrolysis, the less electropositive impurities in the anode, settle down at the bottom and are removed as anode mud.

Let us understand this process by considering electrolytic refining of silver as an example.

Cathode : Pure silver

Anode : Impure silver rods

Electrolyte : Acidified aqueous solution of silver nitrate.

When a current is passed through the electrodes the following reactions will take place

Reaction at anode $Ag(s) \longrightarrow Ag^{+}(aq) + 1e^{-}$

Reaction at cathode $Ag^{+}(aq) + 1e^{-} \longrightarrow Ag(s)$

During electrolysis, at the anode the silver atoms lose electrons and enter the solution. The positively charged silver cations migrate towards the cathode and get discharged by gaining electrons and deposited on the cathode. Other metals such as copper, zinc etc.,can also be refined by this process in a similar manner.

1.6.4 Zone Refining

This method is based on the principles of fractional crystallisation. When an impure metal is melted and allowed to solidify, the impurities will prefer to be in the molten region. i.e. impurities are more soluble in the melt than in the solid state metal. In this process the impure metal is taken in the form of a rod. One end of the rod is heated using a mobile induction heater which results in melting of the metal on that portion of the rod. When the heater is slowly moved to the other end the pure metal crystallises while the impurities will move on to the adjacent molten zone formed due to the movement of the heater. As the heater moves further away, the molten zone containing impurities also moves along with it. The process is repeated several times by moving the heater in the same direction again and again to achieve the desired purity level. This process is carried out in an inert gas atmosphere to prevent the oxidation of metals . Elements such as germanium (Ge), silicon (Si) and galium (Ga) that are used as semiconductor are refined using this process.

1.6.5 Vapour phase method

In this method, the metal is treated with a suitable reagent which can form a volatile compound with the metal. Then the volatile compound is decomposed to give the pure metal. We can understand this method by considering the following process.

Mond process for refining nickel:

The impure nickel is heated in a stream of carbon monoxide at around 350 K. The nickel reacts with the CO to form a highly volatile nickel tetracarbonyl. The solid impurities are left behind.

$$Ni(s) + 4\,CO(g) \longrightarrow Ni(CO)_4(g)$$

On heating the nickel tetracarbonyl around 460 K, the complex decomposes to give pure metal.

$$Ni(CO)_4(g) \longrightarrow Ni(s) + 4\,CO(g)$$

Van-Arkel method for refining zirconium/titanium:

This method is based on the thermal decomposition of metal compounds which lead to the formation of pure metals. Titanium and zirconium can be purified using this method. For example, the impure titanium metal is heated in an evacuated vessel with iodine at a temperature of 550 K to form the volatile titanium tetra-iodide.(TiI_4). The impurities are left behind, as they do not react with iodine.

$$Ti\,(s) + 2I_2\,(s) \longrightarrow TiI_4\,(vapour)$$

The volatile titanium tetraiodide vapour is passed over a tungsten filament at a temperature aroud 1800 K. The titanium tetraiodide is decomposed and pure titanium is deposited on the filament. The iodine is reused.

$$TiI_4\,(vapour) \longrightarrow Ti\,(s) + 2I_2\,(s)$$

1.7 Application metals

1.7.1 Application of Al

Aluminium is the most abundant metal and is a good conductor of electricity and heat. It also resists corrosion. The following are some of its applications.

- Many heat exchangers/sinks and our day to day cooking vessels are made of aluminium.
- It is used as wraps (aluminium foils) and is used in packing materials for food items,
- Aluminium is not very strong, However , its alloys with copper, manganese, magnesium and silicon are light weight and strong and they are used in design of aeroplanes and other forms of transport.
- As Aluminium shows high resistance to corrosion, it is used in the design of chemical reactors, medical equipments,refrigeration units and gas pipelines.
- Aluminium is a good electrical conductor and cheap, hence used in electrical overhead electric cables with steel core for strength.

1.7.1 Application of Zn

- Metallic zinc is used in **galvanising** metals such as iron and steel structures to protect them from rusting and corrosion.
- Zinc is also used to produce die-castings in the automobile, electrical and hardware industries
- Zinc oxide is used in the manufacture of many products such as paints, rubber, cosmetics,

pharmaceuticals, plastics, inks, batteries, textiles and electrical equipment. Zinc sulphide is used in making luminous paints, fluorescent lights and x-ray screens.

- Brass an alloy of zinc is used in water valves and communication equipment as it is highly resistant to corrosion.

1.7.1 Application of Fe

- Iron is one of the most useful metals and its alloys are used everywhere including bridges, electricity pylons, bicycle chains, cutting tools and rifle barrels.
- Cast iron is used to make pipes, valves and pumps stoves etc...
- Magnets can be made from iron and its alloys and compounds.
- An important alloy of iron is stainless steel, and it is very resistant to corrosion. It is used in architecture, bearings, cutlery, surgical instruments and jewellery. Nickel steel is used for making cables, automobiles and aeroplane parts. Chrome steels are used for maufacturing cutting tools and curshing machines

1.7.1 Application of Cu

Copper is the first metal used by the human and extended use of its alloy bronze resulted in a new era,'Bronze age'

Copper is used for making coins and ornaments along with gold and other metals.

Copper and its alloys are used for making wires, water pipes and other electrical parts

1.7.1 Application of Au

- Gold, one of the expensive and precious metals. It is used for coinage, and has been used as standard for monetary systems in some countries.
- It is used extensively in jewellery in its alloy form with copper. It is also used in electroplating to cover other metals with a thin layer of gold which are used in watches, artificial limb joints, cheap jewellery, dental fillings and electrical connectors.
- Gold nanoparticles are also used for increasing the efficiency of solar cells and also used an catalysts.

DO YOU KNOW?

The Iron Pillar – Delhi:

The Iron pillar, also known as Ashoka Pillar, is 23 feet 8 inches high, 16 inches wide and weighs over 6000 kg.

The surprise comes in knowing its age, some 1600 years old,an iron column should have turned into a pile of dust long ago. Despite that, it has avoided corrosion for over the last 1600 years and stands as an evidence of the exquisite skills and knowledge of ancient Indians.

A protective film was created through a complicated combination of the presence of raw and unreduced iron in the pillar and cycles of the weather, which helped to create a thin, uniform layer of misawite on the pillar. Misawite is a compound of iron, oxygen and hydrogen which does not rust and gives corrosion resistance.

Summary

- Metallurgy relates to the science and technology of metals.
- A naturally occurring substance obtained by mining which contains the metal in free state or in the form of compounds like oxides, sulphides etc... is called a **mineral**.
- minerals that contains a high percentage of metal, from which it can be extracted conveniently and economically are called **ores**.
- The extraction of a metal of interest from its ore consists of the following metallurgical processes.
  (i) concentration of the ore
  (ii) extraction of crude metal
  (iii) refining of crude metal
- The extraction of crude metals from the concentrated ores is carried out in two steps namely, (i) conversion of the ore into oxides of the metal of interest and (ii) reduction of the metal oxides to elemental metals.
- The graphical representation of variation of the standard Gibbs free energy of reaction for the formation of various metal oxides with temperature is called Ellingham diagram
- Ellingham diagram helps us to select a suitable reducing agent and appropriate temperature range for reduction.

- Similar to thermodynamic principles, electrochemical principles also find applications in metallurgical process.
- If E^0 is positive then the ΔG is negative and the reduction is spontaneous and hence a redox reaction is planned in such a way that the e.m.f of the net redox reaction is positive. When a more reactive metal is added to the solution containing the relatively less reactive metal ions, the more reactive metal will go into the solution.
- Generally the metal extracted from its ore contains some impurities such as unreacted oxide ore, other metals, nonmetals etc...Removal of such impurities associated with the isolated crude metal is called refining process.

EVALUATION

FEKC9Z

Choose the correct answer:

1. Bauxite has the composition

   a) Al_2O_3 b) $Al_2O_3.nH_2O$ c) $Fe_2O_3.2H_2O$ d) None of these

2. Roasting of sulphide ore gives the gas (A).(A) is a colourless gas. Aqueous solution of (A) is acidic. The gas (A) is

   a) CO_2 b) SO_3 c) SO_2 d) H_2S

3. Which one of the following reaction represents calcinations?

   a) $2Zn + O_2 \longrightarrow 2ZnO$ b) $2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$

   c) $MgCO_3 \longrightarrow MgO + CO_2$ d) Both (a) and (c)

4. The metal oxide which cannot be reduced to metal by carbon is

   a) PbO b) Al_2O_3 c) ZnO d) FeO

5. Which of the metal is extracted by Hall-Heroult process?

   a) Al b) Ni c) Cu d) Zn

6. Which of the following statements, about the advantage of roasting of sulphide ore before reduction is not true?

   a) ΔG_f^0 of sulphide is greater than those for CS_2 and H_2S.

   b) ΔG_r^0 is negative for roasting of sulphide ore to oxide

   c) Roasting of the sulphide to its oxide is thermodynamically feasible.

   d) Carbon and hydrogen are suitable reducing agents for metal sulphides.

7. Match items in column - I with the items of column – II and assign the correct code.

Column-I		Column-II	
A	Cyanide process	(i)	Ultrapure Ge
B	Froth floatation process	(ii)	Dressing of ZnS
C	Electrolytic reduction	(iii)	Extraction of Al
D	Zone refining	(iv)	Extraction of Au
		(v)	Purification of Ni

	A	B	C	B
(a)	(i)	(ii)	(iii)	(iv)
(b)	(iii)	(iv)	(v)	(i)
(c)	(iv)	(ii)	(iii)	(i)
(d)	(ii)	(iii)	(i)	(v)

8. Wolframite ore is separated from tinstone by the process of

a) Smelting
b) Calcination
c) Roasting
d) Electromagnetic separation

9. Which one of the following is not feasible

a) $Zn(s) + Cu^{2+}(aq) \longrightarrow Cu(s) + Zn^{2+}(aq)$
b) $Cu(s) + Zn^{2+}(aq) \longrightarrow Zn(s) + Cu^{2+}(aq)$
c) $Cu(s) + 2Ag^{+}(aq) \longrightarrow 2Ag(s) + Cu^{2+}(aq)$
d) $Fe(s) + Cu^{2+}(aq) \longrightarrow Cu(s) + Fe^{2+}(aq)$

10. Electrochemical process is used to extract

a) Iron
b) Lead
c) Sodium
d) silver

11. Flux is a substance which is used to convert

a) Mineral into silicate
b) Infusible impurities to soluble impurities
c) Soluble impurities to infusible impurities
d) All of these

12. Which one of the following ores is best concentrated by froth – floatation method?

a) Magnetite
b) Haematite
c) Galena
d) Cassiterite

13. In the extraction of aluminium from alumina by electrolysis, cryolite is added to

a) Lower the melting point of alumina
b) Remove impurities from alumina
c) Decrease the electrical conductivity
d) Increase the rate of reduction

14. Zinc is obtained from ZnO by

a) Carbon reduction
b) Reduction using silver
c) Electrochemical process
d) Acid leaching

15. Cupellation is a process used for the refining of

a) Silver
b) Lead
c) Copper
d) iron

16. Extraction of gold and silver involves leaching with cyanide ion. silver is later recovered by (NEET-2017)

a) Distillation
b) Zone refining
c) Displacement with zinc
d) liquation

17. Considering Ellingham diagram, which of the following metals can be used to reduce alumina? (NEET-2018)

a) Fe
b) Cu
c) Mg
d) Zn

18. The following set of reactions are used in refining Zirconium

$$Zr\ (impure) + 2I_2 \xrightarrow{523\ K} ZrI_4$$

$$ZrI_4 \xrightarrow{1800K} Zr\ (pure) + 2I_2$$

This method is known as

a) Liquation
b) van Arkel process
c) Zone refining
d) Mond's process

19. Which of the following is used for concentrating ore in metallurgy?

a) Leaching
b) Roasting
c) Froth floatation
d) Both (a) and (c)

20. The incorrect statement among the following is

a) Nickel is refined by Mond's process

b) Titanium is refined by Van Arkel's process

c) Zinc blende is concentrated by froth floatation

d) In the metallurgy of gold, the metal is leached with dilute sodium chloride solution

21. In the electrolytic refining of copper, which one of the following is used as anode?

a) Pure copper
b) Impure copper
c) Carbon rod
d) Platinum electrode

22. Which of the following plot gives Ellingham diagram

a) ΔS Vs T
b) ΔG^0 Vs T
c) ΔG^0 Vs $\frac{1}{T}$
d) ΔG^0 Vs T^2

23. In the Ellingham diagram, for the formation of carbon monoxide

a) $\left(\frac{\Delta S^0}{\Delta T}\right)$ is negative
b) $\left(\frac{\Delta G^0}{\Delta T}\right)$ is positive
c) $\left(\frac{\Delta G^0}{\Delta T}\right)$ is negative
d) initially $\left(\frac{\Delta T}{\Delta G^0}\right)$ is positive, after 700^0C, $\left(\frac{\Delta G^0}{\Delta T}\right)$ is negative

24. Which of the following reduction is not thermodynamically feasible?

a) $Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr$
b) $Al_2O_3 + 2Cr \longrightarrow Cr_2O_3 + 2Al$
c) $3TiO_2 + 4Al \longrightarrow 2\,Al_2O_3 + 3Ti$
d) none of these

25. Which of the following is not true with respect to Ellingham diagram?

a) Free energy changes follow a straight line. Deviation occurs when there is a phase change.
b) The graph for the formation of CO_2 is a straight line almost parallel to free energy axis.
c) Negative slope of CO shows that it becomes more stable with increase in temperature.
d) Positive slope of metal oxides shows that their stabilities decrease with increase in temperature.

Answer the following questions:

1. What are the differences between minerals and ores?
2. What are the various steps involved in extraction of pure metals from their ores?
3. What is the role of Limestone in the extraction of Iron from its oxide Fe_2O_3?
4. Which type of ores can be concentrated by froth floatation method? Give two examples for such ores.
5. Out of coke and CO, which is better reducing agent for the reduction of ZnO? Why?
6. Describe a method for refining nickel.
7. Explain zone refining process with an example using the Ellingham diagram given below.

8. (A) Predict the conditions under which

   (i) Aluminium might be expected to reduce magnesia.

   (ii) Magnesium could reduce alumina.

   (B) Carbon monoxide is more effective reducing agent than carbon below 983K but, above this temperature, the reverse is true –Explain.

   (c) it is possible to reduce Fe_2O_3 by coke at a temperature around 1200K

9. Give the uses of zinc.

10. Explain the electrometallurgy of aluminium.

11. Explain the following terms with suitable examples.

    (i) Gangue (ii) slag

12. Give the basic requirement for vapour phase refining.

13. Describe the role of the following in the process mentioned.

    (i) Silica in the extraction of copper.

    (ii) Cryolite in the extraction of aluminium.

    (iii) Iodine in the refining of Zirconium.

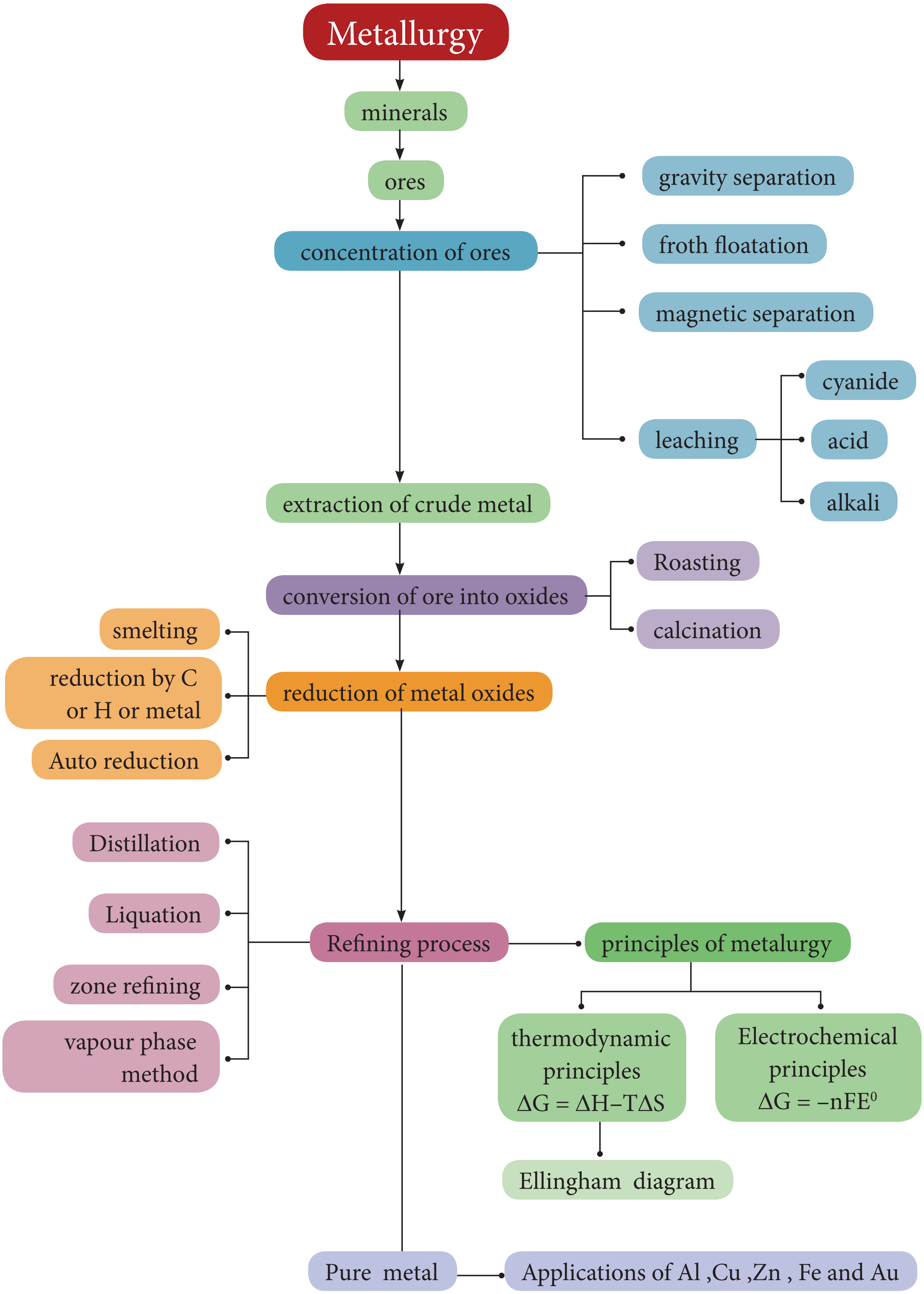
    (iv) Sodium cyanide in froth floatation.

14. Explain the principle of electrolytic refining with an example.

15. The selection of reducing agent depends on the thermodynamic factor: Explain with an example.

16. Give the limitations of Ellingham diagram.

17. Write a short note on electrochemical principles of metallurgy.


Metallurgy
minerals
ores
concentration of ores
gravity separation
froth floatation
magnetic separation
leaching
cyanide
acid
alkali
extraction of crude metal
conversion of ore into oxides
Roasting
calcination
smelting
reduction by C or H or metal
Auto reduction
reduction of metal oxides
Distillation
Liquation
zone refining
vapour phase method
Refining process
principles of metalurgy
thermodynamic principles $\Delta G = \Delta H - T\Delta S$
Electrochemical principles $\Delta G = -nFE^0$
Ellingham diagram
Pure metal
Applications of Al ,Cu ,Zn , Fe and Au

UNIT
2

p-BLOCK ELEMENTS-I

Kenneth wade
(1932–2014)

Kenneth Wade, was a British chemist, and professor emeritus at Durham University. He developed a method for the prediction of shapes of borane clusters. Wade's rules are used to rationalize the shape of borane clusters by calculating the total number of skeletal electron pairs (SEP) available for cluster bonding. For his substantial contribution, Kenneth Wade was granted FRS award from royal society, London In 1989.He received the Tilden prize award in 1999 from the Royal Society of Chemistry for advances in chemistry.

SB76YV

Learning Objectives

After studying this unit, the students will be able to

- describe the general trends in the properties of p-block elements
- explain the anomalous properties of the first element of p-block groups
- discuss the preparation, properties and uses of boron
- discuss the preparation of important, compounds of boron and aluminium
- discuss the preparation and properties of important compounds of carbon and silicon

INTRODUCTION

We have already learnt the classification of elements into four blocks namely s, p, d and f. We have also learnt the properties of s-block elements and their important compounds in the XI standard. This year we learn the elements of remaining blocks, starting with p-block elements.

The elements in which their last electron enters the 'p' orbital, constitute the p-block elements. They are placed in 13th to 18th groups of the modern periodic table and the first member of the groups are B, C, N, O, F and He respectively. These elements have quite varied properties and this block contains nonmetals, metals and metalloids. Nonmetallic elements of this group have more varied properties than metals. The elements of this block and their compounds play an important role in our day to day life, for example, without molecular oxygen we cannot imagine the survival of living system. The most abundant metal aluminium and its alloys have plenty of applications ranging from household utensils to parts of aircraft. The semi conducting nature of elements such as silicon and germanium made a revolutionary change in the field of modern electronics. In this unit we discuss the properties of first three groups (Group 13 - 15) of p-block elements namely boron, carbon and nitrogen family elements and their important compounds.

2.1 General trends in properties of p-block elements:

We already learnt that the properties of elements largely depends on their electronic configuration, size, ionisation enthalpy, electronegativity etc... Let us discuss the general trend in such properties of various p-block elements.

2.1.1 Electronic configuration and oxidation state:

The p-block elements have a general electronic configuration of ns^2, np^{1-6}. The elements of each group have similar outer shell electronic configuration and differ only in the value of n (principal quantum number). The elements of group 18 (inert gases) have completely filled p orbitals, hence they are more stable and have least reactivity. The elements of this block show variable oxidation state and their highest oxidation state (group oxidation state) is equal to the total number of valance electrons present in them. Unlike s-block elements which show only positive oxidation state, some of the p-block elements show negative oxidation states also. The halogens have a strong tendency to gain an electron to give a stable halide ion with completely filled electronic configuration and hence -1 oxidation state is more common in halogens. Similarly, the other elements belonging to pnictogen and chalcogen groups also show negative oxidation states.

Evaluate yourself :

Why group 18 elements are called inert gases? Write the general electronic configuraton of group 18 elements

Table 2.1 General electronic configurations and oxidation states of p-block elements

Group No.	**13**	**14**	**15**	**16**	**17**	**18**
Group Name	Icosagens	Tetragens	Pnictogens	Chalcogens	Halogens	Inert gases
General outer electronic configuration	$ns^2 np^1$	$ns^2 np^2$	$ns^2 np^3$	$ns^2 np^4$	$ns^2 np^5$	$ns^2 np^6$
Highest oxidation state (Group oxidation state)	+3	+4	+5	+6	+7	+8
Other observed oxidation states	+1	+2, -4	+3, -3	+4, +2, -2	+5, +3, +1, -1	+6. +4, +2

2.1.2 Metallic nature:

The tendency of an element to form a cation by loosing electrons is known as electropositive or metallic character. This character depends on the ionisation energy. Generally on descending a group the ionisation energy decreases and hence the metallic character increases.

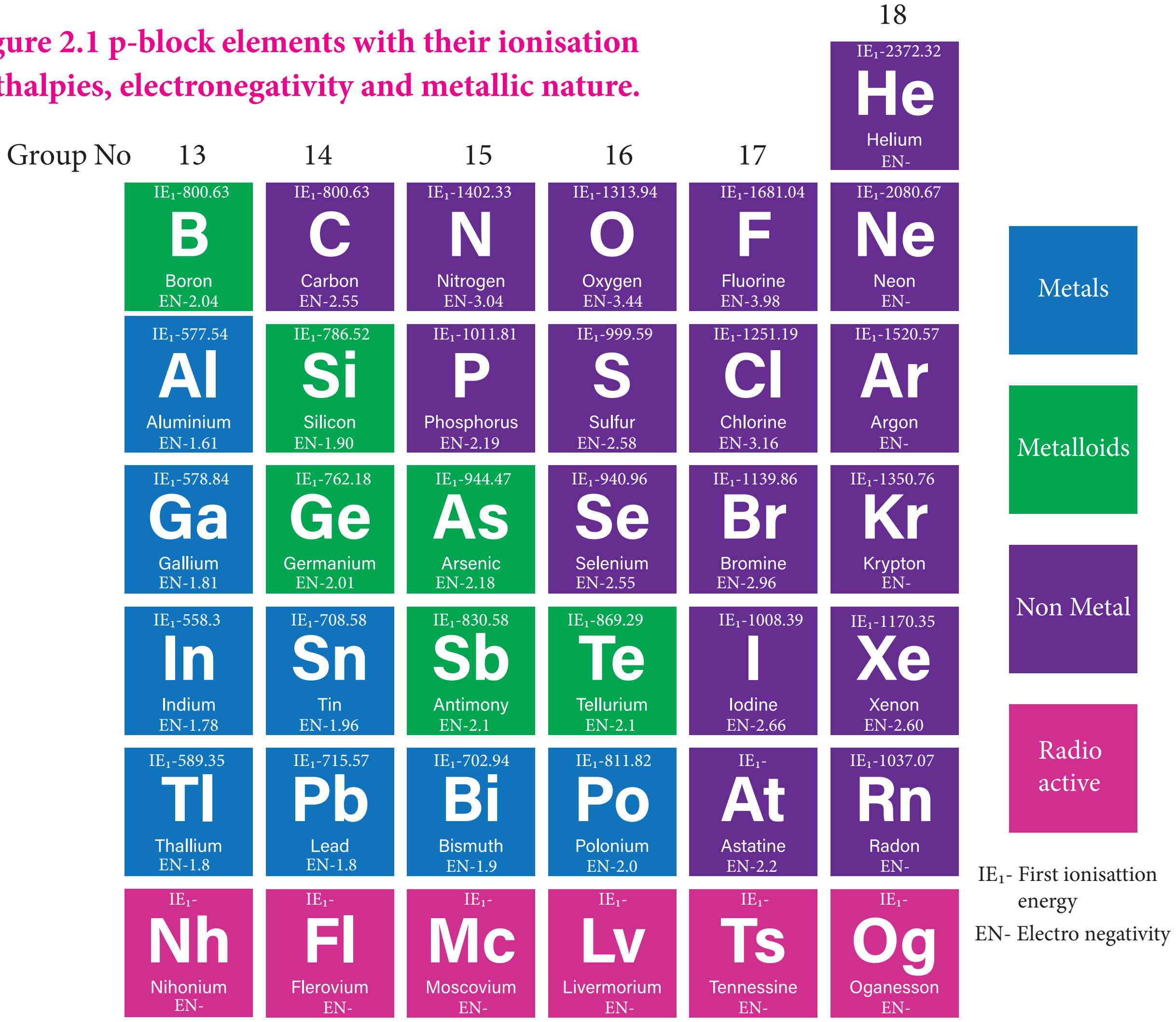


Figure 2.1 p-block elements with their ionisation enthalpies, electronegativity and metallic nature.

Group No	13	14	15	16	17	18
						IE_1-2372.32 He Helium EN-
	IE_1-800.63 B Boron EN-2.04	IE_1-800.63 C Carbon EN-2.55	IE_1-1402.33 N Nitrogen EN-3.04	IE_1-1313.94 O Oxygen EN-3.44	IE_1-1681.04 F Fluorine EN-3.98	IE_1-2080.67 Ne Neon EN-
	IE_1-577.54 Al Aluminium EN-1.61	IE_1-786.52 Si Silicon EN-1.90	IE_1-1011.81 P Phosphorus EN-2.19	IE_1-999.59 S Sulfur EN-2.58	IE_1-1251.19 Cl Chlorine EN-3.16	IE_1-1520.57 Ar Argon EN-
	IE_1-578.84 Ga Gallium EN-1.81	IE_1-762.18 Ge Germanium EN-2.01	IE_1-944.47 As Arsenic EN-2.18	IE_1-940.96 Se Selenium EN-2.55	IE_1-1139.86 Br Bromine EN-2.96	IE_1-1350.76 Kr Krypton EN-
	IE_1-558.3 In Indium EN-1.78	IE_1-708.58 Sn Tin EN-1.96	IE_1-830.58 Sb Antimony EN-2.1	IE_1-869.29 Te Tellurium EN-2.1	IE_1-1008.39 I Iodine EN-2.66	IE_1-1170.35 Xe Xenon EN-2.60
	IE_1-589.35 Tl Thallium EN-1.8	IE_1-715.57 Pb Lead EN-1.8	IE_1-702.94 Bi Bismuth EN-1.9	IE_1-811.82 Po Polonium EN-2.0	IE_1- At Astatine EN-2.2	IE_1-1037.07 Rn Radon EN-
	IE_1- Nh Nihonium EN-	IE_1- Fl Flerovium EN-	IE_1- Mc Moscovium EN-	IE_1- Lv Livermorium EN-	IE_1- Ts Tennessine EN-	IE_1- Og Oganesson EN-

- 🟦 Metals
- 🟩 Metalloids
- 🟪 Non Metal
- 🟥 Radio active

IE_1- First ionisattion energy
EN- Electro negativity

In p-block, the elements present in lower left part are metals while the elements in the upper right part are non metals. Elements of group 13 have metallic character except the first element boron which is a metalloid, having properties intermediate between the metal and nonmetals. The atomic radius of boron is very small and it has relatively high nuclear charge and these properties are responsible for its nonmetallic character. In the subsequent groups the non-metallic character increases. In group 14 elements, carbon is a nonmetal while silicon and germanium are metalloids. In group 15, nitrogen and phosphorus are non metals and arsenic & antimony are metalloids. In group 16, oxygen, sulphur and selenium are non metals and tellurium is a metalloid. All the elements of group 17 and 18 are non metals.

2.1.3 Ionisation Enthalpy:

We have already learnt that as we move down a group, generally there is a steady decrease in ionisation enthalpy of elements due to increase in their atomic radius. In p-block elements, there are some minor deviations to this general trend. In group 13, from boron to aluminium the ionisation enthalpy decreases as expected. But from aluminium to thallium there is only a marginal difference. This is due to the presence of inner d and f-electrons which has poor shielding effect compared to s and p-electrons. As a result, the effective nuclear charge on the valance electrons increases. A similar trend is also observed in group 14. The remaining groups (15 to 18) follow the general trend. In these groups, the ionisation enthalpy decreases, as we move down the group. Here, poor shielding effect of d- and f-electrons are overcome by the increased shielding effect of the additional p-electrons. The ionisation enthalpy of elements in successive groups is higher than the corresponding elements of the previous group as expected.

2.1.4 Electronegativity

As we move down the 13th group, the electronegativity first decreases from boron to aluminium and then marginally increases for Gallium, thereafter there is no appreciable change. Similar trend is also observed in 14 th group as well. In other groups, as we move down the group, the electro negativity decreases. This observed trend can be correlated with their atomic radius.

2.1.5 Anomalous properties of the first elements:

In p-block elements, the first member of each group differs from the other elements of the corresponding group. The following factors are responsible for this anomalous behaviour.

1. Small size of the first member
2. High ionisation enthalpy and high electronegativity
3. Absence of d orbitals in their valance shell

The first member of the group 13, boron is a metalloid while others are reactive metals. Moreover, boron shows diagonal relationship with silicon of group 14. The oxides of boron and silicon are similar in their acidic nature. Both boron and silicon form covalent hydrides that can be easily hydrolysed. Similarly, except boron trifluoride, halides of both elements are readily hydrolysed.

In group 14, the first element carbon is strictly a nonmetal while other elements are metalloids (silicon & germanium) or metals (tin & lead). Unlike other elements of the group carbon can form multiple bonds such as C=C, C=O etc... Carbon has a greater tendency to form a chain of bonds with itself or with other atoms which is known as catenation. There is considerable decrease in catenation property down the group (C>>Si>Ge≈Sn>Pb).

In group 15 also the first element nitrogen differs from the rest of the elements of the group. Like carbon, the nitrogen can from multiple bonds (N=N, C=N, N=O etc...). Nitrogen is a diatomic gas unlike the other members of the group. Similarly in group 16, the first element, oxygen also exists as a diatomic gas in that group. Due to its high electronegativity it forms hydrogen bonds.

The first element of group 17, fluorine the most electronegative element, also behaves quiet differently compared to the rest of the members of group. Like oxygen it also forms hydrogen bonds. It shows only -1 oxidation state while the other halogens have +1, +3, +5 and +7 oxidation states in addition to -1 state. The fluorine is the strongest oxidising agent and the most reactive element among the halogens.

2.1.6 Inert pair effect:

We have already learnt that the alkali and alkaline earth metals have an oxidation state of +1 and +2 respectively, corresponding to the total number of electrons present in them. Similarly, the elements of p-block also show the oxidation states corresponding to the maximum number of valence electrons (group oxidation state). In addition they also show variable oxidation state. In case of the heavier post-transition elements belonging to the groups (13 to 16), the most stable oxidation state is two less than the group oxidation state and there is a reluctance to exhibit the group oxidation state. Let us consider group 13 elements. As we move from boron to heavier elements, there is an increasing tendency to have +1 oxidation state, rather than the group oxidation state, +3. For example Al^{+3} is more stable than Al^{+1} while Tl^{+1} is more stable than Tl^{+3}. Aluminium(III)chloride is stable whereas thallium(III)chloride is highly unstable and disproportionates to thallium(I) chloride and chlorine gas. This shows that in thallium the stable lower oxidation state corresponds to the loss of np electrons only and not ns electrons. Thus in heavier post-transition metals, the outer s electrons (ns) have a tendency to remain inert and show reluctance to take part in the bonding, which is known as inert pair effect. This effect is also observed in groups 14, 15 and 16.

2.1.7 Allotropism in p-block elements:

Some elements exist in more than one crystalline or molecular forms in the same physical state. For example, carbon exists as diamond and graphite. This phenomenon is called allotropism (in greek '*allos*' means another and '*trope*' means change) and the different forms of an element are called allotropes. Many p-block elements show allotropism and some of the common allotropes are listed in the table.

Table 2.2 : Some of common allotropes of p-block elements

Element	**Most common allotropes**
Boron	Amorphous boron, α-rhombohedral boron, β-rhombohedral boron, γ-orthorhombic boron, α-tetragonal boron, β-tetragonal boron
Carbon	Diamond, Graphite, Graphene, Fullerenes, Carbon nanotubes
Silicon	Amorphous silicon, crystalline silicon
Germanium	α-germanium, β-germanium
Tin	Grey tin, white tin, rhombic tin, sigma tin
Phosphorous	White phosphorous, Red phosphorous, Scarlet phosphorous, Violet phosphorous, Black phosphorous.
Arsenic	Yellow arsenic, gray arsenic & Black arsenic
Anitimony	Blue-white antimony, Yellow, Black
Oxygen	Dioxygen, ozone
Sulphur	Rhombus sulphur, monoclinic sulphur
Selenium	Red selenium, Gray selenium, Black selenium, Monoclinic selenium,
Tellurium	Amorphous & Crystalline

2.2 Group 13 (Boron group) elements:

2.2.1 Occurrence:

The boron occurs mostly as borates and its important ores are borax - $Na_2[B_4O_5(OH)_4].8H_2O$ and kernite - $Na_2[B_4O_5(OH)_4].2H_2O$. Aluminium is the most abundant metal and occurs as oxides and also found in aluminosilicate rocks. Commercially it is extracted from its chief ore, bauxite ($Al_2O_3.2H_2O$). The other elements of this group occur only in trace amounts. The other elements Ga, In and Tl occur as their sulphides.

2.2.2 Physical properties:

Some of the physical properties of the group 13 elements are listed below

Table 2.3 Physical properties of group 13 elements

Property	**Boron**	**Aluminum**	**Gallium**	**Indium**	**Thallium**
Physical state at 293 K	Solid	Solid	Solid	Solid	Solid
Atomic Number	5	13	31	49	81
Isotopes	^{11}B	^{27}Al	^{69}Ga	^{115}In	^{205}Tl

Property	Boron	Aluminum	Gallium	Indium	Thallium
Atomic Mass ($g.mol^{-1}$ at 293 K)	10.81	26.98	69.72	114.81	204.38
Electronic configuration	$[He]2s^2\ 2p^1$	$[Ne]3s^2\ 3p^1$	$[Ar]3d^{10}\ 4s^2\ 4p^1$	$[Kr]4d^{10}\ 5s^2\ 5p^1$	$[Xe]\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^1$
Atomic radius (Å)	1.92	1.84	1.87	1.93	1.96
Density ($g.cm^{-3}$ at 293 K)	2.34	2.70	5.91	7.31	11.80
Melting point (K)	2350	933	302.76	429	577
Boiling point (K)	4273	2792	2502	2300	1746

2.2.3 Chemical properties of boron:

Boron is the only nonmetal in this group and is less reactive. However, it shows reactivity at higher temperatures. Many of its compounds are electron deficient and has unusual type of covalent bonding which is due to its small size, high ionisation energy and similarity in electronegativity with carbon and hydrogen.

Formation of metal borides:

Many metals except alkali metals form borides with a general formula M_xB_y (x ranging upto 11 and y ranging upto 66 or higher)

Direct combination of metals with boron:

$$Cr + nB \xrightarrow{1500\ K} CrB_n$$

Reduction of borontrihalides:

Reduction of borontrichloride with a metal assisted by dihydrogen gives metal borides.

$$BCl_3 + W \xrightarrow[H_2]{1500\ K} WB + Cl_2 + HCl$$

Formation of hydrides:

Boron does not react directly with hydrogen. However, it forms a variety of hydrides called boranes. The simplest borane is diborane - B_2H_6. Other larger boranes can be prepared from diborane. Treatment of gaseous boron trifluoride with sodium hydride around 450 K gives diborane. To prevent subsequent pyrolysis, the product diborane is trapped immediately.

$$2BF_3 + 6NaH \xrightarrow{450\ K} B_2H_6 + 6NaF$$

Formation of boron trihalides:

Boron combines with halogen to form boron trihalides at high temperatures.

$$2B + 3X_2 \xrightarrow{\Delta} 2BX_3$$

Formation of boron nitride:

Boron burns with dinitrogen at high temperatures to form boron nitride.

$$2B + N_2 \xrightarrow{\Delta} 2BN$$

Formation of oxides:

When boron is heated with oxygen around 900 K, it forms its oxide.

$$4B + 3O_2 \xrightarrow{900\ K} 2B_2O_3$$

Reaction with acids and alkali:

Halo acids have no reaction with boron. However, boron reacts with oxidising acids such as sulphuric acid and nitric acids and forms boric acid.

$$2B + 3H_2SO_4 \longrightarrow 2H_3BO_3 + 3SO_2$$

$$B + 3HNO_3 \longrightarrow H_3BO_3 + 3NO_2$$

Boron reacts with fused sodium hydroxide and forms sodium borate.

$$2B + 6NaOH \longrightarrow 2Na_3BO_3 + 3H_2$$

Uses of boron:

1. Boron has the capacity to absorb neutrons. Hence, its isotope $^{10}B_5$ is used as moderator in nuclear reactors.
2. Amorphous boron is used as a rocket fuel igniter.
3. Boron is essential for the cell walls of plants.
4. Compounds of boron have many applications. For example eye drops, antiseptics, washing powders etc.. contains boric acid and borax. In the manufacture of Pyrex glass , boric oxide is used.

2.2.4. Borax [$Na_2B_4O_7.10H_2O$]:

Preparation:

Borax is a sodium salt of tetraboric acid. It is obtained from colemanite ore by boiling its solution with sodium carbonate.

$$2Ca_2B_6O_{11} + 2NaCO_3 + H_2O \xrightarrow{\Delta} 3Na_2B_4O_7 + 3CaCO_3 + Ca(OH)_2$$

Borax is normally formulated as $Na_2B_4O_7.10H_2O$. But it contains, tetranuclear units $[B_4O_5.(OH)_4]^{2-}$. This form is known as prismatic form. Borax also exists two other forms namely, jeweller or octahderal borax ($Na_2B_4O_7.5H_2O$) and borax glass ($Na_2B_4O_7$).

Properties

Borax is basic in nature and its solution in hot-water is alkaline as it dissociates into boric acid and sodium hydroxide.

$$Na_2B_4O_7 + 7H_2O \longrightarrow 4H_3BO_3 + 2NaOH$$

On heating it forms a transparent borax beads.

$$Na_2B_4O_7.10H_2O \xrightarrow[-10H_2O]{\Delta} Na_2B_4O_7 \longrightarrow 2NaBO_2 + B_2O_3$$

Borax reacts with acids to form sparingly soluble boric acid.

$$Na_2B_4O_7 + 2HCl + 7H_2O \longrightarrow 4H_3BO_3 + 2NaCl$$

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow 4H_3BO_3 + 2Na_2SO_4$$

When treated with ammonium chloride it forms boron nitride.

$$Na_2B_4O_7 + 2NH_4Cl \longrightarrow 2NaCl + 2BN + B_2O_3 + 4H_2O$$

Uses of Borax:

1. Borax is used for the identification of coloured metal ions
2. In the manufacture optical and borosilicate glass, enamels and glazes for pottery
3. It is also used as a flux in metallurgy and also acts as a preservative

2.2.5. Boric acid [H_3BO_3 or $B(OH)_3$]:

Preparation:

Boric acid can be extracted from borax and colemanite.

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow Na_2SO_4 + 4H_3BO_3$$

$$Ca_2B_6O_{11} + 11H_2SO_4 + SO_2 \longrightarrow Ca(HSO_3)_2 + 6H_3BO_3$$

Properties:

Boric acid is a colourless transparent crystal. It is a very weak monobasic acid and, it accepts hydroxyl ion rather than donating proton.

$$B(OH)_3 + 2H_2O \rightleftharpoons H_3O^+ + [B(OH)_4]^-$$

It reacts with sodium hydroxide to form sodium metaborate and sodium tetraborate.

$$NaOH + H_3BO_3 \longrightarrow NaBO_2 + 2H_2O$$

$$2NaOH + 4H_3BO_3 \longrightarrow Na_2B_4O_7 + 7H_2O$$

Action of Heat:

Boric acid when heated at 373 K gives metaboric acid and at 413 K, it gives tetraboric acid. When heated at red hot, it gives boric anhydride which is a glassy mass.

$$4H_3BO_3 \xrightarrow{373\ K} 4HBO_2 + 4\ H_2O$$

$$4HBO_2 \xrightarrow{413\ K} H_2B_4O_7 + H_2O$$

$$H_2B_4O_7 \xrightarrow{\text{Red hot}} 2B_2O_3 + H_2O$$

Acton of ammonia

Fusion of urea with $B(OH)_3$, in an atmosphere of ammonia at 800 - 1200 K gives boron nitride.

$$B(OH)_3 + NH_3 \xrightarrow{\Delta} BN + 3H_2O$$

When boric acid or borate salt is heated with ethyl alcohol in presence of conc. sulphuric acid, an ester, trialkylborate is formed. The vapour of this ester burns with a green edged flame and this reaction is used to identify the presence of borate.

$$H_3BO_3 + 3C_2H_5OH \xrightarrow[H_2SO_4]{\text{Conc.}} B(OC_2H_5)_3 + 3H_2O$$

Note: The trialkyl borate on reaction with sodium hydride in tetrahydrofuron to form a coordination compound $Na[BH(OR)_3]$, which acts as a powerful reducing agent.

Formation of boron trifluoride:

Boric acid reacts with calcium fluoride in presence of conc. sulphuric acid and gives boron trifluoride.

$$3CaF_2 + 3H_2SO_4 + 2\ B(OH)_3 \longrightarrow 3CaSO_4 + 2BF_3 + 6H_2O$$

Borax when heated with soda ash it gives borax

$$Na_2CO_3 + 4B(OH)_3 \longrightarrow Na_2B_4O_7 + CO_2 + 6H_2O$$

Structure of Boric acid:

Boric acid has a two dimensional layered structure. It consists of $[BO_3]^{3-}$ unit and these are linked to each other by hydrogen bonds as shown in the Figure 2.2.

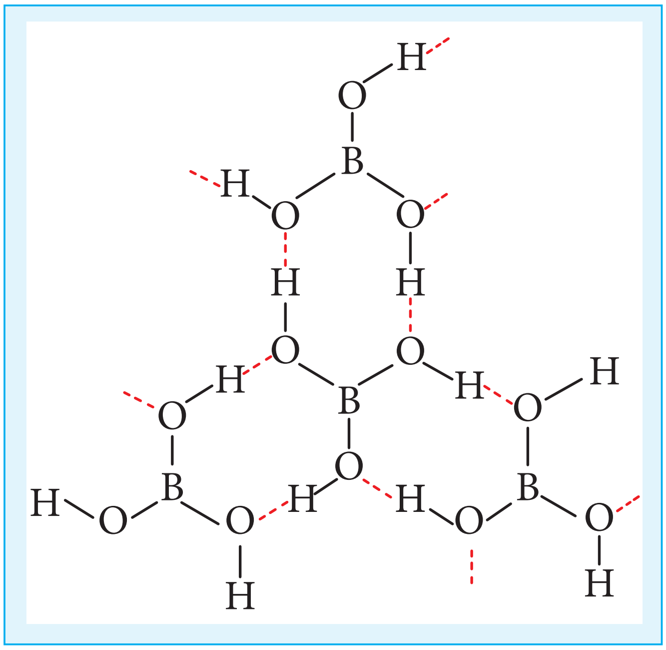


Figure 2.2 Structure of boric acid

Uses of boric acid:

1. Boric acid is used in the manufacture of pottery glases, enamels and pigments.
2. It is used as an antiseptic and as an eye lotion.
3. It is also used as a food preservative.

2.2.6 Diborane

Preparation:

As discussed earlier diborane can be prepared by the action of metal hydride with boron. This method is used for the industrial production.

Diborane can also be obtained in small quantities by the reaction of iodine with sodium borohydride in diglyme.

$$2NaBH_4 + I_2 \longrightarrow B_2H_6 + 2NaI + H_2$$

On heating magnesium boride with HCl a mixture of volatile boranes are obtained.

$$2Mg_3B_2 + 12HCl \longrightarrow 6MgCl_2 + B_4H_{10} + H_2$$

$$B_4H_{10} + H_2 \longrightarrow 2B_2H_6$$

Properties:

Boranes are colourless diamagnetic compounds with low thermal stability. Diborane is a gas at room temperature with sweet smell and it is extremely toxic. It is also highly reactive.

At high temperatures it forms higher boranes liberating hydrogen.

$$5B_2H_6 \xrightarrow[\text{U - tube}]{388\text{ K}} 2B_5H_{11} + 4H_2$$

$$2B_2H_6 \xrightarrow{198 - 373\text{ K}} B_4H_{10} + H_2$$

$$5B_2H_6 \xrightarrow[\text{sealed tube}]{373\text{ K}} B_{10}H_{14} + 8H_2$$

$$5B_2H_6 \xrightarrow{473 - 523\text{ K}} 2B_5H_9 + 6H_2$$

$$10B_2H_6 \xrightarrow{523\text{ K}} 2B_5H_9 + 2B_5H_{10} + 11H_2$$

$$B_2H_6 \xrightarrow{\text{Red hot}} 2B + 3H_2$$

Diboranes reacts with water and alkali to give boric acid and metaborates respectively.

$$B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$$

$$B_2H_6 + 2NaOH + 2H_2O \longrightarrow 2NaBO_2 + 6H_2$$

Action of air:

At room temperature pure diborane does not react with air or oxygen but in impure form it gives B_2O_3 along with large amount of heat.

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O \qquad \Delta H = -2165\text{ KJ mol}^{-1}$$

Diborane reacts with methyl alcohol to give trimethyl Borate.

$$B_2H_6 + 6CH_3OH \longrightarrow 2B(OCH_3)_3 + 6H_2$$

Hydroboration:

Diborane adds on to alkenes and alkynes in ether solvent at room temperature. This reaction is called hydroboration and is highly used in synthetic organic chemistry, especially for anti Markovnikov addition.

$$B_2H_6 + 6RCH{=}CHR \longrightarrow 2B(RCH\text{-}CH_2R)_3$$

Reaction with ionic hydrides

When treated with metal hydrides it forms metal borohydrides

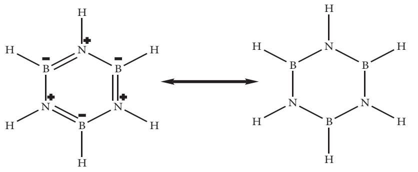
$$B_2H_6 + 2LiH \xrightarrow{\text{Ether}} 2LiBH_4$$
$$B_2H_6 + 2NaH \xrightarrow{\text{Diglyme}} 2NaBH_4$$

Reaction with ammonia:

When treated with excess ammonia at low temperatures diborane gives diboranediammonate. On heating at higher temperatures it gives borazole.

$$3B_2H_6 + 6NH_3 \xrightarrow{-153\text{ K}} 3B_2H_6.2NH_3 \text{ (or) } 3[BH_2(NH_3)_2]^+[BH_4]^-$$

$$3B_2H_6{+}2NH_3 \xrightarrow[\text{Clossed vessel}]{\text{High temp}}$$



$2B_3N_3H_6$ (Borazole or Borazine - Inorganic benzene)

Structure of diborane:

In diborane two BH_2 units are linked by two bridged hydrogens. Therefore, it has eight B-H bonds. However, diborane has only 12 valance electrons and are not sufficient to form normal covalent bonds. The four terminal B-H bonds are normal covalent bonds (two centre - two electron bond or 2c-2e bond). The remaining four electrons have to be used for the bridged bonds. i.e. two three centred B-H-B bonds utilise two electrons each. Hence, these bonds are three centre- two electron bonds (3c-2e). The bridging hydrogen atoms are in a plane as shown in the figure 2.3. In diborne, the boron is sp^3 hybridised.

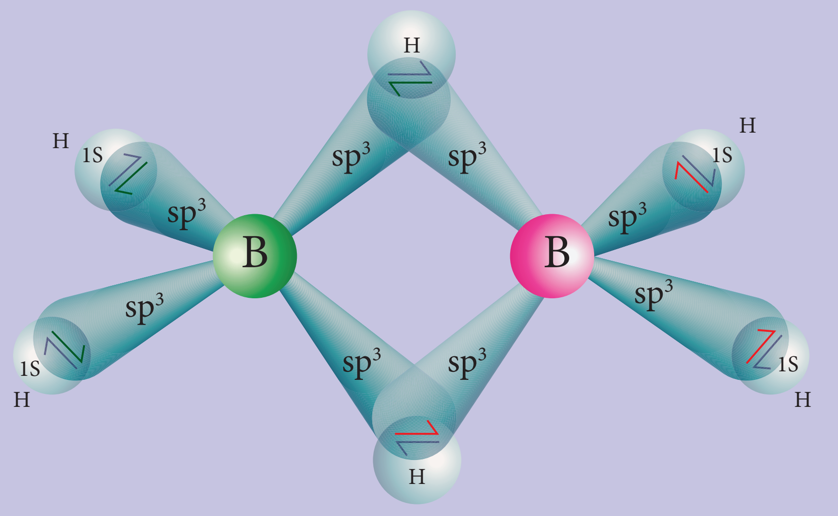


Figure 2.3 Structure of diborane.

Three of the four sp^3 hybridised orbitals contains single electron and the fourth orbital is empty. Two of the half filled hybridised orbitals of each boron overlap with the two hydrogens to form four terminal 2c-2e bonds, leaving one empty and one half filled hybridised orbitals on each boron. The Three centre - two electron bonds), B-H-B bond formation involves overlapping the half filled hybridised orbital of one boron, the empty hybridised orbital of the other boron and the half filled 1s orbital of hydrogen.

Uses of diborane:

1. Diborane is used as a high energy fuel for propellant
2. It is used as a reducing agent in organic chemistry
3. It is used in welding torches

2.2.7 Boron trifluoride:

Preparation:

Boron trifuloride is obtained by the treatment of calcium fluoride with boron trioxide in presence of conc. sulphuric acid.

$$B_2O_3 + 3CaF_2 + 3H_2SO_4 \xrightarrow{\Delta} 2BH_3 + 3CaSO_4 .+ 3H_2O$$

It can also be obtained by treating boron trioxide with carbon and fluorine.

$$B_2O_3 + 3C + 3F_2 \longrightarrow 2BF_3 + 3CO$$

In the laboratory pure BF_3 is prepared by the thermal decomposition of benzene diazonium tetrafluoro borate.

$$PhN_2BF_4 \xrightarrow{\Delta} BF_3 + PhF + N_2$$

Properties:

Boron trifluoride has a planar geometry. It is an electron deficient compound and accepts electron pairs to form coordinate covalent bonds. They form complex of the type $[BX_4]^-$.

$$BF_3 + NH_3 \longrightarrow F_3B \leftarrow NH_3$$
$$BF_3 + H_2O \longrightarrow F_3B \leftarrow OH_2$$

On hydrolysis, boric acid is obtained. This then gets converted into fluoro boric acid.

$$4BF_3 + 12H_2O \longrightarrow 4H_3BO_3 + 12HF$$
$$3H_3BO_3 + 12HF \longrightarrow 3H^+ + 3[BF_4]^- + 9H_2O$$

$$4BF_3 + 3H_2O \longrightarrow H_3BO_3 + 3H^+ + 3[BF_4]^-$$

Uses of Boron trifluoride:

1. Boron trifluoride is used for preparing HBF_4, a catalyst in organic chemistry
2. It is also used as a fluorinating reagent.

2.2.8 Aluminium chloride:

Preparation:

When aluminium metal or aluminium hydroxide is treated with hydrochloric acid, aluminium trichloride is formed. The reaction mixture is evaporated to obtain hydrated aluminium chloride.

$$2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2$$

$$Al(OH)_3 + 3HCl \longrightarrow AlCl_3 + 3H_2O$$

McAfee Process:

Aluminium chloride is obtained by heating a mixture of alumina and coke in a current of chlorine.

$$Al_2O_3 + 3C + 3Cl_2 \longrightarrow 2AlCl_3 + 3CO_2$$

On industrial scale it is prepared by chlorinating aluminium around 1000 K

$$2Al + 3Cl_2 \xrightarrow{1000\ K} 2AlCl_3$$

Properties:

Anhydrous aluminium chloride is a colourless, hygroscopic substance.

An aqueous solution of aluminium chloride is acidic in nature. It also produces hydrogen chloride fumes in moist air.

$$AlCl_3 + 3H_2O \longrightarrow Al(OH)_3 + 3HCl$$

With ammonium hydroxide it forms aluminium hydroxide.

$$AlCl_3 + 3NH_4OH \longrightarrow Al(OH)_3 + 3NH_4Cl$$

With excess of sodium hydroxide it produces metal aluminate

$$AlCl_3 + 4NaOH \longrightarrow NaAlO_2 + 2H_2O + 3NaCl$$

It behaves like a Lewis acid and forms addition compounds with ammonia, phosphine and carbonylchloride etc... Eg. $AlCl_3.6NH_3$.

Uses of aluminium chloride:

1. Anhydrous aluminium chloride is used as a catalyst in Friedels Crafts reactions
2. It is used for the manufacture of petrol by cracking the mineral oils.
3. It is used as a catalyst in the manufacture on dyes, drugs and perfumes.

2.2.9 Alums:

The name alum is given to the double salt of potassium aluminium sulphate [$K_2SO_4.Al_2(SO_4)_3.24.H_2O$]. Now a days it is used for all the double salts with $M'_2SO_4.M''_2(SO_4)_3.24H_2O$, where M' is univalent metal ion or $[NH_4]^+$ and M" is trivalent metal ion.

Examples:

Potash alum [$K_2SO_4.Al_2(SO_4)_3.24.H_2O$]; Sodium alum [$Na_2SO_4.Al_2(SO_4)_3.24.H_2O$] , Ammonium alum [$(NH_4)_2SO_4.Al_2(SO_4)_3.24.H_2O$], Chrome alum [$K_2SO_4.Cr_2(SO_4)_3.24.H_2O$].

Alums in general are more soluble in hot water than in cold water and in solutions they exhibit the properties of constituent ions.

Preparation:

The alunite the alum stone is the naturally occurring form and it is $K_2SO_4.Al_2(SO_4)_3.4Al(OH)_3$. When alum stone is treated with excess of sulphuric acid, the aluminium hydroxide is converted to aluminium sulphate. A calculated quality of potassium sulphate is added and the solution is crystallised to generate potash alum. It is purified by recrystallisation.

$$K_2SO_4.Al_2(SO_4)_3.4Al(OH)_3 + 6H_2SO_4 \longrightarrow K_2SO_4 + 3Al_2(SO_4)_3 + 12\ H_2O$$

$$K_2SO_4 + Al_2(SO_4)_3 + 24\ H_2O \longrightarrow K_2SO_4.Al_2(SO_4)_3.24\ H_2O$$

Properties

Potash alum is a white crystalline solid it is soluble in water and insoluble in alcohol. The aqueous solution is acidic due to the hydrolysis of aluminium sulphate it melts at 365 K on heating. At 475 K loses water of hydration and swells up. The swollen mass is known as burnt alum. Heating to red hot it decomposes into potassium sulphate, alumina and sulphur trioxide.

$$K_2SO_4.Al_2(SO_4)_3.24\ H_2O \xrightarrow{500\ K} K_2SO_4.Al_2(SO_4)_3 + 24\ H_2O$$

$$K_2SO_4.Al_2(SO_4)_3 \xrightarrow{\text{Red hot}} K_2SO_4 + Al_2O_3 + 3SO_3$$

Potash alum forms aluminium hydroxide when treated with ammonium hydroxide.

$$K_2SO_4.Al_2(SO_4)_3.24\ H_2O + 6NH_4OH \longrightarrow K_2SO_4 + 3(NH_4)_2SO_4 + 24\ H_2O + 3Al(OH)_3$$

Uses of Alum:

1. It is used for purification of water
2. It is also used for water proofing and textiles
3. It is used in dyeing, paper and leather tanning industries
4. It is employed as a styptic agent to arrest bleeding.

2.3 Group 14 (Carbon group) elements:

2.3.1 Occurrence:

Carbon is found in the native form as graphite. Coal, crude oil and carbonate rocks such as calcite, magnesite etc... contains large quantities of carbon in its combined form with other elements. Silicon occurs as silica (sand and quartz crystal). Silicate minerals and clay are other important sources for silicon.

2.3.2 Physical properties:

Some of the physical properties of the group 14 elements are listed below

Table 2.4 Physical properties of group 14 elements

Property	Carbon	Silicon	Germanium	Tin	Lead
Physical state at 293 K	Solid	Solid	Solid	Solid	Solid
Atomic Number	6	14	32	50	82
Isotopes	^{12}C, ^{13}C, ^{14}C	^{28}Si, ^{30}Si	^{73}Ge, ^{74}Ge	^{120}Sn	^{208}Pb
Atomic Mass (g.mol^{-1} at 293 K)	12.01	28.09	72.63	118.71	207.2
Electronic configuration	$[He]2s^2\ 2p^2$	$[Ne]3s^2\ 3p^2$	$[Ar]3d^{10}\ 4s^2\ 4p^2$	$[Kr]4d^{10}\ 5s^2\ 5p^2$	$[Xe]\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^2$
Atomic radius (Å)	1.70	2.10	2.11	2.17	2.02
Density (g.cm^{-3} at 293 K)	3.51	2.33	5.32	7.29	11.30
Melting point (K)	Sublimes at 4098	1687	1211	505	601
Boiling point (K)		3538	3106	2859	2022

2.3.3 Tendency for catenation

Catenation is an ability of an element to form chain of atoms. The following conditions are necessary for catenation. (i) the valency of element is greater than or equal to two, (ii) element should have an ability to bond with itself (iii) the self bond must be as strong as its bond with other elements (iv) kinetic inertness of catenated compound towards other molecules. Carbon possesses all the above properties and forms a wide range of compounds with itself and with other elements such as H, O, N, S and halogens.

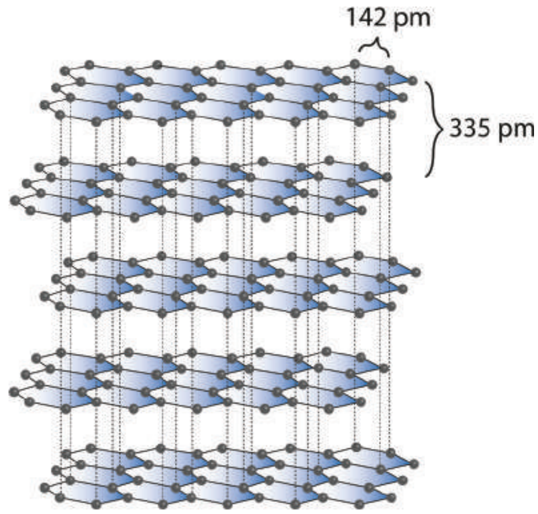


Figure 2.4 Structure of graphite

2.3.4 Allotropes of carbon

Carbon exists in many allotropic forms. Graphite and diamond are the most common allotropes. Other important allotropes are graphene, fullerenes and carbon nanotubes.

Graphite is the most stable allotropic form of carbon at normal temperature and pressure. It is soft and conducts electricity. It is composed of flat two dimensional sheets of carbon atoms. Each sheet is a hexagonal net of sp^2 hybridised carbon atoms with a C-C bond length of 1.41 Å which is close to the

C-C bond distance in benzene (1.40 Å). Each carbon atom forms three σ bonds with three neighbouring carbon atoms using three of its valence electrons and the fourth electron present in the unhybridised p orbital forms a π-bond. These π electrons are delocalised over the entire sheet which is responsible for its electrical conductivity. The successive carbon sheets are held together by weak vander Waals forces. The distance between successive sheet is 3.40 Å. It is used as a lubricant either on its own or as a graphited oil.

Unlike graphite the other allotrope **diamond** is very hard. The carbon atoms in diamond are sp^3 hybridised and bonded to four neighbouring carbon atoms by σ bonds with a C-C bond length of 1.54 Å. This results in a tetrahedral arrangement around each carbon atom that extends to the entire lattice as shown in figure 2.5. Since all four valance electrons of carbon are involved in bonding there is no free electrons for conductivity. Being the hardest element, it used for sharpening hard tools, cutting glasses, making bores and rock drilling.

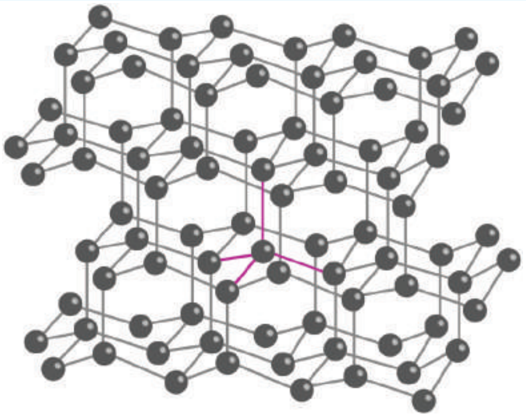


Figure 2.5 Structure of diamond

Fullerenes are newly synthesised allotropes of carbon. Unlike graphite and diamond, these allotropes are discrete molecules such as C_{32}, C_{50}, C_{60}, C_{70}, C_{76} etc.. These molecules have cage like structures as shown in the figure. The C_{60} molecules have a soccer ball like structure and is called buckminster fullerene or buckyballs. It has a fused ring structure consists of 20 six membered rings and 12 five membered rings. Each carbon atom is sp^2 hybridised and forms three σ bonds & a delocalised π bond giving aromatic character to these molecules. The C-C bond distance is 1.44 Å and C=C distance 1.38 Å.

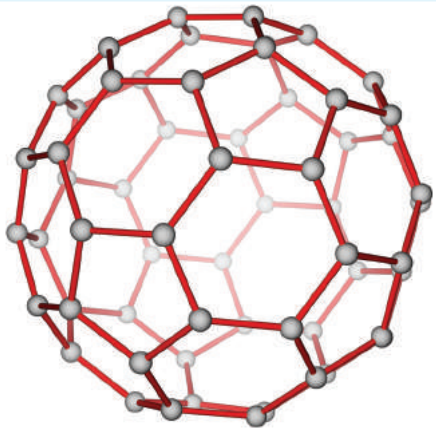


Figure 2.6 Structure of Fullerenes

Carbon nanotubes, another recently discovered allotropes, have graphite like tubes with fullerene ends. Along the axis, these nanotubes are stronger than steel and conduct electricity. These have many applications in nanoscale electronics, catalysis, polymers and medicine.

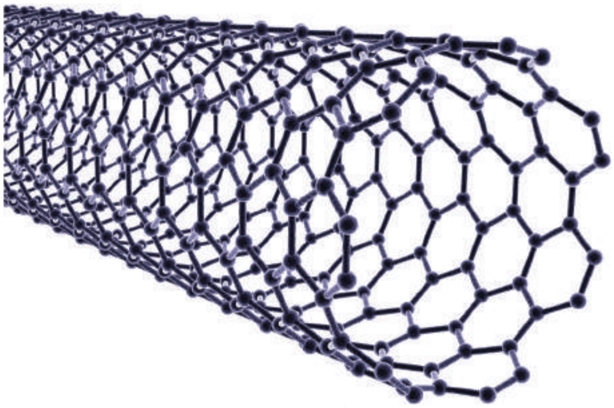


Figure 2.7 Structure of carbon nanotubes

Another allotrophic form of carbon is graphene. It has a single planar sheet of sp^2 hybridised carbon atoms that are densely packed in a honeycomb crystal lattice.

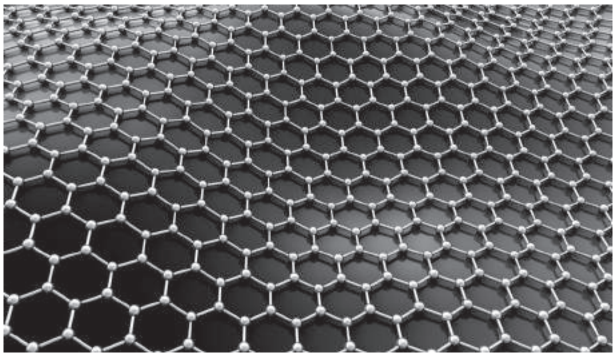


Figure 2.8 Structure of graphene

2.3.5 Carbon monoxide [CO]:

Preparation:

Carbon monoxide can be prepared by the reaction of carbon with limited amount of oxygen.

$$2C + O_2 \longrightarrow 2CO$$

On industrial scale carbon monoxide is produced by the reaction of carbon with air. The carbon monoxide formed will contain nitrogen gas also and the mixture of nitrogen and carbon monoxide is called producer gas.

$$2C + O_2/N_2\ (\text{air}) \longrightarrow \underset{\text{Producers Gas}}{2CO + N_2}$$

The producer gas is then passed through a solution of copper(I)chloride under pressure which results in the formation of $CuCl(CO).2H_2O$. At reduced pressures this solution releases the pure carbon monoxide.

Pure carbon monoxide is prepared by warming methanoic acid with concentrated sulphuric acid which acts as a dehydrating agent.

$$HCOOH + H_2SO_4 \longrightarrow CO + H_2O + H_2SO_4$$

Properties

It is a colourless, odourless, and poisonous gas. It is slightly soluble in water.

It burns in air with a blue flame forming carbon dioxide.

$$2CO + O_2 \longrightarrow 2CO_2$$

When carbon monoxide is treated with chlorine in presence of light or charcoal, it forms a poisonous gas carbonyl chloride, which is also known as phosgene. It is used in the synthesis of isocyanates.

$$CO + Cl_2 \longrightarrow COCl_2$$

Carbon monoxide acts as a strong reducing agent.

$$CO + Fe_2O_3 \longrightarrow 2Fe + 3CO_2$$

Under high temperature and pressure a mixture of carbon monoxide and hydrogen (synthetic gas or syn gas) gives methanol.

$$CO + 2H_2 \longrightarrow CH_3OH$$

In oxo process, ethene is mixed with carbon monoxide and hydrogen gas to produce propanal.

$$CO + C_2H_4 + H_2 \longrightarrow CH_3CH_2CHO$$

Fischer Tropsch synthesis:

The reaction of carbon monoxide with hydrogen at a pressure of less than 50 atm using metal catalysts at 500 - 700 K yields saturated and unsaturated hydrocarbons.

$$nCO + (2n+1)H_2 \longrightarrow C_nH_{(2n+2)} + nH_2O$$

$$nCO + 2nH_2 \longrightarrow C_nH_{2n} + nH_2O$$

Carbon monoxide forms numerous complex compounds with transition metals in which the transition meal is in zero oxidation state. These compounds are obtained by heating the metal with carbon monoxide.

Eg. Nickel tetracarbonyl $[Ni(CO)_4]$, Iron pentacarbonyl $[Fe(CO)_5]$, Chromium hexacarbonyl $[Cr(CO)_6]$.

Structure:

It has a linear structure. In carbon monoxide, three electron pairs are shared between carbon and oxygen. The bonding can be explained using molecular orbital theory as discussed in XI standard. The C-O bond distance is 1.128Å. The structure can be considered as the resonance hybrid of the following two canonical forms.

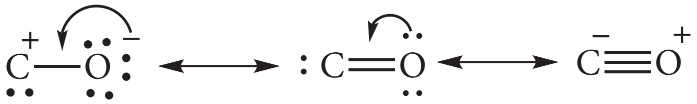


Figure 2.9 Structure of carbon monoxide

Uses of carbon monoxide:

1. Equimolar mixture of hydrogen and carbon monoxide - water gas and the mixture of carbon monoxide and nitrogen - producer gas are important industrial fuels
2. Carbon monoxide is a good reducing agent and can reduce many metal oxides to metals.
3. Carbon monoixde is an important ligand and forms carbonyl compound with transition metals

2.3.6 Carbon dioxide:

Carbon dioxide occurs in nature in free state as well as in the combined state. It is a constituent of air (0.03%). It occurs in rock as calcium carbonate and magnesium carbonate.

Production

On industrial scale it is produced by burning coke in excess of air.

$$2CO + O_2 \longrightarrow 2CO_2 \quad \Delta H = 394 \text{ kJ mol}^{-1}$$

Calcination of lime produces carbon dioxide as by product.

$$CaCO_3 \longrightarrow CaO + CO_2$$

Carbon dioxide is prepared in laboratory by the action of dilute hydrochloric acid on metal carbonates.

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$$

Properties

It is a colourless, nonflammable gas and is heavier than air. Its critical temperature is 31^0 C and can be readily liquefied.

Carbon dioxide is a very stable compound. Even at 3100 K only 76 % decomposes to form carbon monoxide and oxygen. At still higher temperature it decomposes into carbon and oxygen.

$$CO_2 \xrightleftharpoons{\text{3100 K}} CO + \tfrac{1}{2}O_2$$

$$CO_2 \xrightleftharpoons{\text{high temperature}} C + O_2$$

Reducing behaviour:

At elevated temperatures, it acts as a strong reducing agent. For example,

$$CO_2 + Mg \longrightarrow 2MgO + C$$

Water gas equilibrium:

The equilibrium involved in the reaction between carbon dioxide and hydrogen, has many industrial applications and is called water gas equilibrium.

$$CO_2 + H_2 \rightleftharpoons \underbrace{CO + H_2O}_{\text{Water gas}}$$

Acidic behaviour:

The aqueous solution of carbon dioxide is slightly acidic as it forms carbonic acid.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

Structure of carbon dioxide

Carbon dioxide has a liner structure with equal bond distance for the both C-O bonds. In this molecule there is one C-O sigma bond. In addition there is 3c-4e bond covering all the three atoms.

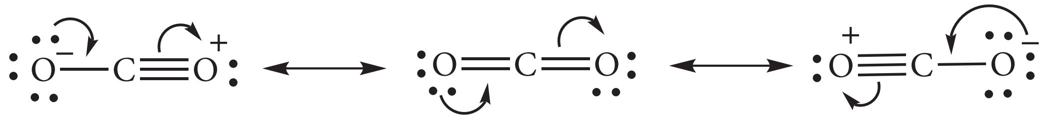


Figure 2.10 Structure of carbon dixide

Uses of carbon dioxide

1. Carbon dioxide is used to produce an inert atomosphere for chemical processing.
2. Biologically, it is important for photosynthesis.

3. It is also used as fire extinguisher and as a propellent gas.
4. It is used in the production of carbonated beverages and in the production of foam.

2.3.7 Silicon tetrachloride:

Preparation:

Silicon tetrachloride can be prepared by passing dry chlorine over an intimate mixture of silica and carbon by heating to 1675 K in a porcelain tube

$$SiO_2 + 2C + 2Cl_2 \longrightarrow SiCl_4 + 2CO$$

On commercial scale, reaction of silicon with hydrogen chloride gas occurs above 600 K

$$Si + 4HCl \longrightarrow SiCl_4 + 2H_2$$

Properties:

Silicon tetrachloride is a colourless fuming liquid and it freezes at -70 ^oC

In moist air, silicon tetrachloride is hydrolysed with water to give silica and hydrochloric acid.

$$SiCl_4 + 4H_2O \longrightarrow 4HCl + Si(OH)_4$$

When silicon tetrachloride is hydrolysed with moist ether, linear perchloro siloxanes are formed $[Cl\text{-}(Si\,Cl_2O)_nSiCl_3$ where n=1-6.

Alcoholysis

The chloride ion in silicon tetrachloride can be substituted by nucleophile such as OH, OR, etc.. using suitable reagents. For example, it forms silicic esters with alcohols.

$$SiCl_4 + C_2H_5OH \longrightarrow \underset{\text{Tetraethoxy silane}}{Si(OC_2H_5)_4} + 4HCl$$

Ammonialysis.

Similarly silicon tetrachloride undergoes ammonialysis to form chlorosilazanes.

$$2SiCl_4 + NH_3 \xrightarrow[\text{Ether}]{330\text{ K}} Cl_3Si\text{-}NH\text{-}SiCl_3$$

Uses:

1. Silicon tetrachloride is used in the production of semiconducting silicon.
2. It is used as a starting material in the synthesis of silica gel, silicic esters, a binder for ceramic materials.

2.3.8 Silcones:

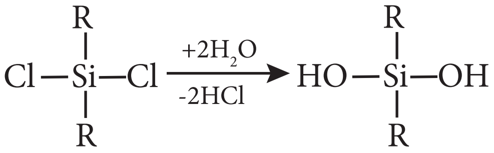
Silicones or poly siloxanes are organo silicon polymers with general empirical formula (R_2SiO). Since their empirical formula is similar to that of ketone (R_2CO), they were named “silicones”. These silicones may be linear or cross linked. Because of their very high thermal stability they are called high –temperature polymers.

Preparation:

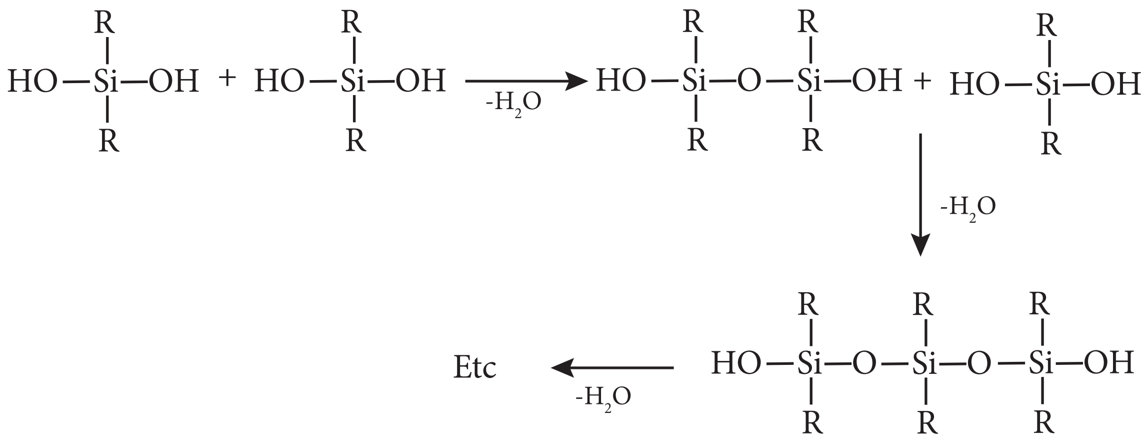
Generally silicones are prepared by the hydrolysis of dialkyldichlorosilanes (R_2SiCl_2) or diaryldichlorosilanes Ar_2SiCl_2, which are prepared by passing vapours of RCl or ArCl over silicon at 570 K with copper as a catalyst.

$$2RCl + Si \xrightarrow{Cu\ /\ 570\ K} R_2SiCl_2$$

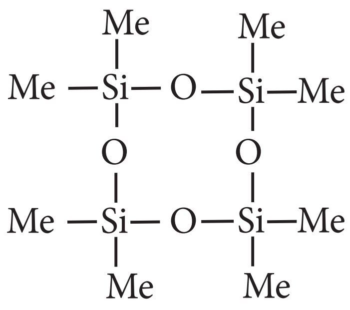
The hydrolysis of dialkylchloro silanes R_2SiCl_2 yields to a straight chain polymer which grown from both the sides

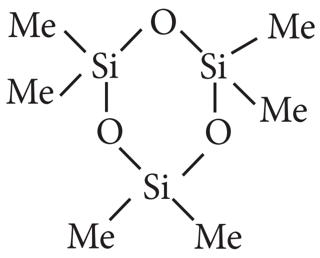


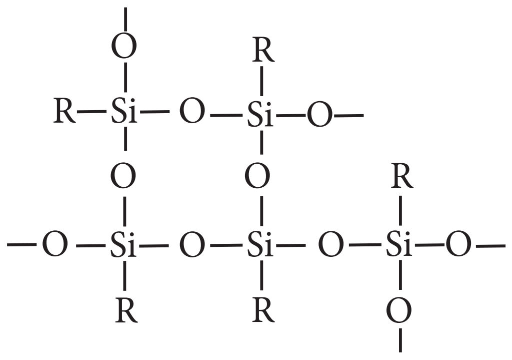
$$Cl-\overset{R}{\underset{R}{Si}}-Cl \xrightarrow[-2HCl]{+2H_2O} HO-\overset{R}{\underset{R}{Si}}-OH$$



The hydrolysis of monoalkylchloro silanes $RSiCl_3$ yields to a very complex cross linked polymer.. Linear silicones can be converted into cyclic or ring silicones when water molecules is removed from the terminal –OH groups.







Types of silicones:

(i) Liner silicones:

They are obtained by the hydrolysis and subsequent condensation of dialkyl or diaryl silicon chlorides.

a) **Silicone rubbers:** These silicones are bridged together by methylene or similar groups

b) **Silicone resins:** They are obtained by blending silicones with organic resins such as acrylic esters.

(ii) Cyclic silicones

These are obtained by the hydrolysis of R_2SiCl_2.

(iii) Cross linked silicones

They are obtained by hydrolysis of $RSiCl_3$

Properties

The extent of cross linking and nature of alkyl group determine the nature of polymer. They range from oily liquids to rubber like solids. All silicones are water repellent. This property arises due to the presence of organic side groups that surrounds the silicon which makes the molecule looks like an alkane. They are also thermal and electrical insulators. Chemically they are inert. Lower silicones are oily liquids whereas higher silicones with long chain structure are waxy solids. The viscosity of silicon oil remains constant and doesn't change with temperature and they don't thicken during winter

Uses:

1. Silicones are used for low temperature lubrication and in vacuum pumps, high temperature oil baths etc...
2. They are used for making water proofing clothes
3. They are used as insulting material in electrical motor and other appliances
4. They are mixed with paints and enamels to make them resistant towards high temperature, sunlight, dampness and chemicals.

2.3.9 Silicates

The mineral which contains silicon and oxygen in tetrahedral $[SiO_4]^{4-}$ units linked together in different patterns are called silicates. Nearly 95 % of the earth crust is composed of silicate minerals and silica. The glass and ceramic industries are based on the chemistry silicates.

Types of Silicates:

Silicates are classified into various types based on the way in which the tetrahedral units, $[SiO_4]^{4-}$ are linked together.

Ortho silicates (Neso silicates): The simplest silicates which contain discrete $[SiO_4]^{4-}$ tetrahedral units are called ortho silicates or neso silicates.

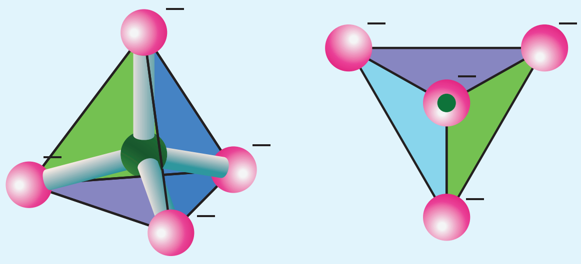


Figure 2.11
Structure of Ortho silicates

Examples : Phenacite - Be_2SiO_4 (Be^{2+} ions are tetrahedrally surrounded by O^{2-} ions), Olivine - $(Fe/Mg)_2SiO_4$ (Fe^{2+} and Mg^{2+} cations are octahedrally surrounded by O^{2-} ions),

Pyro silicate (or) Soro silicates):

Silicates which contain $[Si_2O_7]^{6-}$ ions are called pyro silicates (or) Soro silicates. They are formed by joining two $[SiO_4]^{4-}$tetrahedral units by sharing one oxygen atom at one corner.(one oxygen is removed while joining). Example : Thortveitite - $Sc_2Si_2O_7$

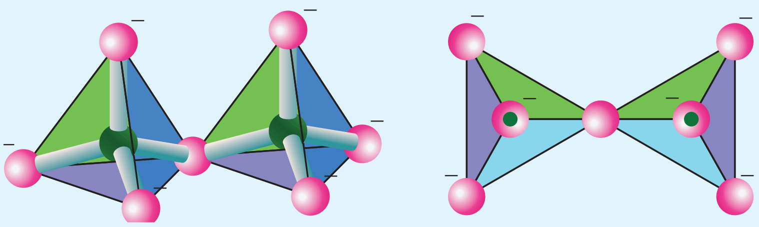


Figure 2.12 Structure of Pyro silicate

Cyclic silicates (or Ring silicates)

Silicates which contain $(SiO_3)_n^{2n-}$ ions which are formed by linking three or more tetrahedral SiO_4^{4-} units cyclically are called cyclic silicates. Each silicate unit shares two of its oxygen atoms with other units.

Example: Beryl $[Be_3Al_2\ (SiO_3)_6]$ (an aluminosilicate with each aluminium is surrounded by 6 oxygen atoms octahedrally)

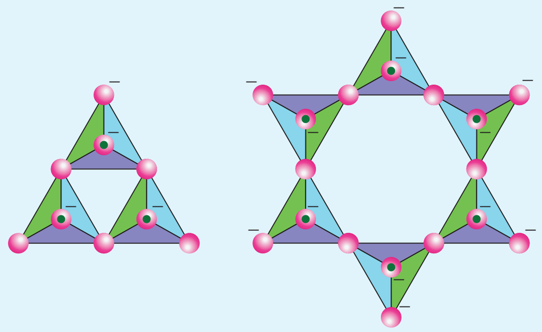


Figure 2.13 Structure of Cyclic silicates

Inosilicates :

Silicates which contain 'n' number of silicate units liked by sharing two or more oxygen atoms are called inosilicates. They are further classified as chain silicates and double chain silicates.

Chain silicates (or pyroxenes): These silicates contain $[(SiO_3)_n]^{2n-}$ ions formed by linking 'n' number of tetrahedral $[SiO_4]^{4-}$units linearly. Each silicate unit shares two of its oxygen atoms with other units.

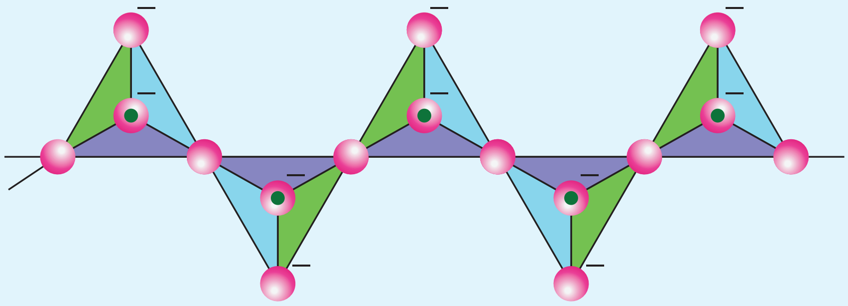


Figure 2.14 Structure of Chain silicates

Example: Spodumene - $LiAl(SiO_3)_2$.

Double chain silicates (or amphiboles): These silicates contains $[Si_4O_{11}]_n^{6n-}$ ions. In these silicates there are two different types of tetrahedra : (i) Those sharing 3 vertices (ii) those sharing only 2 vertices.

Examples:

1) **Asbestos :** These are fibrous and non-combustible silicates. Therefore they are used for thermal insulation material, brake linings, construction material and filters. Asbestos being carcinogenic silicates, their applications are restricted.

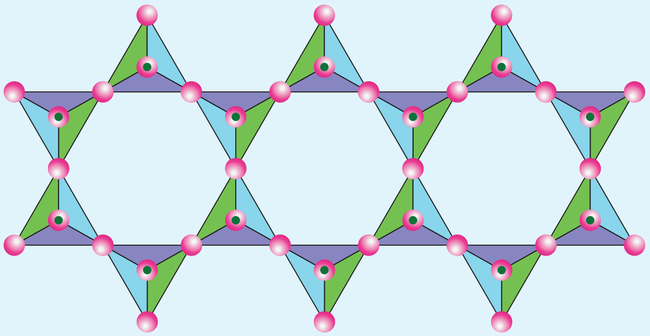


Figure 2.15 Structure of Double chain silicates

Sheet or phyllo silicates

Silicates which contain $(Si_2O_5)_n^{2n-}$ are called sheet or phyllo silicates. In these, Each $[SiO_4]^{4-}$ tetrahedron unit shares three oxygen atoms with others and thus by forming two-dimensional sheets. These sheets silicates form layered structures in which silicate sheets are stacked over each other. The attractive forces between these layers are very week, hence they can be cleaved easily just like graphite.

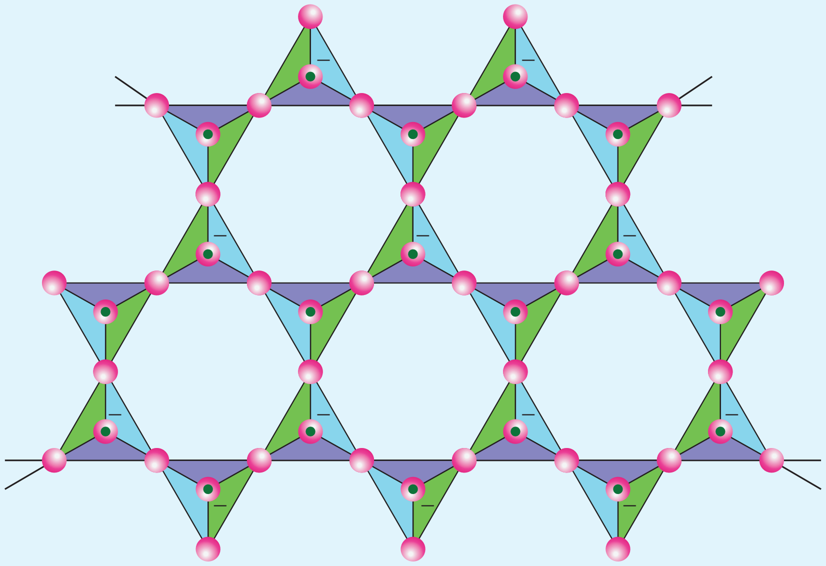


Figure 2.16 Structure of Sheet or phyllo silicates

Example: Talc, Mica etc...

Three dimensional silicates (or tecto silicates):

Silicates in which all the oxygen atoms of $[SiO_4]^{4-}$ tetrahedra are shared with other tetrahedra to form three-dimensional network are called three dimensional or tecto silicates. They have general formula $(SiO_2)_n$.

Examples: Quartz

These tecto silicates can be converted into Three dimentional aluminosilicates by replacing $[SiO_4]^{4-}$ units by $[AlO_4]^{5-}$ units. E.g. Feldspar, Zeolites etc.,

2.3.10 Zeolites:

Zeolites are three-dimensional crystalline solids containing aluminium, silicon, and oxygen in their regular three dimensional framework. They are hydrated sodium alumino silicates with general formula $NaO.(Al_2O_3).x(SiO_2).yH_2O$ (x=2 to 10; y=2 to 6).

Zeolites have porous structure in which the monovalent sodium ions and water molecules are loosely held. The Si and Al atoms are tetrahedrally coordinated with each other through shared oxygen atoms. Zeolites are similar to clay minerals but they differ in their crystalline structure.

Zeolites have a three dimensional crystalline structure looks like a honeycomb consisting of a network of interconnected tunnels and cages. Water molecules moves freely in and out of these pores but the zeolite framework remains rigid. Another special aspect of this structure is that the pore/channel sizes are nearly uniform, allowing the crystal to act as a molecular sieve. We have already discussed in XI standard, the removal of permanent hardness of water using zeolites.

DO YOU KNOW?

Boron Neutron Capture Therapy:

The affinity of Boron-10 for neutrons is the basis of a technique known as boron neutron capture therapy (BNCT) for treating patients suffering from brain tumours.

It is based on the nuclear reaction that occurs when boron-10 is irradiated with low-energy thermal neutrons to give high linear energy α particles and a Li particle.

Boron compounds are injected into a patient with a brain tumour and the compounds collect preferentially in the tumour. The tumour area is then irradiated with thermal neutrons and results in the release of an alpha particle that damages the tissue in the tumour each time a boron-10 nucleus captures a neutron. In this way damage can be limited preferentially to the tumour, leaving the normal brain tissue less affected. BNCT has also been studied as a treatment for several other tumours of the head and neck, the breast, the prostate, the bladder, andthe liver.

Summary

- The elements in which their last electron enters the 'p' orbital, constitute the p-block elements.
- The p-block elements have a general electronic configuration of ns^2, np^{1-6}. The elements of each group have similar outer shell electronic configuration and differ only in the value of n (principal quantum number).
- Generally on descending a group the ionisation energy decreases and hence the metallic character increases.
- The ionisation enthalpy of elements in successive groups is higher than the corresponding elements of the previous group as expected.
- As we move down the 13th group, the electronegativity first decreases from boron to aluminium and then marginally increases.

- In p-block elements, the first member of each group differs from the other elements of the corresponding group.
- In heavier post-transition metals, the outer s electrons (ns) have a tendency to remain inert and show reluctance to take part in the bonding, which is known as inert pair effect.
- Some elements exist in more than one crystalline or molecular forms in the same physical state. For example, carbon exists as diamond and graphite. This phenomenon is called allothropism
- Borax is a sodium salt of tetraboric acid. It is obtained from colemanite ore by boiling its solution with sodium carbonate.
- Boric acid can be extracted from borax and colemanite.
- Boric acid has a two dimensional layered structure.
- The name alum is given to the double salt of potassium aluminium sulphate [K_2SO_4.$Al_2(SO_4)_3$.24.H_2O].
- Carbon is found in the native form as graphite.
- Silicon occurs as silica (sand and quartz crystal). Silicate minerals and clay are other important sources for silicon.
- Catenation is an ability of an element to form chain of atoms
- Carbon nanotubes, another recently discovered allotropes, have graphite like tubes with fullerene ends.
- Silicones or poly siloxanes are organo silicon polymers with general empirical formula (R_2SiO). Because of their very high thermal stability they are called high –temperature polymers.
- The mineral which contains silicon and oxygen in tetrahedral $[SiO_4]^{4-}$ units linked together in different patterns are called silicates.
- Types of Silicates:
  - **Ortho silicates (Neso silicates), Pyro silicate (or) Soro silicates),** Cyclic silicates (or Ring silicates)
  - Inosilicates : **Chain silicates (or pyroxenes), Double chain silicates (or amphiboles):**
  - Sheet or phyllo silicates
  - Three dimensional silicates (or tecto silicates)
- Zeolites are three-dimensional crystalline solids containing aluminium, silicon, and oxygen in their regular three dimensional framework.
- zeolites act as a molecular sieve for the removal of permanent hardness of water

EVALUATION

XTYRAH

Choose the correct answer:

1. An aqueous solution of borax is

   a) neutral b) acidic c) basic d) amphoteric

2. Boric acid is an acid because its molecule (NEET)

   a) contains replaceable H^+ ion

   b) gives up a proton

   c) combines with proton to form water molecule

   d) accepts OH^- from water ,releasing proton.

3. Which among the following is not a borane?

   a) B_2H_6 b) B_3H_6 c) B_4H_{10} d) none of these

4. Which of the following metals has the largest abundance in the earth's crust?

   a) Aluminium b) calcium c) Magnesium d) sodium

5. In diborane, the number of electrons that accounts for banana bonds is

   a) six b) two c) four d) three

6. The element that does not show catenation among the following p-block elements is

   a) Carbon b) silicon c) Lead d) germanium

7. Carbon atoms in fullerene with formula C_{60} have

   a) sp^3 hybridised b) sp hybridised

   c) sp^2 hybridised d) partially sp^2 and partially sp^3 hybridised

8. Oxidation state of carbon in its hydrides

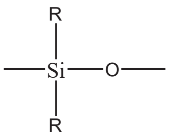
   a) +4 b) -4 c) +3 d) +2

9. The basic structural unit of silicates is (NEET)

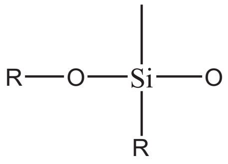
   a) $(SiO_3)^{2-}$ b) $(SiO_4)^{2-}$ c) $(SiO)^{-}$ d) $(SiO_4)^{4-}$

10. The repeating unit in silicone is

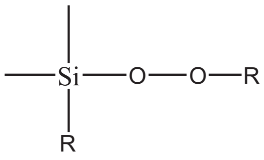
   a) SiO_2

   b) 

   $-\overset{R}{\underset{R}{Si}}-O-$

   c) 

   $R-O-\underset{R}{\overset{|}{Si}}-O$

   d) 

   $-\underset{R}{\overset{|}{Si}}-O-O-R$

11. Which of these is not a monomer for a high molecular mass silicone polymer?

a) Me_3SiCl b) $PhSiCl_3$ c) $MeSiCl_3$ d) Me_2SiCl_2

12. Which of the following is not sp^2 hybridised?

a) Graphite b) graphene c) Fullerene d) dry ice

13. The geometry at which carbon atom in diamond are bonded to each other is

a) Tetrahedral b) hexagonal c) Octahedral d) none of these

14. Which of the following statements is not correct?

a) Beryl is a cyclic silicate

b) Mg_2SiO_4 is an orthosilicate

c) SiO_4^{4-} is the basic structural unit of silicates

d) Feldspar is not aluminosilicate

15. AlF_3 is soluble in HF only in the presence of KF. It is due to the formation of (NEET)

a) $K_3[AlF_3H_3]$ b) $K_3[AlF_6]$

c) AlH_3 d) $K[AlF_3H]$

16. Match items in column - I with the items of column – II and assign the correct code.

Column-I		**Column-II**	
A	Borazole	1	$B(OH)_3$
B	Boric acid	2	$B_3N_3H_6$
C	Quartz	3	$Na_2[B_4O_5(OH)_4]\ 8H_2O$
D	Borax	4	SiO_2

	A	B	C	D
(a)	2	1	4	3
(b)	1	2	4	3
(c)	1	2	4	3
(d)	None of these			

17. Duralumin is an alloy of

a) Cu,Mn b) Cu,Al,Mg c) Al,Mn d) Al,Cu,Mn,Mg

18. Thermodynamically the most stable form of carbon is

a) Diamond b) graphite c) Fullerene d) none of these

19. The compound that is used in nuclear reactors as protective shields and control rods is

a) Metal borides b) metal oxides c) Metal carbonates d) metal carbide

20. The stability of +1 oxidation state increases in the sequence

a) Al < Ga < In < Tl b) Tl < In < Ga < Al

c) In < Tl < Ga < Al d) Ga< In < Al < Tl

Answer the following questions:

1. Write a short note on anamolous properties of the first element of p-block.
2. Describe briefly allotropism in p- block elements with specific reference to carbon.
3. Boron does not react directly with hydrogen. Suggest one method to prepare diborane from BF_3.
4. Give the uses of Borax.
5. What is catenation ? describe briefly the catenation property of carbon.
6. Write a note on Fisher tropsch synthesis.
7. Give the structure of CO and CO_2.
8. Give the uses of silicones.
9. $AlCl_3$ behaves like a lewis acid. Substantiate this statement.
10. Describe the structure of diborane.
11. Write a short note on hydroboration.
12. Give one example for each of the following

    (i) icosogens (ii) tetragen (iii) prictogen (iv) chalcogen

13. Write a note on metallic nature of p-block elements.

14. Complete the following reactions

    a. $B(OH)_3 + NH_3 \longrightarrow$

    b. $Na_2B_4O_7 + H_2SO_4 + H_2O \longrightarrow$

    c. $B_2H_6 + 2NaOH + 2H_2O \longrightarrow$

    d. $B_2H_6 + CH_3OH \longrightarrow$

    e. $BF_3 + 9\,H_2O \longrightarrow$

    f. $HCOOH + H_2SO_4 \longrightarrow$

    g. $SiCl_4 + NH_3 \longrightarrow$

    h. $SiCl_4 + C_2H_5OH \longrightarrow$

    i. $B + NaOH \longrightarrow$

    j. $H_2B_4O_7 \xrightarrow{\text{Red hot}}$

15. How will you identify borate radical?

16. Write a note on zeolites.

17. How will you convert boric acid to boron nitride?

18. A hydride of 2nd period alkali metal (A) on reaction with compound of Boron (B) to give a reducing agent (C). identify A , B and C.

19. A double salt which contains fourth period alkali metal (A) on heating at 500K gives (B). aqueous solution of (B) gives white precipitate with $BaCl_2$ and gives a red colour compound with alizarin. Identify A and B.

20. CO is a reducing agent . justify with an example.

UNIT 3

p-BLOCK ELEMENTS - II

Sir William Ramsay,
(1852 – 1916)

Sir William Ramsay was a Scottish chemist who discovered the noble gases. During the years 1885–1890 he published several important papers on the oxides of nitrogen.In August 1894, Ramsay had isolated a new heavy element of air, and he named it "argon", (the Greek word meaning "lazy").In the following years, he worked with Morris Travers and discovered neon, krypton, and xenon. In 1910 he isolated and characterized radon. In recognition of his services in the discovery of the inert gases, he was awarded a noble prize in chemistry in 1904. His work in isolating noble gases led to the development of a new section of the periodic table.

AQKKZD

Learning Objectives

After studying this unit, the students will be able to

- discuss the preparation and properties of important compounds of nitrogen and phosphorus
- describe the preparation and properties of important compounds of oxygen and sulphur
- describe the preparation, properties of halogens and hydrogen halides
- explain the chemistry of inter-halogen compounds
- describe the occurrence, properties and uses of noble gases
- appreciate the importance of p-block elements and their compounds in day today life.

INTRODUCTION

We have already learnt the general characteristics of p-block elements and the first two group namely icosagens (boron group) and tetragens (carbon group) in the previous unit. In this unit we learn the remaining p-block groups, pnictogens, chalcogens, halogens and inert gases.

3.1 Group 15 (Nitrogen group) elements:

3.1.1 Occurrence:

About 78 % of earth atmosphere contains dinitorgen (N_2) gas. It is also present in earth crust as sodium nitrate (Chile saltpetre) and potassium nitrates (Indian saltpetre). The 11th most abundant element phosphorous, exists as phosphate (fluroapatite, chloroapatite and hydroxyapatite). The other elements arsenic, antimony and bismuth are present as sulphides and are not very abundant.

3.1.2 Physical properties:

Some of the physical properties of the group 15 elements are listed below

Table 3.1 Physical properties of group 15 elements

Property	Nitrogen	Phosphorus	Arsenic	Antimony	Bismuth
Physical state at 293 K	Gas	Solid	Solid	Solid	Solid
Atomic Number	7	15	33	51	83
Isotopes	^{14}N, ^{15}N	^{31}P	^{75}As	^{121}Sb	^{209}Bi
Atomic Mass (g.mol^{-1} at 293 K)	14	30.97	74.92	121.76	209.98
Electronic configuration	[He]$2s^2$ $2p^3$	[Ne]$3s^2$ $3p^3$	[Ar]$3d^{10}$ $4s^2$ $4p^3$	[Kr]$4d^{10}$ $5s^2$ $5p^3$	[Xe] $4f^{14}$ $5d^{10}$ $6s^2$ $6p^3$
Atomic radius (Å)	1.55	1.80	1.85	2.06	2.07
Density (g.cm^{-3} at 293 K)	1.14×10^{-3}	1.82 (white phosphorus)	5.75	6.68	9.79
Melting point (K)	63	317	Sublimes at 889	904	544
Boiling point (K)	77	554		1860	1837

3.1.3 Nitrogen:

Preparation:

Nitrogen, the principle gas of atmosphere (78 % by volume) is separated industrially from liquid air by fractional distillation

Pure nitrogen gas can be obtained by the thermal decomposition of sodium azide about 575 K

$$2NaN_3 \longrightarrow 2\,Na + 3N_2$$

It can also be obtained by oxidising ammonia using bromine water

$$8NH_3 + 3Br_2 \longrightarrow 6NH_4Br + N_2$$

Properties

Nitrogen gas is rather inert. Terrestrial nitrogen contains 14.5% and 0.4% of nitrogen-14 and nitrogen-15 respectively. The later is used for isotopic labelling. The chemically inert character of nitrogen is largely due to high bonding energy of the molecules 225 cal mol^{-1} (946 kJ mol^{-1}). Interestingly the triply bonded species is notable for its less reactivity in comparison with other iso-electronic triply bonded systems such as -C≡C-, C≡O, X-C≡N, X-N≡C, -C≡C-, and -C≡N. These groups can act as donor where as dinitrogen cannot. However, it can form complexes with metal (M→ N≡N) like CO to a less extent

The only reaction of nitrogen at room temperature is with lithium forming Li_3N. With other elements, nitrogen combines only at elevated temperatures. Group 2 metals and Th forms ionic nitrides.

$$6Li + N_2 \longrightarrow 2Li_3N$$

$$3Ca + N_2 \xrightarrow{\text{red hot}} Ca_3N_2$$

$$2B + N_2 \xrightarrow{\text{bright red hot}} 2BN$$

Direct reaction with hydrogen gives ammonia. This reaction is favoured by high pressures and at optimum temperature in presence of iron catalyst. This reaction is the basis of Haber's process for the synthesis of ammonia.

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3 \quad \Delta H_f = -46.2 \text{ kJ mol}^{-1}$$

With oxygen, nitrogen produces nitrous oxide at high temperatures. Even at 3473 K nitrous oxide yield is only 4.4%.

$$2N_2 + O_2 \longrightarrow 2N_2O$$

Uses of nitrogen

1. Nitrogen is used for the manufacture of ammonia, nitric acid and calcium cyanamide etc.
2. Liquid nitrogen is used for producing low temperature required in cryosurgery, and so in biological preservation .

3.1.4 Ammonia (NH_3)

Preparation:

Ammonia is formed by the hydrolysis of urea.

$$NH_2CONH_2 + H_2O \longrightarrow 2NH_3 + CO_2$$

Ammonia is prepared in the laboratory by heating an ammonium salt with a base.

$$2NH_4^+ + OH^- \longrightarrow 2NH_3 + H_2O$$

$$2NH_4Cl + CaO \longrightarrow CaCl_2 + 2NH_3 + H_2O$$

It can also be prepared by heating a metal nitrides such as magnesium nitride with water.

$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$$

It is industrially manufactured by passing nitrogen and hydrogen over iron catalyst (a small amount of K_2O and Al_2O_3 is also used to increase the rate of attainment of equilibrium) at 750 K at 200 atm pressure. In the actual process the hydrogen required is obtained from water gas and nitrogen from fractional distillation of liquid air.

Properties

Ammonia is a pungent smelling gas and is lighter than air. It can readily liquefied by at about 9 atmospheric pressure. The liquid boils at -38.4°C and freezes at -77° C. Liquid ammonia resembles water in its physical properties. i.e. it is highly associated through strong hydrogen bonding. Ammonia is extremely soluble in water (702 Volume in 1 Volume of water) at 20°C and 760mm pressure.

At low temperatures two soluble hydrate $NH_3.H_2O$ and $2NH_3.H_2O$ are isolated. In these molecules ammonia and water are linked by hydrogen bonds. In aqueous solutions also ammonia may be hydrated in a similar manner and we call the same as $(NH_3.H_2O)$

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

The dielectric constant of ammonia is considerably high to make it a fairly good ionising solvent like water.

$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

$$K_{-50^0C} = [NH_4^+][NH_2^-] = 10^{-30}$$

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$K_{23^0C} = [H_3O^+][OH^-] = 10^{-14}$$

Chemical Properties

Action of heat: Above 500°C ammonia decomposes into its elements. The decomposition may be accelerated by metallic catalysts like Nickel, Iron. Almost complete dissociation occurs on continuous sparking.

$$2NH_3 \xrightarrow{>500^0 C} N_2 + 3H_2$$

Reaction with air/oxygen: Ammonia does not burn in air but burns freely in free oxygen with a yellowish flame to give nitrogen steam.

$$4NH_3 + 3O_2 \rightleftharpoons N_2 + 6H_2O$$

In presence of catalyst like platinum, it burns to produce nitric oxide. This process is used for the manufacture of nitric acid and is known as ostwalds process.

$$4NH_3 + 5O_2 \rightleftharpoons 4NO + 6H_2O$$

Reducing property: Ammonia acts as a reducing agent. It reduces the metal oxides to metal when passed over heated metallic oxide.

$$3PbO + 2NH_3 \longrightarrow 3Pb + N_2 + 3H_2O$$

Reaction with acids: When treated with acids it forms ammonium salts. This reaction shows that the affinity of ammonia for proton is greater than that of water.

Reaction with chlorine and chlorides: Ammonia reacts with chlorine and chlorides to give ammonium chloride as a final product. The reactions are different under different conditions as given below.

With excess ammonia

$$2\,NH_3 + 3\,Cl_2 \longrightarrow N_2 + 6\,HCl$$

$$6\,HCl + 6\,NH_3 \longrightarrow 6\,NH_4Cl$$

With excess of chlorine ammonia reacts to give nitrogen trichloride, an explosive substance.

$$2NH_3 + 6Cl_2 \longrightarrow 2NCl_3 + 6\,HCl$$

$$2NH_3(g) + HCl(g) \longrightarrow NH_4Cl\,(s)$$

Reaction of ammonia with HCL

Formation of amides and nitrides: With strong electro positive metals such as sodium, ammonia forms amides while it forms nitrides with metals like magnesium.

$$2Na + 2NH_3 \longrightarrow 2NaNH_2 + H_2$$

$$3Mg + 2NH_3 \longrightarrow Mg_3N_2 + 3H_2$$

With metallic salts: Ammonia reacts with metallic salts to give metal hydroxides (in case of Fe) or forming complexes (in case Cu)

$$Fe^{3+} + 3NH_4^+ \xrightarrow{3\,OH^-} Fe(OH)_3 + 3NH_4^+$$

$$Cu^{2+} + 4NH_3 \longrightarrow \underset{\substack{\text{Tetraamminecopper(II)ion} \\ \text{(a coordination complex)}}}{[Cu(NH_3)_4]^{2+}}$$

Formation of amines: Ammonia forms ammonated compounds by ion dipole attraction. Eg. $[CaCl_2.8NH_3]$. In this, the negative ends of ammonia dipole is attracted to Ca^{2+} ion.

It can also act as a ligand and form coordination compounds such as $[Co(NH_3)_6]^{3+}$, $[Ag(NH_3)_2]^+$. For example when excess ammonia is added to aqueous solution copper sulphate a deep blue colour compound $[Cu(NH_3)_4]^{2+}$ is formed.

Structure of ammonia

Ammonia molecule is pyramidal in shape N-H bond distance is 1.016 Å and H-H bond distance is 1.645 Å with a bond angle 107 °. The structure of ammonia may be regarded as a tetrahedral with

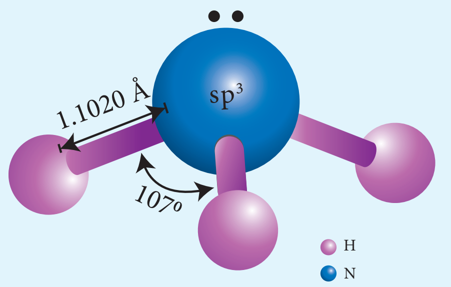


Figure 3.1 Structure of ammonia

one lone pair of electrons in one tetrahedral position hence it has a pyramidal shape as shown in the figure.

3.1.5 Nitric acid

Preparation

Nitric acid is prepared by heating equal amounts of potassium or sodium nitrate with concentrated sulphuric acid.

$$KNO_3 + H_2SO_4 \longrightarrow KHSO_4 + HNO_3$$

The temperature is kept as low as possible to avoid decomposition of nitric acid. The acid condenses to a fuming liquids which is coloured brown by the presence of a little nitrogen dioxide which is formed due to the decomposition of nitric acid.

$$4HNO_3 \longrightarrow 4NO_2 + 2H_2O + O_2$$

Commercial method of preparation

Nitric acid prepared in large scales using Ostwald's process. In this method ammonia from Haber's process is mixed about 10 times of air. This mixture is preheated and passed into the catalyst chamber where they come in contact with platinum gauze. The temperature rises to about 1275 K and the metallic gauze brings about the rapid catalytic oxidation of ammonia resulting in the formation of NO, which then oxidised to nitrogen dioxide.

$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O + 120\text{ kJ}$$

$$2NO + O_2 \longrightarrow 2NO_2$$

The nitrogen dioxide produced is passed through a series of adsorption towers. It reacts with water to give nitric acid. Nitric acid formed is bleached by blowing air.

$$6NO_2 + 3H_2O \longrightarrow 4HNO_3 + 2NO + H_2O$$

Properties

Pure nitric acid is colourless. It boils at 86 °C. The acid is completely miscible with water forming a constant boiling mixture (98% HNO_3, Boiling point 120.5 °C). Fuming nitric acid contains oxides of nitrogen. It decomposes on exposure to sunlight or on being heated, into nitrogen dioxide, water and oxygen.

$$4HNO_3 \longrightarrow 4NO_2 + 2H_2O + O_2$$

Due to this reaction pure acid or its concentrated solution becomes yellow on standing.

In most of the reactions, nitric acid acts as an oxidising agent. Hence the oxidation state changes from +5 to a lower one. It doesn't yield hydrogen in its reaction with metals. Nitric acid can act as an acid, an oxidizing agent and an nitrating agent.

As an acid: Like other acids it reacts with bases and basic oxides to form salts and water

$$ZnO + 2HNO_3 \longrightarrow Zn(NO_3)_2 + H_2O$$

$$3FeO + 10HNO_3 \longrightarrow 3Fe(NO_3)_3 + NO + 5\,H_2O$$

As an oxidising agent: The nonmetals like carbon, sulphur, phosphorus and iodine are oxidised by nitric acid.

$$C + 4HNO_3 \longrightarrow 2H_2O + 4NO_2 + CO_2$$

$$S + 2HNO_3 \longrightarrow H_2SO_4 + 2NO$$

$$P_4 + 20HNO_3 \longrightarrow 4H_3PO_4 + 4H_2O + 20NO_2$$

$$3I_2 + 10HNO_3 \longrightarrow 6HIO_3 + 10NO + 2H_2O$$

$$HNO_3 + F_2 \longrightarrow HF + NO_3F$$

$$3H_2S + 2HNO_3 \longrightarrow 3S + 2NO + 4H_2O$$

As an nitrating agent: In organic compounds replacement of a –H atom with $-NO_2$ is often referred as nitration. For example.

$$C_6H_6 + HNO_3 \xrightarrow{H_2SO_4} C_6H_5NO_2 + H_2O$$

Nitration takes place due to the formation of nitronium ion

$$HNO_3 + H_2SO_4 \longrightarrow NO_2^+ + H_3O^+ + HSO_4^-$$

Action of nitric acid on metals

All metals with the exception of gold, platinum, rhodium, iridium and tantalum reacts with nitric acid. Nitric acid oxidises the metals. Some metals such as aluminium, iron, cobalt, nickel and chromium are rendered passive in concentrated acid due to the formation of a layer of their oxides on the metal surface, which prevents the nitric acid from reacting with pure metal.

With weak electropositive metals like tin, arsenic, antimony, tungsten and molybdenum, nitric acid gives metal oxides in which the metal is in the higher oxidation state and the acid is reduced to a lower oxidation state. The most common products evolved when nitric acid reacts with a metal are gases NO_2, NO and H_2O. Occasionally N_2, NH_2OH and NH_3 are also formed.

$$\overset{+5}{HNO_3} \quad \overset{+4}{NO_2} \quad \overset{+3}{HNO_2} \quad \overset{+2}{NO} \quad \overset{+1}{N_2O} \quad \overset{0}{N_2} \quad \overset{-3}{NH_3}$$

The reactions of metals with nitric acid are explained in 3 steps as follows:

Primary reaction: Metal nitrate is formed with the release of nascent hydrogen

$$M + HNO_3 \longrightarrow MNO_3 + (H)$$

Secondary reaction: Nascent hydrogen produces the reduction products of nitric acid.

$$HNO_3 + 2H \longrightarrow \underset{\text{Nitrous acid}}{HNO_2} + H_2O$$

$$HNO_3 + 6H \longrightarrow \underset{\text{Hydroxylamine}}{NH_2OH} + 2H_2O$$

$$HNO_3 + 8H \longrightarrow \underset{\text{Ammonia}}{NH_3} + 3H_2O$$

$$2HNO_3 + 8H \longrightarrow \underset{\text{Hypo nitrous acid}}{H_2N_2O_2} + 4H_2O$$

Tertiary reaction: The secondary products either decompose or react to give final products

Decomposition of the secondary:

$$3\ \underset{\text{Nitrous acid}}{HNO_2} \longrightarrow \underset{\text{Nitric acid}}{HNO_3} + 2\ \underset{\text{Nitric oxide}}{NO} + H_2O$$

$$2\ \underset{\text{Nitrous acid}}{HNO_2} \longrightarrow \underset{\text{Dinitrogentrioxide}}{N_2O_3} + H_2O$$

$$\underset{\text{Hypo nitrous acid}}{H_2N_2O_2} \longrightarrow \underset{\text{Nitrous oxide}}{N_2O} + H_2O$$

Reaction of secondary products:

$$HNO_2 + NH_3 \longrightarrow N_2 + 2H_2O$$

$$HNO_2 + NH_2OH \longrightarrow N_2O + 2H_2O$$

$$HNO_2 + HNO_3 \longrightarrow 2NO_2 + H_2O$$

Examples:

Copper reacts with nitric acid in the following manner

$$3Cu + 6HNO_3 \longrightarrow 3Cu(NO_3)_2 + 6(H)$$

$$6(H) + 3HNO_3 \longrightarrow 3HNO_2 + 3H_2O$$

$$3HNO_2 \longrightarrow HNO_3 + 2NO + H_2O$$

overall reation

$$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

The concentrated acid has a tendency to form nitrogen dioxide

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

Magnesium reacts with nitric acid in the following way

$$4Mg + 8HNO_3 \longrightarrow 4Mg(NO_3)_2 + 8[H]$$

$$HNO_3 + 8H \longrightarrow NH_3 + 3H_2O$$

$$HNO_3 + NH_3 \longrightarrow NH_4NO_3$$

overall reaction

$$4Mg + 10HNO_3 \longrightarrow 4Mg(NO_3)_2 + NH_4NO_3 + 3H_2O$$

If the acid is diluted we get N_2O

$$4Mg + 10HNO_3 \longrightarrow 4Mg(NO_3)_2 + N_2O + 5H_2O$$

Uses of nitric acid:

3. Nitric acid is used as a oxidising agent and in the preparation of aquaregia.
4. Salts of nitric acid are used in photography ($AgNO_3$) and gunpowder for firearms. ($NaNO_3$)

Evaluate yourself :

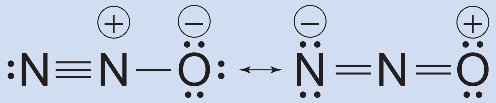
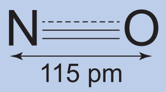
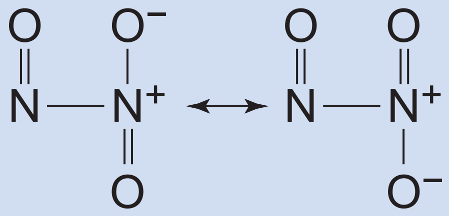
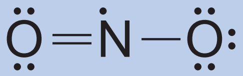
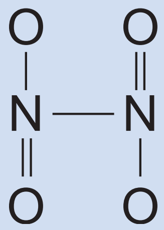
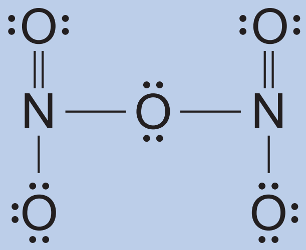
Write the products formed in the reaction of nitric acid (both dilute and concentrated) with zinc.

3.1.6 Oxides and oxoacids of nitrogen

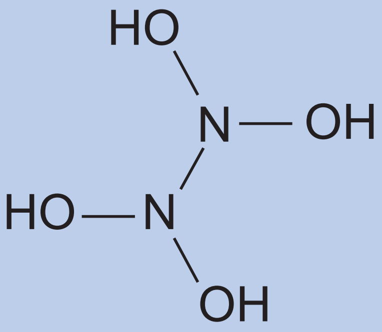
Name	Formula	Oxidation state	Physical properties	Preparation
Nitrous oxide	N_2O	**+1**	Colourless gas & neutral	$NH_4NO_3 \rightarrow N_2O + 2H_2O$
Nitric oxide	**NO**	**+2**	Colourless gas & neutral	$2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$
Dinitrogen trioxide (or) Nitrogen sesquoxide	$\mathbf{N_2O_3}$	**+3**	Blue solid & acidic	$2NO + N_2O_4 \rightarrow 2N_2O_3$
Nitrogen dioxide	$\mathbf{NO_2}$	**+4**	Brown gas & acidic	$2Pb(NO_3)_2 \rightarrow 4NO_2 + 2PbO + 3O_2$
Nitrogen tetraoxide	$\mathbf{N_2O_4}$	**+4**	Colourless solid & acidic	$2NO_2 \rightarrow N_2O_4$
Nitrogen pentoxide	$\mathbf{N_2O_5}$	**+5**	Colourless solid & acidic	$2HNO_3 + P_2O_5 \rightarrow N_2O_5 + 2HPO_3$

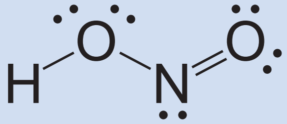
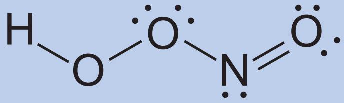
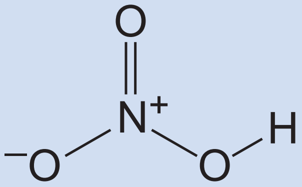
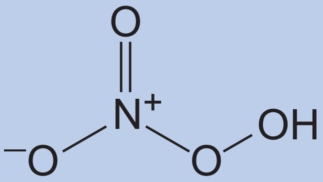
Preparation of nitrogen oxides

Structures of oxides of nitrogen:

Name	Formula	Structure
Nitrous oxide	N_2O	
Nitric oxide	**NO**	
Dinitrogen trioxide (or) Nitrogen sesquoxide	$\mathbf{N_2O_3}$	
Nitrogen dioxide	$\mathbf{NO_2}$	
Nitrogen tetraoxide	$\mathbf{N_2O_4}$	
Nitrogen pentoxide	$\mathbf{N_2O_5}$	

Structures of oxoacids of nitrogen:

Name	Formula	Structure
Hyponitrous acid	$H_2N_2O_2$	$HO-N=N-OH$
Hydronitrous acid	$H_4N_2O_4$	

Nitrous acid	**HNO_2**	
Pernitrous acid	**HOONO**	
Nitric acid	**HNO_3**	
Pernitric acid	**HNO_4**	

Preparation of oxoacids of nitrogen:

Name	Formula	Oxidation state	Preparation
Hyponitrous acid	$H_2N_2O_2$	+1	$Ag_2N_2O_2 + 2HCl \longrightarrow 2AgCl + H_2N_2O_2$
Nitrous acid	HNO_2	+3	$Ba(NO_2)_2 + H_2SO_4 \longrightarrow 2HNO_2 + BaSO_4$
Pernitrous acid	HOONO	+5	$H_2O_2 + ON(OH) \longrightarrow ON(OOH) + H_2O$
Nitric acid	HNO_3	+5	$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$ $2NO + O_2 \longrightarrow NO_2$ $2NO_2 \longrightarrow N_2O_4$ $2N_2O_4 + 2H_2O + O_2 \longrightarrow 4HNO_3$
Pernitric acid	HNO_4	+7	$H_2O_2 + N_2O_5 \longrightarrow NO_2OOH + HNO_3$

3.1.7 Allotropic forms of phosphorus:

Phosphorus has several allotropic modification of which the three forms namely white, red and black phosphorus are most common.

The freshly prepared white phosphorus is colourless but becomes pale yellow due to formation of a layer of red phosphorus upon standing. Hence it is also known as yellow phosphorus. It is poisonous in nature and has a characteristic garlic smell. It glows in the dark due to oxidation which is called phosphorescence. Its ignition temperature is very low and hence it undergoes spontaneous combustion in air at room temperature to give P_2O_5.

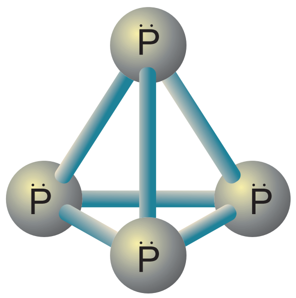


Figure 3.2 Structure of white phosphorous

The white phosphorus can be changed into red phosphorus by heating it to 420 ^{0}C in the absence of air and light. Unlike white phosphorus it is not poisonous and does not show Phosphorescence. It also does not ignite at low temperatures. The red phosphorus can be converted back into white phosphorus by boiling it in an inert atmosphere and condensing the vapour under water.

The phosphorus has a layer structure and also acts as a semiconductor. The four atoms in phosphorus have polymeric structure with chains of P_4 linked tetrahedrally. Unlike nitrogen P≡P is less stable than P-P single bonds. Hence, phosphorus atoms are linked through single bonds rather than triple bonds. In addition to the above two more allotropes namely scarlet and violet phosphorus are also known for phosphorus.

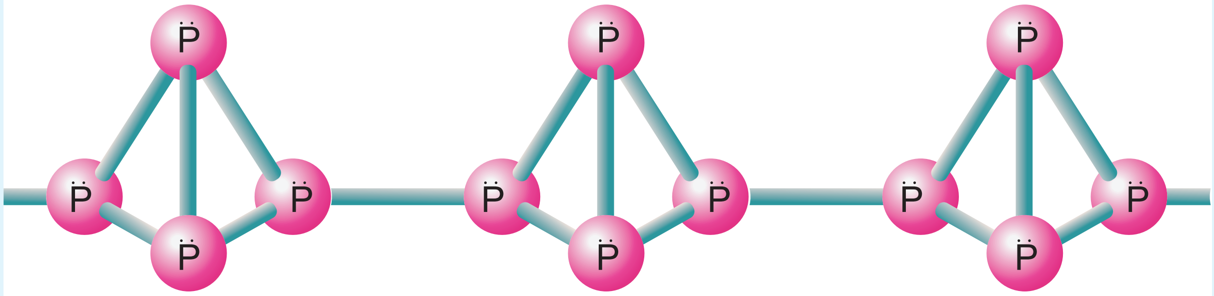


Figure 3.3 Structure of red phosphorous

3.1.8 Properties of phosphorus

Phosphorus is highly reactive and has the following important chemical properties

Reaction with oxygen: Yellow phosphorus readily catches fire in air giving dense white fumes of phosphorus pentoxide. Red phosphorus also reacts with oxygen on heating to give phosphorus trioxide or phosphorus pentoxide.

$$P_4 + 3O_2 \xrightarrow{\Delta} \underset{\text{Phosphoroustrioxide}}{P_4O_6}$$

$$P_4 + 5O_2 \xrightarrow{\Delta} \underset{\text{Phosphorouspentoxide}}{P_4O_{10}}$$

Reaction with chlorine: Phosphorus reacts with chlorine to form tri and penta chloride. Yellow phosphorus reacts violently at room temperature, while red phosphorous reacts on heating

$$P_4 + 6Cl_2 \longrightarrow \underset{\text{Phosphorous tri chloride}}{4PCl_3}$$

$$P_4 + 10Cl_2 \longrightarrow \underset{\text{Phosphorous penta chloride}}{4PCl_5}$$

Reaction with alkali: Yellow phosphorous reacts with alkali on boiling in an inert atmosphere liberating phosphine. Here phosphorus act as reducing agent.

$$P_4 + 3NaOH + 3H_2O \longrightarrow \underset{\text{sodium hypo phosphite}}{3NaH_2PO_2} + \underset{\text{Phosphine}}{PH_3\uparrow}$$

Reaction with nitric acid: When phosphorous is treated with conc. nitric acid it is oxidised to phosphoric acid. This reaction is catalysed by iodine crystals.

$$P_4 + 20HNO_3 \longrightarrow \underset{\text{Ortho phosphoric acid}}{4H_3PO_4} + 20NO_2 + 4H_2O$$

Reaction with metals: Phosphorous reacts with metals like Ca and Mg to give phosphides.. Metals like sodium and potassium react with phosphorus vigorously.

$$P_4 + 6Mg \longrightarrow \underset{\text{Magnesium phosphide}}{2Mg_3P_2}$$

$$P_4 + 6Ca \longrightarrow \underset{\text{Calcium phosphide}}{2Ca_3P_2}$$

$$P_4 + 12Na \longrightarrow \underset{\text{Sodium phosphide}}{4Na_3P} \quad .$$

Uses of phosphorous:

1. The red phosphorus is used in the match boxes
2. It is also used for the production of certain alloys such as phosphor bronze

3.1.9 Phosphine (PH_3)

Phosphine is the most important hydride of phosphorous

Preparation:

Phosphine is prepared by action of sodium hydroxide with white phosphorous in an inert atmosphere of carbon dioxide or hydrogen.

$$P_4 + 3NaOH + 3H_2O \longrightarrow \underset{\text{sodium hypo phosphite}}{3NaH_2PO_2} + \underset{\text{Phosphine}}{PH_3\uparrow}$$

Phosphine is freed from phosphine dihydride(P_2H_4) by passing through a freezing mixture. The dihydride condenses while phosphine does not.

Phosphine can also prepared by the hydrolysis of metallic phosphides with water or dilute mineral acids.

$$Ca_3P_2 + 6H_2O \longrightarrow \underset{\text{Phosphine}}{2PH_3} \uparrow + 3Ca(OH)_2$$

$$AlP + 3HCl \longrightarrow \underset{\text{Phosphine}}{PH_3} \uparrow + AlCl_3$$

Phosphine is prepared in pure form by heating phosphorous acid.

$$\underset{\text{Phosphorous acid}}{4H_3PO_3} \xrightarrow{\Delta} \underset{\text{Ortho phosphoric acid}}{3H_3PO_4} + \underset{\text{Phosphine}}{PH_3} \uparrow$$

A pure sample of phosphine is prepared by heating phosphonium iodide with caustic soda solution.

$$PH_4I + NaOH \xrightarrow{\Delta} \underset{\text{Phosphine}}{PH_3} \uparrow + NaI + H_2O$$

Physical properties:

It is colourless, poisonous gas with rotten fish smell. It is slightly soluble in water and is neutral to litmus test. It condenses to a colourless liquid at 188 K and freezes to a solid at 139.5 K .

Chemical properties:

Thermal stability: Phosphine decomposes into its elements when heated in absence of air at 317 K or when electric current is passed through it.

$$4PH_3 \xrightarrow{317K} P_4 + 6H_2$$

Combustion: When phosphine is heated with air or oxygen it burns to give meta phosphoric acid.

$$4PH_3 + 8O_2 \xrightarrow{\Delta} \underset{\text{Phosphorous pentoxide}}{P_4O_{10}} + 6H_2O$$

$$P_4O_{10} + 6H_2O \xrightarrow{\Delta} \underset{\text{Meta phosphoric acid}}{4HPO_3} + 4H_2O$$

Basic nature: Phosphine is weakly basic and forms phosphonium salts with halogen acids.

$$PH_3 + HI \longrightarrow PH_4I$$

$$PH_4I + H_2O \xrightarrow{\Delta} \underset{\text{Phosphine}}{PH_3} + H_3O^+ + I^-$$

It reacts with halogens to give phosphorus penta halides.

$$PH_3 + 4Cl_2 \longrightarrow PCl_5 + 3HCl$$

Reducing property : Phosphine precipitates some metal from their salt solutions.

$$3AgNO_3 + PH_3 \longrightarrow Ag_3P + 3HNO_3$$

It forms coordination compounds with lewis acids such as boron trichloride.

$$BCl_3 + PH_3 \longrightarrow \underset{\text{Coordination compound}}{[Cl_3B \leftarrow : PH_3]}$$

Structure:

In phosphine, phosphorus shows sp^3 hybridisation. Three orbitals are occupied by bond pair and fourth corner is occupied by lone pair of electrons. Hence, bond angle is reduced to 94°. Phosphine has a pyramidal shape.

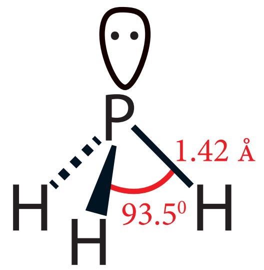


Figure 3.4 Structure of phosphine

Uses of phosphine:

Phosphine is used for producing smoke screen as it gives large smoke. In a ship, a pierced container with a mixture of calcium carbide and calcium phosphide, liberates phosphine and acetylene when thrown into sea. The liberated phosphine catches fire and ignites acetylene. These burning gases serves as a signal to the approaching ships. This is known as **Holmes signal**.

3.1.10 Phosphorous trichloride and pentachloride:

Phosphorous trichloride:

Preparation:

When a slow stream of chlorine is passed over white phosphorous, phosphorous trichloride is formed. It can also be obtained by treating white phosphorous with thionyl chloride.

$$P_4 + 8SOCl_2 \longrightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$$

Properties

When phosphorous trichloride is hydrolysed with cold water it gives phosphorous acid.

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$

This reaction involves the coordination of a water molecule using a vacant 3d orbital on the phosphorous atom following by elimination of HCl which is similar to hydrolysis of $SiCl_4$.

$$PCl_3 + H_2O \longrightarrow PCl_3.H_2O \longrightarrow P(OH)Cl_2 + HCl$$

This reaction is followed by two more steps to give $P(OH)_3$ or H_3PO_3.

$$HPOC1_2 + H_2O \longrightarrow H_2PO_2Cl + HCl$$
$$H_2PO_2Cl + H_2O \longrightarrow H_2PHO_3 + HCl$$

Similar reactions occurs with other molecules that contains alcohols and carboxylic acids.

$$C_2H_5OH + PCl_3 \longrightarrow C_2H_5Cl + H_3PO_3$$
$$C_2H_5COOH + PCl_3 \longrightarrow C_2H_5COCl + H_3PO_3$$

Uses of phosphorus trichloride:

Phosphorus trichloride is used as a chlorinating agent and for the preparation of H_3PO_3.

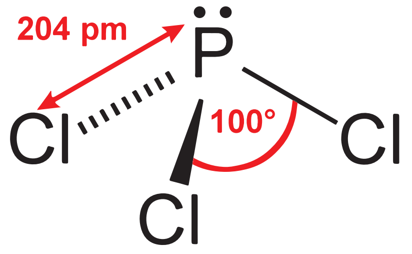


Figure 3.5 Structure of phosphorus trichloride

Phosphorous pentachloride:

Preparation

When PCl_3 is treated with excess chlorine, phosphorous pentachloride is obtained.

$$PCl_3 + Cl_2 \longrightarrow PCl_5$$

Chemical properties

On heating phosphorous pentachloride, it decomposes into phosphorus trichloride and chlorine.

$$PCl_{5}(g) \longrightarrow PCl_{3}(g) + \underset{(Excess)}{Cl_{2}(g)}.$$

Phosphorous pentachloride reacts with water to give phosphoryl chloride and orthophosphoric acid.

$$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$$

$$POCl_3 + 3H_2O \longrightarrow H_3PO_4 + 3HCl$$

Overall reaction

$$PCl_5 + 4H_2O \longrightarrow H_3PO_4 + 5HCl$$

Phosphorous pentachloride reacts with metal to give metal chlorides. It also chlorinates organic compounds similar to phosphorus trichloride.

$$2Ag + 2PCl_5 \longrightarrow 2AgCl + 2PCl_3$$

$$Sn + 4PCl_5 \longrightarrow SnCl_4 + 4PCl_3$$

$$C_2H_5OH + PCl_5 \longrightarrow C_2H_5Cl + HCl + POCl_3$$

$$C_2H_5COOH + PCl_5 \longrightarrow C_2H_5COCl + HCl + POCl_3$$

Uses of phosphorus pentachloride

Phosphorous pentachloride is a chlorinating agent and is useful for replacing hydroxyl groups by chlorine atom.

3.1.11 Structure of oxides and oxoacids of phosphorus

Phosphorous forms phosphorous trioxide, phosphorous tetra oxide and phosphorous pentaoxides

In phosphorous trioxide four phosphorous atoms lie at the corners of a tetrahedron and six oxygen atoms along the edges. The P-O bond distance is 165.6

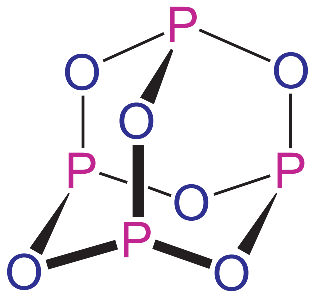


Figure 3.6 Structure of P_2O_3

pm which is shorter than the single bond distance of P-O (184 pm) due to pπ-dπ bonding and results in considerable double bond character.

In P_4O_{10} each P atoms form three bonds to oxygen atom and also an additional coordinate bond with an oxygen atom.

Terminal coordinate P-O bond length is 143 pm, which is less than the expected single bond distance. This may be due to lateral overlap of filled p orbitals of an oxygen atom with empty d orbital on phosphorous.

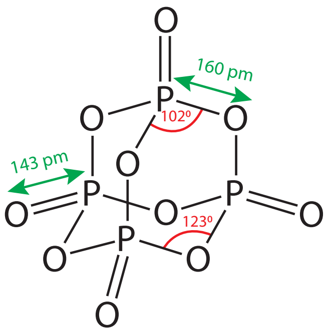
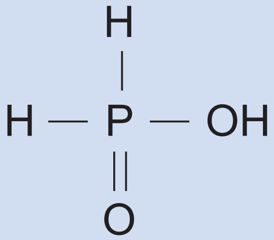
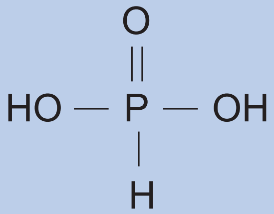
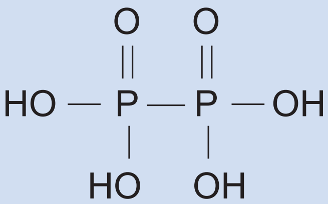
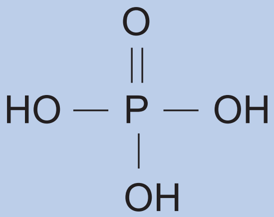
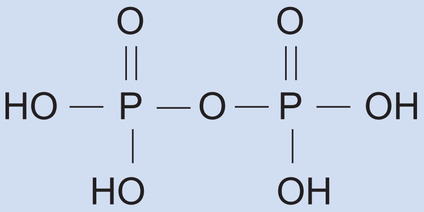


Figure 3.7 Structure of P_4O_{10}

Oxoacids of Phosphorous-Structure:

Name	Formula	Structure
Hypophosphorous acid	H_3PO_2	
Orthophosphrous acid	H_3PO_3	
Hypophosphoric acid	$H_4P_2O_6$	
Orthophosphoric acid	H_3PO_4	
Pyrophosphoric acid	$H_4P_2O_7$	

Oxoacids of Phosphorous-Preparation:

Name	Formula	Oxidation state	Preparation
Hypophosphorous acid	H_3PO_2	+1	$P_4 + 6H_2O \longrightarrow 3H_3PO_2 + PH_3$
Orthophosphrous acid	H_3PO_3	+3	$P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3$
Hypophosphoric acid	$H_4P_2O_6$	+4	$2P + 2O_2 + 2H_2O \longrightarrow H_4P_2O_6$
Orthophosphoric acid	H_3PO_4	+5	$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$
Pyrophosphoric acid	$H_4P_2O_7$	+5	$2H_3PO_3 \longrightarrow H_4P_2O_7 + H_2O$

Group 16 (Oxygen group) elements:

Occurrence:

Elements belonging group 16 are called chalgogens or ore forming elements as most of the ores are oxides or sulphides. First element oxygen, the most abundant element, exists in both as dioxygen in air (above 20 % by weight as well as volume) and in combined form as oxides. Oxygen and sulphur makes up about 46.6 % & 0.034 & of earth crust by weight respectively. Sulphur exists as sulphates (gypsum, epsom etc...) and sulphide (galena, Zinc blende etc...). It is also present in the volcanic ashes. The other elements of this groups are scarce and are often found as selenides, tellurides etc... along with sulphide ores.

Physical properties:

The common physical properties of the group 16 elements are listed in the Table.

Table 3.2 Physical properties of group 16 elements

Property	Oxygen	Sulphur	Selenium	Tellurium	Polonium
Physical state at 293 K	Gas	Solid	Solid	Solid	Solid
Atomic Number	8	16	34	52	84
Isotopes	^{16}O	^{32}S	^{80}Se	^{130}Te	^{209}Po, ^{210}Po
Atomic Mass (g.mol^{-1} at 293 K)	15.99	32.06	78.97	127.60	209
Electronic configuration	[He]$2s^2\ 2p^4$	[Ne]$3s^2\ 3p^4$	[Ar]$3d^{10}\ 4s^2\ 4p^4$	[Kr]$4d^{10}\ 5s^2\ 5p^4$	[Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^4$

Atomic radius (Å)	1.52	1.80	1.90	2.06	1.97
Density ($g.cm^{-3}$ at 293 K)	1.3×10^{-3}	2.07	4.81	6.23	9.20
Melting point (K)	54	388	494	723	527
Boiling point (K)	90	718	958	1261	1235

3.2 Oxygen:

Preparation: The atmosphere and water contain 23% and 83% by mass of oxygen respectively. Most of the world's rock contain combined oxygen. Industrially oxygen is obtained by fractional distillation of liquefied air. In the laboratory, oxygen is prepared by one of the following methods.

The decomposition of hydrogen peroxide in the presence of catalyst (MnO_2) or by oxidation with potassium permanganate.

$$2H_2O_2 \rightleftharpoons 2H_2O + O_2$$

$$5H_2O_2 + 2MnO_4^- + 6H^+ \longrightarrow 5O_2 + 8H_2O + 2Mn^{2+}$$

The thermal decomposition of certain metallic oxides or oxoanions gives oxygen.

$$2HgO \xrightarrow{\Delta} 2Hg + O_2$$

$$2BaO_2 \xrightarrow{\Delta} 2BaO + O_2$$

$$2KClO_3 \xrightarrow[MnO_2]{\Delta} 2KCl + 3O_2$$

$$2KNO_3 \xrightarrow{\Delta} 2KNO_2 + O_2$$

Properties

Under ordinary condition oxygen exists as a diatomic gas. Oxygen is paramagnetic. Like nitrogen and fluorine, oxygen form strong hydrogen bonds. Oxygen exists in two allotropic forms namely dioxygen (O_2) and ozone or trioxygen (O_3). Although negligible amounts of ozone occurs at sea level it is formed in the upper atmosphere by the action of ultraviolet light. In the laboratory ozone is prepared by passing electrical discharge through oxygen. At a potential of 20,000 V about 10% of oxygen is converted into ozone it gives a mixture known as ozonised oxygen. Pure ozone is obtained as a pale blue gas by the fractional distillation of liquefied ozonised oxygen.

$$\underset{\text{Oxygen}}{O_2} \rightleftharpoons \underset{\text{atomic oxygen}}{2(O)}$$

$$O_2 + (O) \rightleftharpoons \underset{\text{Ozone}}{O_3}$$

The ozone molecule have a bent shape and symmetrical with delocalised bonding between the oxygen atoms.

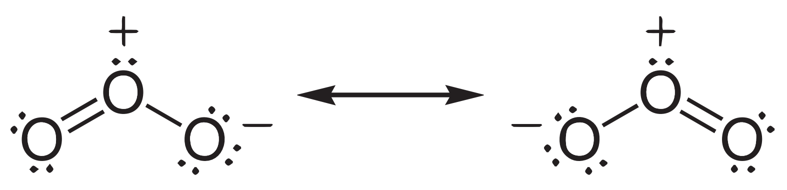


Figure 3.8 Structure of ozone

Chemical properties:

The chemical properties of oxygen and ozone differ vastly. Oxygen combines with many metals and non-metals to form oxides. With some elements such as s-block elements combination of oxygen occurs at room temperature. Some of less reactive metals react when powdered finely and made to react exothermically with oxygen at room temperature but a lump of metal is unaffected under same condition. These finely divided metals are known as pyrophoric and when set the powder on fire, heat is liberated during a reaction.

On the other hand ozone is a powerful oxidising agent and it reacts with many substances under conditions where oxygen will not react. For example, it oxidises potassium iodide to iodine. This reaction is quantitative and can be used for estimation of ozone.

$$O_3 + 2KI + H_2O \longrightarrow 2KOH + O_2 + I_2$$

Ozone is commonly used for oxidation of organic compounds. In acidic solution ozone exceeds the oxidising power of fluorine and atomic oxygen. The rate of decomposition of ozone drops sharply in alkaline solution.

Uses:

1. Oxygen is one of the essential component for the survival of living organisms.
2. It is used in welding (oxyacetylene welding)
3. Liquid oxygen is used as fuel in rockets etc...

3.2.1 Allotrophic forms of sulphur

Sulphur exists in crystalline as well as amorphous allotrophic forms. The crystalline form includes rhombic sulphur (α sulphur) and monoclinic sulphur (β sulphur). Amorphous allotropic form includes plastic sulphur (γ sulphur), milk of sulphur and colloidal sulphur.

Rhombic sulphur also known as α sulphur, is the only thermodynamically stable allotropic form at ordinary temperature and pressure. The crystals have a characteristic yellow colour and composed of S_8 molecules. When heated slowly above 96 ^{0}C, it converts into monoclinic sulphur. Upon cooling below 96 ^{0}C the β form converts back to α form. **Monoclinic sulphur** also contains S_8 molecules in addition to small amount of S_6 molecules. It exists as a long needle like prism and is also called as prismatic sulphur. It is stable between 96 ^{0} - 119 ^{0}C and slowly changes into rhombic sulphur.

When molten sulphur is poured into cold water a yellow rubbery ribbon of plastic sulphur is produced. They are very soft and can be stretched easily. On standing (cooling slowly) it slowly becomes hard and changes to stable rhombic sulphur.

Sulphur also exists in liquid and gaseous states. At around 140 ^{0}C the monoclinic sulphur melts to form mobile pale yellow liquid called λ sulphur. The vapour over the liquid sulphur consists of 90 % of S_8, S_7 & S_6 and small amount of mixture of S_2, S_3, S_4, S_5 molecules.

3.2.2 Sulphur dioxide

Preparation

From sulphur: A large-scale production of sulphur dioxide is done by burning sulphur in air. About 6-8% of sulphur is oxidised to SO_3.

$$S + O_2 \longrightarrow SO_2$$
$$2S + 3O_2 \longrightarrow 2SO_3$$

From sulphides: When sulphide ores such as galena (PbS), zinc blende (ZnS) are roasted in air, sulphur dioxide is liberated. Large amounts of sulphur dioxide required for manufacturing of sulphuric acid and other industrial purpose is prepared by this method.

$$2ZnS + 3O_2 \xrightarrow{\Delta} 2ZnO + 2SO_2$$
$$4FeS_2 + 11O_2 \xrightarrow{\Delta} 2Fe_2O_3 + 8SO_2$$

Laboratory preparation: Sulphur dioxide is prepared in the laboratory treating a metal or metal sulphite with sulphuric acid

$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$$

$$SO_3^{-} + 2H^{+} \longrightarrow H_2O + SO_2$$

Properties:

Sulphur dioxide gas is found in volcanic eruptions. A large amount of sulphur dioxide gas is released into atmosphere from power plants using coal and oil and copper melting plants. It is a colourless gas with a suffocating odour. It is highly soluble in water and it is 2.2 times heavier than air. Sulphur dioxide can be liquefied (boiling point 263 K) at 2.5 atmospheric pressure and 288 K.

Chemical properties

Sulphur dioxide is an acidic oxide. It dissolves in water to give sulphurous acid.

$$SO_2 + H_2O \rightleftharpoons \underset{\text{Sulphurous acid}}{H_2SO_3}$$
$$H_2SO_3 \rightleftharpoons 2H^{+} + SO_3^{2-}$$

Reaction with sodium hydroxide and sodium carbonate: Sulphur dioxide reacts with sodium hydroxide and sodium carbonate to form sodium bisulphite and sodium sulphite respectively.

$$SO_2 + NaOH \longrightarrow \underset{\text{Sodium bisulphite}}{NaHSO_3}$$
$$2SO_2 + Na_2CO_3 + H_2O \longrightarrow 2NaHSO_3 + CO_2$$
$$2\,NaHSO_3 \longrightarrow \underset{\text{Sodium sulphite}}{Na_2SO_3} + H_2O + SO_2$$

Oxidising property: Sulphur dioxide, oxidises hydrogen sulphide to sulphur and magnesium to magnesium oxide.

$$2H_2S + SO_2 \longrightarrow 3S + 2H_2O$$
$$2Mg + SO_2 \longrightarrow 2MgO + S$$

Reducing property: As it can readily be oxidised, it acts as a reducing agent. It reduces chlorine into hydrochloric acid.

$$SO_2 + 2H_2O + Cl_2 \longrightarrow H_2SO_4 + 2HCl$$

It also reduces potassium permanganate and dichromate to Mn^{2+} and Cr^{3+} respectively.

$$2KMnO_4 + 5SO_2 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

$$K_2Cr_2O_7 + 3SO_2 + H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

Reaction with oxygen: Sulphur dioxide is oxidised to sulphur trioxide upon heating with oxygen at high temperature. This reaction is used for the manufacture of sulphuric acid by contact process.

$$SO_2(g) + O_2(g) \xrightarrow[450^0C]{V_2O_5} 2SO_3(g)$$

Bleaching action of sulphur dioxide: In presence of water, sulphur dioxide bleaches coloured wool, silk, sponges and straw into colourless due to its reducing property.

$$SO_2 + 2H_2O \longrightarrow 2\ H_2SO_4 + 2(H)$$

$$\underset{\text{Coloured}}{X} + 2(H) \longrightarrow \underset{\text{Colourless}}{XH_2}$$

However, the bleached product (colourless) is allowed to stand in air, it is reoxidised by atmospheric oxygen to its original colour. Hence bleaching action of sulphur dioxide is temporary.

Uses:

1. Sulphur dioxide is used in bleaching hair, silk, wool etc...
2. It can be used for disinfecting crops and plants in agriculture.

Structure of sulphur dioxide:

In sulphur dioxide, sulphur atom undergoes sp^2 hybridisation. A double bond arises between S and O is due to pπ- dπ overlapping.

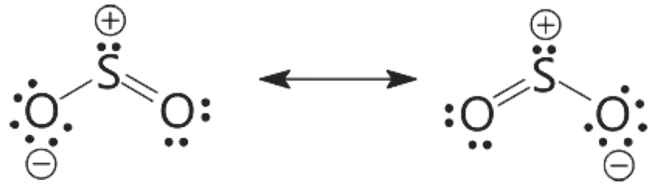


Figure 3.9 Structure of sulphur dioxide.

3.2.3 Sulphuric acid: (H_2SO_4)

Preparation:

Sulphuric acid can be manufactured by lead chamber process, cascade process or contact process. Here we discuss the contact process.

Manufacture of sulphuric acid by contact process:

The contact process involves the following steps.

i. Initially sulphur dioxide is produced by burning sulphur or iron pyrites in oxygen/air.

$$S + O_2 \longrightarrow SO_2$$

$$4FeS_2 + 11O_2 \longrightarrow 2Fe_2O_3 + 8SO_2$$

ii. Sulphur dioxide formed is oxidised to sulphur trioxide by air in the presence of a catalyst such as V_2O_5 or platinised asbestos.

iii. The sulphur trioxide is absorbed in concentrated sulphuric acid and produces oleum ($H_2S_2O_7$). The oleum is converted into sulphuric acid by diluting it with water.

$$SO_3 + H_2SO_4 \longrightarrow H_2S_2O_7 \xrightarrow{H_2O} 2H_2SO_4$$

To maximise the yield the plant is operated at 2 bar pressure and 720 K. The sulphuric acid obtained in this process is over 96 % pure.

Physical properties:

Pure sulphuric acid is a colourless, viscous liquid (Density: 1.84 g/mL at 298 K). High boiling point and viscosity of sulphuric acid is due to the association of molecules together through hydrogen bonding.

The acid freezes at 283.4 K and boils at 590 K. It is highly soluble in water and has strong affinity towards water and hence it can be used as a dehydrating agent. When dissolved in water, it forms mono ($H_2SO_4.H_2O$) and dihydrates ($H_2SO_4.2H_2O$) and the reaction is exothermic.

The dehydrating property can also be illustrated by its reaction with organic compounds such as sugar, oxalic acid and formic acid.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2SO_4 \longrightarrow 12C + H_2SO_4.11H_2O$$

$$\underset{\text{Formic acid}}{HCOOH} + H_2SO_4 \longrightarrow CO + H_2SO_4.H_2O$$

$$\underset{\text{Oxalic acid}}{(COOH)_2} + H_2SO_4 \longrightarrow CO + CO_2 + H_2SO_4.H_2O$$

Chemical Properties:

Sulphuric acid is highly reactive. It can act as strong acid and an oxidising agent.

Decomposition: Sulphuric acid is stable, however, it decomposes at high temperatures to sulphur trioxide.

$$H_2SO_4 \longrightarrow H_2O + SO_3$$

Acidic nature: It is a strong dibasic acid. Hence it forms two types of salts namely sulphates and bisulphates.

$$H_2SO_4 + NaOH \longrightarrow \underset{\text{sodium bisulphate}}{NaHSO_4} + H_2O$$

$$H_2SO_4 + 2NaOH \longrightarrow \underset{\text{sodium sulphate}}{Na_2SO_4} + 2H_2O$$

$$H_2SO_4 + 2NH_3 \longrightarrow \underset{\text{Ammonium sulphate}}{(NH_4)_2SO_4}$$

Oxidising property: Sulphuric acid is an oxidising agent as it produces nascent oxygen as shown below.

$$H_2SO_4 \longrightarrow H_2O + SO_2 + \underset{\text{nascent oxygen}}{(O)}$$

Sulphuric acid oxidises elements such as carbon, sulphur and phosphorus. It also oxides bromide and iodide to bromine and iodine respectively.

$$C + 2H_2SO_4 \longrightarrow 2SO_2 + 2H_2O + CO_2$$
$$S + 2H_2SO_4 \longrightarrow 3SO_2 + 2H_2O$$
$$P_4 + 10H_2SO_4 \longrightarrow 4H_3PO_4 + 10SO_2 + 4H_2O$$
$$H_2S + H_2SO_4 \longrightarrow SO_2 + 2H_2O + S$$
$$H_2SO_4 + 2HI \longrightarrow 2SO_2 + 2H_2O + I_2$$
$$H_2SO_4 + 2HBr \longrightarrow 2SO_2 + 2H_2O + Br_2$$

Reaction with metals: Sulphuric acid reacts with metals and gives different product depending on the reactants and reacting condition.

Dilute sulphuric acid reacts with metals like tin, aluminium, zinc to give corresponding sulphates.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2 \uparrow$$
$$2Al + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2 \uparrow$$

Hot concentrated sulphuric acid reacts with copper and lead to give the respective sulphates as shown below.

$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + 2H_2O + SO_2 \uparrow$$
$$Pb + 2H_2SO_4 \longrightarrow PbSO_4 + 2H_2O + SO_2 \uparrow$$

Sulphuric acid doesn't react with noble metals like gold, silver and platinum.

Reaction with salts: It reacts with different metal salts to give metal sulphates and bisulphates.

$$KCl + H_2SO_4 \longrightarrow KHSO_4 + HCl$$
$$KNO_3 + H_2SO_4 \longrightarrow KHSO_4 + HNO_3$$
$$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2$$
$$2NaBr + 3H_2SO_4 \longrightarrow 2NaHSO_4 + 2H_2O + Br_2 + SO_2$$

Reaction with organic compounds: It reacts organic compounds such as benzene to give sulphonic acids.

$$\underset{\text{Benzene}}{C_6H_6} + H_2SO_4 \longrightarrow \underset{\text{Benzene sulphonic acid}}{C_6H_5SO_3H} + H_2O$$

Uses of sulphuric acid:

1. Sulphuric acid is used in the manufacture of fertilisers, ammonium sulphate and super phosphates and other chemicals such as hydrochloric acid, nitric acid etc...
2. It is used as a drying agent and also used in the preparation of pigments, explosives etc..

Test for sulphate/sulphuric acid:

Dilute solution of sulphuric acid/aqueous solution of sulphates gives white precipitate (barium sulphate) with barium chloride solution. It can also be detected using lead acetate solution. Here a white precipitate of lead sulphate is obtained.

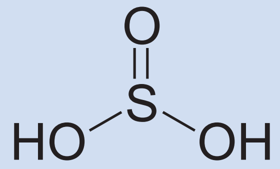
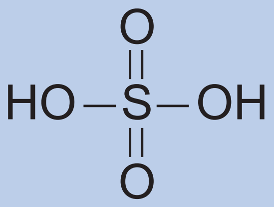
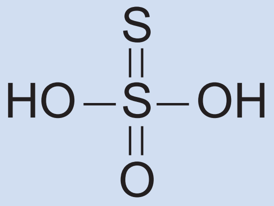
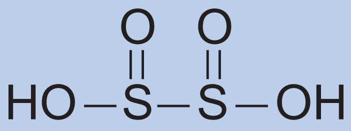
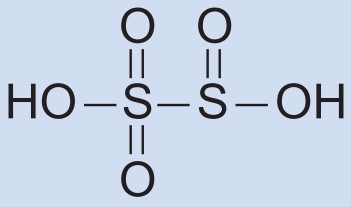
$$BaCl_2 + H_2SO_4 \longrightarrow \underset{\substack{\text{Barium sulphate} \\ \text{(White precipitate)}}}{BaSO_4 \downarrow} + 2HCl$$

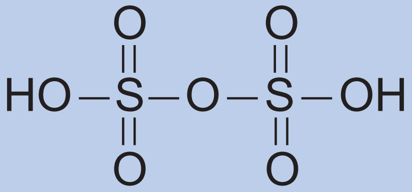
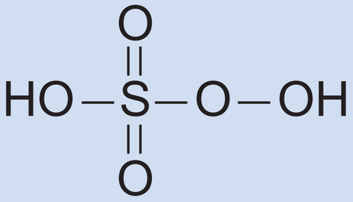
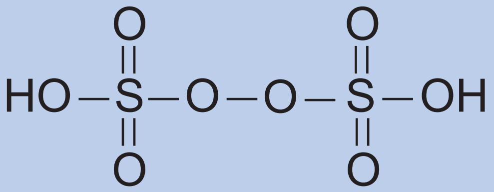
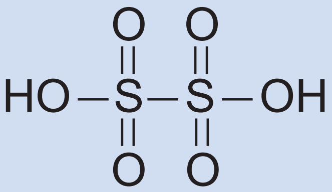
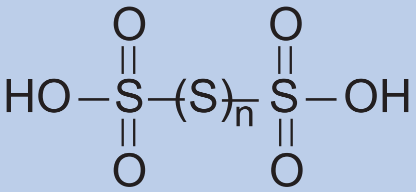
$$(CH_3COO)_2Pb + H_2SO_4 \longrightarrow \underset{\substack{\text{Lead sulphate} \\ \text{(White precipitate)}}}{PbSO_4 \downarrow} + 2CH3COOH$$

Structure of oxoacids of sulphur:

Sulphur forms many oxoacids. The most important one is sulphuric acid. Some acids like sulphurous and dithionic acids are known in the form of their salts only since the free acids are unstable and cannot be isolated.

Various oxo acids of sulphur with their structures are given below

Name	Molecular Formula	Structure
Sulphurous acid	H_2SO_3	
Sulphuric acid	H_2SO_4	 $HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$
Thiosulphuric acid	$H_2S_2O_3$	 $HO-\overset{\overset{S}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$
Dithionous acid	$H_2S_2O_4$	 $HO-\overset{\overset{O}{\|}}{S}-\overset{\overset{O}{\|}}{S}-OH$
Dithionic acid	$H_2S_2O_5$	 $HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-\overset{\overset{O}{\|}}{S}-OH$

Name	Molecular Formula	Structure
Disulphuric acid or pyrosulphuric acid	$H_2S_2O_7$	 $HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$
Peroxymono sulphuric acid	H_2SO_5	 $HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-OH$
Peroxodisulphuric acid. Marshall’s acid	$H_2S_2O_8$	 $HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$
Dithionic acid	$H_2S_2O_6$	 $HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$
Polythionic acid	$H_2S_{n+2}O_6$	 $HO-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-(S)_n-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$

3.3 Group 17 (Halogen group) elements:

3.3.1 Chlorine

Occurrence:

The halogens are present in combined form as they are highly reactive. The main source of fluorine is fluorspar or fluorite. The other ores of fluorine are cryolite, fluroapatite. The main source of chlorine is sodium chloride from sea water. Bromides and iodides also occur in sea water.

Physical properties:

The common physical properties of the group 17 elements are listed in the table.

Table 3.3 Physical properties of group 17 elements

Property	Fluorine	Chlorine	Bromine	Iodine	Astatine
Physical state at 293 K	Gas	Gas	Liquid	Solid	Solid
Atomic Number	9	17	35	53	85
Isotopes	^{19}F	^{35}Cl, ^{37}Cl	^{79}Br	^{127}I	^{210}At, ^{211}At
Atomic Mass (g.mol^{-1} at 293 K)	18.99	35.45	79.9	126.9	210
Electronic configuration	$[He]2s^2\ 2p^5$	$[Ne]3s^2\ 3p^5$	$[Ar]3d^{10}\ 4s^2\ 4p^5$	$[Kr]4d^{10}\ 5s^2\ 5p^5$	$[Xe]\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^5$
Atomic radius (Å)	1.47	1.75	1.85	1.98	2.02
Density (g.cm^{-3} at 293 K)	1.55×10^{-3}	2.89×10^{-3}	3.10	4.93	-
Melting point (K)	53	171	266	387	573
Boiling point (K)	85	239	332	457	623

Properties:

Chlorine is highly reactive hence it doesn't occur free in nature. It is usually distributed as various metal chlorides. The most important chloride is sodium chloride which occurs in sea water.

Preparation:

Chlorine is prepared by the action of conc. sulphuric acid on chlorides in presence of manganese dioxide.

$$4NaCl + MnO_2 + 4H_2SO_4 \longrightarrow Cl_2 + MnCl_2 + 4NaHSO_4 + 2H_2O$$

It can also be prepared by oxidising hydrochloric acid using various oxidising agents such as manganese dioxide, lead dioxide, potassium permanganate or dichromate.

$$PbO_2 + 4HCl \longrightarrow PbCl_2 + 2H_2O + Cl_2$$

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$$

$$2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$

$$K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$$

When bleaching powder is treated with mineral acids chlorine is liberated

$$CaOCl_2 + 2HCl \longrightarrow CaCl_2 + H_2O + Cl_2$$

$$CaOCl_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + Cl_2$$

3.3.1 Manufacture of chlorine:

Chlorine is manufactured by the electrolysis of brine in electrolytic process or by oxidation of HCl by air in Deacon's process.

Electrolytic process: When a solution of brine (NaCl) is electrolysed, Na^+ and Cl^- ions are formed. Na^+ ion reacts with OH^- ions of water and forms sodium hydroxide. Hydrogen and chlorine are liberated as gases.

$NaCl \longrightarrow Na^+ + Cl^-$	At the cathode,	At the anode,
$H_2O \longrightarrow H^+ + OH^-$	$H^+ + e^- \longrightarrow H$	$Cl^- \longrightarrow Cl + e^-$
$Na^+ + OH^- \longrightarrow NaOH$	$H + H \longrightarrow H_2$	$Cl + Cl \longrightarrow Cl_2$

Deacon's process: In this process a mixture of air and hydrochloric acid is passed up a chamber containing a number of shelves, pumice stones soaked in cuprous chloride are placed. Hot gases at about 723 K are passed through a jacket that surrounds the chamber.

$$4HCl + O_2 \xrightarrow[Cu_2Cl_2]{400^0C} 2H_2O + Cl_2 \uparrow$$

The chlorine obtained by this method is dilute and is employed for the manufacture of bleaching powder. The catalysed reaction is given below,

$$2Cu_2Cl_2 + O_2 \longrightarrow \underset{\text{Cuprous oxy chloride}}{2Cu_2OCl_2}$$

$$Cu_2OCl_2 + 2HCl \longrightarrow \underset{\text{Cupric chloride}}{2CuCl_2} + H_2O$$

$$2CuCl_2 \longrightarrow \underset{\text{Cuprous chloride}}{Cu_2Cl_2} + Cl_2$$

Physical properties:

Chlorine is a greenish yellow gas with a pungent irritating odour. It produces headache when inhaled even in small quantities whereas inhalation of large quantities could be fatal. It is 2.5 times heavier than air.

Chlorine is soluble in water and its solution is referred as chlorine water. It deposits greenish yellow crystals of chlorine hydrate ($Cl_2.8H_2O$). It can be converted into liquid (Boiling point – 34.6° C) and yellow crystalline solid (Melting point -102° C)

Chemical properties:

Action with metals and non-metals: It reacts with metals and non metals to give the corresponding chlorides.

$$2Na + Cl_2 \longrightarrow 2NaCl$$

$$2Fe + 3Cl_2 \longrightarrow 2FeCl_3$$

$$2Al + 3Cl_2 \longrightarrow 2AlCl_3$$

$$Cu + Cl_2 \longrightarrow CuCl_2$$

$$H_2 + Cl_2 \longrightarrow 2HCl \quad ; \quad \Delta H = -44kCal$$

$$2B + 3Cl_2 \longrightarrow 2BCl_3$$

$$2S + Cl_2 \longrightarrow \underset{\text{disulphur dichloride}}{S_2Cl_2}$$

$$P_4 + 6Cl_2 \longrightarrow 4PCl_3$$

$$2As + 3Cl_2 \longrightarrow 2AsCl_3$$

$$2Sb + 3Cl_2 \longrightarrow 2SbCl_3$$

Affinity for hydrogen : When burnt with turpentine it forms carbon and hydrochloric acid.

$$C_{10}H_{16} + 8Cl_2 \longrightarrow 10C + 16HCl$$

It forms dioxygen when reacting with water in presence of sunlight. When chlorine in water is exposed to sunlight it loses its colour and smell as the chlorine is converted into hydrochloric acid.

$$2Cl_2 + 2H_2O \longrightarrow O_2 + 4HCl$$

Chlorine reacts with ammonia to give ammonium chloride and other products as shown below:

With excess ammonia,

$$2NH_3 + 3Cl_2 \longrightarrow N_2 + 6HCl$$

$$6HCl + 6\,NH_3 \longrightarrow 6\,NH_4Cl$$

overall reaction

$$8NH_3 + 3Cl_2 \longrightarrow N_2 + 6\,NH_4Cl$$

With excess chlorine,

$$NH_3 + 3Cl_2 \longrightarrow NCl_3 + 3HCl$$

$$3HCl + 3NH_3 \longrightarrow 3NH_4Cl$$

overall reaction

$$4NH_3 + 3Cl_2 \longrightarrow NCl_3 + 3NH_4Cl$$

Chlorine oxidises hydrogen sulphide to sulphur and liberates bromine and iodine from iodides and bromides. However, it doesn't oxidise fluorides

$$H_2S + Cl_2 \longrightarrow 2HCl + S$$

$$Cl_2 + 2KBr \longrightarrow 2KCl + Br_2$$

$$Cl_2 + 2KI \longrightarrow 2KCl + I_2$$

Reaction with alkali: Chlorine reacts with cold dilute alkali to give chloride and hypochlorite while with hot concentrated alkali chlorides and chlorates are formed.

$$Cl_2 + H_2O \longrightarrow HCl + HOCl$$

$$HCl + NaOH \longrightarrow NaCl + H_2O$$

$$HOCl + NaOH \longrightarrow NaOCl + H_2O$$

overall reaction

$$Cl_2 + 2NaOH \longrightarrow \underset{\text{sodium hypo chlorite}}{NaOCl} + NaCl + H_2O$$

$$(Cl_2 + H_2O \longrightarrow HCl + HOCl) \times 3$$
$$(HCl + NaOH \longrightarrow NaCl + H_2O) \times 3$$
$$(HOCl + NaOH \longrightarrow NaOCl + H_2O) \times 3$$
$$3NaOCl \longrightarrow NaClO_3 + 2NaCl$$

overall reaction

$$3Cl_2 + 6NaOH \longrightarrow NaClO_3 + 5NaCl + 3H_2O$$

Oxidising and bleaching action: Chlorine is a strong oxidising and bleaching agent because of the nascent oxygen.

$$H_2O + Cl_2 \longrightarrow HCl + \underset{\text{Hypo chlorous acid}}{HOCl}$$
$$HOCl \longrightarrow HCl + (O)$$

Colouring matter + Nascent oxygen → Colourless oxidation product

The bleaching of chlorine is permanent. It oxidises ferrous salts to ferric, sulphites to sulphates and hydrogen sulphide to sulphur.

$$2FeCl_2 + Cl_2 \longrightarrow 2FeCl_3$$
$$Cl_2 + H_2O \longrightarrow HCl + HOCl$$
$$2FeSO_4 + H_2SO_4 + HOCl \longrightarrow Fe_2(SO_4)_3 + HCl + H_2O$$

overall reaction

$$2FeSO_4 + H_2SO_4 + Cl_2 \longrightarrow Fe_2(SO_4)_3 + 2HCl$$
$$Cl_2 + H_2O \longrightarrow HCl + HOCl$$
$$Na_2SO_3 + HOCl \longrightarrow Na_2SO_4 + HCl$$

overall reaction

$$Na_2SO_3 + H_2O + Cl_2 \longrightarrow Na_2SO_4 + 2HCl$$
$$Cl_2 + H_2S \longrightarrow 2HCl + S$$

Preparation of bleaching powder: Bleaching powder is produced by passing chlorine gas through dry slaked lime (calcium hydroxide).

$$Ca(OH)_2 + Cl_2 \longrightarrow CaOCl_2 + H_2O$$

Displacement redox reactions: Chlorine displaces bromine from bromides and iodine from iodide salts.

$$Cl_2 + 2KBr \longrightarrow 2KCl + Br_2$$
$$Cl_2 + 2KI \longrightarrow 2KCl + I_2$$

Formation of addition compounds: Chlorine forms addition products with sulphur dioxide, carbon monoixde and ethylene. It forms substituted products with alkanes/arenes.

$$SO_2 + Cl_2 \longrightarrow \underset{\text{Sulphuryl chloride}}{SO_2Cl_2}$$
$$CO + Cl_2 \longrightarrow \underset{\text{Carbonyl chloride}}{COCl_2}$$

$$C_2H_4 + Cl_2 \longrightarrow \underset{\text{ethylene dichloride}}{C_2H_4Cl_2}$$

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$

$$C_6H_6 + Cl_2 \xrightarrow{FeCl_3} C_6H_5Cl + HCl$$

Uses of chlorine:

It is used in

1. Purification of drinking water
2. Bleaching of cotton textiles, paper and rayon
3. Extraction of gold and platinum

3.3.2 Hydrochloric acid:

Laboratory preparation:

It is prepared by the action of sodium chloride and concentrated sulphuric acid.

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$$

$$NaHSO_4 + NaCl \longrightarrow Na_2SO_4 + HCl$$

Dry hydrochloric acid is obtained by passing the gas through conc. sulphuric acid

Properties:

Hydrogen chloride is a colourless, pungent smelling gas, easily liquefied to a colourless liquid (boiling point 189K) and frozen into a white crystalline solid (melting point 159K). It is extremely soluble in water.

$$HCl\,(g) + H_2O\,(l) \longrightarrow H_3O^+ + Cl^-$$

Chemical properties:

Like all acids it liberates hydrogen gas from metals and carbon dioxide from carbonate and bicarbonate salts.

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$$

$$Mg + 2HCl \longrightarrow MgCl_2 + H_2$$

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + CO_2 + H_2$$

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + CO_2 + H_2$$

$$NaHCO_3 + 2HCl \longrightarrow 2NaCl + CO_2 + H_2O$$

It liberates sulphur dioxide from sodium sulphate

$$Na_2SO_4 + 2HCl \longrightarrow 2NaCl + H_2O + SO_2$$

When three parts of concentrated hydrochloric acid and one part of concentrated nitric acid are mixed, Aquaregia (Royal water) is obtained. This is used for dissolving gold, platinum etc...

$$Au + 4H^+ + NO_3^- + 4\,Cl^- \longrightarrow AuCl_4^- + NO + 2H_2O$$

$$Pt + 8H^+ + 4NO_3^- + 6Cl^- \longrightarrow [PtCl_6]^{2-} + 4NO_2 + 4H_2O$$

Uses of hydrochloric acid:

1. Hydrochloric acid is used for the manufacture of chlorine, ammonium chloride, glucose from corn starch etc.,
2. It is used in the extraction of glue from bone and also for purification of bone black

3.3.3 Trends in physical and chemical properties of hydrogen halides:

Preparation:

Direct combination is a useful means of preparing hydrogen chloride. The reaction between hydrogen and fluorine is violent while the reaction between hydrogen and bromine or hydrogen and iodine are reversible and don't produce pure forms.

Displacement reactions:

Concentrated sulphuric acid displaces hydrogen chloride from ionic chlorides. At higher temperatures the hydrogen sulphate formed react with further ionic chloride. Displacement can be used for the preparation of hydrogen fluorides from ionic fluorides. Hydrogen bromide and hydrogen iodide are oxidised by concentrated sulphuric acid and can't be prepared in this method.

Hydrolysis of phosphorus trihalides:

Gaseous hydrogen halides are produced when water is added in drops to phosphorus tri halides except phosphorus trifluoride.

$$PX_3 + 3H_2O \longrightarrow H_3PO_3 + 3HX$$

Hydrogen bromide may be obtained by adding bromine dropwise to a paste of red phosphorous and water while hydrogen iodide is conveniently produced by adding water dropwise to a mixture of red phosphorous and iodine.

$$2P + 3X_2 \longrightarrow 2PX_3$$

$$2PX_3 + 3H_2O \longrightarrow H_3PO_3 + 3HX$$

(where X=Br or I)

Any halogen vapours which escapes with the hydrogen halide is removed by passing the gases through a column of moist red phosphorous.

From covalent hydrides:

Halogens are reduced to hydrogen halides by hydrogen sulphide.

$$H_2S + X_2 \longrightarrow 2HX + S$$

Hydrogen chloride is obtained as a by-product of the reactions between hydrocarbon of halogens.

Table 3.4: General Properties:

	HF	HCl	HBr	HI
Bond dissolution enthalphy	+562	+431	+366	+299
% of ionic character	43	17	113	7

In line with the decreasing bond dissociation enthalpy, the thermal stability of hydrogen halides decreases from fluoride to iodide.

For example, Hydrogen iodide decomposes at 400° C while hydrogen fluoride and hydrogen chloride are stable at this temperature.

At room temperature, hydrogen halides are gases but hydrogen fluoride can be readily liquefied. The gases are colourless but, with moist air gives white fumes due to the production of droplets of hydrohalic acid. In HF, due to the presence of strong hydrogen bond it has high melting and boiling points. This effect is absent in other hydrogen halides.

Acidic properties:

The hydrogen halides are extremely soluble in water due to the ionisation.

$$HX + H_2O \longrightarrow H_3O^+ + X^-$$

(X – F, Cl, Br, or I)

Solutions of hydrogen halides are therefore acidic and known as hydrohalic acids. Hydrochloric, hydrobromic and hydroiodic acids are almost completely ionised and are therefore strong acids but HF is a weak acid i.e. 0.1mM solution is only 10% ionised, but in 5M and 15M solution HF is stronger acid due to the equilibrium.

$$HF + H_2O \rightleftharpoons H_3O^+ + F^-$$

$$HF + F^- \rightleftharpoons HF_2^-$$

At high concentration, the equilibrium involves the removal of fluoride ions is important. Since it affects the dissociation of hydrogen fluoride and increases and hydrogen ion concentration Several stable salts $NaHF_2$, KHF_2 and NH_4HF_2 are known. The other hydrogen halides do not form hydrogen dihalides.

Hydrohalic acid shows typical acidic properties. They form salts with acids, bases and reacts with metals to give hydrogen. Moist hydrofluoric acid (not dry) rapidly react with silica and glass.

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$

$$Na_2SiO_3 + 6HF \longrightarrow Na_2SiF_6 + 3H_2O$$

Oxidation: Hydrogen iodide is readily oxidised to iodine hence it is a reducing agent.

$$2HI \rightleftharpoons 2H^+ + I_2 + 2e^-$$

Acidic solution of iodides is readily oxidised. A positive result is shown by liberation of iodine which gives a blue-black colouration with starch.

Hydrogen bromide is more difficult to oxidise than HI. HBr reduces slowly H_2SO_4 into SO_2

$$2HBr + H_2SO_4 \longrightarrow 2H_2O + Br_2 + SO_2$$

But hydrogen iodide and ionic iodides are rapidly reduced by H_2SO_4 into H_2S and not into SO_2.

$$8HI + H_2SO_4 \longrightarrow 4H_2O + 4I_2 + H_2S$$

Reducing property of hydrogen iodide can be also explained by using its reaction with alcohols into ethane. It converts nitric acid into nitrous acid and dinitrogen dioxide into ammonium.

Hydrogen chloride is unaffected by concentrated sulphuric aid by only strong oxidising agents like MnO_2, potassium permanganate or potassium chloride.

To summarize the trend,

Table 3.5

Property	Order
Reactivity of hydrogen	Decreases from fluorine to iodine
Stability	Decreases from HF to HI
Volatility of the hydrides	HF < HI < HBr < HCl
Thermal stability	HF > HI > HBr > HCl
Boiling point	HCl < HBr < HI
Acid strength	Increases from HF to HI

3.3.4 Inter halogen compounds:

Each halogen combines with other halogens to form a series of compounds called inter halogen compounds. In the given table of inter halogen compounds a given compound A is less electronegative than B.

Table 3.6

AB	AB_3	AB_5	AB_7
ClF	ClF_3	IF_5	IF_7
BrF	BrF_3	BrF_5	
IF	IF_3		
BrCl	ICl_3		
ICl			
IBr			

Properties of inter halogen compounds:

i. The central atom will be the larger one

ii. It can be formed only between two halogen and not more than two halogens.

iii. Fluorine can't act as a central metal atom being the smallest one

iv. Due to high electronegativity with small size fluorine helps the central atom to attain high coordination number

v. They can undergo the auto ionization.

$$2\ \mathrm{ICl} \rightleftharpoons \mathrm{I}^{+} + \mathrm{ICl}_2^{-}$$

$$2\ \mathrm{ICl}_3 \rightleftharpoons \mathrm{ICl}_2^{+} + \mathrm{ICl}_4^{-}$$

vi. They are strong oxidizing agents

Reaction with alkali:

When heated with the alkalis, larger halogen form oxyhalogens and the smaller forms halide.

$$\mathrm{BrF}_5 \xrightarrow{{}^{-}\mathrm{OH}} 5\mathrm{F}^{-} + \underset{\text{Bromate ion}}{\mathrm{BrO}_3^{-}}$$

$$\mathrm{ICl} \xrightarrow{{}^{-}\mathrm{OH}} \mathrm{Cl}^{-} + \underset{\text{Hypo iodite ion}}{\mathrm{OI}^{-}}$$

Structure of inter halogen compounds:

The structures of different type of interhalogen compunds can be easily explained using VSEPR theory. The details are given below.

Table 3.7

Type	Structure	Hybridisation	bond pairs / lone pairs
AX	Linear	sp^3	1 / 3
AX_3	T shaped	sp^3d	3 / 2
AX_5	Square pyrimidal	sp^3d^2	5 / 1
AX_7	Pentagonal bipyramidal	sp^3d^3	7 / 0

3.3.5 Oxides of halogen

Fluorine reacts readily with oxygen and forms difluorine oxide (F_2O) and difluorine dioxide (F_2O_2) where it has a -1 oxidation state. Other halogens do not react with oxygen readily. But the following oxides can be prepared by some indirect methods. Except fluorine all the other halogens have positive oxidation states.

Table 3.8

Type	X_2O	XO_2	XO_3	X_2O_6	X_2O_7	Others
Oxidation state	+1	+4	+5	+6	+7	-
F	-	-	-	-	-	OF_2 (-1) O_2F_2 (-1) O_4F_2 (-1)
Cl	Cl_2O	ClO_2	-	Cl_2O_6	Cl_2O_7	Cl_2O_4 (+4)

Br	Br_2O	BrO_2	-	-	-	-
I	-	-	I_2O_5	-	-	I_4O_9 I_2O_4 (+4)

3.3.6 Oxoacids of halogens:

Chlorine forms four types of oxoacids namely hypochlorus acid, chlorous acid, chloric acid and perchloric acid. Bromine and iodine forms the similar acids except halous acid. Howeve, flurine only forms hypofulric acid. The oxidizing power oxo acids follows the order:

$$\mathbf{HOX > HXO_2 > HXO_3 > HXO_4}$$

Table 3.9

Type	HOX	HXO_2	HXO_3	HXO_4
Common Name	Hypohalous acid	Halous acid	Halic acid	Perhalic acid
Oxidation state	+1	+3	+5	+7
F	HOF	-	-	-
Cl	HOCl	$HClO_2$	$HClO_3$	$HClO_4$
Br	HOBr		$HBrO_3$	$HBrO_4$
I	HOI		HIO_3	HIO_4
Structure				

3.4 Group 18 (Inert gases) elements:

3.4.1 Occurrence:

All the noble gases occur in the atmosphere.

Physical properties:

As we move along the noble gas elements, their atomic radius and boiling point increases from helium to radon. The first ionization energy decreases from helium to radon. Noble gases have the largest ionisation energy compared to any other elements in a given row as they have completely filled orbital in their outer most shell. They are extremely stable and have a small tendency to gain or lose electrons. The common physical properties of the group 18 elements are listed in the Table.

Property	Neon	Argon	Krypton	Xenon	Radon
Physical state at 293 K	Gas	Gas	Gas	Gas	Gas
Atomic Number	10	18	36	54	86

Isotopes	^{20}Ne	^{40}Ar	^{84}Kr	^{132}Xe	^{211}Rn, ^{220}Rn, ^{222}Rn
Atomic Mass (g.mol^{-1} at 293 K)	20.18	39.95	77.92	131.29	[222]
Electronic configuration	[He]2s^2 2p^6	[Ne]3s^2 3p^6	[Ar]3d^{10} 4s^2 4p^6	[Kr]4d^{10} 5s^2 5p^6	[Xe] 4f^{14} 5d^{10} 6s^2 6p^6
Atomic radius (Å)	1.54	1.88	2.02	2.16	2.20
Density (g.cm^{-3} at 293 K)	8.25 x 10^{-4}	1.63 x 10^{-3}	3.42 x 10^{-3}	5.37 x 10^{-3}	9.07 x 10^{-3}
Melting point (K)	24.56	83.81	115.78	161.4	202
Boiling point (K)	27.104	87.30	119.74	165.05	211.5

Table 3.10 Physical properties of group 18 elements

Properties of inert gases:

Physical properties:

Noble gases are monoatomic, odourless, colourless, tasteless, and non-inflammable. They are highly unreactive. They are non-metallic in nature.

Chemical Properties:

Only the xenon and krypton show some chemical reactivity. Xenon fluorides are prepare by direct reaction of xenon and fluorine under different conditions as shown below.

$$Xe + F_2 \xrightarrow[400^0C]{Ni} XeF_2$$

$$Xe + 2F_2 \xrightarrow[400^0C]{Ni/acetone} XeF_4$$

$$Xe + 3F_2 \xrightarrow[400^0C]{Ni/200\ atm} XeF_6$$

When XeF_6 is heated at 50 °C in a sealed quartz vessel it forms $XeOF_4$.

$$2XeF_6 + SiO_2 \xrightarrow{50^0C} 2XeOF_4 + SiF_4$$

When the reaction is continued the following reaction takes place.

$$2XeOF_4 + SiO_2 \longrightarrow 2XeO_2F_2 + SiF_4$$

$$2XeO_2F_2 + SiO_2 \longrightarrow 2XeO_3 + SiF_4$$

On hydrolysis with water vapour XeF_6 gives XeO_3

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

When XeF_6 reacts with 2.5 M NaOH, sodium per xenate is obtained.

$$2XeF_6 + 16NaOH \longrightarrow Na_4XeO_6 + Xe + O_2 + 12NaF + 8H_2O$$

Sodium per xenate is very much known for its strong oxidizing property. For example, it oxidises manganese (II) ion into permanganate ion even in the absence of the catalyst.

$$5XeO_6^{4-} + 2Mn^{2+} + 14H^+ \longrightarrow 2MnO_4^- + 5XeO_3 + 7H_2O$$

Xenon reacts with PtF_6 and gave an orange yellow solid $[XePtF_6]$ and this is insoluble in CCl_4.

Xenon difluoride forms addition compounds $XeF_2.2SbF_5$ and $XeF_2.2TaF_5$. Xenon hexa fluorides forms compound with boron and alkali metals. Eg : $XeF_6.BF_3$, XeF_6MF, M-alkali metals.

There is some evidence for existence of xenon dichloride $XeCl_2$.

Krypton form krypton difluoride when an electric discharge is passes through Kr and fluorine at 183° C or when gases are irradiated with SbF_5 it forms $KrF_2.2SbF_3$.

Table 3.11 Structures of compounds of Xenon:

Compound	Hybridisation	Shape / Structure
XeF	sp^3d	Linear
XeF_4	sp^3d^2	Square planar
XeF_6	sp^3d^3	Distorted octahedron
$XeOF_2$	sp^3d	T Shaped
$XeOF_4$	sp^3d^2	Square pyramidal
XeO_3	sp^3	Pyramidal

Uses of noble gases:

The inertness of noble gases is an important feature of their practical uses.

Helium:

1. Helium and oxygen mixture is used by divers in place of air oxygen mixture. This prevents the painful dangerous condition called bends.
2. Helium is used to provide inert atmosphere in electric arc welding of metals
3. Helium has lowest boiling point hence used in cryogenics (low temperature science).
4. It is much less denser than air and hence used for filling air balloons

Neon:

Neon is used in advertisement as neon sign and the brilliant red glow is caused by passing electric current through neon gas under low pressure.

Argon:

Argon prevents the oxidation of hot filament and prolongs the life in filament bulbs

Krypton:

Krypton is used in fluorescent bulbs, flash bulbs etc...

Lamps filed with krypton are used in airports as approaching lights as they can penetrate through dense fog.

Xenon:

Xenon is used in fluorescent bulbs, flash bulbs and lasers.

Xenon emits an intense light in discharge tubes instantly. Due to this it is used in high speed electronic flash bulbs used by photographers

Radon:

Radon is radioactive and used as a source of gamma rays

Radon gas is sealed as small capsules and implanted in the body to destroy malignant i.e. cancer growth

Summary

- **Occurrence:** About 78 % of earth atmosphere contains dinitorgen (N_2) gas. It is also present in earth crust as sodium nitrate (Chile saltpetre) and potassium nitrates (Indian saltpetre).
- **Nitrogen**, the principle gas of atmosphere (78 % by volume) is separated industrially from liquid air by fractional distillation
- Ammonia is formed by the hydrolysis of urea.
- Nitric acid is prepared by heating equal amounts of potassium or sodium nitrate with concentrated sulphuric acid.
- In most of the reactions, nitric acid acts as an oxidising agent. Hence the oxidation state changes from +5 to a lower one. It doesn't yield hydrogen in its reaction with metals.
- The reactions of metals with nitric acid are explained in 3 steps as follows:
    - **Primary reaction:** Metal nitrate is formed with the release of nascent hydrogen
    - **Secondary reaction:** Nascent hydrogen produces the reduction products of nitric acid.
    - **Tertiary reaction:** The secondary products either decompose or react to give final products
- Phosphorus has several allotropic modification of which the three forms namely white, red and black phosphorus are most common.
- yellow phosphorus is poisonous in nature and has a characteristic garlic smell. It glows in the dark due to oxidation which is called phosphorescence.
- Yellow phosphorus readily catches fire in air giving dense white fumes of phosphorus pentoxide.
- Phosphine is prepared by action of sodium hydroxide with white phosphorous in an inert atmosphere of carbon dioxide or hydrogen.

- Phosphine is used for producing smoke screen as it gives large smoke.
- When a slow stream of chlorine is passed over white phosphorous, phosphorous trichloride is formed.
- phosphorus trichloride: and Phosphorous pentachloride are used as a chlorinating agent
- Oxygen is paramagnetic. It exists in two allotropic forms namely dioxygen (O_2) and ozone or trioxygen (O_3).
- Ozone is commonly used for oxidation of organic compounds.
- Sulphur exists in crystalline as well as amorphous allotrophic forms. The crystalline form includes rhombic sulphur (α sulphur) and monoclinic sulphur (β sulphur). Amorphous allotropic form includes plastic sulphur (γ sulphur), milk of sulphur and colloidal sulphur.
- Sulphuric acid can be manufactured by lead chamber process, cascade process or contact process.
- When dissolved in water, it forms mono ($H_2SO_4.H_2O$) and dihydrates ($H_2SO_4.2H_2O$) and the reaction is exothermic.
- Halogens are present in combined form as they are highly reactive.
- Chlorine is manufactured by the electrolysis of brine in electrolytic process or by oxidation of HCl by air in Deacon's process.
- Chlorine is a strong oxidising and bleaching agent because of the nascent oxygen.
- When three parts of concentrated hydrochloric acid and one part of concentrated nitric acid are mixed, Aquaregia (Royal water) is obtained. This is used for dissolving gold, platinum etc...
- Hydrogen halides are extremely soluble in water due to the ionisation.
- Each halogen combines with other halogens to form a series of compounds called inter halogen compounds.
- Fluorine reacts readily with oxygen and forms difluorine oxide (F_2O) and difluorine dioxide (F_2O_2) where it has a -1 oxidation state.
- All the noble gases occur in the atmosphere.
- They are extremely stable and have a small tendency to gain or lose electrons.
- Sodium per xenate is very much known for its strong oxidizing property.
- The inertness of noble gases is an important feature of their practical uses.

EVALUATION

MM7FP9

Choose the best answer:

1. In which of the following , NH_3 is not used?

    a) Nessler's reagent

    b) Reagent for the analysis of IV group basic radical

    c) Reagent for the analysis of III group basic radical

    d) Tollen's reagent

2. Which is true regarding nitrogen?

    a) least electronegative element

    b) has low ionisation enthalpy than oxygen

    c) d- orbitals available

    d) ability to form $p\pi - p\pi$ bonds with itself

3. An element belongs to group 15 and 3 rd period of the periodic table, its electronic configuration would be

    a) $1s^2 2s^2 2p^4$

    b) $1s^2 2s^2 2p^3$

    c) $1s^2 2s^2 2p^6 3s^2 3p^2$

    d) $1s^2 2s^2 2p^6 3s^2 3p^3$

4. Solid (A) reacts with strong aqueous NaOH liberating a foul smelling gas(B) which spontaneously burn in air giving smoky rings. A and B are respectively

    a) P_4(red) and PH_3

    b) P_4(white) and PH_3

    c) S_8 and H_2S

    d) P_4(white) and H_2S

5. In the brown ring test, brown colour of the ring is due to

    a) a mixture of No and NO_2

    b) Nitroso ferrous sulphate

    c) Ferrous nitrate

    d) Ferric nitrate

6. On hydrolysis, PCl_3 gives

    a) H_3PO_3

    b) PH_3

    c) H_3PO_4

    d) $POCl_3$

7. P_4O_6 reacts with cold water to give

    a) H_3PO_3

    b) $H_4P_2O_7$

    c) HPO_3

    d) H_3PO_4

8. The basicity of pyrophosphorous acid ($H_4P_2O_5$) is

a) 4
b) 2
c) 3
d) 5

9. The molarity of given orthophosphoric acid solution is 2M. its normality is

a) 6N
b) 4N
c) 2N
d) none of these

10. Assertion : bond dissociation energy of fluorine is greater than chlorine gas

Reason: chlorine has more electronic repulsion than fluorine

a) Both assertion and reason are true and reason is the correct explanation of assertion.
b) Both assertion and reason are true but reason is not the correct explanation of assertion.
c) Assertion is true but reason is false.
d) Both assertion and reason are false.

11. Among the following, which is the strongest oxidizing agent?

a) Cl_2
b) F_2
c) Br_2
d) l_2

12. The correct order of the thermal stability of hydrogen halide is

a) HI > HBr > HCl > HF
b) HF > HCl > HBr > HI
c) HCl > HF > HBr > HI
d) HI > HCl > HF > HBr

13. Which one of the following compounds is not formed?

a) $XeOF_4$
b) XeO_3
c) XeF_2
d) NeF_2

14. Most easily liquefiable gas is

a) Ar
b) Ne
c) He
d) Kr

15. XeF_6 on complete hydrolysis produces

a) $XeOF_4$
b) XeO_2F_2
c) XeO_3
d) XeO_2

16. On oxidation with iodine, sulphite ion is transformed to

a) $S_4O_6^{2-}$
b) $S_2O_6^{2-}$

c) SO_4^{2-}

d) SO_3^{2-}

17. Which of the following is strongest acid among all?

a) HI

b) HF

c) HBr

d) HCl

18. Which one of the following orders is correct for the bond dissociation enthalpy of halogen molecules? (NEET)

a) $Br_2 > I_2 > F_2 > Cl_2$

b) $F_2 > Cl_2 > Br_2 > I_2$

c) $I_2 > Br_2 > Cl_2 > F_2$

d) $Cl_2 > Br_2 > F_2 > I_2$

19. Among the following the correct order of acidity is (NEET)

a) $HClO_2 < HClO < HClO_3 < HClO_4$

b) $HClO_4 < HClO_2 < HClO < HClO_3$

c) $HClO_3 < HClO_4 < HClO_2 < HClO$

d) $HClO < HClO_2 < HClO_3 < HClO_4$

20. When copper is heated with conc HNO_3 it produces

a) $Cu(NO_3)_2$, NO and NO_2

b) $Cu(NO_3)_2$ and N_2O

c) $Cu(NO_3)_2$ and NO_2

d) $Cu(NO_3)_2$ and NO

Answer the following questions:

1. What is inert pair effect?
2. Chalcogens belongs to p-block. Give reason.
3. Explain why fluorine always exhibit an oxidation state of -1?
4. Give the oxidation state of halogen in the following.

   a) OF_2 b) O_2F_2 c) Cl_2O_3 d) I_2O_4

5. What are interhalogen compounds? Give examples.
6. Why fluorine is more reactive than other halogens?
7. Give the uses of helium.
8. What is the hybridisation of iodine in IF_7? Give its structure.
9. Give the balanced equation for the reaction between chlorine with cold NaOH and hot NaOH.
10. How will you prepare chlorine in the laboratory?
11. Give the uses of sulphuric acid.
12. Give a reason to support that sulphuric acid is a dehydrating agent.

13. Write the reason for the anamolous behaviour of Nitrogen.

14. Write the molecular formula and structural formula for the following molecules.

    a) Nitric acid
    b) dinitrogen pentoxide
    c) phosphoric acid
    d) phosphine

15. Give the uses of argon.

16. Write the valence shell electronic configuration of group-15 elements.

17. Give two equations to illustrate the chemical behaviour of phosphine.

18. Give a reaction between nitric acid and a basic oxide.

19. What happens when PCl_5 is heated?

20. Suggest a reason why HF is a weak acid, whereas binary acids of the all other halogens are strong acids.

21. Deduce the oxidation number of oxygen in hypofluorous acid – HOF.

22. What type of hybridisation occur in

    a) BrF_5 b) BrF_3

23. Complete the following reactions.

    1. $NaCl + MnO_2 + H_2SO_4 \longrightarrow$
    2. $NaNO_2 + HCl \longrightarrow$
    3. $IO_3^- + I^- + H^+ \longrightarrow$
    4. $I_2 + S_2O_3^{2-} \longrightarrow$
    5. $P_4 + NaOH + H_2O \longrightarrow$
    6. $AgNO_3 + PH_3 \longrightarrow$
    7. $Mg + HNO_3 \longrightarrow$
    8. $KClO_3 \xrightarrow{\Delta}$
    9. $Cu + \overset{\text{Hot conc}}{H_2SO_4} \longrightarrow$
    10. $Sb + Cl_2 \longrightarrow$
    11. $HBr + H_2SO_4 \longrightarrow$
    12. $XeF_6 + H_2O \longrightarrow$
    13. $XeO_6^{4-} + Mn^{2+} + H^+ \longrightarrow$
    14. $XeOF_4 + SiO_2 \longrightarrow$
    15. $Xe + F_2 \xrightarrow[400^0C]{Ni / 200 atm}$

UNIT
4

TRANSITION AND INNER TRANSITION ELEMENTS

Martin Heinrich Klaproth, (1743— 1817)

Martin Heinrich Klaproth, German chemist who discovered uranium, zirconium and cerium . He described them as distinct elements, though he did not obtain them in the pure metallic state. He verified the discoveries of titanium, tellurium, and strontium, His role is the most significant in systematizing analytical chemistry and mineralogy.

ZITAE5

Learning Objectives

After studying this unit, the students will be able to

- recognise the position of d and f block elements in the periodic table
- describe the general trend in properties of elements of 3d series
- discuss the trends in M^{n+}/M standard electrode potential
- predict the oxidising and reducing property based in E^{o} values
- explain the tendencies of d-block elements towards the formation of alloy, complex and interstitial compounds
- describe the preparation and properties of potassium permanganate and potassium dichromate
- describe the properties of f-block elements
- compare the properties of lanthanoides and actinides

INTRODUCTION

Generally the metallic elements that have incompletely filled d or f sub shell in the neutral or cationic state are called transition metals. This definition includes lanthanoides and actinides. However, IUPAC defines transition metal as an element whose atom has an incomplete d sub shell or which can give rise to cations with an incomplete d sub shell. They occupy the central position of the periodic table, between s and p block elements, and their properties are transitional between highly reactive metals of s block and elements of p block which are mostly non metals. Except group- 11 elements all transition metals are hard and have very high melting point.

Transition metals, iron and copper play an important role in the development of human civilization. Many other transition elements also have important applications such as tungsten in light bulb filaments, titanium in manufacturing artificial joints, molybdenum in boiler plants, platinum in catalysis etc. They also play vital role in living system, for example iron in hemoglobin, cobalt in vitamin B_{12} etc.,

In this unit we study the general trend in properties of d block elements with specific reference to 3d series, their characteristics, chemical reactivity, some important compounds $KMnO_4$ and $K_2Cr_2O_7$, we also discuss the f-block elements later in this unit.

4.1 Position of d- block elements in the periodic table:

We have already learnt the periodic classification of elements in XI std. the transition metals occupy from group –3 to group-12 of the modern periodic table.

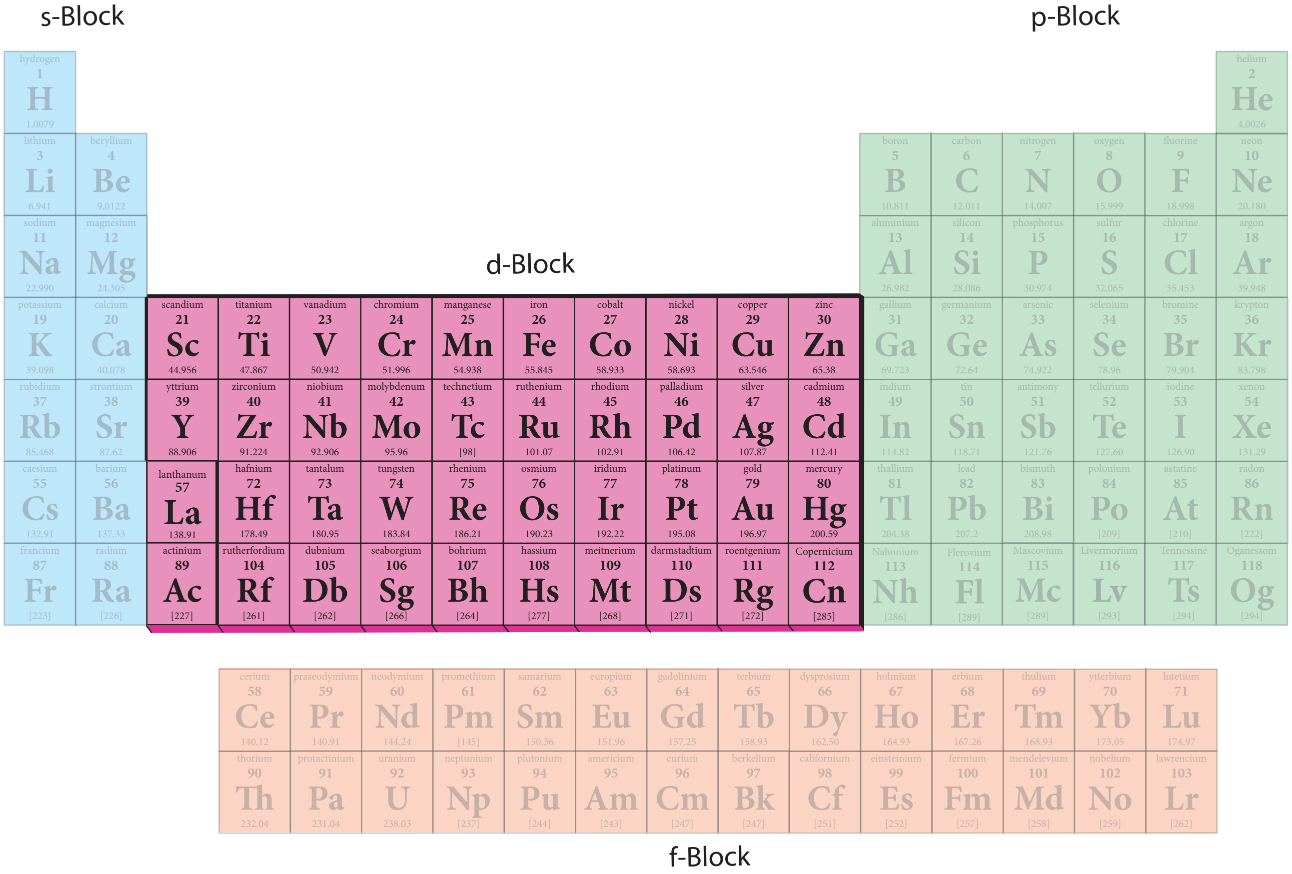


Figure 4.1-Position of d- block elements in the periodic table

d- Block elements composed of 3d series (4th period) Scandium to Zinc (10 elements), 4d series (5th period) Yttrium to Cadmium (10 elements) and 5d series (6th period) Lanthanum, Haffinium to mercury. As we know that the group-12 elements Zinc, Cadmium and Mercury do not have partially filled d-orbital either in their elemental state or in their normal oxidation states. However they are treated as transition elements, because their properties are an extension of the properties of the respective transition elements. As per the IUPAC definition, the seventh period elements, starting from Ac, Rf to Cn also belong to transition metals. All of them are radioactive. Except Actinium; all the remaining elements are synthetically prepared and have very low half life periods.

4.2 Electronic configuration:

We have already learnt in XI STD to write the electronic configuration of the elements using Aufbau principle, Hund's rule etc. According to Aufbau principle, the electron first fills the 4s orbital before 3d orbital. Therefore filling of 3d orbital starts from Sc, its electronic configuration is $[Ar]3d^1\ 4s^2$ and the electrons of successive elements are progressively filled in 3d orbital and the filling of 3d orbital is complete in Zinc, whose electronic configuration is $[Ar]\ 3d^{10}\ 4s^2$. However, there are two exceptions in the above mentioned progressive filling of 3d orbitals; if there is a chance of acquiring half filled or fully filled 3d sub shell, it is given priority as they are the stable configuration, for example Cr and Cu.

The electronic configurations of Cr and Cu are $[Ar]\ 3d^5\ 4s^1$ and $[Ar]\ 3d^{10}\ 4s^1$ respectively. The extra stability of half filled and fully filled d orbitals, as already explained in XI STD, is due to symmetrical distribution of electrons and exchange energy.

Note: The extra stability due to symmetrical distribution can also be visualized as follows. When the d orbitals are considered together, they will constitute a sphere. So the half filled and fully filled configuration leads to complete symmetrical distribution of electron density. On the other hand, an unsymmetrical distribution of electron density as in the case of partially filled configuration will result in building up of a potential difference. To decrease this and to achieve a tension free state with lower energy, a symmetrical distribution is preferred.

With these two exceptions and minor variation in certain individual cases, the general electronic configuration of d- block elements can be written as [Noble gas] $(n-1)d^{1-10}ns^{1-2}$, Here, $n = 4 \text{ to } 7$. In periods 6 and 7, (except La and Ac) the configuration includes $((n-2)f$ orbital ; [Noble gas] $(n-2)f^{14}(n-1)d^{1-10}ns^{1-2}$.

4.3 General trend in properties:

4.3.1 Metallic behavior:

All the transition elements are metals. Similar to all metals the transition metals are good conductors of heat and electricity. Unlike the metals of Group-1 and group-2, all the transition metals except group 11 elements are hard. Of all the known elements, silver has the highest electrical conductivity at room temperature.

Most of the transition elements are hexagonal close packed, cubic close packed or body centrered cubic which are the characteristics of true metals.

21 Sc HCP	22 Ti HCP	23 V BCC	24 Cr BCC	25 Mn BCC	26 Fe BCC	27 Co HCP	28 Ni FCC	29 Cu FCC	30 Zn HCP
39 Y HCP	40 Zr HCP	41 Nb BCC	42 Mo BCC	43 Tc HCP	44 Ru HCP	45 Rh FCC	46 Pd FCC	47 Ag FCC	48 Cd HCP
57* La DHCP	72 Hf HCP	73 Ta BCC/ TETR	74 W BCC	75 Re HCP	76 Os HCP	77 Ir FCC	78 Pt FCC	79 Au FCC	80 Hg RHO
89** Ac FCC	104 Rf [HCP]	105 Db [BCC]	106 Sg [BCC]	107 Bh [HCP]	108 Hs [HCP]	109 Mt [FCC]	110 Ds [BCC]	111 Rg [BCC]	112 Cn [BCC]

Figure 4.2 lattice structures of 3d, 4d and 5d transition metals

As we move from left to right along the transition metal series, melting point first increases as the number of unpaired d electrons available for metallic bonding increases, reach a maximum value and then decreases, as the d electrons pair up and become less available for bonding.

For example, in the first series the melting point increases from Scandium (m.pt 1814K) to a maximum of 2183 K for vanadium, which is close to 2180K for chromium. However, manganese in 3d series and Tc in 4d series have low melting point. The maximum melting point at about the middle of transition metal series indicates that d^5 configuration is favorable for strong interatomic attraction. The following figure shows the trends in melting points of transition elements.

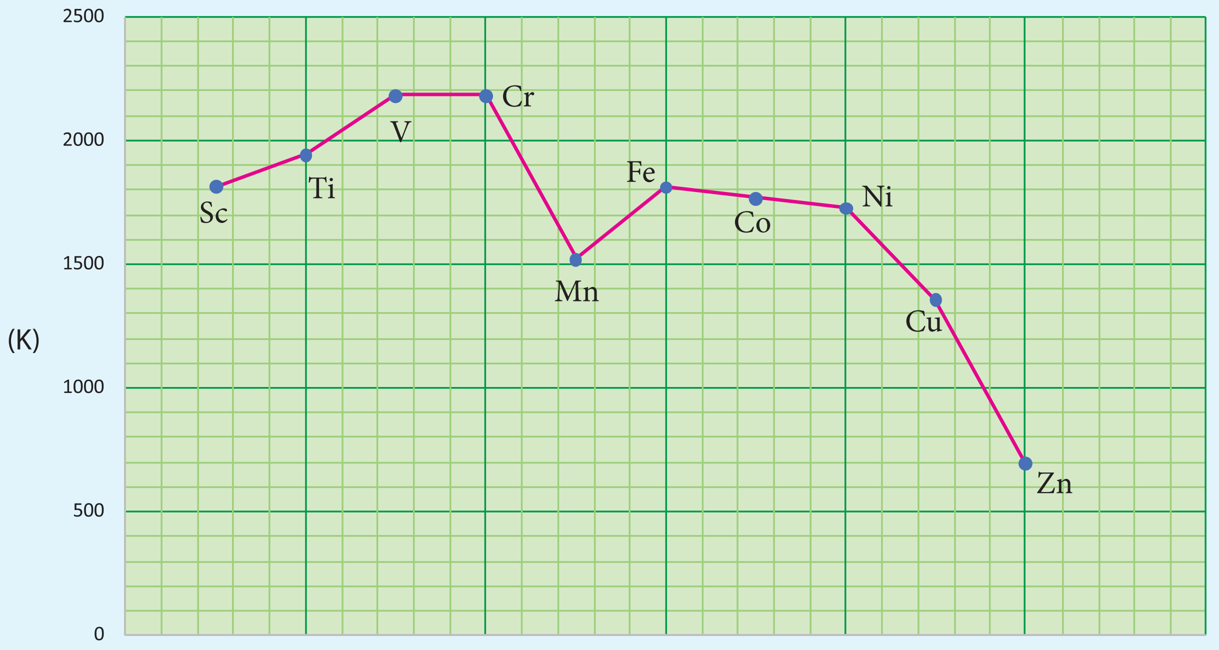


Figure 4.3-Variation in melting point of 3d series elements

4.3.2 Variation of atomic and ionic size:

It is generally expected a steady decrease in atomic radius along a period as the nuclear charge increases and the extra electrons are added to the same sub shell. But for the 3d transition elements, the expected decrease in atomic radius is observed from Sc to V , thereafter up to Cu the atomic radius nearly remains the same. As we move from Sc toZn in 3d series the extra electrons are added to the 3d orbitals, the added 3d electrons only partially shield the increased nuclear charge and hence the effective nuclear charge increases slightly. However, the extra electrons added to the 3d sub shell strongly repel the 4s electrons and these two forces are operated in opposite direction and as they tend to balance each other, it leads to constancy in atomic radii.

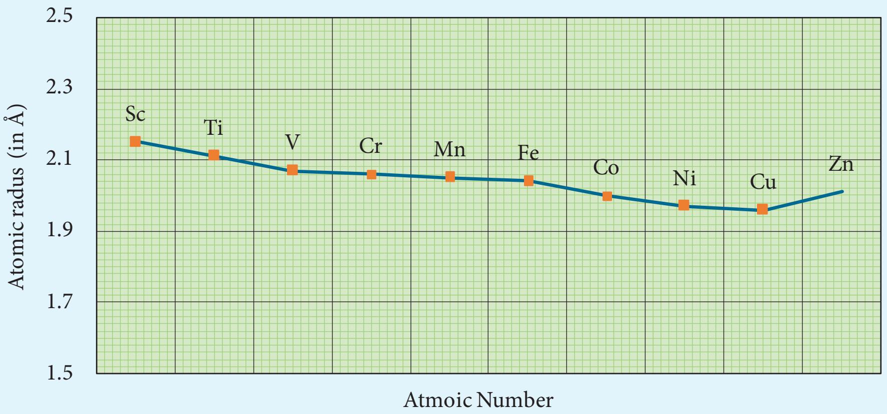


Figure 4.4 (a) Atomic radius of 3d Elements

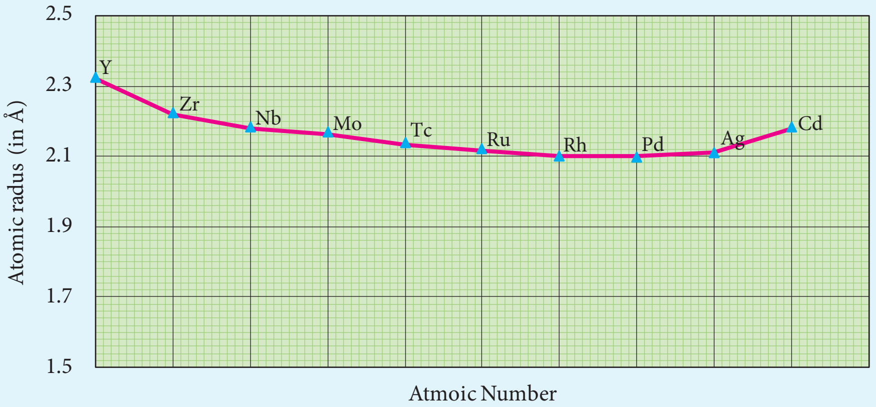


Figure 4.4 (b) Atomic radius of 4d Elements

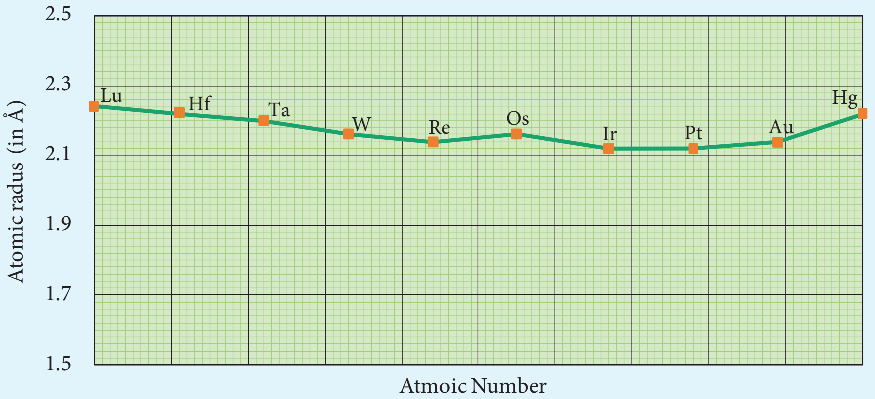


Figure 4.4 (c) Atomic radius of 5d Elements

At the end of the series, d – orbitals of Zinc contain 10 electrons in which the repulsive interaction between the electrons is more than the effective nuclear charge and hence, the orbitals slightly expand and atomic radius slightly increases.

Generally as we move down a group atomic radius increases, the same trend is expected in d block elements also. As the electrons are added to the 4d sub shell, the atomic radii of the 4d elements are higher than the corresponding elements of the 3d series. However there is an unexpected observation in the atomic radius of 5d elements which have nearly same atomic radius as that of corresponding 4d elements. This is due to lanthanoide contraction which is to be discussed later in this unit under inner transition elements.

4.3.3 Ionization enthalpy:

Ionization energy of transition element is intermediate between those of s and p block elements. As we move from left to right in a transition metal series, the ionization enthalpy increases as expected. This is due to increase in nuclear charge corresponding to the filling of d electrons. The following figure show the trends in ionisation enthalpy of transition elements.

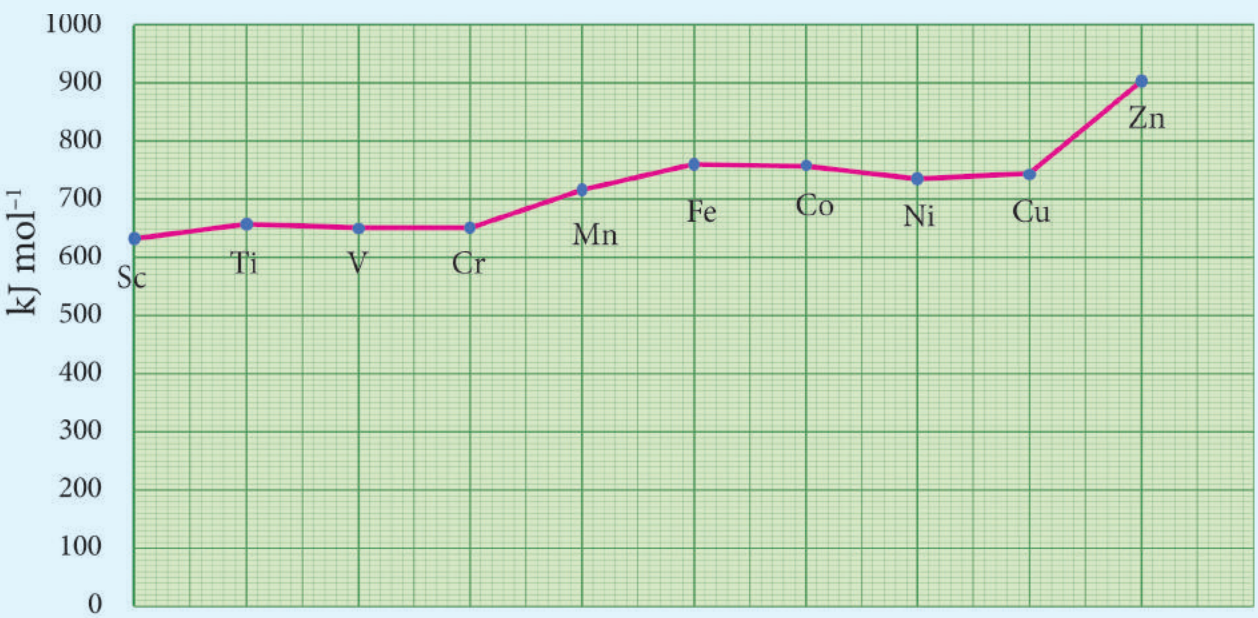


Figure 4.5 Variation in ionisation energy of 3d series elements

The increase in first ionisation enthalpy with increase in atomic number along a particular series is not regular. The added electron enters (n-1)d orbital and the inner electrons act as a shield and decrease the effect of nuclear charge on valence ns electrons. Therefore, it leads to variation in the ionization energy values.

The ionisation enthalpy values can be used to predict the thermodynamic stability of their compounds. Let us compare the ionisation energy required to form Ni^{2+} and Pt^{2+} ions.

For Nickel, $IE_1 + IE_2 = (737 + 1753)$

$= 2490\ kJmol^{-1}$

For Platinum, $IE_1 + IE_2 = (864 + 1791)$

$= 2655\ kJmol^{-1}$

Since, the energy required to form Ni^{2+} is less than that of Pt^{2+}, Ni(II) compounds are thermodynamically more stable than Pt(II) compounds.

Evaluate yourself:

Compare the stability of Ni^{4+} and Pt^{4+} from their ionisation enthalpy values.

IE	Ni	Pt
I	737	864
II	1753	1791
III	3395	2800
IV	5297	4150

4.3.4 Oxidation state:

The first transition metal Scandium exhibits only +3 oxidation state, but all other transition elements exhibit variable oxidation states by loosing electrons from (n-1)d orbital and ns orbital as the energy difference between them is very small. Let us consider the 3d series; the following table summarizes the oxidation states of the 3d series elements.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
				+7				
			+6	+6	+6			
		+5	+5	+5				
	+4	+4	+4	+4	+4	+4	+4	
+3	+3	+3	+3	+3	+3	+3	+3	
	+2	+2	+2	+2	+2	+2	+2	+2
								+1

At the beginning of the series, +3 oxidation state is stable but towards the end +2 oxidation state becomes stable.

The number of oxidation states increases with the number of electrons available, and it decreases as the number of paired electrons increases. Hence, the first and last elements show less number of oxidation states and the middle elements with more number of oxidation states. For example, the first element Sc has only one oxidation state +3; the middle element Mn has six different oxidation states from +2 to +7. The last element Cu shows +1 and +2 oxidation states only.

The relative stability of different oxidation states of 3d metals is correlated with the extra stability of half filled and fully filled electronic configurations. Example: $Mn^{2+}\left(3d^5\right)$ is more stable than $Mn^{4+}\left(3d^3\right)$

The oxidation states of 4d and 5d metals vary from +3 for Y and La to +8 for Ru and Os. The highest oxidation state of 4d and 5d elements are found in their compounds with the higher electronegative elements like O, F and Cl. for example: RuO_4, OsO_4 and WCl_6. Generally in going down a group, a stability of the higher oxidation state increases while that of lower oxidation state decreases.It is evident from the Frost diagram (ΔG^0 vs oxidation number) as shown below,For titanium,vanadium and chromium, the most thermodynamically stable oxidation state is +3. For iron, the stabilities of +3 and +2 oxidation states are similar.Copper is unique in 3d series having a stable +1 oxidation state. It is prone to disproportionate to the +2 and 0 oxidation states.

Evaluate yourself:

Why iron is more stable in +3 oxidation state than in +2 and the reverse is true for Manganese?

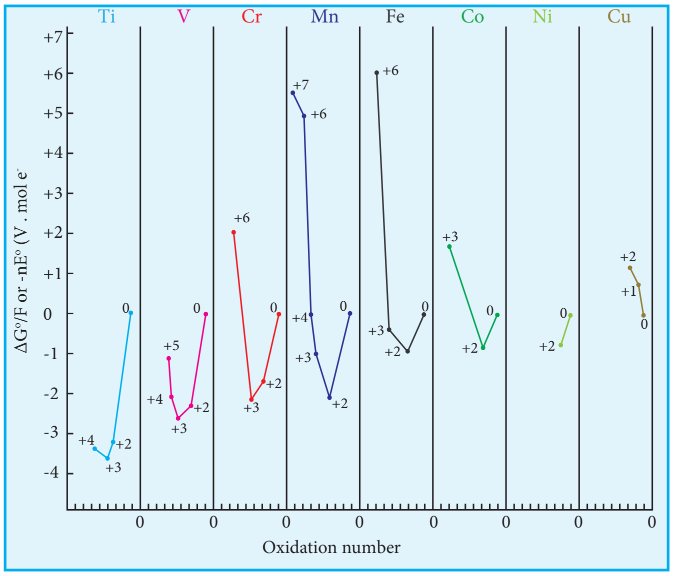


Figure 4.6 Frost diagram

4.3.5 Standard electrode potentials of transition metals

Redox reactions involve transfer of electrons from one reactant to another. Such reactions are always coupled, which means that when one substance is oxidised, another must be reduced. The substance which is oxidised is a reducing agent and the one which is reduced is an oxidizing agent. The oxidizing and reducing power of an element is measured in terms of the standard electrode potentials.

Standard electrode potential is the value of the standard emf of a cell in which molecular hydrogen under standard pressure (1atm) and temperature (273K) is oxidised to solvated protons at the electrode.

If the standard electrode potential (E^0), of a metal is large and negative, the metal is a powerful reducing agent, because it loses electrons easily. Standard electrode potentials (reduction potential) of few first transition metals are given in the following table.

Reaction	Standard reduction potential (V)
$Ti^{2+} + 2e^- \longrightarrow Ti$	−1.63
$V^{2+} + 2e^- \longrightarrow V$	−1.19
$Cr^{2+} + 2e^- \longrightarrow Cr$	−0.91
$Mn^{2+} + 2e^- \longrightarrow Mn$	−1.18
$Fe^{2+} + 2e^- \longrightarrow Fe$	−0.44
$Co^{2+} + 2e^- \longrightarrow Co$	−0.28
$Ni^{2+} + 2e^- \longrightarrow Ni$	−0.23
$Cu^{2+} + 2e^- \longrightarrow Cu$	+0.34
$Zn^{2+} + 2e^- \longrightarrow Zn$	−0.76

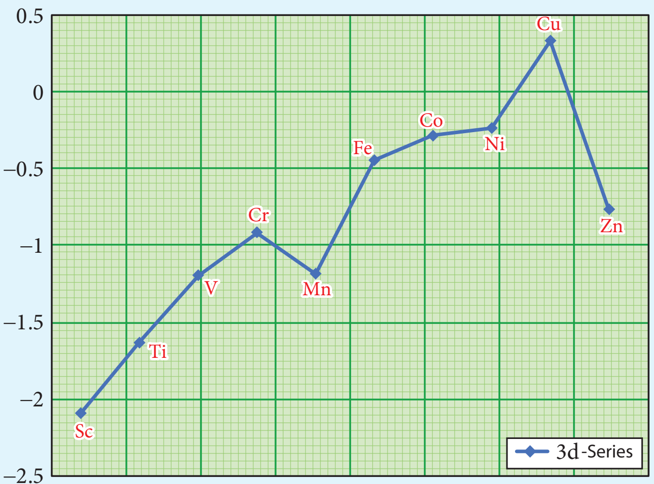


Figure 4.7 (a) $\left(E^0_{M^{2+}/M}\right)$ **-3d series**

In 3d series as we move from Ti to Zn, the standard reduction potential $\left(E^0_{M^{2+}/M}\right)$ value is approaching towards less negative value and copper has a positive reduction potential. i.e., elemental copper is more stable than Cu^{2+}. There are two deviations., In the general trend, Fig shows that $\left(E^0_{M^{2+}/M}\right)$ value for manganese and zinc are more negative than the regular trend. It is due to extra stability which arises due to the half filled d^5 configuration in Mn^{2+} and completely filled d^{10} configuration in Zn^{2+}.

Transition metals in their high oxidation states tend to be oxidizing . For example, Fe^{3+} is moderately a strong oxidant, and it oxidises copper to Cu^{2+} ions. The feasibility of the reaction is predicted from the following standard electrode potential values.

$$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+} \quad E^0 = 0.77V$$

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \quad E^0 = +0.34\ V$$

The standard electrode potential for the M^{3+}/M^{2+} half-cell gives the relative stability between M^{3+} and M^{2+}. The reduction potential values are tabulated as below.

Reaction	Standard reduction potential (V)
$Ti^{3+} + e^- \longrightarrow Ti^{2+}$	–0.37
$V^{3+} + e^- \longrightarrow V^{2+}$	–0.26
$Cr^{3+} + e^- \longrightarrow Cr^{2+}$	–0.41
$Mn^{3+} + e^- \longrightarrow Mn^{2+}$	+1.51
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	+0.77
$Co^{3+} + e^- \longrightarrow Co^{2+}$	+1.81

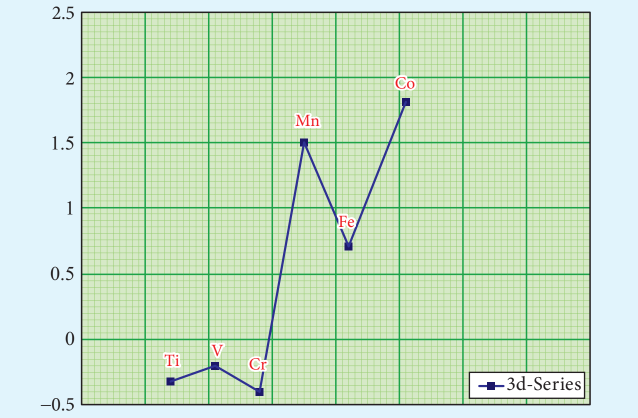


Figure 4.7 (b) M^{3+}/M^{2+} -3d series

The negative values for titanium, vanadium and chromium indicate that the higher oxidation state is preferred. If we want to reduce such a stable Cr^{3+} ion, strong reducing agent which has high negative value for reduction potential like metallic zinc $\left(E^0 = -0.76\ V\right)$ is required.

The high reduction potential of Mn^{3+}/Mn^{2+} indicates Mn^{2+} is more stable than Mn^{3+}. For Fe^{3+}/Fe^{2+} the reduction potential is 0.77V, and this low value indicates that both Fe^{3+} and Fe^{2+} can exist under normal conditions. The drop from Mn to Fe is due to the electronic structure of the ions concerned.Mn^{3+} has a $3d^4$ configuration while that of Mn^{2+} is $3d^5$. The extra stability associated with a half filled d sub shell makes the reduction of Mn^{3+} very feasible ($E^0 = +1.51V$).

4.3.6 Magnetic properties

Most of the compounds of transition elements are paramagnetic. Magnetic properties are related to the electronic configuration of atoms. We have already learnt in XI STD that the electron is spinning around its own axis, in addition to its orbital motion around the nucleus. Due to these motions, a tiny magnetic field is generated and it is measured in terms of magnetic moment. On the basis of magnetic properties, materials can be broadly classified as (i) paramagnetic materials (ii) diamagnetic materials, besides these there are ferromagnetic and antiferromagnetic materials.

Materials with no elementary magnetic dipoles are diamagnetic, in other words a species with all paired electrons exhibits diamagnetism. This kind of materials are repelled by the magnetic field because the presence of external magnetic field, a magnetic induction is introduced to the material which generates weak magnetic field that oppose the applied field.

Paramagnetic solids having unpaired electrons possess magnetic dipoles which are isolated from one another. In the absence of external magnetic field, the dipoles are arranged at random and hence the solid shows no net magnetism. But in the presence of magnetic field, the dipoles are aligned parallel to the direction of the applied field and therefore, they are attracted by an external magnetic field.

Ferromagnetic materials have domain structure and in each domain the magnetic dipoles are arranged. But the spin dipoles of the adjacent domains are randomly oriented. Some transition elements or ions with unpaired d electrons show ferromagnetism.

3d transition metal ions in paramagnetic solids often have a magnetic dipole moments corresponding to the electron spin contribution only. The orbital moment L is said to be quenched. So the magnetic moment of the ion is given by

$$\mu = g\sqrt{S(S+1)}\ \mu_B$$

Where S is the total spin quantum number of the unpaired electrons and is μ_B Bohr Magneton.

For an ion with n unpaired electrons $S = \frac{n}{2}$ and for an electron g=2

Therefore the spin only magnetic moment is given by

$$\mu = 2\sqrt{\left(\frac{n}{2}\right)\left(\frac{n}{2}+1\right)}\ \mu_B$$

$$\mu = 2\sqrt{\left(\frac{n(n+2)}{4}\right)}\ \mu_B$$

$$\mu = \sqrt{n(n+2)}\ \mu_B$$

The magnetic moment calculated using the above equation is compared with the experimental values in the following table. In most of the cases, the agreement is good.

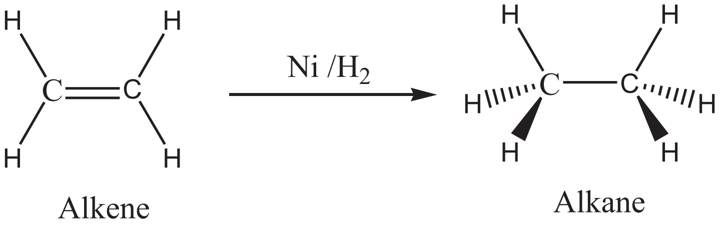
Ion	**Configuration**	**n**	$\mu = \sqrt{n(n+2)}\ \mu_B$	**μ (observed)**
Sc^{3+}, Ti^{4+}, V^{5+}	d^0	0	$\mu = \sqrt{0(0+2)} = 0\ \mu_B$	diamagnetic
Ti^{3+}, V^{4+}	d^1	1	$\mu = \sqrt{1(1+2)} = \sqrt{3} = 1.73\ \mu_B$	1.75
Ti^{2+}, V^{3+}	d^2	2	$\mu = \sqrt{2(2+2)} = \sqrt{8} = 2.83\ \mu_B$	2.76
Cr^{3+}, Mn^{4+}, V^{2+}	d^3	3	$\mu = \sqrt{3(3+2)} = \sqrt{15} = 3.87\ \mu_B$	3.86
Cr^{2+}, Mn^{3+}	d^4	4	$\mu = \sqrt{4(4+2)} = \sqrt{24} = 4.89\ \mu_B$	4.80
Mn^{2+}, Fe^{3+}	d^5	5	$\mu = \sqrt{5(5+2)} = \sqrt{35} = 5.91\ \mu_B$	5.96
Co^{3+}, Fe^{2+}	d^6	4	$\mu = \sqrt{4(4+2)} = \sqrt{24} = 4.89\ \mu_B$	5.3-5.5
Co^{2+}	d^7	3	$\mu = \sqrt{3(3+2)} = \sqrt{15} = 3.87\ \mu_B$	4.4-5.2
Ni^{2+}	d^8	2	$\mu = \sqrt{2(2+2)} = \sqrt{8} = 2.83\ \mu_B$	2.9-3.4
Cu^{2+}	d^9	1	$\mu = \sqrt{1(1+2)} = \sqrt{3} = 1.732\ \mu_B$	1.8-2.2
Cu^{+}, Zn^{2+}	d^{10}	0	$\mu = \sqrt{0(0+2)} = 0\ \mu_B$	diamagnetic

4.3.7 Catalytic properties

The chemical industries manufacture a number of products such as polymers, flavours, drugs etc., Most of the manufacturing processes have adverse effect on the environment so there is an interest for eco friendly alternatives. In this context, catalyst based manufacturing processes are advantageous, as they require low energy, minimize waste production and enhance the conversion of reactants to products.

Many industrial processes use transition metals or their compounds as catalysts. Transition metal has energetically available d orbitals that can accept electrons from reactant molecule or metal can form bond with reactant molecule using its d electrons. For example, in the catalytic hydrogenation of an alkene, the alkene bonds to an active site by using its π electrons with an empty d orbital of the catalyst.

The σ bond in the hydrogen molecule breaks, and each hydrogen atom forms a bond with a d electron on an atom in the catalyst. The two hydrogen atoms then bond with the partially broken π -bond in the alkene to form an alkane.

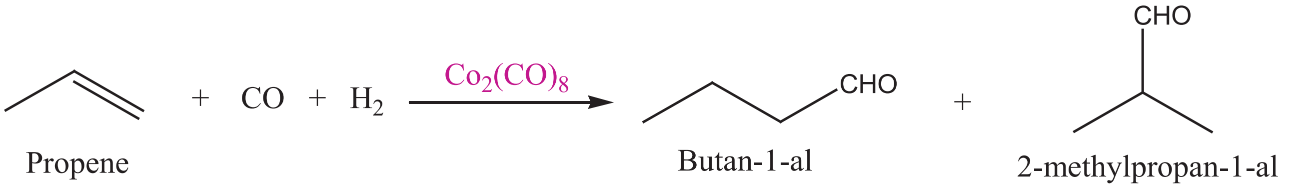


In certain catalytic processes the variable oxidation states of transition metals find applications. For example, in the manufacture of sulphuric acid from SO_3, vanadium pentoxide

(V_2O_5) is used as a catalyst to oxidise SO_2. In this reaction V_2O_5 is reduced to vanadium (IV) Oxide (VO_2).

Some more examples are discussed below,

(i) Hydroformylation of olefins



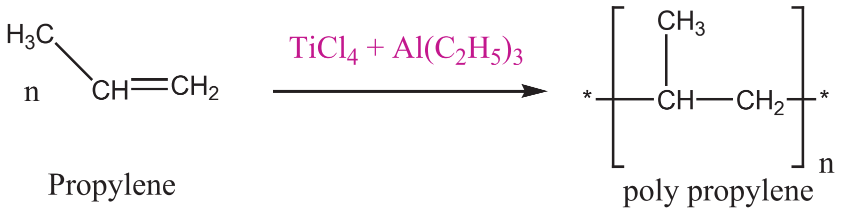
(ii) Preparation acetic acid from acetaldehyde.

$$CH_3\text{- }CHO + CO \xrightarrow{\text{Rh / Ir complex}} CH_3\text{- }COOH$$

Acetaldehyde Acetic acid

(iii) Zeigler – Natta catalyst

A mixture of TiCl4 and trialkyl aluminium is used for polymerization.



4.3.8 Alloy formation

An alloy is formed by blending a metal with one or more other elements. The elements may be metals or non-metals or both. The bulk metal is named as solvent, and the other elements in smaller portions are called solute. According to Hume-Rothery rule to form a substitute alloy the difference between the atomic radii of solvent and solute is less than 15%. Both the solvent and solute must have the same crystal structure and valence and their electro negativity difference must be close to zero. Transition metals satisfying these mentioned conditions form a number of alloys among themselves, since their atomic sizes are similar and one metal atom can be easily replaced by another metal atom from its crystal lattice to form an alloy. The alloys so formed are hard and often have high melting points. Examples: Ferrous alloys, gold – copper alloy, chrome alloys etc.,

4.3.9 Formation of interstitial compounds

An interstitial compound or alloy is a compound that is formed when small atoms like hydrogen, boron, carbon or nitrogen are trapped in the interstitial holes in a metal lattice. They are usually non-stoichiometric compounds.Transition metals form a number of interstitial compounds such as TiC, $ZrH_{1.92}$, Mn_4N etc. The elements that occupy the metal lattice provide them new properties.

(i) They are hard and show electrical land thermal conductivity

(ii) They have high melting points higher than those of pure metals

(iii) Transition metal hydrides are used as powerful reducing agents

(iv) Metallic carbides are chemically inert.

4.3.10 Formation of complexes

Transition elements have a tendency to form coordination compounds with a species that has an ability to donate an electron pair to form a coordinate covalent bond. Transition metal ions are small and highly charged and they have vacant low energy orbitals to accept an electron pair donated by other groups. Due to these properties, transition metals form large number of complexes. Examples: $[Fe(CN)_6]^{4-}$, $[Co(NH_3)_6]^{3+}$, etc..

The chemistry of coordination compound is discussed in unit 5.

4.4 important compound of Transition elements

Oxides and Oxoanions of Metals

Generally, transition metal oxides are formed by the reaction of transition metals with molecular oxygen at high temperatures. Except the first member of 3d series, Scandium, all other transition elements form ionic metal oxides. The oxidation number of metal in metal oxides ranges from +2 to +7. As the oxidation number of a metal increases, ionic character decreases, for example, Mn_2O_7 is covalent. Mostly higher oxides are acidic in nature, Mn_2O_7 dissolves in water to give permanganic acid ($HMnO_4$) , similarly CrO_3 gives chromic acid (H_2CrO_4) and dichromic acid ($H_2Cr_2O_7$). Generally lower oxides may be amphoteric or basic, for example, Chromium (III) oxide - Cr_2O_3, is amphoteric and Chromium(II) oxide, CrO, is basic in nature.

Potassium dichromate $K_2Cr_2O_7$

Preparation:

Potassium dichromate is prepared from chromate ore. The ore is concentrated by gravity separation. It is then mixed with excess sodium carbonate and lime and roasted in a reverbratory furnace.

$$4\,FeCr_2O_4 + 8\,Na_2CO_3 + 7\,O_2 \xrightarrow{900\text{ - }1000^0C} 8\,Na_2CrO_4 + 2\,Fe_2O_3 + 8\,CO_2\uparrow$$

The roasted mass is treated with water to separate soluble sodium chromate from insoluble iron oxide. The yellow solution of sodium chromate is treated with concentrated sulphuric acid which converts sodium chromate into sodium dichromate.

$$\underset{\substack{\text{sodium chromate}\\\text{(yellow)}}}{2\,Na_2CrO_4} + H_2SO_4 \longrightarrow \underset{\substack{\text{sodium dichromate}\\\text{(orange red)}}}{Na_2Cr_2O_7} + Na_2SO_4 + H_2O$$

The above solution is concentrated to remove less soluble sodium sulphate. The resulting solution is filtered and further concentrated. It is cooled to get the crystals of $Na_2SO_4.2H_2O$.

The saturated solution of sodium dichromate in water is mixed with KCl and then concentrated to get crystals of NaCl. It is filtered while hot and the filtrate is cooled to obtain $K_2Cr_2O_7$ crystals.

$$\underset{\substack{\text{sodium dichromate}\\ \text{(orange red)}}}{Na_2Cr_2O_7} + 2KCl \longrightarrow \underset{\substack{\text{potassium dichromate}\\ \text{(orange red)}}}{K_2Cr_2O_7} + 2NaCl$$

Physical properties:

Potassium dichromate is an orange red crystalline solid which melts at 671K and it is moderately soluble in cold water, but very much soluble in hot water. On heating it decomposes and forms Cr_2O_3 and molecular oxygen. As it emits toxic chromium fumes upon heating, it is mainly replaced by sodium dichromate.

$$4\ \underset{\substack{\text{potassium}\\ \text{dichromate}}}{K_2Cr_2O_7} \xrightarrow{\Delta} 4\ \underset{\substack{\text{potassium}\\ \text{chromate}}}{K_2CrO_4} + 2\ \underset{\substack{\text{chromium(III)}\\ \text{oxide}}}{Cr_2O_3} + 3O_2\uparrow$$

Structure of dichromate ion:

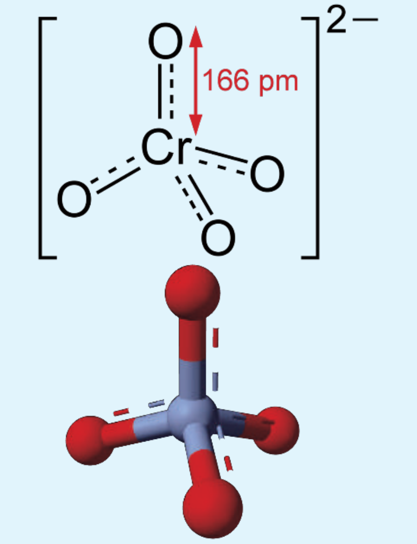


Figure 4.8 (a) Structure of chromate ion

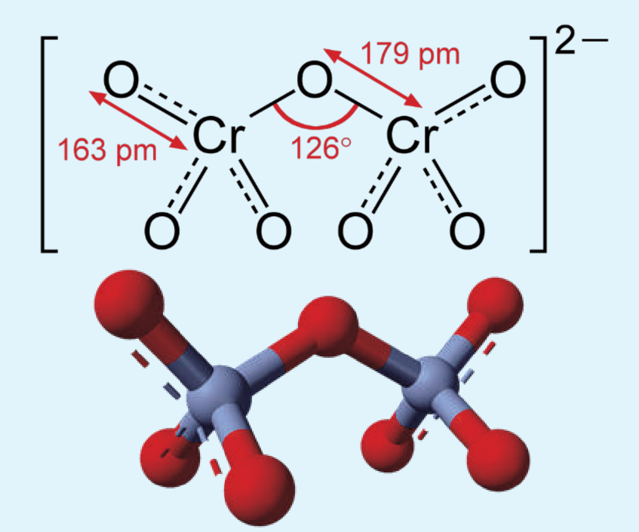


Figure 4.8 (b) Structure of dichromate ion

Both chromate and dichromate ion are oxo anions of chromium and they are moderately strong oxidizing agents. In these ions chromium is in +6 oxidation state. In an aqueous solution, chromate and dichromate ions can be interconvertible, and in an alkaline solution chromate ion is predominant, whereas dichromate ion becomes predominant in acidic solutions. Structures of these ions are shown in the figure.

Chemical properties:

1. Oxidation

Potassium dichromate is a powerful oxidising agent in acidic medium. Its oxidising action in the presence of H+ ions is shown below. You can note that the change in the oxidation state of chromium from Cr^{6+} to Cr^{3+}.Its oxidising action is shown below.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow Cr^{3+} + 7\ H_2O$$

The oxidising nature of potassium dichromate (dichromate ion) is illustrated in the following examples.

(i) It oxidises ferrous salts to ferric salts.

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

(ii) It oxidises iodide ions to iodine

$$Cr_2O_7^{2-} + 6I^- + 14H^+ \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

(iii) It oxidises sulphide ion to sulphur

$$Cr_2O_7^{2-} + 3S^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 3S + 7H_2O$$

(iv) It oxidises sulphur dioxide to sulphate ion

$$Cr_2O_7^{2-} + 3SO_2 + 2H^+ \longrightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O$$

(v) It oxidises stannous salts to stannic salt

$$Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 3Sn^{4+} + 7H_2O$$

(vi) It oxidises alcohols to acids.

$$2K_2Cr_2O_7 + 8H_2SO_4 + 3CH_3CH_2OH \longrightarrow 2K_2SO_4 + 2Cr_2\left(SO_4\right)_3 + 3CH_3COOH + 11H_2O$$

2. Chromyl chloride test:

When potassium dichromate is heated with any chloride salt in the presence of Conc H_2SO_4, orange red vapours of chromyl chloride (CrO_2Cl_2) is evolved. This reaction is used to confirm the presence of chloride ion in inorganic qualitative analysis.

$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \longrightarrow 2KHSO_4 + 4NaHSO_4 + \underset{\text{Chromyl chloride}}{2CrO_2Cl_2} \uparrow + 3H_2O$$

The chromyl chloride vapours are dissolved in sodium hydroxide solution and then acidified with acetic acid and treated with lead acetate. A yellow precipitate of lead chromate is obtained.

$$CrO_2Cl_2 + 4NaOH \longrightarrow Na_2CrO_4 + 2NaCl + 2H_2O$$

$$Na_2CrO_4 + \left(CH_3COO\right)_2 Pb \longrightarrow \underset{\substack{\text{Leadchromate} \\ \text{(Yellowprecipitate)}}}{PbCrO_4} \downarrow + 2CH_3COONa$$

Uses of potassium dichromate:

Some important uses of potassium dichromate are listed below.

1. It is used as a strong oxidizing agent.
2. It is used in dyeing and printing.
3. It used in leather tanneries for chrome tanning.
4. It is used in quantitative analysis for the estimation of iron compounds and iodides.

Potassium permanganate - $KMnO_4$

Preparation:

Potassium permanganate is prepared from pyrolusite (MnO_2) ore. The preparation involves the following steps.

(i) Conversion of MnO_2 to potassium manganate:
Powdered ore is fused with KOH in the presence of air or oxidising agents like KNO_3 or $KClO_3$. A green coloured potassium manganate is formed.

$$2MnO_2 + 2KOH + O_2 \longrightarrow \underset{\substack{\textit{potassium manganate} \\ \textit{(Green)}}}{K_2MnO_4} + 2H_2O$$

(ii) Oxidation of potassium manganate to potassium permanganate:
Potassium manganate thus obtained can be oxidised in two ways , either by chemical oxidation or electrolytic oxidation.

Chemical oxidation:

In this method potassium manganate is treated with ozone (O_3) or chlorine to get potassium permanganate.

$$2MnO_4^{2-} + O_3 + H_2O \longrightarrow 2MnO_4^{-} + 2OH^{-} + O_2$$
$$2MnO_4^{2-} + Cl_2 \longrightarrow 2MnO_4^{-} + 2Cl^{-}$$

Electrolytic oxidation

In this method aqueous solution of potassium manganate is electrolyzed in the presence of little alkali.

$$K_2MnO_4 \rightleftharpoons 2K^{+} + MnO_4^{2-}$$
$$H_2O \rightleftharpoons H^{+} + OH^{-}$$

Manganate ions are converted into permanganate ions at anode.

$$\underset{\textit{Green}}{MnO_4^{2-}} \rightleftharpoons \underset{\textit{purple}}{MnO_4^{-}} + e^{-}$$

$H_2$is liberated at the cathode.

$$2H^{+} + 2e^{-} \longrightarrow H_2 \uparrow$$

The purple coloured solution is concentrated by evaporation and forms crystals of potassium permanganate on cooling.

Physical properties:

Potassium permanganate exists in the form of dark purple crystals which melts at 513 K. It is sparingly soluble in cold water but, fairly soluble in hot water.

Structure of permanganate ion

Permanganate ion has tetrahedral geometry in which the central Mn^{7+} is sp^3 hybridised.

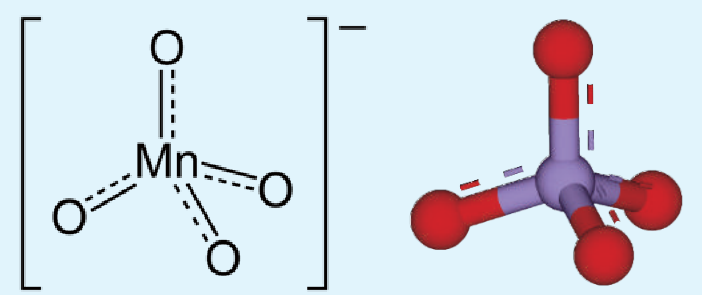


Figure 4.9 Structure of permanganate ion

Chemical properties:

1. **Action of heat:**

When heated, potassium permanganate decomposes to form potassium manganate and manganese dioxide.

$$2KMnO_4 \longrightarrow 2K_2MnO_4 + MnO_2 + O_2$$

2. **Action of conc H_2SO_4**

On treating with cold conc H_2SO_4, it decomposes to form manganese heptoxide, which subsequently decomposes explosively.

$$2KMnO_4 + \underset{\text{(cold)}}{2H_2SO_4} \longrightarrow Mn_2O_7 + 2KHSO_4 + H_2O$$

$$Mn_2O_7 \xrightarrow{\Delta} 2MnO_2 + 3O_2$$

But with hot conc H_2SO_4, potassium permanganate give $MnSO_4$

$$4KMnO_4 + \underset{\text{(hot)}}{6H_2SO_4} \longrightarrow 4MnSO_4 + 2K_2SO_4 + 6H_2O + 5O_2$$

3. **Oxidising property:**

Potassium permanganate is a strong oxidising agent, its oxidising action differs in different reaction medium.

a) In neutral medium:

In neutral medium, it is reduced to MnO_2.

$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$$

(i) It oxidises H_2S to sulphur

$$2MnO_4^- + 3H_2S \longrightarrow 2MnO_2 + 3S + 2OH^- + 2H_2O$$

(ii) It oxidises thiosulphate into sulphate

$$8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow 6SO_4^{2-} + 8MnO_2 + 2OH^-$$

b) In alkaline medium:

In the presence of alkali metal hydroxides, the permanganate ion is converted into manganate.

$$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$$

This manganate is further reduced to MnO_2 by some reducing agents.

$$MnO_4^{2-} + H_2O \longrightarrow MnO_2 + 2OH^- + [O]$$

So the overall reaction can be written as follows.

$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$$

This reaction is similar as that for neutral medium.

Bayer's reagent:

Cold dilute alkaline $KMnO_4$ is known as Bayer's reagent. It is used to oxidise alkenes into diols. For example, ethylene can be converted into ethylene glycol and this reaction is used as a test for unsaturation.

c) In acid medium:

In the presence of dilute sulphuric acid, potassium permanganate acts as a very strong oxidising agent. Permanganate ions is converted into Mn^{2+} ion.

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

The oxidising nature of potassium permanganate (permanganate ion) in acid medium is illustrated in the following examples.

(i) It oxidises ferrous salts to ferric salts.

$$2MnO_4^- + 10Fe^{2+} + 16H^+ \longrightarrow 2Mn^{2+} + 10Fe^{3+} + 8H_2O$$

(ii) It oxidises iodide ions to iodine

$$2MnO_4^- + 10\,I^- + 16H^+ \longrightarrow 2Mn^{2+} + 5I_2 + 8H_2O$$

(iii) It oxidises oxalic acid to CO_2

$$2MnO_4^- + 5(COO)^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

(iv) It oxidises sulphide ion to sulphur

$$2MnO_4^- + 5\,S^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 5\,S + 8H_2O$$

(v) It oxidises nitrites to nitrates

$$2MnO_4^- + 5NO_2^- + 6H^+ \longrightarrow 2Mn^{2+} + 5NO_3^- + 3H_2O$$

(vi) It oxidises alcohols to aldehydes.

$$2KMnO_4 + 3H_2SO_4 + 5CH_3CH_2OH \longrightarrow 2K_2SO_4 + 2MnSO_4 + 5CH_3CHO + 8H_2O$$

(vii) It oxidises sulphite to sulphate

$$2MnO_4^- + 5SO_3^{2-} + 6H^+ \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$$

Uses of potassium permanganate:

Some important uses of potassium permanganate are listed below.

1. It is used as a strong oxidizing agent.
2. It is used for the treatment of various skin infections and fungal infections of the foot.
3. It used in water treatment industries to remove iron and hydrogen sulphide from well water.
4. It is used as a Bayer's reagent for detecting unsaturation in an organic compound.
5. It is used in quantitative analysis for the estimation of ferrous salts, oxalates, hydrogen peroxide and iodides.

Note HCl cannot be used for making the medium acidic since it reacts with $KMnO_4$ as follows.

$$2MnO_4^- + 10\,Cl^- + 16H^+ \longrightarrow 2Mn^{2+} + 5Cl_2 + 8H_2O$$

HNO_3 also cannot be used since it is good oxidising agent and reacts with reducing agents in the reaction.

However,H_2SO_4 is found to be most suitable since it does not react with potassium permanganate.

Note

$$\text{Equivalent weight of } KMnO_4 \text{ in acid medium} = \frac{\text{Molecular weight of } KMnO_4}{\text{no of mols of electrons transferred}} = \frac{158}{5} = 31.6$$

$$\text{Equivalent weight of } KMnO_4 \text{ in basic medium} = \frac{\text{Molecular weight of } KMnO_4}{\text{no of mols of electrons transferred}} = \frac{158}{1} = 158$$

$$\text{Equivalent weight of } KMnO_4 \text{ in neutral medium} = \frac{\text{Molecular weight of } KMnO_4}{\text{no of mols of electrons transferred}} = \frac{158}{3} = 52.67$$

f-block elements – Inner transition elements

In the inner transition elements there are two series of elements.

1) Lanthanoids (previously called lanthanides)
2) Actinoids (previously called actinides)

Lanthanoid series consists of fourteen elements from Cerium ($_{58}Ce$) to Lutetium ($_{71}Lu$) following Lanthanum ($_{57}La$).These elements are characterised by the preferential filling of 4f orbitals, Similarly actinoids consists of 14 elements from Thorium ($_{90}Th$) to Lawrencium ($_{103}Lr$) following Actinium ($_{89}Ac$).These elements are characterised by the preferential filling of 5f orbital.

The position of Lanthanoids in the periodic table

The actual position of Lanthanoids in the periodic table is at group number 3 and period number 6.However, in the sixth period after lanthanum, the electrons are preferentially filled in inner 4f sub shell and these fourteen elements following lanthanum show similar chemical properties. Therefore these elements are grouped together and placed at the bottom of the periodic table. This position can be justified as follows.

1. Lanthanoids have general electronic configuration [Xe] $4f^{1-14}$ $5d^{0-1}$ $6s^2$
2. The common oxidation state of lanthanoides is +3
3. All these elements have similar physical and chemical properties.

Similarly the fourteen elements following actinium resemble in their physical and chemical properties. If we place these elements after Lanthanum in the periodic table below 4d series, the properties of the elements belongs to a group would be different and it would affect the proper structure of the periodic table. Hence a separate position is provided to the inner transition elements as shown in the figure.

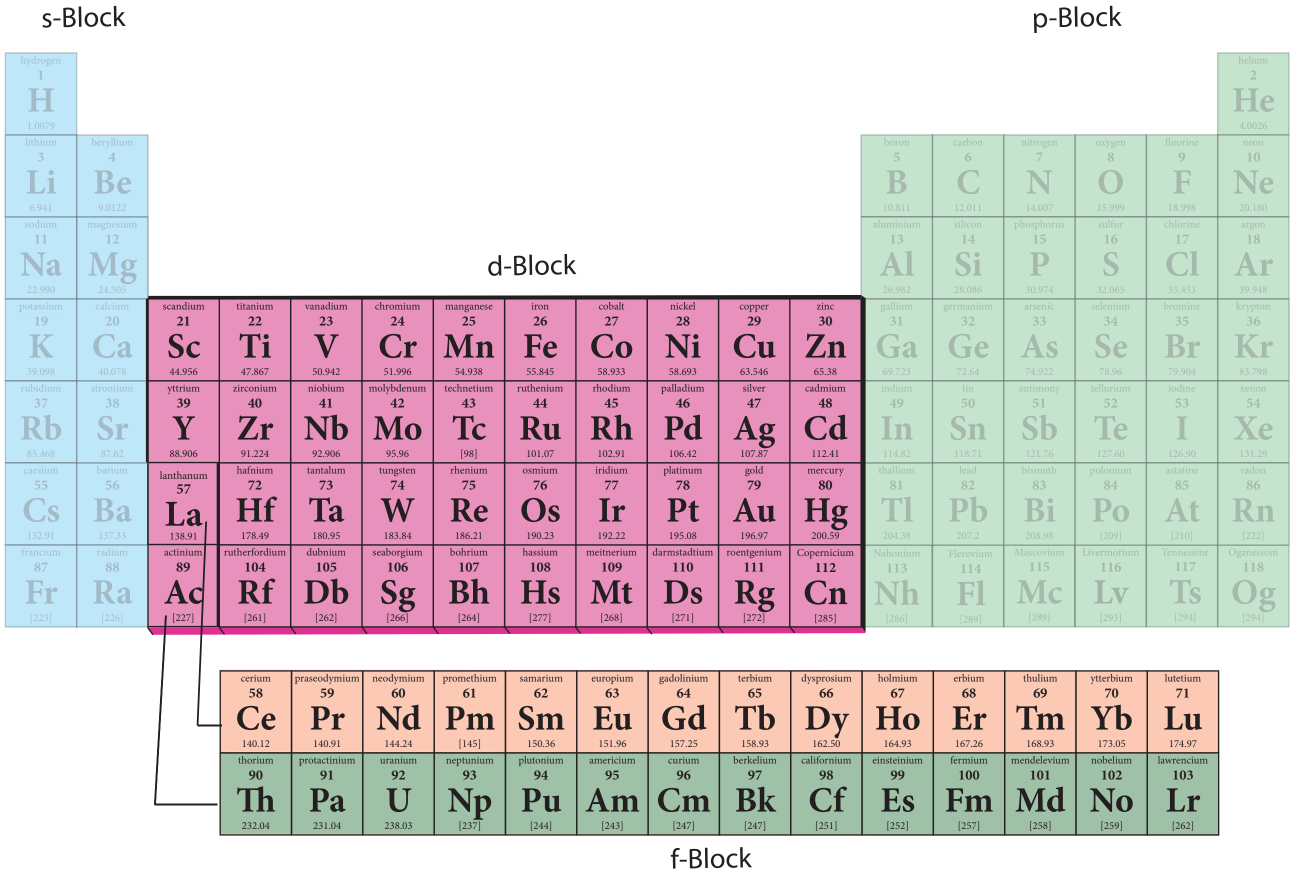


Figure 4.10 position of inner transition elements

Electronic configuration of Lanthanoids:

We know that the electrons are filled in different orbitals in the order of their increasing energy in accordance with Aufbau principle. As per this rule after filling 5s,5p and 6s and 4f level begin to fill from lanthanum, and hence the expected electronic configuration of Lanthanum(La) is [Xe] $4f^1$ $5d^0$ $6s^2$ but the actual electronic configuration of Lanthanum is

$[Xe]\ 4f^0\ 5d^1\ 6s^2$ and it belongs to d block. Filling of 4f orbital starts from Cerium (Ce) and its electronic configuration is $[Xe]\ 4f^1\ 5d^1\ 6s^2$. As we move from Cerium to other elements the additional electrons are progressively filled in 4f orbitals as shown in the table.

Table : electronic configuration of Lanthanum and Lanthanoids

Name of the element	**Atomic number**	**Symbol**	**Electronic configuration**
Lanthanum	57	La	$[Xe]\ 4f^0\ 5d^1\ 6s^2$
Cerium	58	Ce	$[Xe]\ 4f^1\ 5d^1\ 6s^2$
Praseodymium	59	Pr	$[Xe]\ 4f^3\ 5d^0\ 6s^2$
Neodymium	60	Nd	$[Xe]\ 4f^4\ 5d^0\ 6s^2$
Promethium	61	Pm	$[Xe]\ 4f^5\ 5d^0\ 6s^2$
Samarium	62	Sm	$[Xe]\ 4f^6\ 5d^0\ 6s^2$
Europium	63	Eu	$[Xe]\ 4f^7\ 5d^0\ 6s^2$
Gadolinium	64	Gd	$[Xe]\ 4f^7\ 5d^1\ 6s^2$
Terbium	65	Tb	$[Xe]\ 4f^9\ 5d^0\ 6s^2$
Dysprosium	66	Dy	$[Xe]\ 4f^{10}\ 5d^0\ 6s^2$
Holmium	67	Ho	$[Xe]\ 4f^{11}\ 5d^0\ 6s^2$
Erbium	68	Er	$[Xe]\ 4f^{12}\ 5d^0\ 6s^2$
Thulium	69	Tm	$[Xe]\ 4f^{13}\ 5d^0\ 6s^2$
Ytterbium	70	Yb	$[Xe]\ 4f^{14}\ 5d^0\ 6s^2$
Lutetium	71	Lu	$[Xe]\ 4f^{14}\ 5d^1\ 6s^2$

In Gadolinium (Gd) and Lutetium (Lu) the 4f orbitals, are half-filled and completely filled, and one electron enters 5d orbitals. Hence the general electronic configuration of 4f series of elements can be written as $[Xe]\ 4f^{2-14}\ 5d^{0-1}\ 6s^2$

Oxidation state of lanthanoids:

The common oxidation state of lanthanoids is +3. In addition to that some of the lanthanoids also show either +2 or +4 oxidation states.

Gd^{3+} and Lu^{3+} ions have extra stability, it is due to the fact that they have exactly half filled and completely filled f-orbitals respectively.their electronic c onfigurations are

$$Gd^{3+} : [Xe]4f^7$$

$$Lu^{3+} : [Xe]4f^{14}$$

Similarly Cerium and terbium attain $4f^0$ and $4f^7$ configurations respectively in the +4 oxidation states. Eu^{2+} and Yb^{2+} ions have exactly half filled and completely filled f orbitals respectively.

The stability of different oxidation states has an impact on the properties of these elements. the following table shows the different oxidation states of lanthanoids.

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
		+2		+2	+2						+2	+2	
+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3
+4	+4	+4					+4	+4					

Atomic and ionic radii:

As we move across 4f series, the atomic and ionic radii of lanthanoids show gradual decrease with increse in atomic number. This decrease in ionic size is called lanthanoid contraction.

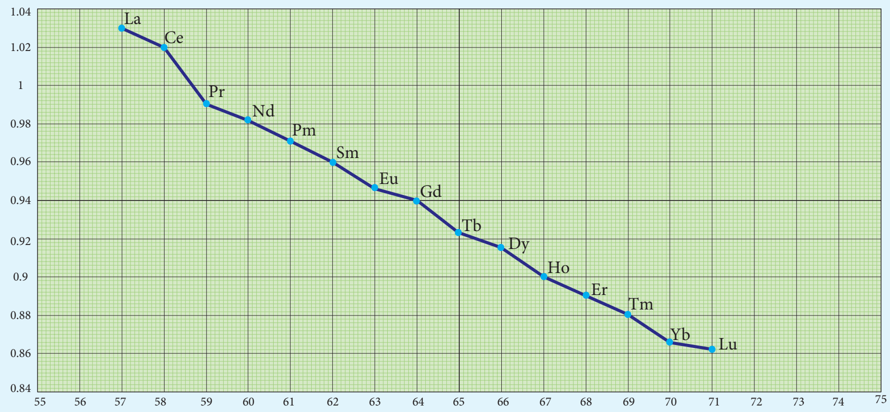


Figure 4.11 Variation of atomic radii of lanthanoids

Cause of lanthanoid contraction:

As we move from one element to another in 4f series (Ce to Lu) the nuclear charge increases by one unit and an additional electron is added into the same inner 4f sub shell. We know that 4f sub shell have a diffused shapes and therefore the shielding effect of 4f elelctrons relatively poor.hence, with increase of nuclear charge, the valence shell is pulled slightly towards nucleus. As a result, the effetive nuclear charge experienced by the 4f elelctorns increases and the size of Ln^{3+} ions decreases. Lanthanoid contraction of various lanthanoids is shown in the graph

Consequences of lanthanoid contraction:

1. Basicity differences

As we from Ce^{3+} to Lu^{3+} , the basic character of Ln^{3+} ions decrease. Due to the decrease in the size of Ln3+ ions, the ionic character of $Ln–OH$ bond decreases (covalent character increases) which results in the decrease in the basicity.

2. Similarities among lanthanoids:

In the complete f - series only 10 pm decrease in atomic radii and 20 pm decrease in ionic radii is observed. because of this very small change in radii of lanthanoids, their chemical properties are quite similar.

The elements of the second and third transition series resemble each other more closely than the elements of the first and second transition series. For example

Series	Element	Atomic radius
3d Series	Ti	132 pm
4d Series	Zr	145 pm
5d Series	Hf	144 pm

Actinoids:

The fourteen elements following actinium ,i.e., from thorium (Th) to lawrentium (Lr) are called actinoids. Unlike the lanthanoids, all the actinoids are radioactive and most of them have short half lives. Only thorium and uranium(U) occur in significant amount in nature and a trace amounts of Plutonium(Pu) is also found in Uranium ores.Neptunium(Np) and successive heavier elements are produced synthetically by the artificial transformation of naturally occuring elements by nuclear reactions.

Similar to lanthanoids, they are placed at the bottom of the periodic table.

Electronic configuration:

The electronic configuration of actinoids is not definite. The general valence shell electronic configuration of 5f elements is represented as $[Rn]5f^{2-14}6d^{0-2}7s^2$. The following table show the electronic configuration of actinoids.

Table : electronic configuration of actinoids

Name of the element	Atomic number	Symbol	Electronic configuration
Actinium	89	Ac	$[Rn]\ 5f^0\ 6d^1\ 7s^2$
Thorium	90	Th	$[Rn]\ 5f^0\ 6d^2\ 7s^2$
Protactinium	91	Pa	$[Rn]\ 5f^2\ 6d^1\ 7s^2$
Uranium	92	U	$[Rn]\ 5f^3\ 6d^1\ 7s^2$
Neptunium	93	Np	$[Rn]\ 5f^4\ 6d^1\ 7s^2$
Plutonium	94	Pu	$[Rn]\ 5f^6\ 6d^0\ 7s^2$
Americium	95	Am	$[Rn]\ 5f^7\ 6d^0\ 7s^2$
Curium	96	Cm	$[Rn]\ 5f^7\ 6d^1\ 7s^2$
Berkelium	97	Bk	$[Rn]\ 5f^9\ 6d^0\ 7s^2$
Californium	98	Cf	$[Rn]\ 5f^{10}\ 6d^0\ 7s^2$

Name of the element	Atomic number	Symbol	Electronic configuration
Einstenium	99	Es	[Rn] $5f^{11}$ $6d^0$ $7s^2$
Fermium	100	Fm	[Rn] $5f^{12}$ $6d^0$ $7s^2$
Mendelevium	101	Md	[Rn] $5f^{13}$ $6d^0$ $7s^2$
Nobelium	102	No	[Rn] $5f^{14}$ $6d^0$ $7s^2$
Lowrentium	103	Lr	[Rn] $5f^{14}$ $7s^2$ $7p^1$

Oxidation state of actinoids:

Like lanthanoids, the most common state of actinoids is +3. In addition to that actinoids show variable oxidation states such as +2 , +3 , +4 ,+5,+6 and +7.

The elements Americium(Am) and Thorium (Th) show +2 oxidation state in some compounds , for example thorium iodide (ThI_2). The elements Th , Pa, U ,Np , Pu and Am show +5 oxidation states. Np and Pu exhibit +7 oxidation state.

Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
+2					+2								
+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3	+3
+4	+4	+4	+4	+4	+4	+4	+4						
+5	+5	+5	+5	+5	+5								
		+6	+6	+6	+6								
			+7	+7	+7								

Differences between lanthanoids and actinoids:

s.no	Lanthanoids	Actinoids
1	Differentiating electron eneters in 4f orbital	Differentiating electron eneters in 5f orbital
2	Binding energy of 4f orbitals are higher	Binding energy of 5f orbitals are lower
3	They show less tendency to form complexes	They show greater tendency to form complexes
4	Most of the lanthanoids are colourless	Most of the actinoids are coloured. For example. U^{3+} (red), U^{4+} (green) , UO_2^{2+} (yellow)

s.no	Lanthanoids	Actinoids
5	They do not form oxo cations	They do form oxo cations such as UO_2^{2+}, NpO_2^{2+} etc
6	Besides +3 oxidation states lanthanoids show +2 and +4 oxidation states in few cases.	Besides +3 oxidation states actinoids show higher oxidation states such as +4, +5, +6 and +7.

Summary

- IUPAC defines transition metal as an element whose atom has an incomplete d sub shell or which can give rise to cations with an incomplete d sub shell. They occupy the central position of the periodic table, between s and p block elements,
- d- Block elements composed of 3d series (4th period) Scandium to Zinc (10 elements), 4d series (5th period) Yttrium to Cadmium (10 elements) and 5d series (6th period) Lanthanum, Haffinium to mercury.
- the general electronic configuration of d- block elements can be written as $[\text{Noble gas}]\,(n-1)d^{1-10}ns^{1-2}$,
  Here, $n = 4$ to 7. In periods 6 and 7, the configuration includes $((n-2)f$ orbital; $[\text{Noble gas}]\,(n-2)f^{14}\,(n-1)d^{1-10}ns^{1-2}$.
- All the transition elements are metals. Similar to all metals the transition metals are good conductors of heat and electricity. Unlike the metals of Group-1 and group-2, all the transition metals except group 11 elements are hard.
- As we move from left to right along the transition metal series, melting point first increases as the number of unpaired d electrons available for metallic bonding increases, reach a maximum value and then decreases, as the d electrons pair up and become less available for bonding.
- Ionization energy of transition element is intermediate between those of s and p block elements. As we move from left to right in a transition metal series, the ionization enthalpy increases as expected.
- The first transition metal Scandium exhibits only +3 oxidation state, but all other transition elements exhibit variable oxidation states by loosing electrons from (n-1)d orbital and ns orbital as the energy difference between them is very small.
- In 3d series as we move from Ti to Zn, the standard reduction potential $\left(E^0_{M^{2+}/M}\right)$ value is approaching towards less negative value and copper has a positive reduction potential. i.e., elemental copper is more stable than Cu^{2+}.

- Most of the compounds of transition elements are paramagnetic. Magnetic properties are related to the electronic configuration of atoms.
- Many industrial processes use transition metals or their compounds as catalysts. Transition metal has energetically available d orbitals that can accept electrons from reactant molecule or metal can form bond with reactant molecule using its d electrons.
- Transition metals form a number of interstitial compounds such as TiC, $ZrH_{1.92}$, Mn_4N etc .
- Transition elements have a tendency to form coordination compounds with a species that has an ability to donate an electron pair to form a coordinate covalent bond.
- In the inner transition elements there are two series of elements. 1) Lanthanoids (previously called lanthanides) 2) Actinoids (previously called actinides)
- Lanthanoids have general electronic configuration $[Xe]\ 4f^{1-14}\ 5d^{0-1}\ 6s^2$
- The common oxidation state of lanthanoides is +3
- As we move across 4f series, the atomic and ionic radii of lanthanoids show gradual decrease with increse in atomic number. This decrese in ionic size is called lanthanoid contraction.
- The electronic configuration of actinoids is not definite. The general valence shell electronic configuration of 5f elements is represented as $[Rn]5f^{2-14}6d^{0-2}7s^2$.
- Like lanthanoids, the most common state of actinoids is +3. In addition to that actinoids show variable oxidation states such as +2 , +3 , +4 ,+5,+6 and +7.

EVALUATION

CFF541

Choose the best answer:

1. Sc(Z=21) is a transition element but Zinc (z=30) is not because

   a) both Sc^{3+} and Zn^{2+} ions are colourless and form white compounds.

   b) in case of Sc, 3d orbital are partially filled but in Zn these are completely filled

   c) last electron as assumed to be added to 4s level in case of zinc

   d) both Sc and Zn do not exhibit variable oxidation states

2. Which of the following d block element has half filled penultimate d sub shell as well as half filled valence sub shell?

   a) Cr　　b) Pd

   c) Pt　　d) none of these

3. Among the transition metals of 3d series, the one that has highest negative $\left(M^{2+}/M\right)$ standard electrode potential is

a) Ti b) Cu c) Mn d) Zn

4. Which one of the following ions has the same number of unpaired electrons as present in V^{3+}?

a) Ti^{3+} b) Fe^{3+}

c) Ni^{2+} d) Cr^{3+}

5. The magnetic moment of Mn^{2+} ion is

a) 5.92BM b) 2.80BM

c) 8.95BM d) 3.90BM

6. Which of the following compounds is colourless?

a) Fe^{3+} b) Ti^{4+}

c) Co^{2+} d) Ni^{2+}

7. the catalytic behaviour of transition metals and their compounds is ascribed mainly due to

a) their magnetic behaviour

b) their unfilled d orbitals

c) their ability to adopt variable oxidation states

d) their chemical reactivity

8. The correct order of increasing oxidizing power in the series

a) $VO_2^+ < Cr_2O_7^{2-} < MnO_4^-$ b) $Cr_2O_7^{2-} < VO_2^+ < MnO_4^-$

c) $Cr_2O_7^{2-} < MnO_4^- < VO_2^+$ d) $MnO_4^- < Cr_2O_7^{2-} < VO_2^+$

9. The alloy of copper that contain Zinc is

a) Monel metal b) Bronze

c) bell metal d) brass

10. Which of the following does not give oxygen on heating?

a) $K_2Cr_2O_7$ b) $(NH_4)_2Cr_2O_7$

c) $KClO_3$ d) $Zn(ClO_3)_2$

11. In acid medium, potassium permanganate oxidizes oxalic acid to

a) oxalate b) Carbon dioxide

c) acetate d) acetic acid

12. Which of the following statements is not true?

a) on passing H_2S, through acidified $K_2Cr_2O_7$ solution, a milky colour is observed.

b) $Na_2Cr_2O_7$ is preferred over $K_2Cr_2O_7$ in volumetric analysis

c) $K_2Cr_2O_7$ solution in acidic medium is orange in colour

d) $K_2Cr_2O_7$ solution becomes yellow on increasing the P^H beyond 7

13. Permanganate ion changes to _________ in acidic medium

a) MnO_4^{2-} b) Mn^{2+}

c) Mn^{3+} d) MnO_2

14. A white crystalline salt (A) react with dilute HCl to liberate a suffocating gas (B) and also forms a yellow precipitate . The gas (B) turns potassium dichromate acidified with dil H_2SO_4 to a green coloured solution(C). A,B and C are respectively

a) Na_2SO_3 , SO_2 , $Cr_2(SO_4)_3$ b) $Na_2S_2O_3$, SO_2 , $Cr_2(SO_4)_3$

c) Na_2S , SO_2 , $Cr_2(SO_4)_3$ d) Na_2SO_4 , SO_2 , $Cr_2(SO_4)_3$

15. MnO_4^- react with Br^- in alkaline P^H to give

a) BrO_3^- , MnO_2 b) Br_2, MnO_4^{2-}

c) Br_2, MnO_2 d) BrO^-, MnO_4^{2-}

16. How many moles of I_2 are liberated when 1 mole of potassium dichromate react with potassium iodide?

a) 1 b) 2

c) 3 d) 4

17. The number of moles of acidified $KMnO_4$ required to oxidize 1 mole of ferrous oxalate(FeC_2O_4) is

a) 5 b) 3 c) 0.6 d) 1.5

18. When a brown compound of Mn (A) ids treated with HCl , it gives a gas (B) . The gas (B) taken in excess reacts with NH_3 to give an explosive compound (C). The compound A, B and C are

a) MnO_2, Cl_2 , NCl_3 b) MnO, Cl_2 , NH_4Cl

c) Mn_3O_4, Cl_2 , NCl_3 d) MnO_3, Cl_2 , NCl_2

19. Which one of the following statements related to lanthanons is incorrect?

a) Europium shows +2 oxidation state.

b) The basicity decreases as the ionic radius decreases from Pr to Lu.

c) All the lanthanons are much more reactive than aluminium.

d) Ce^{4+} solutions are widely used as oxidising agents in volumetric analysis.

20. Which of the following lanthanoid ions is diamagnetic?

a) Eu^{2+} b) Yb^{2+}

c) Ce^{2+} d) Sm^{2+}

21. Which of the following oxidation states is most common among the lanthanoids?

a) 4 b) 2

c) 5 d) 3

22. Assertion : Ce^{4+} is used as an oxidizing agent in volumetric analysis.
Reason: Ce^{4+} has the tendency of attaining +3 oxidation state.
a) Both assertion and reason are true and reason is the correct explanation of assertion.
b) Both assertion and reason are true but reason is not the correct explanation of assertion.
c) Assertion is true but reason is false.
d) Both assertion and reason are false.

23. The most common oxidation state of actinoids is

a) +2 b) +3

c) +4 d) +6

24. The actinoid elements which show the highest oxidation state of +7 are

a) Np, Pu ,Am b) U, Fm, Th

c) U, Th, Md d) Es, No, Lr

25. Which one of the following is not correct?

a) $La(OH)_3$ is less basic than $Lu(OH)_3$

b) In lanthanoid series ionic radius of Ln^{3+} ions decreases

c) La is actually an element of transition metal series rather than lanthanide series

d) Atomic radii of Zr and Hf are same because of lanthanide contraction

Answer the following questions:

1. What are transition metals? Give four examples.
2. Explain the oxidation states of 4d series elements.
3. What are inner transition elements?
4. Justify the position of lanthanides and actinides in the periodic table.
5. What are actinides? Give three examples.
6. Why Gd^{3+} is colourless?
7. Explain why compounds of Cu^{2+} are coloured but those of Zn^{2+} are colourless.
8. Describe the preparation of potassium dichromate.

9. What is lanthanide contraction and what are the effects of lanthanide contraction?

10. complete the following
    - a. $MnO_4^{2-} + H^+ \longrightarrow ?$
    - b. $C_6H_5CH_3 \xrightarrow[KMnO_4]{acidified} ?$
    - c. $MnO_4^- + Fe^{2+} \longrightarrow ?$
    - d. $KMnO_4 \xrightarrow[\text{Red hot}]{\Delta} ?$
    - e. $Cr_2O_7^{2-} + I^- + H^+ \longrightarrow ?$
    - f. $Na_2Cr_2O_7 + KCl \longrightarrow ?$

11. What are interstitial compounds?

12. Calculate the number of unpaired electrons in Ti^{3+} , Mn^{2+} and calculate the spin only magnetic moment.

13. Write the electronic configuration of Ce^{4+} and Co^{2+}.

14. Explain briefly how +2 states becomes more and more stable in the first half of the first row transition elements with increasing atomic number.

15. Which is more stable? Fe^{3+} or Fe^{2+} - explain.

16. Explain the variation in $E^0_{M^{3+}/M^{2+}}$ 3d series.

17. Compare lanthanides and actinides.

18. Explain why Cr^{2+} is strongly reducing while Mn^{3+} is strongly oxidizing.

19. Compare the ionization enthalpies of first series of the transition elements.

20. Actinoid contraction is greater from element to element than the lanthanoid contraction, why?

21. Out of $Lu(OH)_3$ and $La(OH)_3$ which is more basic and why?

22. Why europium (II) is more stable than Cerium (II)?

23. Why do zirconium and Hafnium exhibit similar properties?

24. Which is stronger reducing agent Cr^{2+} or Fe^{2+}?

25. The $E^0_{M^{2+}/M}$ value for copper is positive. Suggest a possible reason for this.

26. predict which of the following will be coloured in aqueous solution Ti^{2+} , V^{3+} Sc^{4+}, Cu^+ ,Sc^{3+}, Fe^{3+}, Ni^{2+} and Co^{3+}

27. Describe the variable oxidation state of 3d series elements.

28. Which metal in the 3d series exhibits +1 oxidation state most frequently and why?

29. Why first ionization enthalpy of chromium is lower than that of zinc?

30. Transition metals show high melting points why?

UNIT 5

COORDINATION CHEMISTRY

Alfred Werner
(1866 –1919)

Alfred Werner was a Swiss chemist who explainedthe bonding in coordination complexes. Werner proposed his coordination theory in 1893. It must be remembered that this imaginative theory was proposed before the electron had been discovered by J.J. Thompson in 1896. Werner did not have any modern instrumental techniques at his time and all his studies were made using simple reaction chemistry. Complexes must have been a complete mystery without any knowledge of bonding or structure. This theory and his painstaking work over the next 20 years won Alfred Werner the Nobel Prize for Chemistry in 1913.He was the first inorganic chemist to win the Nobel Prize.

PC1YSW

Learning Objectives

After studying this unit, students will be able to

- define important terms in coordination chemistry
- nomenclate the coordination compounds in accordance with the guidelines of IUPAC
- describe different types of isomerism in coordination compounds
- discuss the postulates of Werner's theory of coordination compounds
- predict the geometry of coordination compounds using valance bond theory
- apply crystal field theory to explain the colour and magnetic properties of coordination compounds
- differentiate high spin and low spin coordination compounds
- explain the stability of coordination compounds interms of stability constants.
- explain the applications of coordination compounds in day to day life

INTRODUCTION

We have already learnt in the previous unit that the transition metals have a tendency to form complexes (**coordination compounds**). The name is derived from the Latin words '*complexus*' and '*coordinate*' which mean '*hold*' and '*to arrange*' respectively. The complexes of transition metals have interesting properties and differ from simple ionic and covalent compounds. For example, chromium(III)chloride hexahydrate, $CrCl_3.6H_2O$, exists as purple, pale green or dark green compound. In addition to metals, certain non metals also form coordination compounds but have less tendency than d block elements. Coordination compounds play a vital role in the biological functions, and have wide range of catalytic applications in chemical industries. For example, haemoglobin, the oxygen transporter of human is a coordination compound of iron, and cobalamine, an essential vitamin is a coordination compound of cobalt. Chlorophyll, a pigment present in plants acting as a photo sensitiser in the photosynthesis is also a coordination compound. Various coordination compounds such as Wilkinson's compound, Ziegler Natta compound are used as catalysts in industrial processes. Hence, it is important to understand the chemistry of coordination compounds. In this unit we study the nature, bonding, nomenclature, isomerism and applications of the coordination compounds.

5.1 Coordination compounds and double salts:

When two or more stable compounds in solution are mixed together and allowed to evaporate, in certain cases there is a possibility for the formation of double salts or coordination compounds. For example when an equimolar solution of ferrous sulphate and ammonium sulphate are mixed and allowed to crystallise, a double salt namely Mohr's salt (Ferrous ammonium sulphate, $FeSO_4.(NH_4)_2SO_4.6H_2O$) is formed. Let us recall the blood red colour formation in the inorganic qualitative analysis of ferric ion, the reaction between ferric chloride and potassium thiocyanate solution gives a blood red coloured coordination compound, potassium ferrithiocyanate $K_3[Fe(SCN)_6]$. If we perform a qualitative analysis to identify the constituent ions present in both the compounds, Mohr's salt answers the presence of Fe^{2+} ,NH_4^+ and SO_4^{2-}ions, whereas the potassium ferrithiocyanate will not answer Fe^{3+} and SCN^- ions. From this we can infer that the double salts loose their identity and dissociates into their constituent simple ions in solutions , whereas the complex ion in coordination compound, does not loose its identity and never dissociate to give simple ions.

5.2 Werner's theory of coordination compounds:

Swiss chemist Alfred Werner was the first one to propose a theory of coordination compounds to explain the observed behaviour of them.

Let us consider the different coloured complexes of cobalt(III) chloride with ammonia which exhibit different properties as shown below.

Complex	Colour	No. of moles of AgCl precipitated on reaction of one mole of complex with excess Ag^+
$CoCl_3.6NH_3$	Yellow	3
$CoCl_3.5NH_3$	Purple	2
$CoCl_3.4NH_3$	Green	1
$CoCl_3.4NH_3$	Violet	1

In this case, the valences of the elements present in both the reacting molecules, cobalt(III) chloride and ammonia are completely satisfied. Yet these substances react to form the above mentioned complexes.

To explain this behaviour Werner postulated his theory as follows

1. Most of the elements exhibit, two types of valence namely primary valence and secondary valence and each element tend to satisfy both the valences.In modern terminology, the primary valence is referred as the oxidation state of the metal atom and the secondary valence as the coordination number. For example, according to Werner, the primary and secondary valences of cobalt are 3 and 6 respectively.
2. The primary valence of a metal ion is positive in most of the cases and zero in certain cases. They are always satisfied by negative ions. For example in the complex $CoCl_3.6NH_3$, The primary valence of Co is +3 and is satisfied by $3Cl^-$ ions.
3. The secondary valence is satisfied by negative ions, neutral molecules, positive ions or the combination of these. For example, in $CoCl_3.6NH_3$ the secondary valence of cobalt is 6 and is satisfied by six neutral ammonia molecules, whereas in $CoCl_3.5NH_3$ the secondary valence of cobalt is satisfied by five neutral ammonia molecules and a Cl^- ion.
4. According to Werner, there are two spheres of attraction around a metal atom/ion in a complex. The inner sphere is known as coordination sphere and the groups present in this sphere are firmly attached to the metal. The outer sphere is called ionisation sphere. The groups present in this sphere are loosely bound to the central metal ion and hence can be separated into ions upon dissolving the complex in a suitable solvent.

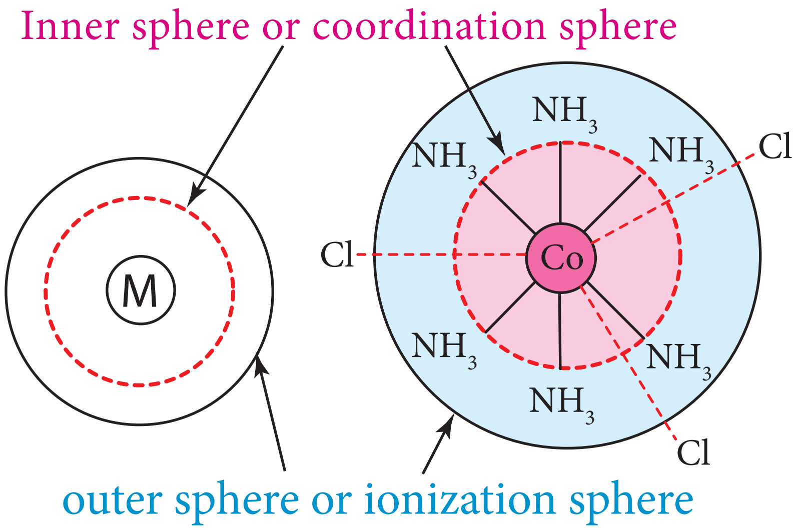


Figure 5.1 inner and outer spheres of attraction in coordination compounds

1. The primary valences are non-directional while the secondary valences are directional. The geometry of the complex is determined by the spacial arrangement of the groups which satisfy the secondary valence. For example, if a metal ion has a secondary valence of six, it has an octahedral geometry. If the secondary valence is 4, it has either tetrahedral or square planar geometry.

The following table illustrates the Werner's postulates.

Complex	**Groups satisfy the secondary valence (non-ionaisable, inner coordination sphere)**	**No. of ionisable Cl^- ions in the complex (outer coordination sphere)**	**No. of moles of AgCl formed = no. of moles of ionisable Cl^-**
$CoCl_3.6NH_3$	6 NH_3	3 Cl^-	3 AgCl
$CoCl_3.5NH_3$	5 NH_3 & 1 Cl^-	2 Cl^-	2 AgCl
$CoCl_3.4NH_3$	4 NH_3 & 2 Cl^-	1 Cl^-	1 AgCl
$CoCl_3.4NH_3$	4 NH_3 & 2 Cl^-	1 Cl^-	1 AgCl

5.2.1 Limitations of Werner's theory:

Even though, Werner's theory was able to explain a number of properties of coordination compounds, it does not explain their colour and the magnetic properties.

Evaluate yourself 1:

When a coordination compound $CrCl_3.4H_2O$ is mixed with silver nitrate solution, one mole of silver chloride is precipitated per mole of the compound. There are no free solvent molecules in that compound. Assign the secondary valence to the metal and write the structural formula of the compound.

5.3 Definition of important terms pertaining to co-ordination compounds

5.3.1 Coordination entity:

Coordination entity is an ion or a neutral molecule, composed of a central atom, usually a metal and the array of other atoms or groups of atoms (ligands) that are attached to it. In the formula, the coordination entity is enclosed in square brackets. For example, in potassium ferrocyanide, $K_4[Fe(CN)_6]$, the coordination entity is $[Fe(CN)_6]^{4-}$. In nickel tetracarbonyl, the coordination entity is $[Ni(CO)_4]$.

5.3.2 Central atom/ion:

The central atom/ion is the one that occupies the central position in a coordination entity and binds other atoms or groups of atoms (ligands) to itself, through a coordinate covalent bond. For example, in $K_4[Fe(CN)_6]$, the central metal ion is Fe^{2+}. In the coordination entity $[Fe(CN)_6]^{4-}$, the Fe^{2+} accepts an electron pair from each ligand, CN^- and thereby forming six coordinate covalent bonds with them. since, the central metal ion has an ability to accept electron pairs, it is referred to as a Lewis acid.

5.3.3 Ligands:

The ligands are the atoms or groups of atoms bound to the central atom/ion. The atom in a ligand that is bound directly to the central metal atom is known as a donor atom. For example, in $K_4[Fe(CN)_6]$, the ligand is CN^- ion, but the donor atom is carbon and in $[Co(NH_3)_6]Cl_3$ the ligand is NH_3 molecule and the donor atom is nitrogen.

Coordination sphere:

The complex ion of the coordination compound containing the central metal atom/ion and the ligands attached to it, is collectively called coordination sphere and are usually enclosed in square brackets with the net charge. The other ionisable ions, are written outside the bracket are called counter ions. For example, the coordination compound $K_4[Fe(CN)_6]$ contains the complex ion $[Fe(CN)_6]^{4-}$ and is referred as the coordination sphere. The other associated ion K^+ is called the counter ion.

Coordination polyhedron:

The three dimensional spacial arrangement of ligand atoms/ions that are directly attached to the central atom is known as the coordination polyhedron (or polygon). For example, in $K_4[Fe(CN)_6]$, the coordination polyhedra is octrahedral. The coordination polyhedra of $[Ni(CO)_4]$ is tetrahedral.

Coordination number:

The number of ligand donor atoms bonded to a central metal ion in a complex is called the coordination number of the metal. In other words, the coordination number is equal to the number of σ-bonds between ligands and the central atom.

For example,

i. In $K_4[Fe(CN)_6]$, the coordination number of Fe^{2+} is 6.

ii. In $[Ni(en)_3]Cl_2$, the coordination number of Ni^{2+} is also 6. Here the ligand 'en' represents ethane-1,2-diamine (NH_2-CH_2-CH_2-NH_2) and it contains two donor atoms (Nitrogen) Each ligand forms two coordination bonds with nickel. So,totally there are six coordination bonds between them.

Oxidation state (number):

The oxidation state of a central atom in a coordination entity is defined as the charge it would bear if all the ligands were removed along with the electron pairs that were shared with the central atom. In naming a complex, it is represented by a Roman numeral. For example, in the coordination entity $[Fe(CN)_6]^{4-}$, the oxidation state of iron is represented as (II). The net charge on the complex ion is equal to the sum of the oxidation state of the central metal and the charge the on the ligands attached to it. Using this relation the oxidation number can be calculated as follows

Net charge = (oxidation state of the central metal) + [(No. of ligands) X (charge on the ligand)]

Example 1:

In $[Fe(CN)_6]^{4-}$, let the oxidation number of iron is x :

The net charge: -4 = x + 6 (-1) => x = +2

Example 2:

In $[Co(NH_3)_5Cl]^{2+}$, let the oxidation number of cobalt is x :

The net charge: +2 = x + 5 (0) + 1 (-1) => x = +3

Evaluate yourself 2:

2. In the complex, $[Pt(NO_2)(H_2O)(NH_3)_2]Br$, identify the following
   - i. Central metal atom/ion
   - ii. Ligand(s) and their types
   - iii. Coordination entity
   - iv. Oxidation number of the central metal ion
   - v. Coordination number

Types of complexes:

The coordination compounds can be classified into the following types based on (i) the net charge of the complex ion, (ii) kinds of ligands present in the coordination entity.

Classification based on the net charge on the complex:

A coordination compound in which the complex ion

i. carries a net positive charge is called a cationic complex. Examples: $[Ag(NH_3)_2]^+$, $[Co(NH_3)_6]^{3+}$, $[Fe(H_2O)_6]^{2+}$, etc

ii. carries a net negative charge is called an anionic complex. Examples: $[Ag(CN)_2]^-$, $[Co(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$, etc

iii. bears no net charge, is called a neutral complex. Examples: $[Ni(CO)_4]$, $[Fe(CO)_5]$, $[Co(NH_3)_3(Cl)_3]$,

Classification based on kind of ligands:

A coordination compound in which

i. the central metal ion/atom is coordinated to only one kind of ligands is called a homoleptic complex. Examples: $[Co(NH_3)_6]^{3+}$, $[Fe(H_2O)_6]^{2+}$,

ii. the central metal ion/atom is coordinated to more than one kind of ligands is called a heteroleptic complex. Example, $[Co(NH_3)_5Cl]^{2+}$, $[Pt(NH_3)_2Cl_2)]$

4.3 Nomenclature of coordination compounds

In the earlier days, the compounds were named after their discoverers. For example, $K[PtCl_3(C_2H_4)]$ was called Zeise's salt and $[Pt(NH_3)_4][PtCl_4]$ is called Magnus's green salt etc... There are numerous coordination compounds that have been synthesised and characterised. The International Union of Pure and Applied Chemistry (IUPAC) has developed an elaborate system of nomenclature to name them systematically. The guidelines for naming coordination compounds based on IUPAC recommendations (2005) are as follows:

1. The cation is named first, followed by the anion regardless of weather the ion is simple or complex. For example
   - In $K_4[Fe(CN)_6]$, the cation K^+ is named first followed by $[Fe(CN)_6]^{4-}$.
   - In $[Co(NH_3)_6]Cl_3$, the complex cation $[Co(NH_3)_6]^{3+}$ is named first followed by the anion Cl^-
   - In $[Pt(NH_3)_4][PtCl_4]$, the complex cation $[Pt(NH_3)_4]^{2+}$is named first followed by the complex anion $[PtCl_4]^{2-}$
2. The simple ions are named as in other ionic compounds. For example,

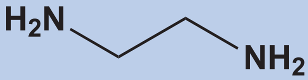
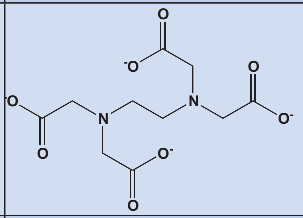
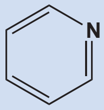
Simple cation	Symbol	Simple anion	Symbol
Sodium	Na^+	Chloride	Cl^-
Potassium	K^+	Nitrate	NO_3^-
Copper	Cu^{2+}	Sulphate	SO_4^{2-}

3. To name a complex ion, the ligands are named first followed by the central metal atom/ion. When a complex ion contains more than one kind of ligands they are named in alphabetical order.

a. Naming the ligands:

i. The name of anionic ligands ends with the letter 'o' and the cationic ligand ends with 'ium'. The neutral ligands are usually called with their molecular names with fewer exceptions namely, H_2O (aqua), CO (carbonyl), NH_3 (ammine) and NO (nitrosyl).

ii. A κ-term is used to denote an ambidendate ligand in which more than one coordination mode is possible. For example, the ligand thiocyanate can bind to the central atom/ion, through either the sulfur or the nitrogen atom. In this ligand, if sulphur forms a coordination bond with metal then the ligand is named thiocyanato-κS and if nitrogen is involved, then it is named thiocyanato-κN.

Common name	Formula	IUPAC ligand name
Bromide	Br^-	bromido
Chloride	Cl^-	chlorido
Furoride	F^-	fluorido
Cyanide	CN^-	cyanido
Hydroxide	OH^-	hydroxido
Carbonate	CO_3^{2-}	carbonato
Nitrate	NO_3^-	nitrato
Nitrite	NO_2^-	$\leftarrow NO_2^-$; nitrito-κN $\leftarrow ONO^-$; nitrito-κO
Sulphate	SO_4^{2-}	sulphato
Sulphide	S^{2-}	sulphido
Oxalate (ox)	$C_2O_4^{2-}$	oxalato
Ethylenediamine (en)		ethane-1,2-diamine
Ethylenediaminetetraacetate (EDTA)		2,2',2'',2'''-(ethane-1,2-diyldinitrilo)tetraacetato
Triphenylphosphine	$P(Ph)_3$	triphenylphosphane
Pyridine (py)		pyridine

iii. If the coordination entity contains more than one ligand of a particular type, the multiples of ligand (2, 3, 4 etc...) is indicated by adding appropriate Greek prefixes (di, tri, tetra, etc...) to the name of the ligand. If the name of a ligand itself contains a Greek prefix (eg. ethylenediamine), use an alternate prefixes (bis, tris, tetrakis etc..) to specify the multiples of such ligands. These numerical prefixes are not taken into account for alphabetising the name of ligands.

b. **Naming the central metal:** In cationic/neutral complexes, the element name is used as such for naming the central metal atom/ion, whereas, a suffix 'ate' is used along with the element name in anionic complexes. The oxidation state of the metal is written immediately after the metal name using roman numerals in parenthesis.

Element	**Name of the metal in**	
	cationic complex	**anionic complex**
Cr	Chromium	Chromate
Zn	Zinc	Zincate
Al	Aluminum	Aluminate
Fe	Iron	Ferrate
Cu	Copper	Cuprate
Co	Cobalt	Cobaltate
Pb	Lead	Plumbate
Ag	Silver	Argentate
Sn	Tin	Stannate
Au	Gold	Aurate
Pt	Platinum	Platinate

Naming of coordination compounds using IUPAC guidelines.

Example 1:

Coordination Compound : $K_4[Fe(CN)_6]$		
Cation (Simple)	K^+	Potassium
Anion (complex)	$[Fe(CN)6]^{4-}$	
Ligands	CN^-	
Name of the ligand with prefix	6 ligands - prefix: hexa Anionic ligand: cyanido-κC (Coordinating atom in CN^- is carbon)	hexacyanido-κC
Central metal	Fe (in anionic complex)	ferrate
Oxidation state of central metal (x)	$x + 6(-1) = -4$ $x = -4 + 6 = +2$	(II)
IUPAC Name: Postassium hexacyanido-κC ferrate(II)		

Example 2: Coordination Compound : $[Co(NH_3)_4Cl_2]Cl$		
Cation (complex)	$[Co(NH_3)_4Cl_2]^+$	
ligands	NH_3 and Cl^-	
Name of the ligand (NH_3) with prefix	4 ligands - prefix: tetra Neutral ligand: ammine	tetraamminiedichlorido (alphabatically ammine comes before chlorido)
	2 ligands - prefix: di Anionic ligand: chlorido	
Central metal	Co (in cationic complex)	cobalt
Oxidation state of central metal (x)	$x + 4 (0) + 2 (-1) = +1$ $x = 1 + 2 = +3$	(III)
Anion (simple)	Cl^-	chloride
IUPAC Name: Tetraamminedichloridocobalt(III) chloride		

Example 3:. Coordination Compound : $[Cr(en)_3][CrF_6]$		
Cation (complex)	$[Cr(en)_3]^{3+}$	
ligands	en - (ethylenediamine)	
Name of the ligand with prefix (Ligand itself contains a Greek prefix - di, use alternate prefix)	3 ligands - prefix: tris Neutral ligand: ethane-1,2-diamine	tris(ethane-1,2-diamine)
central metal	Cr (in cationic complex)	chromium
Oxidation state of central metal (x)	$x + 3 (0) = +3$ $x = +3$	(III)
Anion (Complex)	$[CrF_6]^{3-}$	
ligands	$6 F^-$	
Name of the ligand with prefix	4 ligands - prefix: hexa Anionic ligand: Fluorido	hexafluorido
central metal	Cr (in anionic complex)	chromate
Oxidation state of central metal (x)	$x + 6 (-1) = -3$ $x = -3 + 6 = +3$	(III)
IUPAC Name: Tris(ethane-1,2-diamine)chromium(III) hexafluoridochromate(III)		

More examples with names are given in the list below for better understanding of IUPAC Nomenclature:

i.	$[Ag(NH_3)_2]Cl$	Diamminesilver(I) chloride
ii.	$[Co(en)_2Cl_2]Cl$	Dichloridobis(ethane-1,2-diamine)cobalt(III) chloride
iii.	$[Cu(NH_3)_4]SO_4$	Tetraamminecopper(II) sulphate
iv.	$[Co(CO_3)(NH_3)_4]Cl$	Tetraamminecarbonatocobalt(III) chloride
v.	$[Cr(NH_3)_3(H_2O)_3]Cl_3$	Triamminetriaquachromium(III) chloride
vi.	$K_3[Fe(CN)_5\ NO]$	Potassiumpentacyanidonitrosylferrate(II)
vii.	$Na_2[Ni(EDTA)]$	Sodium 2,2',2'',2'''-(ethane-1,2-diyldinitrilo) tetraacetatonickelate(II)
viii.	$[PdI_2(ONO)_2(H_2O)_2]$	Diaquadiiododinitrito-κO palladium(IV)
ix.	$[Cr(PPh_3)(CO)_5]$	Pentacarbonyltriphenylphosphanechromium(0)
x.	$[Co(NO_2)_3(NH_3)_3]$	Triamminetrinirito-κNcobalt(III)
xi.	$[Co(NH_3)_5CN][Co(NH_3)(CN)_5]$	Pentaamminecyanido-κCcobalt(III) amminepentacyanido-κCcobaltate(III)
xii.	$[Pt(py)_4][PtCl_4]$	Tetrapyridineplatinum(II) tetrachloridoplatinate(II)
xiii.	$[Co(NH_3)_4Cl_2]_3\ [Cr(CN)_6]$	Tetraamminedichloridocobalt(III) hexacyanido-κCchromate(III)
xiv.	$[Ag(NH_3)_2]^+$	diamminesilver(I) ion
xv.	$[Co(NH_3)_5\ Cl]^{2+}$	pentaamminechlorocobalt(III) ion
xvi.	$[FeF_6]^{4-}$	Hexafluoridoferrate(II)ion

Evaluate yourself 1:

14. Write the IUPAC name for the following compounds.

(i) $K_2\left[Fe(CN)_3(Cl)_2(NH_3)\right]$

(ii) $\left[Cr(CN)_2(H_2O)_4\right]\left[Co(ox)_2(en)\right]$

(iii) $\left[Cu(NH_3)_2Cl_2\right]$

(iv) $\left[Cr(NH_3)_3(NC)_2(H_2O)\right]^+$

(v) $\left[Fe(CN)_6\right]^{4-}$

15. Give the structure for the following compounds.

1. (i) diamminesilver(I) dicyanidoargentate(I)
2. (ii)Pentaammine nitrito-κNcobalt (III) ion
3. (iii)hexafluorido cobaltate (III) ion
4. (iv)dichloridobis(ethylenediamine) Cobalt (III) sulphate
5. (v) Tetracarbonylnickel (0)

4.4 Isomerism in coordination compounds

We have already learnt the concept of isomerism in the context of organic compounds, in the previous year chemistry classes. Similarly, coordination compounds also exhibits isomerism. Isomerism is the phenomenon in which more than one coordination compounds having the same molecular formula have different physical and chemical properties due to different arrangement of ligands around the central metal atom. The following flow chart gives an overview of the common types of isomerism observed in coordination compounds,

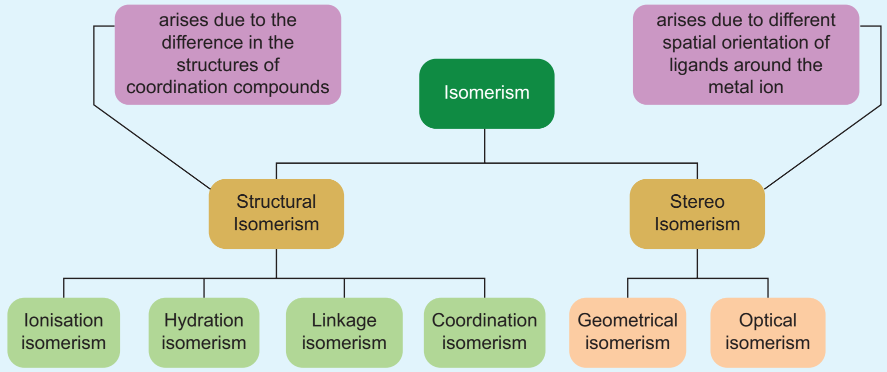


Figure 5.2 Isomerism in coordination compounds

4.4.1 Structural isomers

The coordination compounds with same formula, but have different connections among their constituent atoms are called structural isomers or constitutional isomers. Four common types of structural isomers are discussed below.

Linkage isomers:

This type of isomers arises when an ambidentate ligand is bonded to the central metal atom/ion through either of its two different donor atoms. In the below mentioned examples, the nitrite ion is bound to the central metal ion Co^{3+} through a nitrogen atom in one complex,and through oxygen atom in other complex.

$[Co(NH_3)_5(NO_2)]^{2+}$

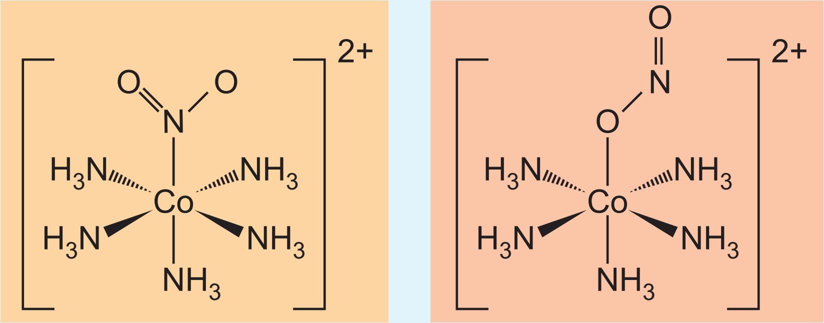


Figure 5.3 Linkage isomers

Coordination isomers:

This type of isomers arises in the coordination compounds having both the cation and anion as complex ions. The interchange of one or more ligands between the cationic and the anionic coordination entities result in different isomers.

For example, in the coordination compound, $[Co(NH_3)_6][Cr(CN)_6]$ the ligands ammonia and cyanide were bound respectively to cobalt and chromium while in its coordination isomer $[Cr(NH_3)_6][Co(CN)_6]$ they are reversed.

Some more examples for coordination isomers

1. $[Cr(NH_3)_5CN][Co(NH_3)(CN)_5]$ and $[Co(NH_3)_5CN][Cr(NH_3)(CN)_5]$
2. $[Pt(NH_3)_4][Pd(Cl)_4]$ and $[Pd(NH_3)_4][Pt(Cl)_4]$

Ionisation isomers:

This type of isomers arises when an ionisable counter ion (simple ion) itself can act as a ligand. The exchange of such counter ions with one or more ligands in the coordination entity will result in ionisation isomers. These isomers will give different ions in solution. For example, consider the coordination compound $[Pt(en)_2Cl_2]Br_2$. In this compound, both Br^- and Cl^- have the ability to act as a ligand and the exchange of these two ions result in a different isomer $[Pt(en)_2Br_2]Cl_2$. In solution the first compound gives Br^- ions while the later gives Cl^- ions and hence these compounds are called ionisaiton isomers.

Some more example for the isomers,

1. $[Cr(NH_3)_4ClBr]NO_2$ and $[Cr(NH_3)_4Cl\ NO_2]Br$
2. $[Co(NH_3)_4Br_2]Cl$ and $[Co(NH_3)_4Cl\ Br]Br$

Evaluate yourself :

3. A solution of $[Co(NH_3)_4I_2]Cl$ when treated with $AgNO_3$ gives a white precipitate. What should be the formula of isomer of the dissolved complex that gives yellow precipitate with $AgNO_3$. What are the above isomers called?

Solvate isomers.

The exchange of free solvent molecules such as water , ammonia, alcohol etc.. in the crystal lattice with a ligand in the coordination entity will give different isomers. These type of isomers are called solvate isomers. If the solvent molecule is water, then these isomers are called hydrate isomers. For example, the complex with chemical formula $CrCl_3.6H_2O$ has three hydrate isomers as shown below.

$[Cr(H_2O)_6]Cl_3$	a violet colour compound and gives three chloride ions in solution,
$[Cr(H_2O)_5Cl]Cl_2.H_2O$	a pale green colour compound and gives two chloride ions in solution and,
$[Cr(H_2O)_4Cl_2]Cl.2H_2O$	dark green colour compound and gives one chloride ion in solution

4.4.2 Stereoisomers:

Similar to organic compounds, coordination compounds also exhibit stereoisomerism. The stereoisomers of a coordination compound have the same chemical formula and connectivity between the central metal atom and the ligands. But they differ in the spatial arrangement of ligands in three dimensional space. They can be further classified as geometrical isomers and optical isomers.

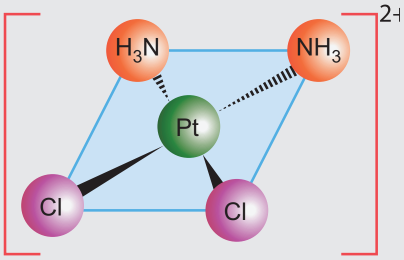
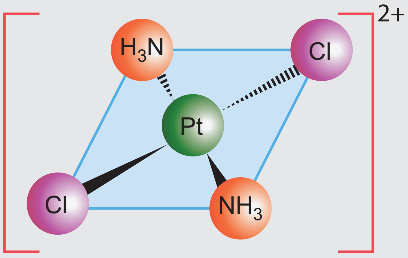
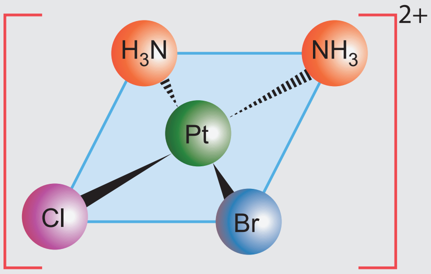
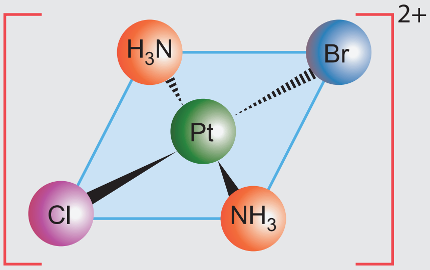
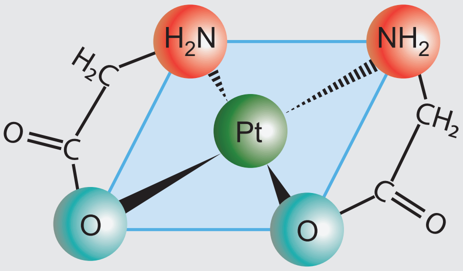
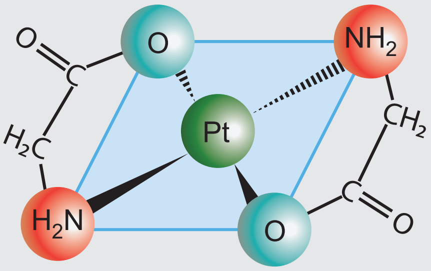
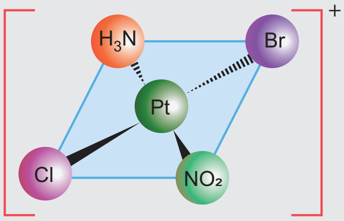
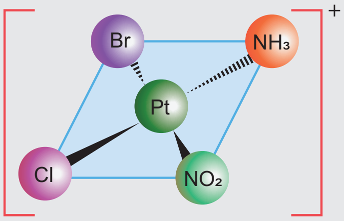
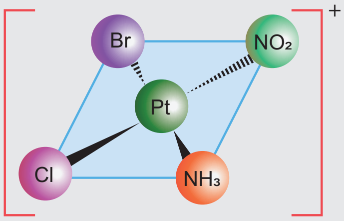
Geometrical isomers:

Geometrical isomerism exists in heteroleptic complexes due to different possible three dimensional spatial arrangements of the ligands around the central metal atom. This type of isomerism exists in square planer and octahedral complexes.

In square planar complexes of the form $[MA_2B_2]^{n\pm}$ and $[MA_2BC]^{n\pm}$ (where A, B and C are mono dentate ligands and M is the central metal ion/atom), Similar groups (A or B) present either on same side or on the opposite side of the central metal atom (M) give rise to two different geometrical isomers, and they are called, *cis* and *trans* isomers respectively.

The square planar complex of the type $[M(xy)_2]^{n\pm}$ where xy is a bidentate ligand with two different coordinating atoms also shows *cis-trans* isomerism. Square planar complex of the form $[MABCD]^{n\pm}$ also shows geometrical isomerism. In this case, by considering any one of the ligands (A, B, C or D) as a reference, the rest of the ligands can be arranged in three different ways leading to three geometrical isomers.

Figure 5.4 MA_2B_2 MA_2BC $M(xy)_2$ MABCD - isomers

Type	Example	
	Cis Isomer	Trans isomer
MA_2B_2		
MA_2BC		
$M(xy)_2$		
MABCD	  	

Octahedral complexes:

Octahedral complexes of the type $[MA_2B_4]^{n\pm}$, $[M(xx)_2B_2]^{n\pm}$ shows *cis-trans* isomerism. Here A and B are monodentate ligands and xx is bidentate ligand with two same kind of donor atoms. In the octahedral complex, the position of ligands is indicated by the following numbering scheme.

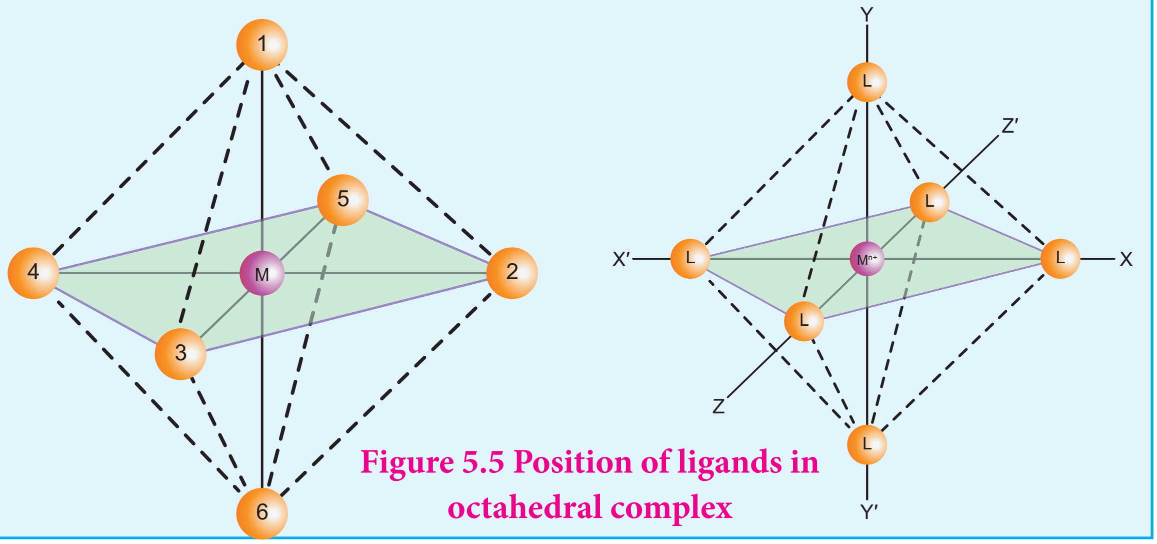


Figure 5.5 Position of ligands in octahedral complex

In the above scheme, the positions (1,2), (1,3), (1,4), (1,5), (2,3), (2,5), (2,6), (3,4), (3,6), (4,5), (4,6), and (5,6) are identical and if two similar groups are present in any one of these positions, the isomer is referred as a *cis* isomer. Similarly, positions (1,6), (2,4), and (3,5) are identical and if similar ligands are present in these positions it is referred as a *trans*-isomer.

Octahedral complex of the type $[MA_3B_3]^{n\pm}$ also shows geometrical isomerism. If the three similar ligands (A) are present in the corners of one triangular face of the octahedron and the other three ligands (B) are present in the opposing triangular face, then the isomer is referred as a facial isomer (*fac* isomer)- Figure 5.6 (a).

If the three similar ligands are present around the meridian which is an imaginary semicircle from one apex of the octahedral to the opposite apex as shown in the figure 5.6(b), the isomer is called as a meridional isomer (*mer* isomer). This is called meridional because each set of ligands can be regarded as lying on a meridian of an octahedron.

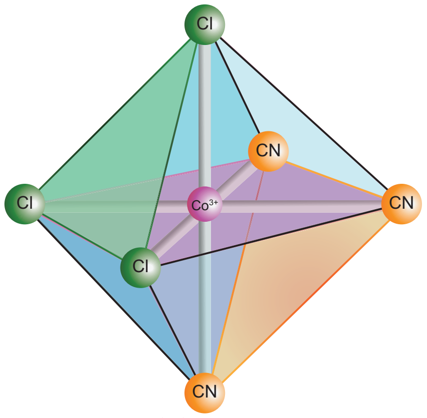


Figure 5.6 (a) Facial isomer

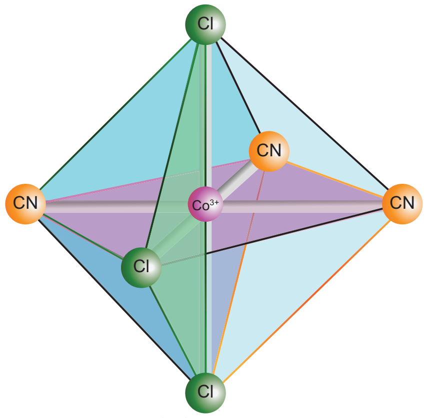


Figure 5.6 (b) Meridional isomer

As the number of different ligands increases, the number of possible isomers also increases. For the octahedral compled of the type [MABCDEF]$^{n\pm}$, where A, B, C, D, E and F are monodentate ligands, fifteen different orientation are possible corresponding to 15 geometrical isomers. It is difficult to generate all the possible isomers.

Evaluate yourself 1:

5. Three compounds A ,B and C have empirical formula $CrCl_3.6H_2O$. they are kept in a container with a dehydrating agent and they lost water and attaining constant weight as shown below.

Compound	Initial weight of the compound(in g)	Constant weight after dehydration (in g)
A	4	3.46
B	0.5	0.466
C	3	3

6. Indicate the possible type of isomerism for the following complexes and draw their isomers

(i) $[Co(en)_3][Cr(CN)_6]$ (ii) $[Co(NH_3)_5(NO_2)]^{2+}$ (iii) $[Pt(NH_3)_3(NO_2)]Cl$

4.4.4 Optical Isomerism

Coordination compounds which possess chairality exhibit optical isomerism similar to organic compounds. The pair of two optically active isomers which are mirror images of each other are called enantiomers. Their solutions rotate the plane of the plane polarised light either clockwise or anticlockwise and the corresponding isomers are called 'd' (dextro rotatory) and 'l' (levo rotatory) forms respectively. The octahedral complexes of type $[M(xx)_3]^{n\pm}$, $[M(xx)_2AB]^{n\pm}$ and $[M(xx)_2B_2]^{n\pm}$ exhibit optical isomerism.

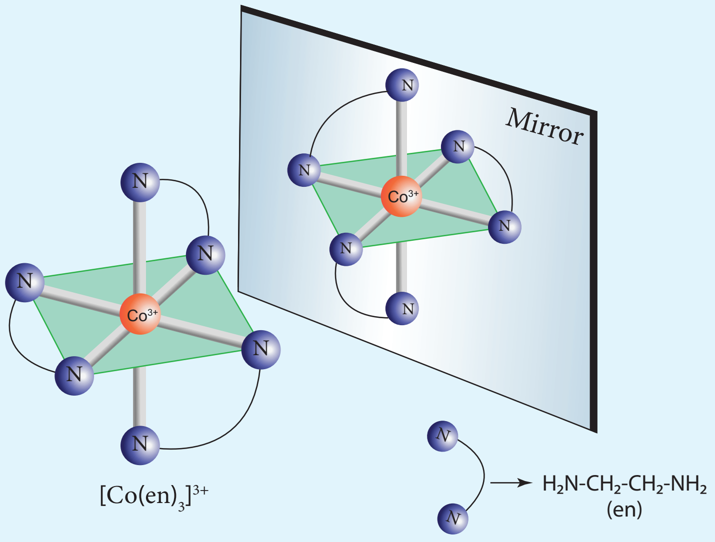


Figure 5.7 - Optical isomer

Examples:

The optical isomers of $[Co(en)_3]^{3+}$ are shown in figure 5.7.

The coordination complex $[CoCl_2(en)_2]^+$ has three isomers, two optically active cis forms and one optically inactive trans form. These structures are shown below.

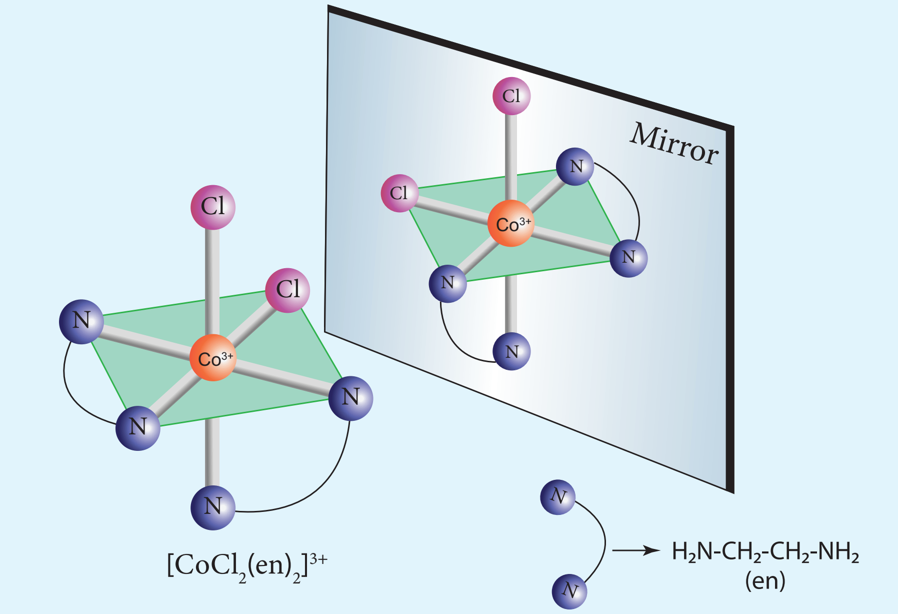


Figure 5.8 - Optical isomers

Evaluate yourself 1:

10. Draw all possible stereo isomers of a complex $Ca[Co(NH_3)Cl(Ox)_2]$

4.5 Theories of coordination compound

Alfred Werner considered the bonding in coordination compounds as the bonding between a lewis acid and a lewis base. His approach is useful in explaining some of the observed properties of coordination compounds. However, properties such as colour, magnetic property etc.. of complexes could not be explained on the basis of his approach. Following werner theory, Linus pauling proposed the Valance Bond Theory (VBT) which assumes that the bond formed between the central metal atom and the ligand is purely covalent. Bethe and Van vleck treated the interaction between the metal ion and the ligands as electrostatic and extended the Crystal Field Theory (CFT) to explain the properties of coordination compounds. Further, Ligand field theory and Molecular orbital have been developed to explain the nature of bonding in the coordination compounds. In this porton we learn the elementry treatment of VBT and CFT to simple coordination compounds.

4.5.1 Valence Bond Theory

According to this theory, the bond formed between the central metal atom and the ligand is due to the overlap of filled ligand orbitals containing a lone pair of electron with the vacant hybrid orbitals of the central metal atom.

Main assumptions of VBT:

1. The ligand → metal bond in a coordination complex is covalent in nature. It is formed by sharing of electrons (provided by the ligands) between the central metal atom and the ligand.

2. Each ligand should have at least one filled orbital containing a lone pair of electrons.
3. In order to accommodate the electron pairs donated by the ligands, the central metal ion present in a complex provides required number (coordination number) of vacant orbitals.
4. These vacant orbitals of central metal atom undergo hybridisation, the process of mixing of atomic orbitals of comparable energy to form equal number of new orbitals called hybridised orbitals with same energy.
5. The vacant hybridised orbitals of the central metal ion, linearly overlap with filled orbitals of the ligands to form coordinate covalent sigma bonds between the metal and the ligand.
6. The hybridised orbitals are directional and their orientation in space gives a definite geometry to the complex ion.

Coordination number	Hybridisation	Geometry	Examples
2	sp	Linear	$[CuCl_2]^-$, $[Ag(CN)_2]^-$
3	sp^2	Trigonal planar	$[HgI_3]^-$
4	sp^3	Tetrahedral	$[Ni(CO)_4]$, $[NiCl_4]^{2-}$
4	dsp^2	Square planar	$[Ni(CN)_4]^{2-}$, $[Pt(NH_3)_4]^{2+}$
5	dsp^3 *($d_{x^2-y^2}$ orbital is involved)*	Trigonal bipyramidal	$Fe(CO)_5$
6	d^2sp^3 *(d_{z^2} and $d_{x^2-y^2}$ orbitals of inner shell are involved)*	Octahedral	$[Ti(H_2O)_6]^{3+}$, $[Fe(CN)_6]^{2-}$, $[Fe(CN)_6]^{3-}$, $[Co(NH_3)_6]^{3+}$ *(Inner orbital complexes)*
6	sp^3d^2 *(d_{z^2} and $d_{x^2-y^2}$ orbitals of the outer shell are involved)*	Octahedral	$[FeF_6]^{4-}$,$[CoF_6]^{4-}$, $[Fe(H_2O)_6]^{2+}$ *(Outer orbital complexes)*

7. In the octahedral complexes, if the (n-1) d orbitals are involved in hybridisation, then they are called inner orbital complexes or low spin complexes or spin paired complexes. If the nd orbitals are involved in hybridisation, then such complexes are called outer orbital or high spin or spin free complexes. Here n represents the principle quantum number of the outermost shell.
8. The complexes containing a central metal atom with unpaired electron(s) are paramagnetic. If all the electrons are paired, then the complexes will be diamagnetic.

9. Ligands such as CO, CN^-, en, and NH_3 present in the complexes cause pairing of electrons present in the central metal atom. Such ligands are called strong field ligands.

10. Greater the overlapping between the ligand orbitals and the hybridised metal orbital, greater is the bond strength.

Let us illustrate the VBT by considering the following examples.

Illustration 1

Complex	**$[Ni(CO)_4]$**
Central metal atom and its outer electronic configuration	Ni: $3d^8$, $4s^2$
Outer orbitals of metal atom/ion	↑↓ ↑↓ ↑↓ ↑ ↑ ($3d^8$) ↑↓ ($4s^2$) ☐☐☐ (4p)
Nature of ligand	CO Strong field ligand causes the pairing of 4s electron with 3d electrons in the metal
Outer orbitals of metal atom/ion in presence of ligand	↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ($3d^{10}$) ☐ ($4s^0$) ☐☐☐ ($4p^0$)
Hybridisation	Coordination number - 4 Hybridsation - sp^3
Hybridised orbitals of the metal atom in the complex	↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ($3d^{10}$) ↑↓ ↑↓ ↑↓ ↑↓ (sp^3 Hybridised orbitals)
Geometry	Tetrahedral
Magnetic property	No. of unparied electrons = 0; Hence diamagnetic
Magnetic moment (Using spin only formula)	$\mu_s = \sqrt{n(n+2)} = 0$

Illustration 2

Complex	$[Ni(CN)_4]^{4-}$
Central metal atom/ion and its outer electronic configuration	Ni^{2+}: $3d^8$, $4s^0$
Outer orbitals of metal atom/ion	↑↓ ↑↓ ↑↓ ↑ ↑ $3d^8$ $4s^2$ 4p
Nature of ligand	CN^- Strong field ligand causes the pairing of 3d electrons in the metal
Outer orbitals of metal atom/ion in presence of ligands	↑↓ ↑↓ ↑↓ ↑↓ $3d^8$ $4s^0$ $4p^0$
Hybridisation	Coordination number - 4 Hybridsation - dsp2
Hybridised orbitals of the metal atom in the complex	↑↓ ↑↓ ↑↓ ↑↓ $3d^8$ ↑↓ ↑↓ ↑↓ ↑↓ dsp^2 Hybridised orbitals $4p_z^0$
Geometry	Square planar
Magnetic property	No. of unparied electrons = 0; Hence diamagnetic
Magnetic moment **(Using spin only formula)**	$\mu_s = \sqrt{n(n+2)} = 0$

Illustration 3

Complex	$[Fe(CN)6]^{3-}$
Central metal atom/ion and its outer electronic configuration	Fe^{3+}: $3d^5$, $4s^0$
Outer orbitals of metal atom/ion	↑ ↑ ↑ ↑ ↑ $3d^5$ $4s^0$ $4p^0$
Nature of ligand	CN^- Strong field ligand causes the pairing of 3d electrons in the metal

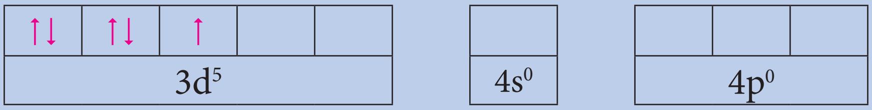
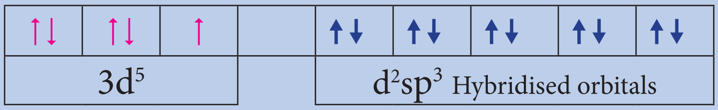
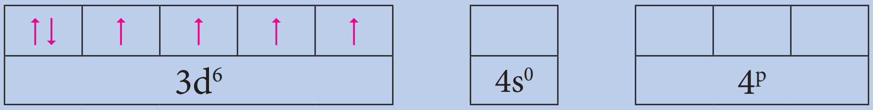
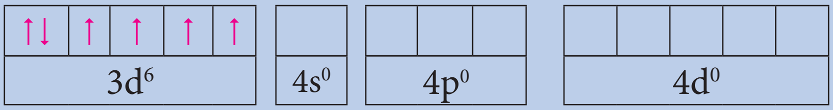
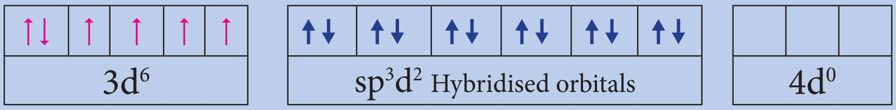
Complex	**$[Fe(CN)_6]^{3-}$**
Outer orbitals of metal atom/ion in presence of ligands	
Hybridisation	Coordination number - 6 Hybridsation - d^2sp^3
Hybridised orbitals of the metal ion in the complex	
Geometry	Octahedral In this complex inner d orbitals are involved in hybridisaion and hence the complex is called inner orbital complex
Magnetic property	No. of unparied electrons = 1; Hence paramagnetic
Magnetic moment **(Using spin only formula)**	$\mu_s = \sqrt{n(n+2)} = \sqrt{1(1+2)} = 1.732\ \text{BM}$

Illustration 4

Complex	**$[CoF_6]^{3-}$**
Central metal atom and its outer electronic configuration	Co^{3+}: $3d^6$, $4s^0$
Outer orbitals of metal atom/ion	
Nature of ligand	F^- Weak field ligand and hence no pairing of 3d electrons in the metal
Outer orbitals of metal atom/ion in presence of ligand	
Hybridisation	Coordination number - 6 Hybridsation - sp^3d^2

Complex	**$[CoF_6]^{3-}$**
Hybridised orbitals of the metal atom in the complex	
Geometry	Octahedral In this complex outer d orbitals are involved in the hybridisaion and hence the complex is called outer orbital complex
Magnetic property	No. of unparied electrons = 4; Hence paramagnetic
Magnetic moment **(Using spin only formula)**	$\mu_s = \sqrt{n(n+2)} = \sqrt{4(4+2)} = 4.899\ \text{BM}$

Limitations of VBT

Eventhough VBT explains many of the observed properties of complexes, it still has following limitations

1. It does not explain the colour of the complex
2. It considers only the spin only magnetic moments and does not consider the other components of magnetic moments.
3. It does not provide a quantitative explanation as to why certain complexes are inner orbital complexes and the others are outer orbital complexes for the same metal. For example, $[Fe(CN)_6]^{4-}$ is diamagnetic (low spin) whereas $[FeF_6]^{4-}$ is paramagnetic (high spin).

Evaluate yourself 1:

7. The spin only magnetic moment of Tetrachloridomanganate(II)ion is 5.9 BM. On the basis of VBT, predict the type of hybridisation and geometry of the compound.

8. Predict the number of unpaired electrons in $[CoCl_4]^{2-}$ ion on the basis of VBT.

9. A metal complex having composition $Co(en)_2Cl_2Br$ has been isolated in two forms A and B. (B) reacted with silver nitrate to give a white precipitate readily soluble in ammonium hydroxide. Whereas A gives a pale yellow precipitate. Write the formula of A and B. state the hybridization of Co in each and calculate their spin only magnetic moment.

4.5.2 Crystal Field Theory

Valance bond theory helps us to visualise the bonding in complexes. However, it has limitations as mentioned above.Hence Crystal Field Theory to expalin some of the properties like colour, magnetic behavior etc.,This theory was originally used to explain the nature of bonding in ionic crystals. Later on, it is used to explain the properties of transition metals and their complexes. The salient features of this theory are as follows.

1. Crystal Field Theory (CFT) assumes that the bond between the ligand and the central metal atom is purely ionic. i.e. the bond is formed due to the electrostatic attraction between the electron rich ligand and the electron deficient metal.

2. In the coordination compounds, the central metal atom/ion and the ligands are considered as point charges (in case of charged metal ions or ligands) or electric dipoles (in case of neutral metal atoms or ligands).

3. According to crystal field theory, the complex formation is considered as the following series of hypothetical steps.

Step 1: In an isolated gaseous state, all the five d orbitals of the central metal ion are degenerate. Initially, the ligands form a spherical field of negative charge around the metal. In this filed, the energies of all the five d orbitals will increase due to the repulsion between the electrons of the metal and the ligand.

Step 2: The ligands are approaching the metal atom in actual bond directions. To illustrate this let us consider an octahedral field, in which the central metal ion is located at the origin and the six ligands are coming from the +x, -x, +y, -y, +z and -z directions as shown below.

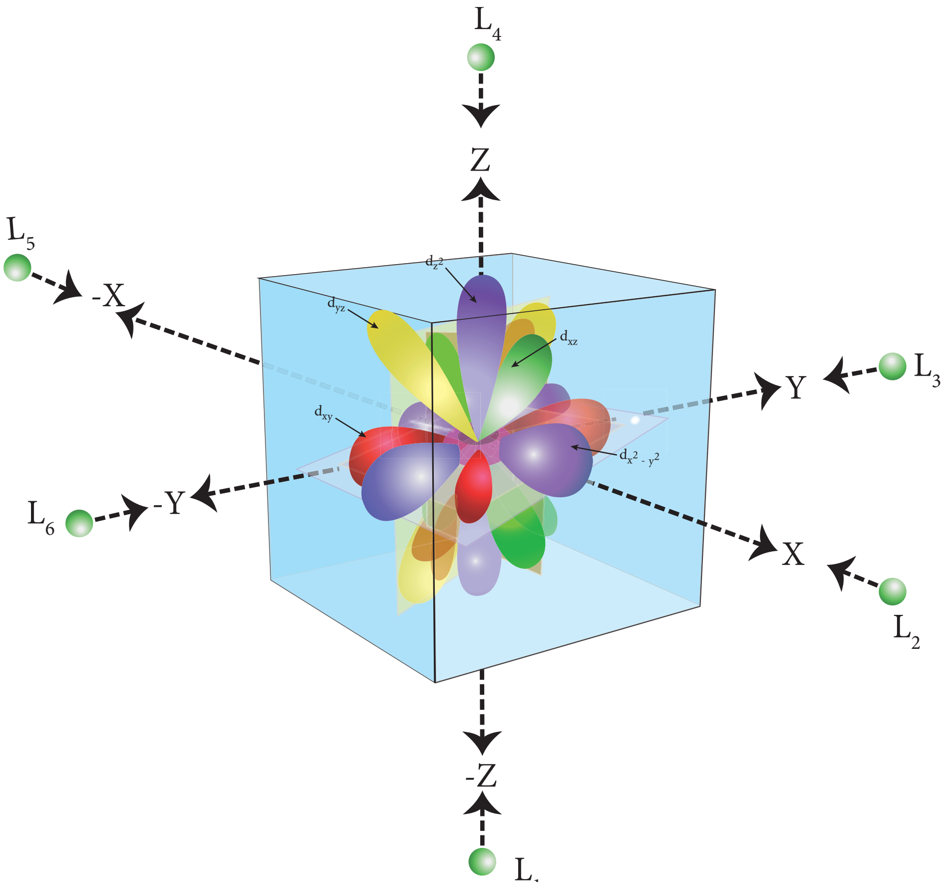


Figure 5.9 octahedral ligand field

As shown in the figure, the orbitals lying along the axes dx^2-y^2 and dz^2 orbitals will experience strong repulsion and raise in energy to a greater extent than the orbitals with lobes directed between the axes (d_{xy}, d_{yz} and d_{zx}). Thus the degenerate d orbitals now split into two sets and the process is called crystal field splitting.

Step 3: Up to this point the complex formation would not be favoured. However, when the ligands approach further, there will be an attraction between the negatively charged electron and the positively charged metal ion, that results in a net decrease in energy. This decrease in energy is the driving force for the complex formation.

Crystal field splitting in octahedral complexes:

During crystal field splitting in octahedral field, in order to maintain the average energy of the orbitals (barycentre) constant, the energy of the orbitals $d_{x^2-y^2}$ and d_{z^2} (represented as e_g orbitals) will increase by $3/5\Delta_o$ while that of the other three orbitals d_{xy}, d_{yz} and d_{zx} (represented as t_{2g} orbitals) decrease by $2/5\Delta_o$. Here, Δ_o represents the crystal field splitting energy in the octahedral field.

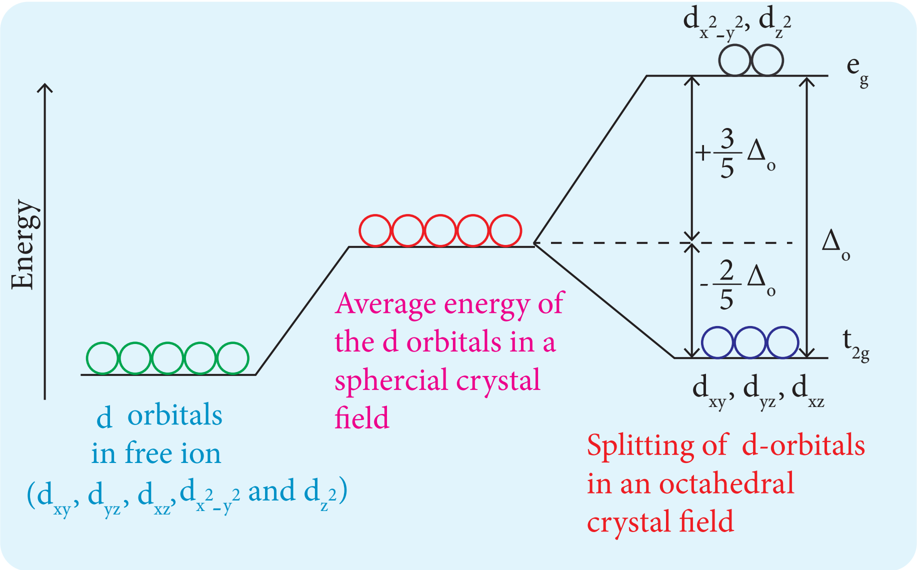


Figure: 5.10 - Crystal field splitting in octahedral field

Crystal field splitting in tetrahedral complexes:

The approach of ligands in tetrahedral field can be visualised as follows. Consider a cube in which the central metal atom is placed at its centre (i.e. origin of the coordinate axis as shown in the figure). The four ligands approach the central metal atom along the direction of the leading diagonals drawn from alternate corners of the cube.

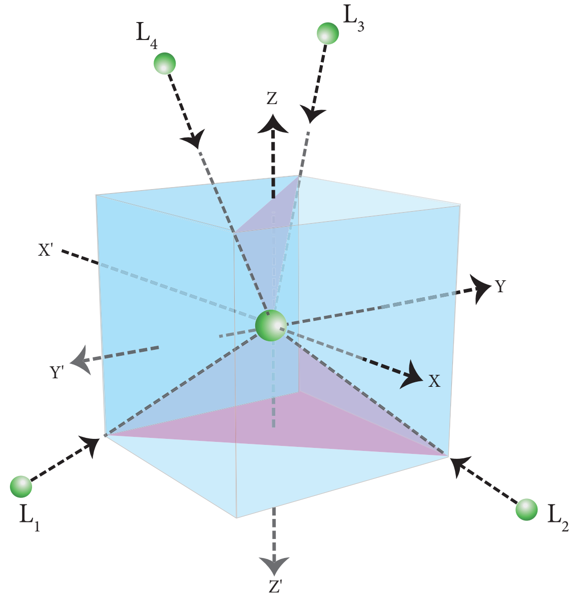


Figure 5.11 tetrahedral ligand field

In this field, none of the d orbitals point dirctly towards the ligands,however the t_2 orbitals (d_{xy}, d_{yz} and d_{zx}) are pointing close to the direction in which ligands are approaching than the e orbitals ($d_{x^2-y^2}$ and d_{z^2}).

As a result, the energy of t_2 orbitals increases by $2/5\Delta_t$ and that of e orbitals decreases by $3/5\Delta_t$ as shown below. when compared to the octahedral field, this splitting is inverted and the spliting energy is less. The relation between the crystal field splitting energy in octahedral and tetrahedral ligand field is given by the expression; $\Delta_t = \frac{4}{9}\Delta_0$

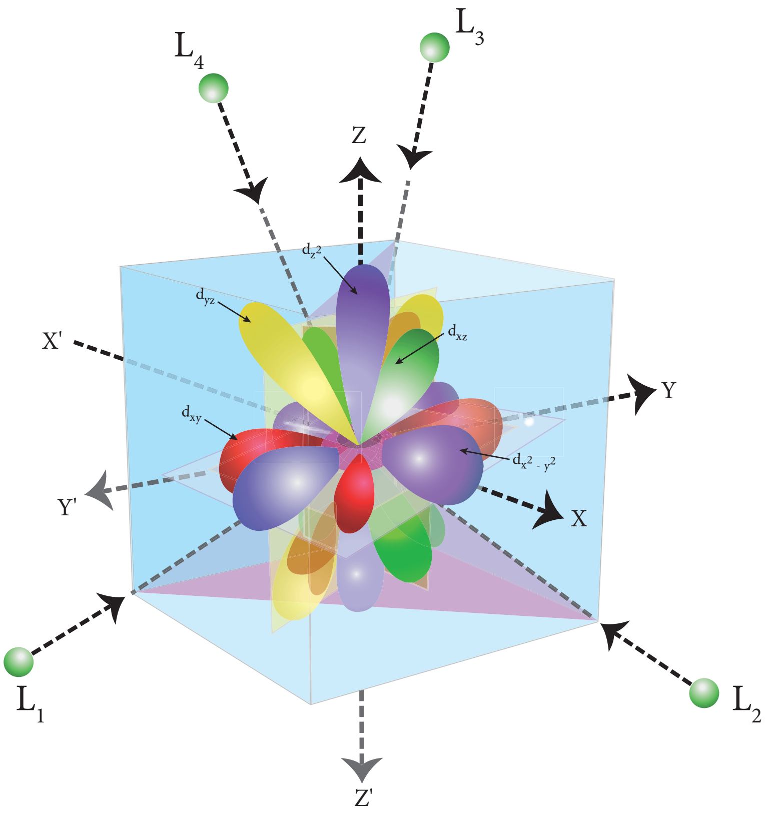


Figure 5.12 d-orbitals in tetrahedral ligand field

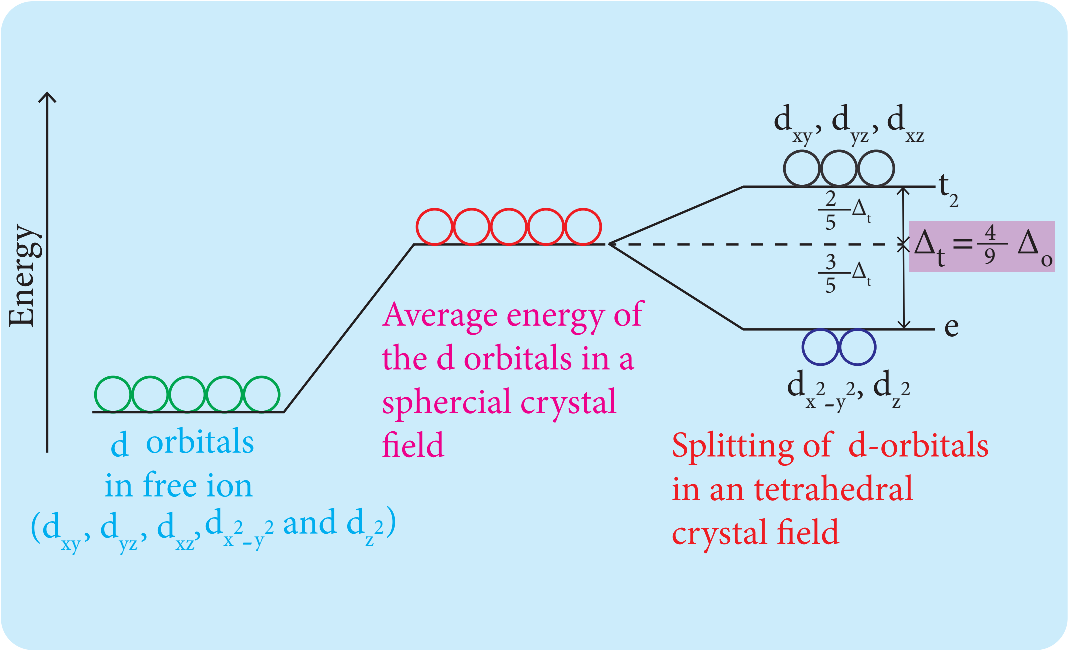


Figure: 5.13 - Crystal field splitting in tetrahedral field

Crystal filed splitting Energy and nature of ligands:

The magnitude of crystal field splitting energy not only depends on the ligand field as discussed above but also depends on the nature of the ligand, the nature of the central metal atom/ion and the charge on it. Let us understand the effect of the nature of ligand on crystal field splitting by calculating the crystal field splitting energy of the octahedral complexes of titanium(III) with different ligands such as fluoride, bromide and water using their absorption spectral data. The absorption wavelengths of complexes $[TiBr_6]^{3-}$, $[TiF_6]^{3-}$ and $[Ti(H_2O)_6]^{3+}$ are 12500, 19000 and 20000 cm^{-1} respectively. The energy associated with the absorbed wavelength of light (λ), corresponds to the crystal field splitting energy (Δ) and is given by the following expression,

$$\Delta = h\nu = \frac{hc}{\lambda} = hc\bar{\nu}$$

where h is the Plank' s constant; c is velocity of light, **υ** is the wave number of absorption maximum which is equal to 1/λ

$[TiBr_6]^{3-}$	$[TiF_6]^{3-}$	$[Ti(H_2O)_6]^{3+}$
$\Delta = hc\bar{\nu}$	$\Delta = hc\bar{\nu}$	$\Delta = hc\bar{\nu}$
$= (6.626 \times 10^{-34}$ Js $)$ $\times (3 \times 10^{8}$ ms$^{-1})$ $\times (12500 \times 10^{2}$ m$^{-1})$	$= (6.626 \times 10^{-34}$ Js $)$ $\times (3 \times 10^{8}$ ms$^{-1})$ $\times (19000 \times 10^{2}$ m$^{-1})$	$= (6.626 \times 10^{-34}$ Js $)$ $\times (3 \times 10^{8}$ ms$^{-1})$ $\times (20000 \times 10^{2}$ m$^{-1})$
$= 248 \times 10^{-24}$ J $= 2.48 \times 10^{-16}$ kJ	$= 377682 \times 10^{-24}$ J $= 3.78 \times 10^{-16}$ kJ	$= 397560 \times 10^{-24}$ J $= 3.98 \times 10^{-16}$ kJ
To express Δ on a per mole basis, multiply it by Avogadro number	To express Δ on a per mole basis, multiply it by Avogadro number	To express Δ on a per mole basis, multiply it by Avogadro number
$= (2.48 \times 10^{-16}$ kJ$)$ $\times (6.023 \times 10^{23}mol^{-1})$	$= (3.78 \times 10^{-16}$ kJ$)$ $\times (6.023 \times 10^{23}mol^{-1})$	$= (3.98 \times 10^{-16}$ kJ$)$ $\times (6.023 \times 10^{23}mol^{-1})$
$= 149.4$ kJ mol^{-1}	$= 227.7$ kJ mol^{-1}	$= 239.7$ kJ mol^{-1}

From the above calculations, it is clear that the crystal filed splitting energy of the Ti^{3+} in complexes,the three ligands is in the order; $Br^- < F^- < H_2O$. Similarly, it has been found form the spectral data that the crystal field splitting power of various ligands for a given metal ion, are in the following order

$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- \approx$ urea $<$ ox$^{2-} < H_2O <$ NCS$^- <$ EDTA$^{4-} < NH_3 <$ en $< NO_2^- < CN^- <$ CO

The above series is known as spectrochemcial series. The ligands present on the right side of the series such as carbonyl causes relatively larger crystal field splitting and are called strong ligands or strong field ligands, while the ligands on the left side are called weak field ligands and causes relatively smaller crystal field splitting.

Distribution of d electrons in octahedral complexes:

The filling of electrons in the d orbitals in the presence of ligand field also follows Hund's rule. In the octahedral complexes with d^2 and d^3 configurations, the electrons occupy different degenerate t_{2g} orbitals and remains unpaired. In case of d^4 configuration, there are two possibilities. The fourth electron may either go to the higher energy e_g orbitals or it may pair with one of the t_{2g} electrons. In this scenario, the preferred configuration will be the one with lowest energy.

If the octahedral crystal field splitting energy (Δ_o) is greater than the pairing energy (P), it is necessary to cause paring of electrons in an orbital, then the fourth electron will pair up with an the electron in the t_{2g} orbital. Conversely, if the Δ_o is lesser than P, then the fourth electron will occupy one of the degenerate higher energy e_g orbitals.

For example, let us consider two different iron(III) complexes $[Fe(H_2O)_6]^{3+}$ (weak field complex; Δ_o is 14000 cm^{-1}) and $[Fe(CN)_6]^{3-}$ (Strong field complex; Δ_o is 35000 cm^{-1}). The pairing energy of Fe^{3+} is 30000 cm^{-1}. In both these complexes the Fe^{3+} has d^5 configuration. In aqua complex, the $\Delta_o < P$ hence, the fourth & fifth electrons enter e_g orbitals and the configuration is $t_{2g}^{\ 3}, e_g^{\ 2}$. In the cyanido complex $\Delta_o > P$ and hence the fourth & fifth electrons pair up with the electrons in the t_{2g} orbitals and the electronic configuration is $t_{2g}^{\ 5}, e_g^{\ 0}$.

The actual distribution of electrons can be ascertained by calculating the crystal field stabilisation energy (CFSE). The crystal field stabilisation energy is defined as the energy difference of electronic configurations in the ligand filed (E_{LF}) and the isotropic field/barycentre (E_{iso}).

$$\text{CFSE } (\Delta E_o) = \{E_{LF}\} - \{E_{iso}\}$$

$$= \{[n_{t_{2g}}(-0.4)+n_{e_g}(0.6)]\ \Delta_o + n_p P\} - \{n'_p\ P\}$$

Here, $n_{t_{2g}}$ is the number of electrons in t_{2g} orbitals; n_{e_g} is number of electrons in e_g orbitals; n_p is number of electron pairs in the ligand field; & n'_p is the number of electron pairs in the isotropic field (barycentre).

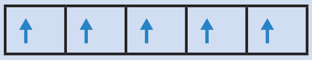
Calculating the CFSE for the Iron complexes

Complex: $[Fe(H_2O)_6]^{3+}$

High Spin Complex	Low spin complex
Electronic configuration in isotropic field : d^5 ↑ ↑ ↑ ↑ ↑	
No. of paired electrons (n'p)= 0 ; Therefore, E_{iso} = 0	

High Spin Complex	**Low spin complex**
Electronic configuration(for high spin complex) : $t^3_{2g}\ e^2_g$ CFSE = $\{[3(-0.4)+2\ (0.6)]\ \Delta_o + 0 \times P\} - \{0\}$ = 0	Electronic configuration (for low spin complex) : $t^5_{2g}\ e^0_g$ CFSE = $\{[5(-0.4)+0\ (0.6)]\ \Delta_o + 2 \times P\} - \{0\}$ = $-2\ \Delta_o + 2P$ = $(-2 \times 14000) + (2 \times 30000)$ = $32000\ cm^{-1}$ High positive CFSE value indicates that low spin complex is not a favourable one.
Actual nature of $[Fe(H_2O)_6]^{3+}$	High spin (Spin free)
Electronic configuration of central metal ion	$t^3_{2g}\ e^2_g$
Magnetic property	No. of unparied electrons = 5; Hence paramagnetic
Magnetic moment (Using spin only formula)	$\mu_s = \sqrt{n(n+2)} = \sqrt{5(5+2)} = 5.916$ BM

Complex: $[Fe(CN)_6]^{3-}$

High Spin Complex	**Low spin complex**
Electronic configuration in isotropic field : d5  No. of paired electrons (n'p)= 0 ; Therefore, $E_{iso} = 0$	
Ligand field: Electronic configuration : $t^3_{2g}\ e^2_g$ CFSE = $\{[3(-0.4)+2\ (0.6)]\ \Delta_o + 0 \times P\} - \{0\}$ = 0	Ligand field Electronic configuration : $t^5_{2g}\ e^0_g$ CFSE = $\{[5(-0.4)+0\ (0.6)]\ \Delta_o + 2 \times P\} - \{0\}$ = $-2\ \Delta_o + 2P$ = $(-2 \times 35000) + (2 \times 30000)$ = $-10000\ cm^{-1}$ Negative CFSE value indicates that low spin complex is favoured

Nature of the complex	Low spin (Spin paired)
Electronic configuration of central metal ion	$t^{5}_{2g}\, e^{0}_{g}$
Magnetic property	No. of unparied electrons = 1; Hence paramagnetic
Magnetic moment (Using spin only formula)	$\mu_s = \sqrt{n(n+2)} = \sqrt{1(1+2)} = 1.732\ \text{BM}$

Colour of the complex and crystal field splitting energy:

Most of the transition metal complexes are coloured. A substance exhibits colour when it absorbs the light of a particular wavelength in the visible region and transmit the rest of the visible light. When this transmitted light enters our eye, our brain recognises its colour. The colour of the transmitted light is given by the complementary colour of the absorbed light. For example, the hydrated copper(II) ion is blue in colour as it absorbs orange light, and transmit its complementary colour, blue. A list of absorbed wavelength and their complementary colour is given in the following table.

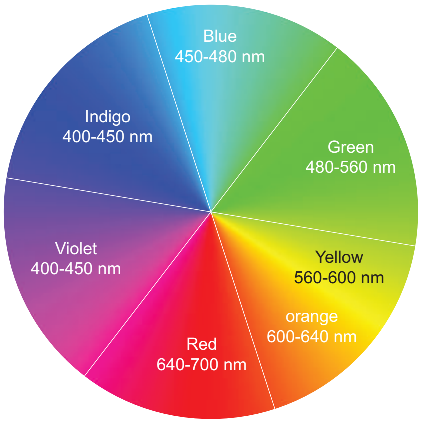


Figure 5.15 Colour Wheel - Complementary colours are shown on opposite sides.

Wave length(λ) of absorbed light (Å)	Wave number(ν) of the absorbed light (cm-1)	Colour of absorbed light	Observed Colour
4000	25000	Violet	Yellow
4750	21053	Blue	Orange
5100	19608	Green	Red
5700	17544	Yellow	Violet
5900	16949	Orange	Blue
6500	15385	Red	Green

The observed colour of a coordination compound can be explained using crystal field theory. We learnt that the ligand field causes the splitting of d orbitals of the central metal atom into two sets (t_{2g} and e_g). When the white light falls on the complex ion, the central metal ion absorbs visible light corresponding to the crystal filed splitting energy and transmits rest of the light which is responsible for the colour of the complex.

This absorption causes excitation of d-electrons of central metal ion from the lower energy t_{2g} level to the higher energy e_g level which is known as d-d transition.

Let us understand the d-d transitions by considering $[Ti(H_2O)_6]^{3+}$ as an example. In this complex the central metal ion is Ti^{3+}, which has d^1 configuration. This single electron occupies one of the t_{2g} orbitals in the octahedral aqua ligand field. When white light falls on this complex the d electron absorbs light and promotes itself to e_g level. The spectral data show the absorption maximum is at 20000 cm^{-1} corresponding to the crystal field splitting energy (Δ_o) 239.7 kJ mol^{-1}. The transmitted colour associated with this absorption is purple and hence ,the complex appears purple in colour.

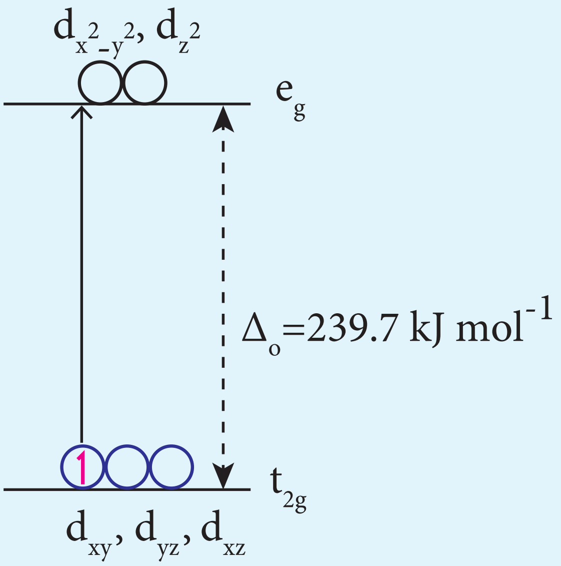


Figure 5.16 d-d Transition

The octahedral titanium(III) complexes with other ligands such as bromide and fluoride have different colours. This is due to the difference in the magnitude of crystal field splitting by these ligands (Refer page 156). However, the complexes of central metal atom such as of Sc^{3+}, Ti^{4+}, Cu^+, Zn^{2+}, etc... are colourless. This is because the d-d transition is not possible in complexes with central metal having d^0 or d^{10} configuration.

Evaluate yourself 1:

11. The mean pairing energy and octahedral field splitting energy of $[Mn(CN)_6]^{3-}$ are 28,800 cm^{-1} and 38500 cm^{-1} respectively. Whether this complex is stable in low spin or high spin?

12. Draw energy level diagram and indicate the number of electrons in each level for the complex $[Cu(H_2O)_6]^{2+}$. Whether the complex is paramagnetic or diamagnetic?

13. For the $[CoF_6]^{3-}$ ion the mean pairing energy is found to be 21000 cm^{-1} . The magnitude of Δ_0 is 13000cm^{-1}. Calculate the crystal field stabilization energy for this complex ion corresponding to low spin and high spin states.

Metallic carbonyls

Metal carbonyls are the transition metal complexes of carbon monoxide, containing Metal-Carbon bond. In these complexes CO molecule acts as a neutral ligand. The first homoleptic carbonyl $\left[Ni(CO)_4\right]$ nickel tetra carbonyl was reported by Mond in 1890.These metallic carbonyls are widely studied because of their industrial importance, catalytic properties and their ability to release carbon monoxide.

Classification:

Generally metal carbonyls are classified in two different ways as described below.

(i) Classification based on the number of metal atoms present.

Depending upon the number of metal atoms present in a given metallic carbonyl, they are classified as follows.

a. Mononuclear carbonyls

These compounds contain only one metal atom, and have comparatively simple structures. For example, $\left[Ni(CO)_4\right]$ - nickel tetracarbonyl is tetrahedral, $\left[Fe(CO)_5\right]$ - Iron pentacarbonyl is trigonalbipyramidal, and $\left[Cr(CO)_6\right]$ - Chromium hexacarbonyl is octahedral.

b. Poly nuclear carbonyls

Metallic carbonyls containing two or more metal atoms are called poly nuclear carbonyls. Poly nuclear metal carbonyls may be Homonuclear $\left(\left[Co_2(CO)_8\right], \left[Mn_2(CO)_{10}\right], \left[Fe_3(CO)_{12}\right]\right)$ or hetero nuclear $\left(\left[MnCo(CO)_9\right], \left[MnRe(CO)_{10}\right]\right)$ etc.

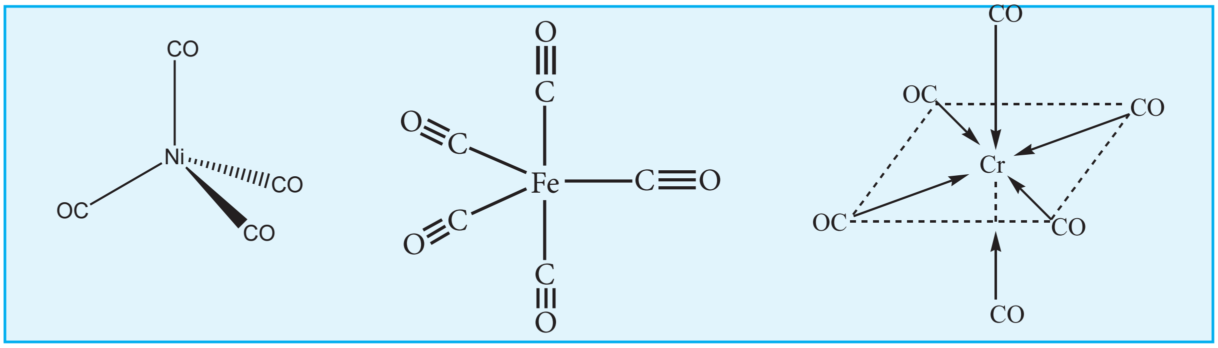
(ii) Classification based on the structure:

The structures of the binuclear metal carbonyls involve either metal–metal bonds or bridging CO groups, or both. The carbonyl ligands that are attached to only one metal atom are referred to as **terminal** carbonyl groups, whereas those attached to two metal atoms simultaneously are called *bridging* carbonyls. Depending upon the structures, metal carbonyls are classified as follows.

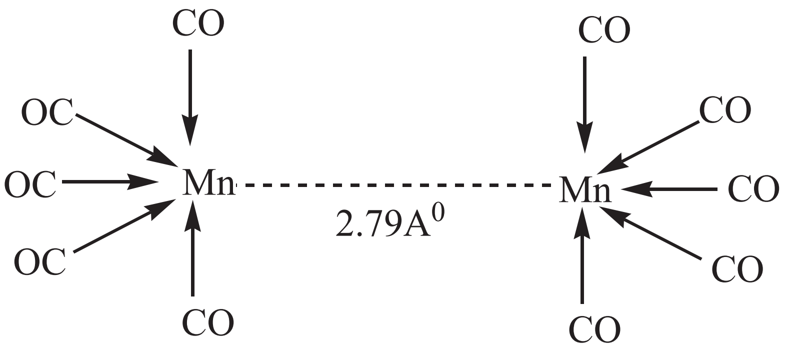
a. Non-bridged metal carbonyls:

These metal carbonyls do not contain any bridging carbonyl ligands. They may be of two types.

(i) Non- bridged metal carbonyls which contain only terminal carbonyls. Examples: $\left[Ni(CO)_4\right]$, $\left[Fe(CO)_5\right]$ and $\left[Cr(CO)_6\right]$



(ii) Non- bridged metal carbonyls which contain terminal carbonyls as well as Metal-Metal bonds. For examples,The structure of $Mn_2(CO)_{10}$actually involve only a metal–metal bond, so the formula is more correctly represented as $(CO)_5Mn–Mn(CO)_5$.

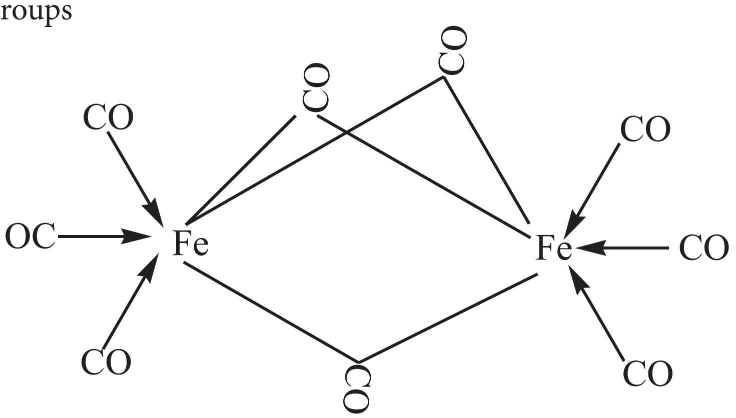


Other examples of this type are, $Tc_2(CO)_{10}$, and $Re_2(CO)_{10}$.

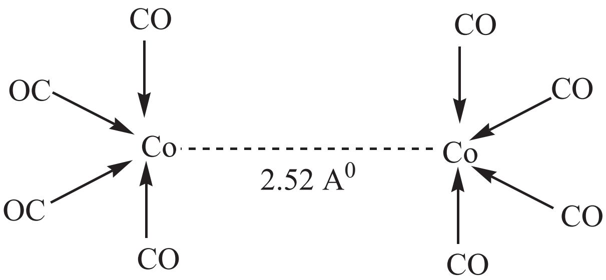
b. Bridged carbonyls:

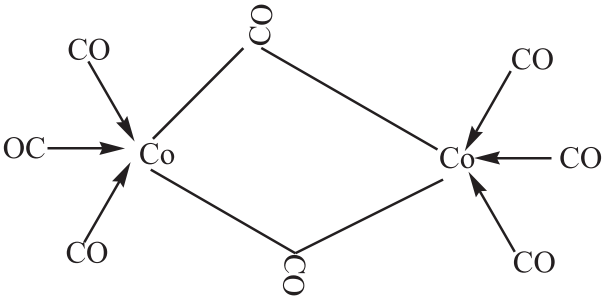
These metal carbonyls contain one or more bridging carbonyl ligands along with terminal carbonyl ligands and one or more Metal-Metal bonds. For example,

(i) The structure of $Fe_2(CO)_9$, di-iron nona carbonyl molecule consists of three bridging CO ligands, six terminal CO groups



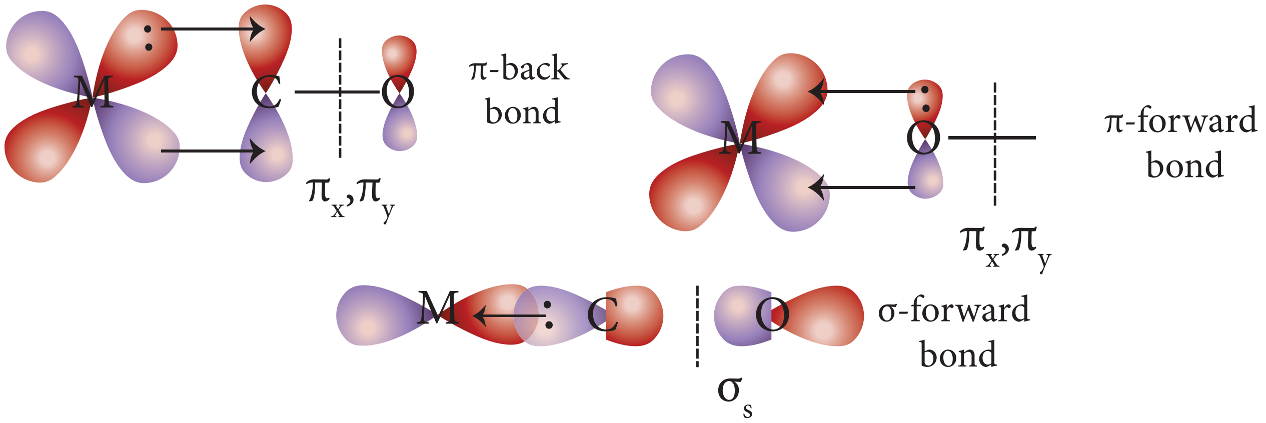
(ii) For dicobaltoctacarbonyl $Co_2(CO)_8$ two isomers are possible. The one has a metal–metal bond between the cobalt atoms, and the other has two bridging CO ligands.





Bonding in metal carbonyls

In metal carbonyls, the bond between metal atom and the carbonyl ligand consists of two components. The first component is an electron pair donation from the carbon atom of carbonyl ligand into a vacant d-orbital of central metal atom. This electron pair donation forms $M \xleftarrow{\sigma \text{ bond}} CO$ sigma bond. This sigma bond formation increases the electron density in metal d orbitals and makes the metal electron rich. In order to compensate for this increased electron density, a filled metal d-orbital interacts with the empty π* orbital on the carbonyl ligand and transfers the added electron density back to the ligand. This second component is called π-back bonding . Thus in metal carbonyls, electron density moves from ligand to metal through sigma bonding and from metal to ligand through pi bonding, this synergic effect accounts for strong $M \leftarrow CO$ bond in metal carbonyls. This phenomenon is shown diagrammatically as follows.



5.11. Stability of metal complexes:

The stability of coordination complexes can be interpreted in two different ways. The first one is thermodynamic stability and second one is kinetic stability. Thermodynamic stability of a coordination complex refers to the free energy change (ΔG) of a complex formation reaction. Kinetic stability of a coordination complex refers to the ligand substitution. In some cases, complexes can undergo rapid ligand substitution; such complexes are called labile complexes. However, some complexes undergo ligand substitution very slowly (or sometimes no substitution), such complexes are called inert complexes.

Stability constant:(β)

The stability of a coordination complex is a measure of its resistance to the replacement of one ligand by another. The stability of a complex refers to the degree of association between two species involved in an equilibrium. Let us consider the following complex formation reaction

$$Cu^{2+} + 4NH_3 \rightleftharpoons \left[Cu\left(NH_3\right)_4\right]^{2+}$$

$$\beta = \frac{\left[Cu\left(NH_3\right)_4\right]^{2+}}{\left[Cu^{2+}\right]\left[NH_3\right]^4} \qquad \text{---------}(1)$$

So, as the concentration of $\left[Cu\left(NH_3\right)_4\right]^{2+}$ increases the value of stability complexes also increases. Therefore the greater the value of stability constant greater is the stability of the complex.

Generally coordination complexes are stable in their solutions; however, the complex ion can undergo dissociation to a small extent. Extent of dissociation depends on the strength of the metal ligand bond, thus Stronger the $M \leftarrow L$, lesser is the dissociation.

In aqueous solutions, when complex ion dissociates, there will be equilibrium between undissociated complex ion and dissociated ions. Hence the stability of the metal complex can be expressed in terms of dissociation equilibrium constant or instability constant (α). For example let us consider the dissociation of $\left[Cu(NH_3)_4\right]^{2+}$ in aqueous solution.

$$\left[Cu(NH_3)_4\right]^{2+} \rightleftharpoons Cu^{2+} + 4NH_3$$

The dissociation equilibrium constant or instability constant is represented as follows,

$$\alpha = \frac{[Cu^{2+}][NH_3]^4}{\left[Cu(NH_3)_4\right]^{2+}} \qquad \text{---------}(2)$$

From (1) and (2) we can say that, the reciprocal of dissociation equilibrium constant (α) is called as formation equilibrium constant or stability constant (β).

$$\beta = \left(\frac{1}{\alpha}\right)$$

Significance of stability constants

The stability of coordination complex is measured in terms of its stability constant (β). Higher the value of stability constant for a complex ion, greater is the stability of the complex ion. Stability constant values of some important complexes are listed in table

Complex ion	Instability constant value (α)	stability constant value (β)
$\left[Fe(SCN)\right]^{2+}$	1.0×10^{-3}	1.0×10^{3}
$\left[Cu(NH_3)_4\right]^{2+}$	1.0×10^{-12}	1.0×10^{12}
$\left[Ag(CN)_2\right]^{-}$	1.8×10^{-19}	5.4×10^{18}
$\left[Co(NH_3)_6\right]^{3+}$	6.2×10^{-36}	1.6×10^{35}
$\left[Hg(CN)_4\right]^{2-}$	4.0×10^{-42}	2.5×10^{41}

By comparing stability constant values in the above table, we can say that among the five complexes listed, $\left[Hg(CN)_4\right]^{2-}$ is most stable complex ion and $\left[Fe(SCN)\right]^{2+}$ is least stable.

5.11.1. Stepwise formation constants and overall formation constants

When a free metal ion is in aqueous medium, it is surrounded by (coordinated with) water molecules. It is represented as $[MS_6]$. If ligands which are stronger than water are added to this metal salt solution, coordinated water molecules are replaced by strong ligands.

Let us consider the formation of a metal complex ML_6 in aqueous medium.(Charge on the metal ion is ignored) complex formation may occur in single step or step by step.

If ligands added to the metal ion in single step, then

$$[MS_6] + 6L \rightleftharpoons [ML_6] + 6S$$

$$\beta_{overall} = \frac{[ML_6][S]^6}{[MS_6][L]^6}$$

$\beta_{overall}$ is called as overall stability constant. As solvent is present in large excess, its concentration in the above equation can be ignored.

$$\therefore \beta_{overall} = \frac{[ML_6]}{[MS_6][L]^6}$$

If these six ligands are added to the metal ion one by one, then the formation of complex $[ML_6]$ can be supposed to take place through six different steps as shown below. Generally step wise stability constants are represented by the symbol k.

$$[MS_6] + L \rightleftharpoons [MS_5L] + S \qquad k_1 = \frac{[MS_5L]}{[MS_6][L]}$$

$$[MS_5L] + L \rightleftharpoons [MS_4L_2] + S \qquad k_2 = \frac{[MS_4L_2]}{[MS_5L][L]}$$

$$[MS_4L_2] + L \rightleftharpoons [MS_3L_3] + S \qquad k_3 = \frac{[MS_3L_3]}{[MS_4L_2][L]}$$

$$[MS_3L_3] + L \rightleftharpoons [MS_2L_4] + S \qquad k_4 = \frac{[MS_2L_4]}{[MS_3L_3][L]}$$

$$[MS_2L_4] + L \rightleftharpoons [MSL_5] + S \qquad k_5 = \frac{[MSL_5]}{[MS_2L_4][L]}$$

$$[MSL_5] + L \rightleftharpoons [ML_6] + S \qquad k_6 = \frac{[ML_6]}{[MSL_5][L]}$$

In the above equilibrium, the values k_1, k_2, k_3, k_4, k_5 and k_6 are called step wise stability constants. By carrying out small a mathematical manipulation, we can show that overall stability constant β is the product of all step wise stability constants k_1, k_2, k_3, k_4, k_5 and k_6.

$$\beta = k_1 \times k_2 \times k_3 \times k_4 \times k_5 \times k_6$$

On taking logarithm both sides

$$\log(\beta) = \log(k_1) + \log(k_2) + \log(k_3) + \log(k_4) + \log(k_5) + \log(k_6)$$

5.12. Importance and applications of coordination complexes:

The coordination complexes are of great importance. These compounds present in many plants, animals and in minerals. Some Important applications of coordination complexes are described below.

1. Phthalo blue – a bright blue pigment is a complex of Copper (II) ion and it is used in printing ink and in the packaging industry.
2. Purification of Nickel by Mond's process involves formation $[Ni(CO)_4]$, which Yields 99.5% pure Nickel on decomposition.
3. EDTA is used as a chelating ligand for the separation of lanthanides,in softening of hard water and also in removing lead poisoning.
4. Coordination complexes are used in the extraction of silver and gold from their ores by forming soluble cyano complex. These cyano complexes are reduced by zinc to yield metals. This process is called as Mac-Arthur –Forrest cyanide process.
5. Some metal ions are estimated more accurately by complex formation. For example, Ni^{2+} ions present in Nickel chloride solution is estimated accurately for forming an insoluble complex called $[Ni(DMG)_2]$
6. Many of the complexes are used as catalysts in organic and inorganic reactions. For example,
   (i) Wilkinson's catalyst - $\left[(PPh_3)_3 RhCl\right]$ is used for hydrogenation of alkenes.
   (ii) Ziegler-Natta catalyst - $[TiCl_4] + Al(C_2H_5)_3$ is used in the polymerization of ethene.
7. In order to get a fine and uniform deposit of superior metals (Ag, Au, Pt etc.,) over base metals, Coordination complexes $\left[Ag(CN)_2\right]^-$ and $\left[Au(CN)_2\right]^-$ etc., are used in electrolytic bath.
8. Many complexes are used as medicines for the treatment of various diseases. For example,
   (1) Ca-EDTA chelate, is used in the treatment of lead and radioactive poisoning. That is for removing lead and radioactive metal ions from the body.
   (2) Cis-platin is used as an antitumor drug in cancer treatment.
9. In photography, when the developed film is washed with sodium thio sulphatesolution (hypo), the negative film gets fixed. Undecomposed AgBr forms a soluble complex called sodiumdithiosulphatoargentate(I) which can be easily removed by washing the film with water.

$$AgBr + 2\,Na_2S_2O_3 \longrightarrow Na_3\left[Ag(S_2O_3)_2\right] + 2\,NaBr$$

10. **Many biological systems contain metal complexes. For example,**

(i) A red blood corpuscles (RBC) is composed of heme group, which is Fe^{2+}- Porphyrin complex.it plays an important role in carrying oxygen from lungs to tissues and carbon dioxide from tissues to lungs.

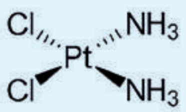
(ii) Chlorophyll, a green pigment present in green plants and algae, is a coordination complex containing Mg^{2+} as central metal ion surrounded by a modified Porphyrin ligand called corrin ring. It plays an important role in photosynthesis, by which plants converts CO_2 and water into carbohydrates and oxygen.

(iii) Vitamin B_{12}(cyanocobalamine) is the only vitamin consist of metal ion. it is a coordination complex in which the central metal ion is Co^{+} surrounded by Porphyrin like ligand.

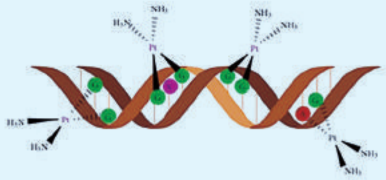
(iv) Many enzymes are known to be metal complexes, they regulate biological processes. For example, Carboxypeptidase is a protease enzyme that hydrolytic enzyme important in digestion, contains a zinc ion coordinated to the protein.

DO YOU KNOW?

Cisplatin:



Cisplatin is a square planar coordination complex (cis- $[Pt(NH_3)_2Cl_2]$), in which two similar ligands are in adjacent positions.



It is a Platinum-based anticancer drugThis drug undergoes hydrolysis and reacts with DNA to produce various crosslinks. These crosslinks hinder the DNA replication and transcription, which results in cell growth inhibition and ultimately cell death.

It also crosslinks with cellular proteins and inhibits mitosis.

Summary

- When two or more stable compounds in solution are mixed together and allowed to evaporate, in certain cases there is a possibility for the formation of double salts or coordination compounds. The double salts loose their identity and dissociates into their constituent simple ions in solutions , whereas the complex ion in coordination compound, does not loose its identity and never dissociate to give simple ions.
- According to werner, most of the elements exhibit, two types of valence namely primary valence and secondary valence and each element tend to satisfy both the valences.In modern terminology, the primary valence is referred as the oxidation state of the metal atom and the secondary valence as the coordination number.
- Coordination entity is an ion or a neutral molecule, composed of a central atom, usually a metal and the array of other atoms or groups of atoms (ligands) that are attached to it.

- The central atom/ion is the one that occupies the central position in a coordination entity and binds other atoms or groups of atoms (ligands) to itself, through a coordinate covalent bond.
- The ligands are the atoms or groups of atoms bound to the central atom/ion. The atom in a ligand that is bound directly to the central metal atom is known as a donor atom.
- The complex ion of the coordination compound containing the central metal atom/ion and the ligands attached to it, is collectively called coordination sphere and are usually enclosed in square brackets with the net charge.
- The three dimensional spacial arrangement of ligand atoms/ions that are directly attached to the central atom is known as the coordination polyhedron (or polygon).
- The number of ligand donor atoms bonded to a central metal ion in a complex is called the coordination number of the metal.
- The oxidation state of a central atom in a coordination entity is defined as the charge it would bear if all the ligands were removed along with the electron pairs that were shared with the central atom.
- This type of isomers arises when an ambidentate ligand is bonded to the central metal atom/ion through either of its two different donor atoms.
- This type of isomers arises in the coordination compounds having both the cation and anion as complex ions. The interchange of one or more ligands between the cationic and the anionic coordination entities result in different isomers.
- **Ionisation isomers** arises when an ionisable counter ion (simple ion) itself can act as a ligand. The exchange of such counter ions with one or more ligands in the coordination entity will result in ionisation isomers.
- Geometrical isomerism exists in heteroleptic complexes due to different possible three dimensional spatial arrangements of the ligands around the central metal atom. This type of isomerism exists in square planer and octahedral complexes.
- Coordination compounds which possess chairality exhibit optical isomerism similar to organic compounds. The pair of two optically active isomers which are mirror images of each other are called enantiomers.
- Linus pauling proposed the Valance Bond Theory (VBT) which assumes that the bond formed between the central metal atom and the ligand is purely covalent. Bethe and Van vleck treated the interaction between the metal ion and the ligands as electrostatic and extended the Crystal Field Theory (CFT) to explain the properties of coordination compounds.

EVALUATION

UUTJ4I

Choose the correct answer:

1. The sum of primary valance and secondary valance of the metal M in the complex $\left[M(en)_2(Ox)\right]Cl$ is L

   a) 3　　b) 6　　c) -3　　d) 9

2. An excess of silver nitrate is added to 100ml of a 0.01M solution of pentaaquachloridochromium(III)chloride. The number of moles of AgCl precipitated would be

   a)0.02　　b) 0.002　　c) 0.01　　d) 0.2

3. A complex has a molecular formula $MSO_4Cl.\ 6H_2O$ .The aqueous solution of it gives white precipitate with Barium chloride solution and no precipitate is obtained when it is treated with silver nitrate solution. If the secondary valence of the metal is six, which one of the following correctly represents the complex?

   a)$\left[M(H_2O)_4Cl\right]SO_4.2H_2O$　　b)$\left[M(H_2O)_6\right]SO_4$

   c)$\left[M(H_2O)_5Cl\right]SO_4.H_2O$　　d) $\left[M(H_2O)_3Cl\right]SO_4.3H_2O$

4. Oxidation state of Iron and the charge on the ligand NO in $\left[Fe(H_2O)_5NO\right]SO_4$ are

   a) +2 and 0 respectively　　b) +3 and 0 respectively

   c) +3 and -1 respectively　　d) +1 and +1 respectively

5. As per IUPAC guidelines, the name of the complex $\left[Co(en)_2(ONO)Cl\right]Cl$ is

   a) chlorobisethylenediaminenitritocobalt(III) chloride

   b) chloridobis(ethane-1,2-diamine)nitro κ-Ocobaltate(III) chloride

   c) chloridobis(ethane-1,2-diammine)nitrito κ-Ocobalt(II) chloride

   d) chloridobis(ethane-1,2-diamine)nitro κ-Ocobalt(III) chloride

6. IUPAC name of the complex $K_3\left[Al(C_2O_4)_3\right]$ is

   a) potassiumtrioxalatoaluminium(III)

   b) potassiumtrioxalatoaluminate(II)

   c) potassiumtrisoxalatoaluminate(III)

   d) potassiumtrioxalatoaluminate(III)

7. A magnetic moment of 1.73BM will be shown by one among the following (NEET)

a) $TiCl_4$ b) $[CoCl_6]^{4-}$

c) $[Cu(NH_3)_4]^{2+}$ d) $[Ni(CN)_4]^{2-}$

8. Crystal field stabilization energy for high spin d^5 octahedral complex is

a) $-0.6\Delta_0$ b) 0

c) $2(P-\Delta_0)$ d) $2(P+\Delta_0)$

9. In which of the following coordination entities the magnitude of Δ_0 will be maximum?

a) $[Co(CN)_6]^{3-}$ b) $[Co(C_2O_4)_3]^{3-}$

c) $[Co(H_2O)_6]^{3+}$ d) $[Co(NH_3)_6]^{3+}$

10. Which one of the following will give a pair of enantiomorphs?

a) $[Cr(NH_3)_6][Co(CN)_6]$ b) $[Co(en)_2Cl_2]Cl$

c) $[Pt(NH_3)_4][PtCl_4]$ d) $[Co(NH_3)_4Cl_2]NO_2$

11. Which type of isomerism is exhibited by $[Pt(NH_3)_2Cl_2]$?

a) Coordination isomerism b) Linkage isomerism

c) Optical isomerism d) Geometrical isomerism

12. How many geometrical isomers are possible for $[Pt(Py)(NH_3)(Br)(Cl)]$?

a) 3 b) 4 c) 0 d) 15

13. Which one of the following pairs represents linkage isomers?

a) $[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$

b) $[Co(NH_3)_5(NO_3)]SO_4$ and $[Co(NH_3)_5(ONO)]$

c) $[Co(NH_3)_4(NCS)_2]Cl$ and $[Co(NH_3)_4(SCN)_2]Cl$

d) both (b) and (c)

14. Which kind of isomerism is possible for a complex $[Co(NH_3)_4Br_2]Cl$?

a) geometrical and ionization b) geometrical and optical

c) optical and ionization d) geometrical only

15. Which one of the following complexes is not expected to exhibit isomerism?

a) $[Ni(NH_3)_4(H_2O)_2]^{2+}$ b) $[Pt(NH_3)_2Cl_2]$

c) $[Co(NH_3)_5SO_4]Cl$ d) $[Fe(en)_3]^{3+}$

16. A complex in which the oxidation number of the metal is zero is

a) $K_4\left[Fe(CN)_6\right]$ b) $\left[Fe(CN)_3(NH_3)_3\right]$

c) $\left[Fe(CO)_5\right]$ d) both (b) and (c)

17. Formula of tris(ethane-1,2-diamine)iron(II)phosphate

a) $\left[Fe(CH_3\text{-}CH(NH_2)_2)_3\right](PO_4)_3$ b) $\left[Fe(H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2)_3\right](PO_4)$

c) $\left[Fe(H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2)_3\right](PO_4)_2$ d) $\left[Fe(H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2)_3\right]_3(PO_4)_2$

18. Which of the following is paramagnetic in nature?

a) $\left[Zn(NH_3)_4\right]^{2+}$ b) $\left[Co(NH_3)_6\right]^{3+}$

c) $\left[Ni(H_2O)_6\right]^{2+}$ d) $\left[Ni(CN)_4\right]^{2-}$

19. Fac-mer isomerism is shown by

a) $\left[Co(en)_3\right]^{3+}$ b) $\left[Co(NH_3)_4(Cl)_2\right]^{+}$

c) $\left[Co(NH_3)_3(Cl)_3\right]$ d) $\left[Co(NH_3)_5Cl\right]SO_4$

20. Choose the correct statement.

a) Square planar complexes are more stable than octahedral complexes

b) The spin only magnetic moment of $\left[Cu(Cl)_4\right]^{2-}$ is 1.732 BM and it has square planar structure.

c) Crystal field splitting energy (Δ_0) of $[FeF_6]^{4-}$ is higher than the (Δ_0) of $\left[Fe(CN)_6\right]^{4-}$

d) crystal field stabilization energy of $\left[V(H_2O)_6\right]^{2+}$ is higher than the crystal field stabilization of $\left[Ti(H_2O)_6\right]^{2+}$

Answer the following questions:

1. Write the IUPAC names for the following complexes.

i) $Na_2\left[Ni(EDTA)\right]$

ii) $\left[Ag(CN)_2\right]^{-}$

iii) $\left[Co(en)_3\right]_2(SO_4)_3$

iv) $\left[Co(ONO)(NH_3)_5\right]^{2+}$

v) $\left[Pt(NH_3)_2Cl(NO_2)\right]$

2. Write the formula for the following coordination compounds.

   a) potassiumhexacyanidoferrate(II)

   b) pentacarbonyliron(0)

   c) pentaamminenitrito $-\kappa-\mathrm{N}$ -cobalt(III)ion

   d) hexaamminecobalt(III)sulphate

   e) sodiumtetrafluoridodihydroxidochromate(III)

3. Arrange the following in order of increasing molar conductivity

   i) $\mathrm{Mg}\left[\mathrm{Cr}\ (\mathrm{NH}_3)(\mathrm{Cl})_5\right]$ ii) $\left[\mathrm{Cr}\left(\mathrm{NH}_3\right)_5\mathrm{Cl}\right]_3\left[\mathrm{CoF}_6\right]_2$

   iii) $\left[\mathrm{Cr}\left(\mathrm{NH}_3\right)_3\mathrm{Cl}_3\right]$

4. Ni^{2+} is identified using alcoholic solution of dimethyl glyoxime. Write the structural formula for the rosy red precipitate of a complex formed in the reaction.

5. $\left[\mathrm{CuCl}_4\right]^{2-}$ exists while $\left[\mathrm{CuI}_4\right]^{2-}$ does not exist why?

6. Calculate the ratio of $\dfrac{\left[\mathrm{Ag}^+\right]}{\left[\mathrm{Ag}\left(\mathrm{NH}_3\right)_2\right]^+}$ in 0.2 M solution of NH_3. If the stability constant for the complex $\left[\mathrm{Ag}\left(\mathrm{NH}_3\right)_2\right]^+$ is 1.7×10^7

7. Give an example of coordination compound used in medicine and two examples of biologically important coordination compounds.

8. Based on VB theory explain why $\left[\mathrm{Cr}\left(\mathrm{NH}_3\right)_6\right]^{3+}$ is paramagnetic, while $\left[\mathrm{Ni}\left(\mathrm{CN}\right)_4\right]^{2-}$ is diamagnetic.

9. Draw all possible geometrical isomers of the complex $\left[\mathrm{Co}\left(\mathrm{en}\right)_2\mathrm{Cl}_2\right]^+$ and identify the optically active isomer.

10. $\left[\mathrm{Ti}\left(\mathrm{H}_2\mathrm{O}\right)_6\right]^{3+}$ is coloured, while $\left[\mathrm{Sc}\left(\mathrm{H}_2\mathrm{O}\right)_6\right]^{3+}$ is colourless- explain.

11. Give an example for complex of the type $\left[\mathrm{Ma}_2\mathrm{b}_2\mathrm{c}_2\right]$ where a, b, c are monodentate ligands and give the possible isomers.

12. Give one test to differentiate $\left[\mathrm{Co}\left(\mathrm{NH}_3\right)_5\mathrm{Cl}\right]\mathrm{SO}_4$ and $\left[\mathrm{Co}\left(\mathrm{NH}_3\right)_5\mathrm{SO}_4\right]\mathrm{Cl}$.

13. In an octahedral crystal field, draw the figure to show splitting of d orbitals.

14. What is linkage isomerism? Explain with an example.

15. Write briefly about the applications of coordination compounds in volumetric analysis.

16. Classify the following ligand based on the number of donor atoms.

   a) NH_3 b) en c) ox^{2-} d) triaminotriethylamine e) pyridine

17. Give the difference between double salts and coordination compounds.

18. Write the postulates of Werner's theory.

19. $\left[Ni(CN)_4\right]^{2-}$ is diamagnetic, while $[NiCl_4]^{2-}$ is paramagnetic , explain using crystal field theory.

20. Why tetrahedral complexes do not exhibit geometrical isomerism.

21. Explain optical isomerism in coordination compounds with an example.

22. What are hydrate isomers? Explain with an example.

23. What is crystal field splitting energy?

24. What is crystal field stabilization energy (CFSE) ?

25. A solution of $\left[Ni(H_2O)_6\right]^{2+}$ is green, whereas a solution of $\left[Ni(CN)_4\right]^{2-}$ is colorless - Explain

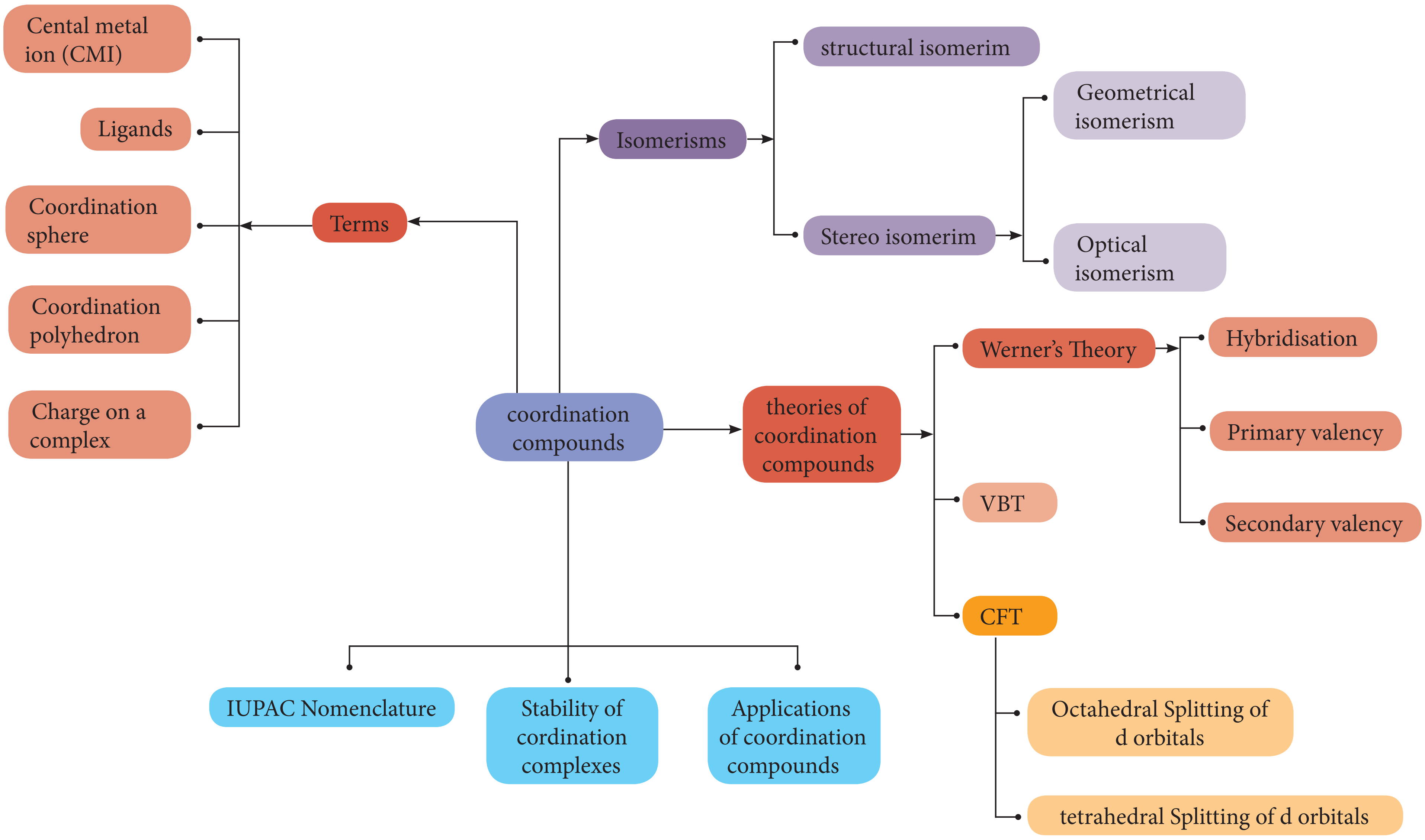
26. Discuss briefly the nature of bonding in metal carbonyls.

27. What is the coordination entity formed when excess of liquid ammonia is added to an aqueous solution of copper sulphate?

28. On the basis of VB theory explain the nature of bonding in $\left[Co(C_2O_4)_3\right]^{3-}$.

29. What are the limitations of VB theory?

30. Write the oxidation state, coordination number , nature of ligand, magnetic property and electronic configuration in octahedral crystal field for the complex $K_4\left[Mn(CN)_6\right]$.


coordination compounds
Terms
Cental metal ion (CMI)
Ligands
Coordination sphere
Coordination polyhedron
Charge on a complex
Isomerisms
structural isomerim
Stereo isomerim
Geometrical isomerism
Optical isomerism
theories of coordination compounds
Werner's Theory
Hybridisation
Primary valency
Secondary valency
VBT
CFT
Octahedral Splitting of d orbitals
tetrahedral Splitting of d orbitals
IUPAC Nomenclature
Stability of cordination complexes
Applications of coordination compounds

ICT Corner

CRYSTAL FIELD THEORY

By using this tool you can understand the crystal field splitting of different metal ions in octahedral and tetrahedral ligand field and also calculate the Crystal Field Stabilisation Energy (CFSE) of a complex using crystal field theory.

Please go to the URL http://vlab.amrita.edu/index.php?sub=2&brch=193&sim=610&cnt=4
(or) Scan the QR code on the right side

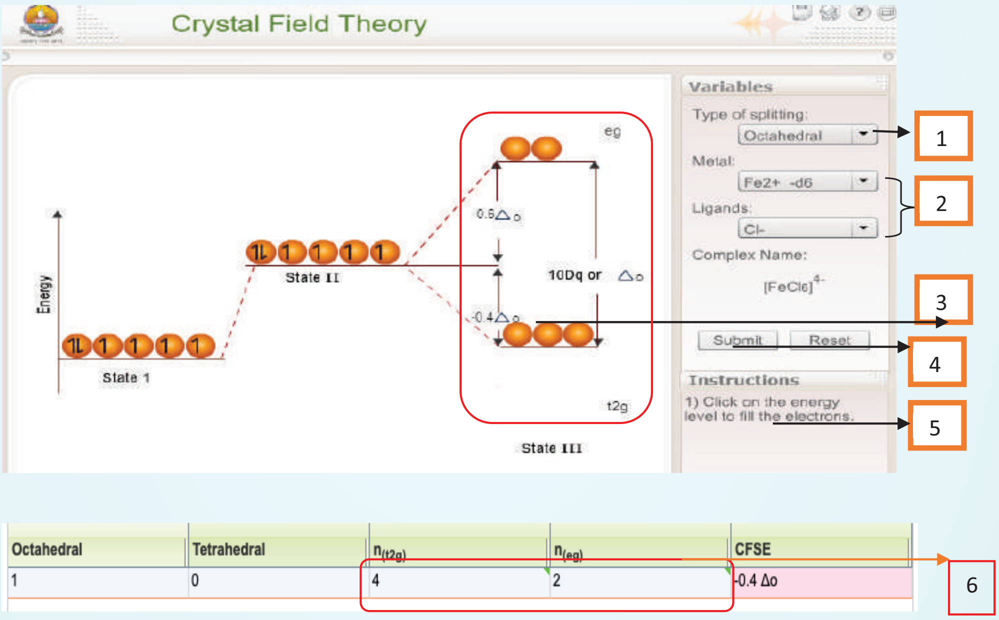
B264_12_CHEMISTRY_EM

Steps

- Open the browser and type the URL given (or) Scan the QR Code. You will see the webpage as shown in the figure.

  Note: *One time sign up is needed to access this webpage. Login using your username and password. Once logged in click the simulation tab.*

- You can select a suitable ligand field splitting using the drop down menu (box 1). Select a metal of interest and a ligand using the drop down menu (box 2). Now crystal field splitting for the selected complex appears on the screen.
- Apply crystal field theory to the selected complex and fill the d-electrons in the t_{2g} and eg orbitals by clicking each orbital. Click on the orbitals thrice to remove electrons. After completion, click submit button (box 4). Now you can check the correctness of the electron distribution. If wrong try again.
- Enter the number of electrons in the t_{2g} & e_g orbitlals in the work sheet at the bottom of the page (box 6), The calculated Crystal Field Stabilisation Energy (CFSE) will be displayed.



Type of splitting: Octahedral

Metal: Fe2+ -d6

Ligands: Cl-

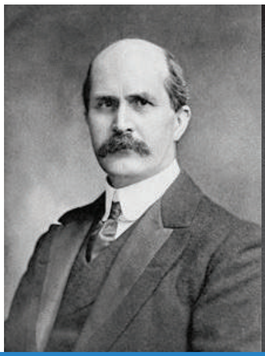
Complex Name: $[FeCl_6]^{4-}$

1) Click on the energy level to fill the electrons.

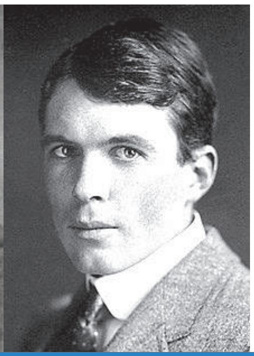
Octahedral	Tetrahedral	$n_{(t2g)}$	$n_{(eg)}$	CFSE
1	0	4	2	-0.4 Δo

UNIT
6

SOLID STATE



Sir William Henry Bragg
(1862 –1942)



Sir Lawrence Bragg
(1890 –1971)

Sir William Henry Bragg was a British physicist, chemist, and a mathematician. Sir William Henry Bragg and his son Lawrence Bragg worked on X-rays with much success. They invented the X-ray spectrometer and founded the new science of X-ray crystallography, the analysis of crystal structure using X-ray diffraction. Bragg was joint winner (with his son, Lawrence Bragg) of the Nobel Prize in Physics in 1915, for their services in the "analysis of crystal structure by means of ray". The mineral Braggite (a sulphide ore of platinum, palladium and Nickel) is named after him and his son.

7RFDTE

Learning Objectives

After studying this unit, the students will be able to

- describe general characteristics of solids
- distinguish amorphous and crystalline solids
- define unit cell
- describe different types of voids and close packed structures
- calculate the packing efficiency of different types of cubic unit cell
- solve numerical problems involving unit cell dimensions
- explain point defects in solids

INTRODUCTION

Matter may exist in three different physical states namely solid, liquid and gas. If you look around, you may find mostly solids rather than liquids and gases. Solids differ from liquids and gases by possessing definite volume and definite shape. In the solids the atoms or molecules or ion are tightly held in an ordered arrangement and there are many types of solids such as diamond, metals, plastics etc., and most of the substances that we use in our daily life are in the solid state. We require solids with different properties for various applications. Understanding the relation between the structure of solids and their properties is very much useful in synthesizing new solid materials with different properties.

In this chapter, we study the characteristics of solids, classification, structure and their properties; we also discuss the crystal defects and their significance.

6.1 General characteristics of solids

We have already learnt in XI STD that gas molecules move randomly without exerting reasonable forces on one another. Unlike gases, in solids the atoms , ions or molecules are held together by strong force of attraction. The general characteristics of solids are as follows,

(i) Solids have definite volume and shape.

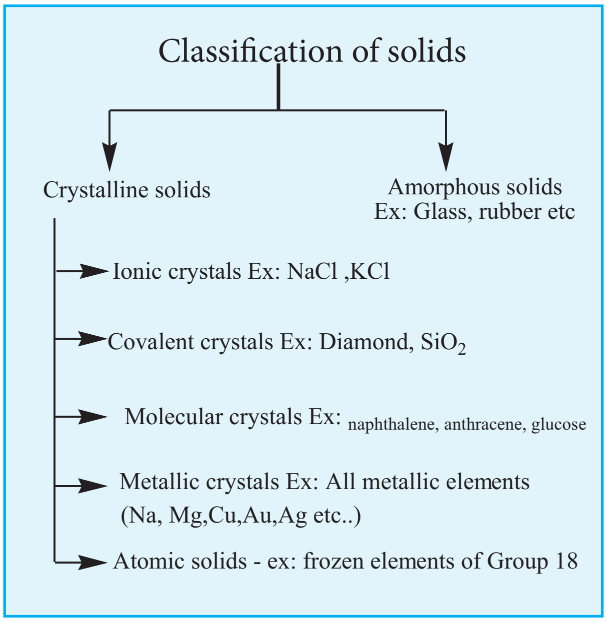
(ii) Solids are rigid and incompressible

(iii) Solids have strong cohesive forces.

(iv) Solids have short inter atomic, ionic or molecular distances.

(v) Their constituents (atoms , ions or molecules) have fixed positions and can only oscillate about their mean positions

6.2 Classification of solids:



We can classify solids into the following two major types based on the arrangement of their constituents.

(i) Crystalline solids

(ii) Amorphous solids.

The term crystal comes from the Greek word "krystallos" which means clear ice. This term was first applied to the transparent quartz stones, and then the name is used for solids bounded by many flat, symmetrically arranged faces.

A crystalline solid is one in which its constituents (atoms, ions or molecules), have an orderly arrangement extending over a long range. The arrangement of such constituents in a crystalline solid is such that the potential energy of the system is at minimum. In contrast, in amorphous solids (In Greek, amorphous means no form) the constituents are randomly arranged.

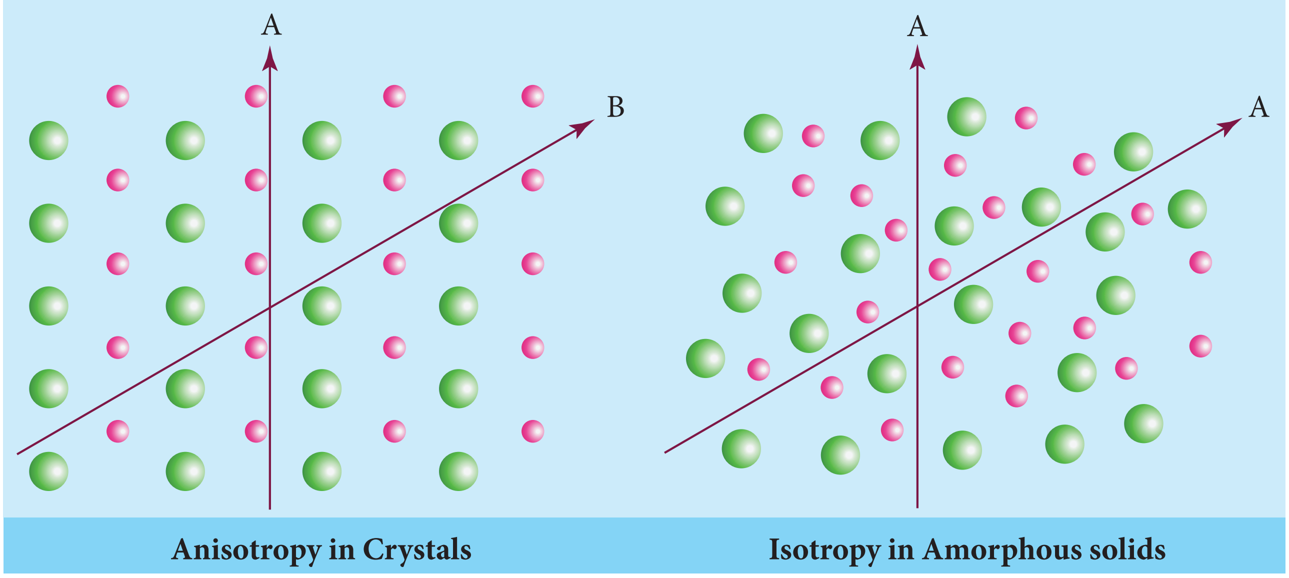
The following table shows the differences between crystalline and amorphous solids.

S.no	Crystalline solids	Amorphous solids
1	Long range orderly arrangement of constituents.	Short range, random arrangement of constituents.
2	Definite shape	Irregular shape
3	Generally crystalline solids are anisotropic in nature	They are isotropic* like liquids
4	They are true solids	They are considered as pseudo solids (or) super cooled liquids
5	Definite Heat of fusion	Heat of fusion is not definite
6	They have sharp melting points.	Gradually soften over a range of temperature and so can be moulded.
7	Examples: NaCl , diamond etc.,	Examples: Rubber , plastics, glass etc

Table 6.1 differences between crystalline and amorphous solids

*Isotropy

Isotropy means uniformity in all directions. In solid state isotropy means having identical values of physical properties such as refractive index, electrical conductance etc., in all directions, whereas anisotropy is the property which depends on the direction of measurement. Crystalline solids are anisotropic and they show different values of physical properties when measured along different directions. The following figure illustrates the anisotropy in crystals due to different arrangement of their constituents along different directions.



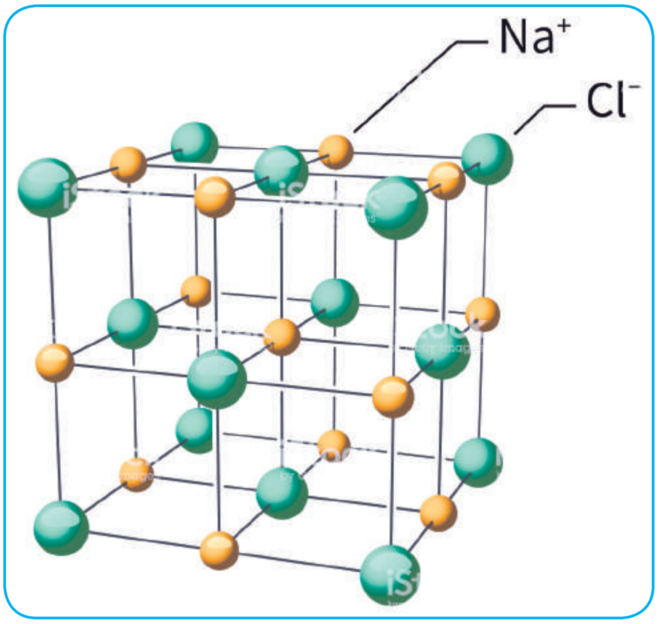
Anisotropy in Crystals

Isotropy in Amorphous solids

6.3 Classification of crystalline solids:

6.3.1 Ionic solids:

The structural units of an ionic crystal are cations and anions. They are bound together by strong electrostatic attractive forces. To maximize the attractive force, cations are surrounded by as many anions as possible and vice versa. Ionic crystals possess definite crystal structure; many solids are cubic close packed. Example: The arrangement of Na^+ and Cl^- ions in NaCl crystal.



Characteristics:

1. Ionic solids have high melting points.
2. These solids do not conduct electricity, because the ions are fixed in their lattice positions.
3. They do conduct electricity in molten state (or) when dissolved in water because, the ions are free to move in the molten state or solution.
4. They are hard as only strong external force can change the relative positions of ions.

6.3.2 Covalent solids:

In covalent solids, the constituents (atoms) are bound together in a three dimensional network entirely by covalent bonds. Examples: Diamond, silicon carbide etc. Such covalent network crystals are very hard, and have high melting point. They are usually poor thermal and electrical conductors.

6.3.3 Molecular solids:

In molecular solids, the constituents are neutral molecules. They are held together by weak van der Waals forces. Generally molecular solids are soft and they do not conduct electricity. These molecular solids are further classified into three types.

DO YOU KNOW?

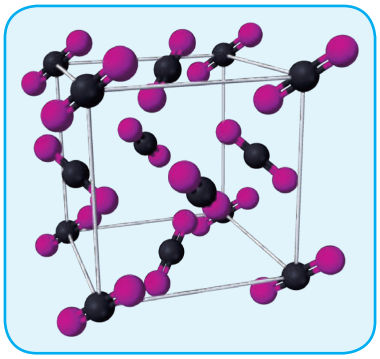
Graphite is used inside pencils.it slips easily off the pencil onto the paper and leaves a blackmark. Graphite is also a component of many lubricants , for example bicycle chain oil , because it is slippery

(i) Non-polar molecular solids:

In non polar molecular solids constituent molecules are held together by weak dispersion forces or London forces.

They have low melting points and are usually in liquids or gaseous state at room temperature. Examples: naphthalene, anthracene etc.,

(ii) Polar molecular solids



The constituents are molecules formed by polar covalent bonds. They are held together by relatively strong dipole-dipole interactions. They have higher melting points than the non-polar molecular solids. Examples are solid CO_2 , solid NH_3 etc.

(iii) Hydrogen bonded molecular solids

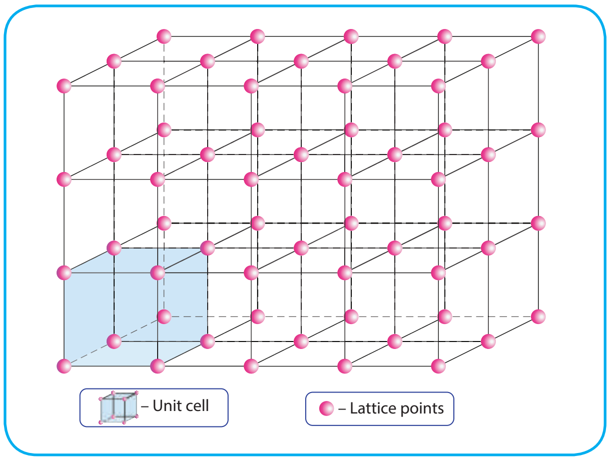
The constituents are held together by hydrogen bonds. They are generally soft solids under room temperature. Examples: solid ice (H_2O), glucose, urea etc.,

6.3.4 Metallic solids:

You have already studied in XI STD about the nature of metallic bonding. In metallic solids, the lattice points are occupied by positive metal ions and a cloud of electrons pervades the space. They are hard, and have high melting point. Metallic solids possess excellent electrical and thermal conductivity. They possess bright lustre. Examples: Metals and metal alloys belong to this type of solids, for example Cu,Fe,Zn, Ag ,Au, Cu-Zn etc.

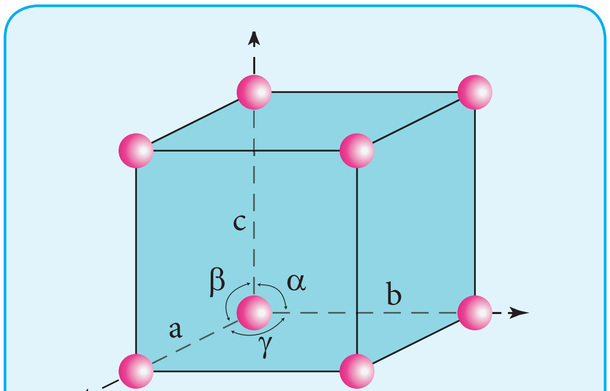
6.4 Crystal lattice and unit cell:

Crystalline solid is characterised by a definite orientation of atoms, ions or molecules, relative to one another in a three dimensional pattern. The regular arrangement of these species throughout the crystal is called a crystal lattice. A basic repeating structural unit of a crystalline solid is called a unit cell. The following figure illustrates the lattice point and the unit cell.



A crystal may be considered to consist of large number of unit cells, each one in direct contact with its nearer neighbour and all similarly oriented in space. The number of nearest neighbours that surrounding a particle in a crystal is called the coordination number of that particle.

A unit cell is characterised by the three edge lengths or lattice constants a ,b and c and the angle between the edges α, β and γ

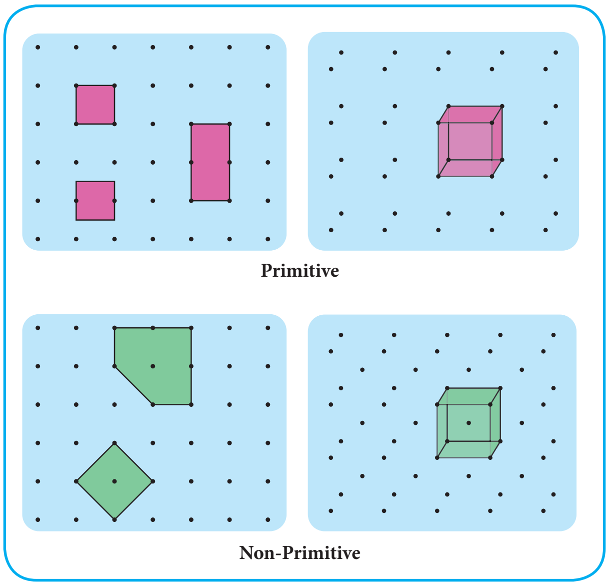


Unit cell

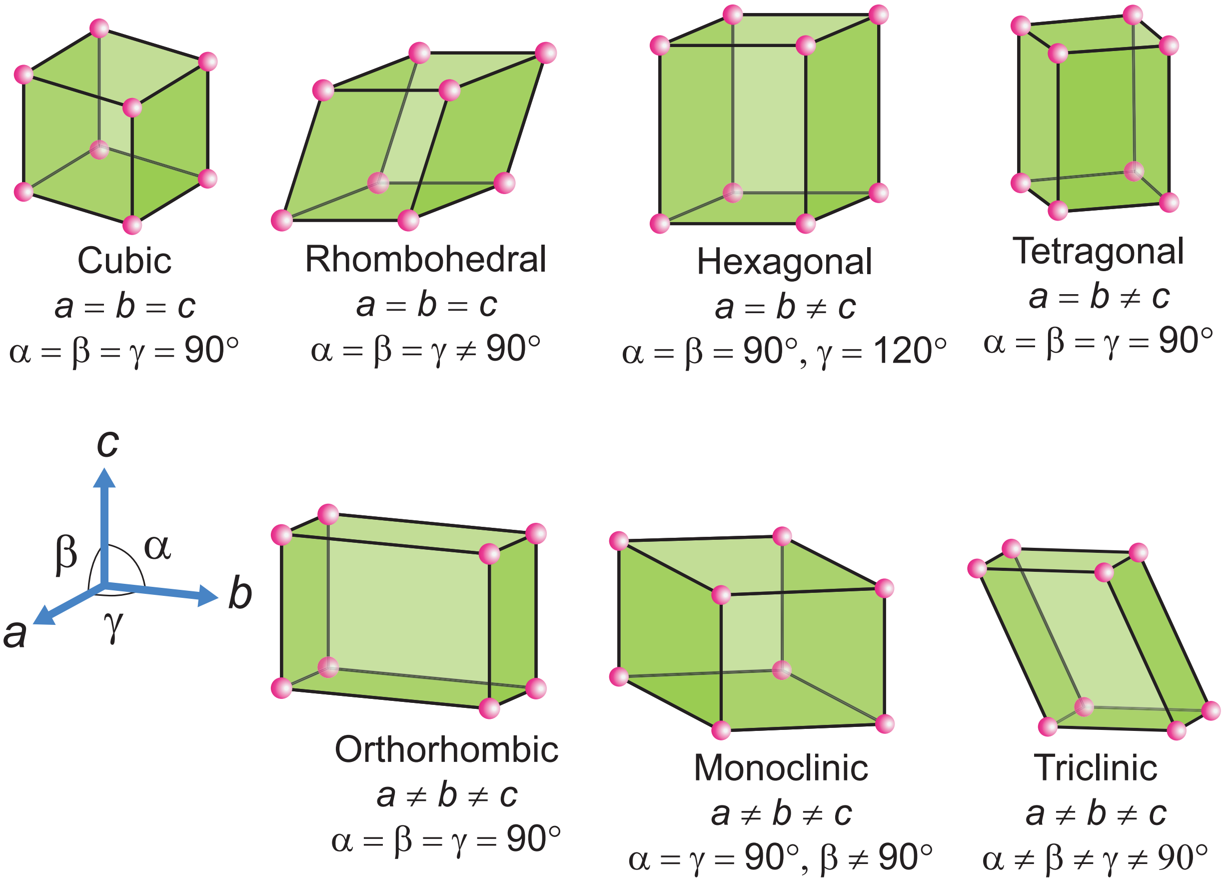
6.5 Primitive and non-primitive unit cell

There are two types of unit cells: primitive and non-primitive. A unit cell that contains only one lattice point is called a primitive unit cell, which is made up from the lattice points at each of the corners.

In case of non-primitive unit cells, there are additional lattice points, either on a face of the unit cell or with in the unit cell.



There are seven primitive crystal systems; cubic, tetragonal, orthorhombic, hexagonal, monoclinic, triclinic and rhombohedral. They differ in the arrangement of their crystallographic axes and angles. Corresponding to the above seven, Bravis defined 14 possible crystal systems as shown in the figure.



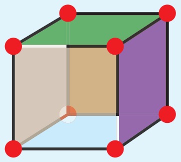
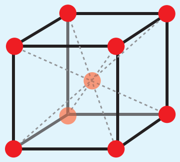
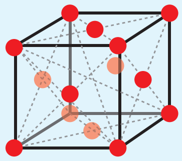
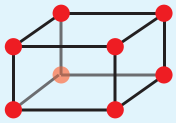
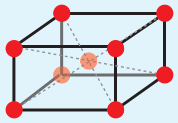
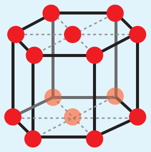
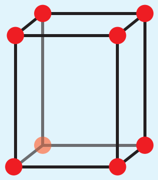
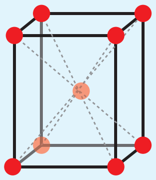
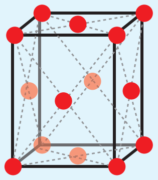
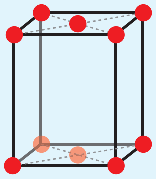
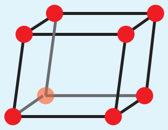
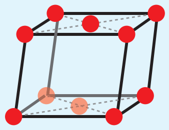
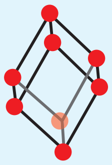
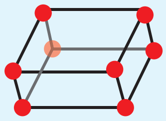
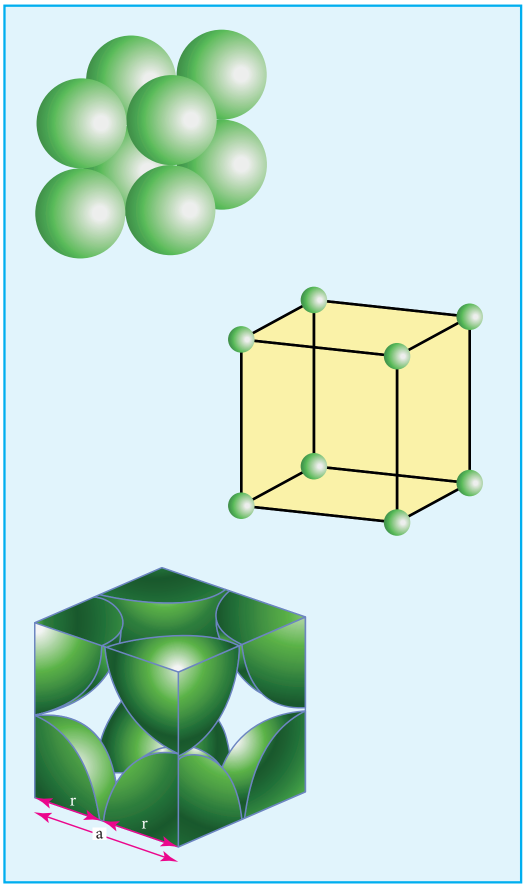
cubic	 primitive	 body centered	 face centered
tetragonal	 primitive	 body centered	
hexagonal			
orthorhombic	 primitive	 body centered	 face centered  basis face centered
monoclinic	 primitive		 basis face centered
trigonal			
triclinic			

Table 6.2 14 Bravais Lattices

Number of atoms in a cubic unit cell:

6.5.1 Primitive (or) simple cubic unit cell.(SC)



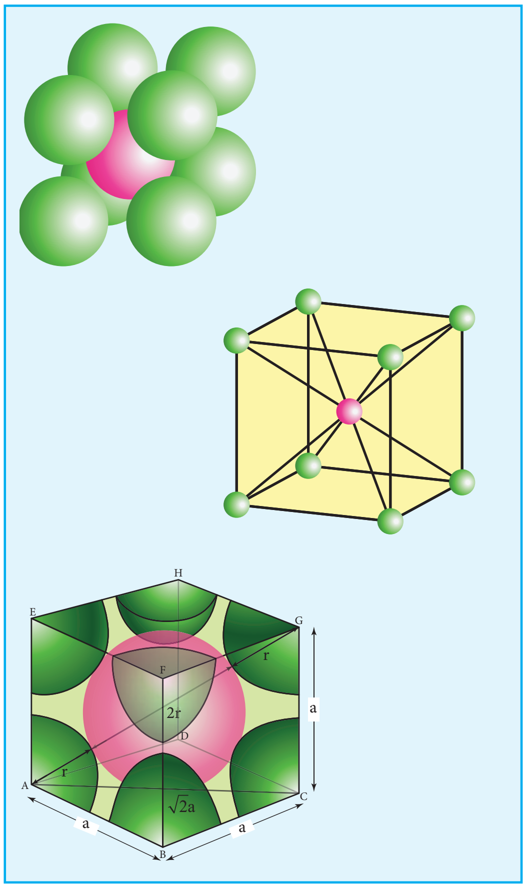
In the simple cubic unit cell, each corner is occupied by an identical atoms or ions or molecules. And they touch along the edges of the cube, do not touch diagonally. The coordination number of each atom is 6.

Each atom in the corner of the cubic unit cell is shared by 8 neighboring unit cells and therefore atoms `per unit cell is equal to $\frac{N_c}{8}$, where N_c is the number of atoms at the corners.

$$\therefore no\ of\ atoms\ in\ a\ \mathrm{SC}\ unit\ cell = \left(\frac{Nc}{8}\right)$$

$$= \left(\frac{8}{8}\right) = 1$$

6.5.2 Body centered cubic unit cell. (BCC)



In a body centered cubic unit cell, each corner is occupied by an identical particle and in addition to that one atom occupies the body centre. Those atoms which occupy the corners do not touch each other, however they all touch the one that occupies the body centre. Hence, each atom is surrounded by eight nearest neighbours and coordination number is 8. An atom present at the body centre belongs to only to a particular unit cell i.e unshared by other unit cell.

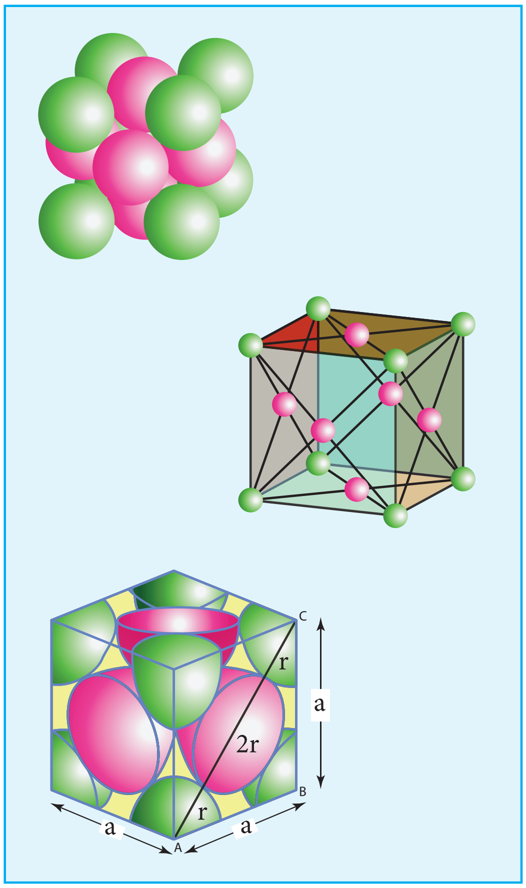
$$\therefore \text{Number of atoms in a bccunitcell} = \left(\frac{Nc}{8}\right) + \left(\frac{N_b}{1}\right)$$

$$= \left(\frac{8}{8} + \frac{1}{1}\right)$$

$$= (1+1)$$

$$= 2$$

6.5.3 Face centered cubic unit cell.(FCC)



In a face centered cubic unit cell, identical atoms lie at each corner as well as in the centre of each face. Those atoms in the corners touch those in the faces but not each other. The atoms in the face centre is being shared by two unit cells, each atom in the face centers makes $\left(\frac{1}{2}\right)$ contribution to the unit cell.

$$\therefore \text{Number of atoms in a fcc unitcell} = \left(\frac{N_c}{8}\right) + \left(\frac{N_f}{2}\right)$$

$$= \left(\frac{8}{8} + \frac{6}{2}\right)$$

$$= (1+3)$$

$$= 4$$

Drawing the crystal lattice on paper is not an easy task. The constituents in a unit cell touch each other and form a three dimensional network. This can be simplified by drawing crystal structure with the help of small circles (spheres) corresponding constituent particles and connecting neighbouring particles using a straight line as shown in the figure.

6.5.4 Calculations involving unit cell dimensions:

X-Ray diffraction analysis is the most powerful tool for the determination of crystal structure. The inter planar distance (d) between two successive planes of atoms can be calculated using the following equation form the X-Ray diffraction data

$$2d\sin\theta = n\lambda$$

The above equation is known as Bragg's equation.

Where

λ is the wavelength of X-ray used for diffraction.

θ is the angle of diffraction

By knowing the values of θ, λ and n we can calculate the value of d.

$$d = \frac{n\lambda}{2\sin\theta}$$

Using these values the edge of the unit cell can be calculated.

6.5.5 Calculation of density:

Using the edge length of a unit cell, we can calculate the density (ρ) of the crystal by considering a cubic unit cell as follows.

$$\text{Density of the unit cell } \rho = \frac{\text{mass of the unit cell}}{\text{volume of the unit cell}} \quad ...(1)$$

$$\text{mass of the unit cell} = \left\{\begin{array}{l}\text{total number of} \\ \text{atoms belongs to} \\ \text{that unit cell}\end{array}\right\} \times \left\{\begin{array}{l}\text{mass of} \\ \text{one atom}\end{array}\right\} \qquad \text{...(2)}$$

$$\text{mass of one atom} = \frac{\text{molar mass (gmol}^{-1}\text{)}}{\text{Avagadro number (mol}^{-1}\text{)}}$$

$$m = \frac{M}{N_A} \qquad \text{...(3)}$$

Substitute (3) in (2)

$$\text{mass of the unit cell} = n \times \frac{M}{N_A} \qquad \text{...(4)}$$

For a cubic unit cell, all the edge lengths are equal i.e , a=b=c

$$\text{volume of the unit cell} = a \times a \times a = a^3 \qquad \text{...(5)}$$

$$\therefore \textbf{Density of the unit cell } \rho = \frac{n\,M}{a^3 N_A} \qquad \text{...(6)}$$

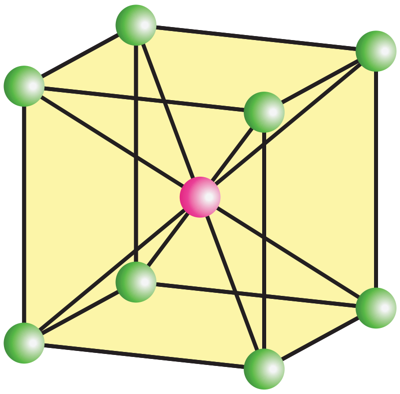
Equation (6) contains four variables namely ρ , n , M and a . If any three variables are known, the fourth one can be calculated.

Example 2

Barium has a body centered cubic unit cell with a length of 508pm along an edge. What is the density of barium in g cm^{-3}?

Solution:

$$\rho = \frac{n\,M}{a^3 N_A}$$



In this case,

n=2 ; M=137.3 $gmol^{-1}$; a = 508pm= 5.08X10^{-8}cm

$$\rho = \frac{2 \text{ atoms} \times 137.3 \text{ g mol}^{-1}}{\left(5.08 \times 10^{-8} \text{ cm}\right)^3 \left(6.023 \times 10^{23} \text{ atoms mol}^{-1}\right)}$$

$$\rho = \frac{2 \times 137.3}{(5.08)^3 \times 10^{-24} \times 6.023 \times 10^{23}} \text{ g cm}^{-3}$$

$$\rho = 3.5 \text{ g cm}^{-3}$$

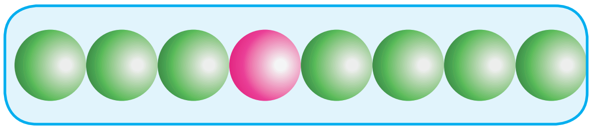
Evaluate yourself -1

1. An element has a face centered cubic unit cell with a length of 352.4 pm along an edge. The density of the element is 8.9 gcm^{-3}. How many atoms are present in 100 g of an element?
2. Determine the density of CsCl which crystallizes in a bcc type structure with an edge length 412.1 pm.
3. A face centered cubic solid of an element (atomic mass 60) has a cube edge of $4\overset{0}{A}$. Calculate its density.

6.6 Packing in crystals:

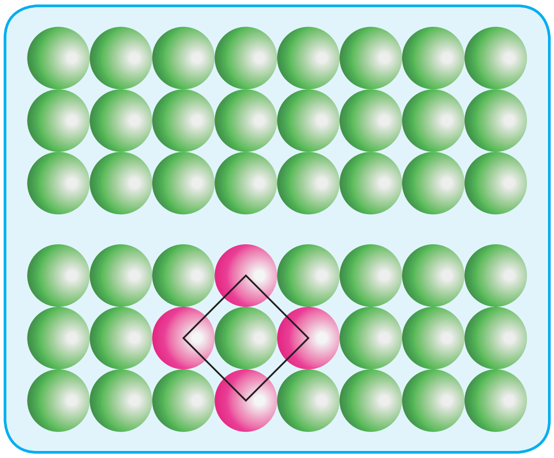
Let us consider the packing of fruits for display in fruit stalls. They are in a closest packed arrangement as shown in the following fig. we can extend this analogy to visualize the packing of constituents (atoms / ions / molecules) in crystals, by treating them as hard spheres. To maximize the attractive forces between the constituents, they generally tend to pack together as close as possible to each other. In this portion we discuss how to pack identical spheres to create cubic and hexagonal unit cell. Before moving on to these three dimensional arrangements, let us first consider the two dimensional arrangement of spheres for better understanding.

6.6.1 Linear arrangement of spheres in one direction:



In a specific direction, there is only one possibility to arrange the spheres in one direction as shown in the fig. in this arrangement each sphere is in contact with two neighbouring spheres on either side.

6.6.2 Two dimensional close packing:



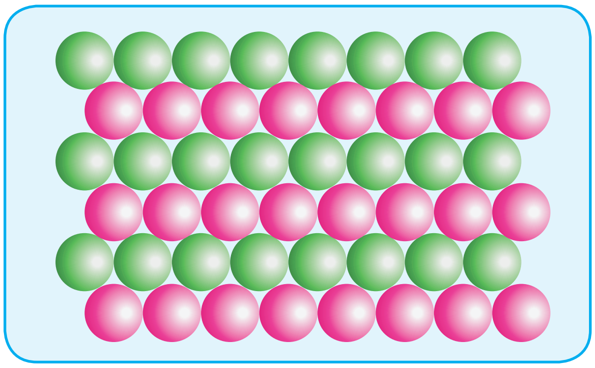
Two dimensional planar packing can be done in the following two different ways.

(i) AAA… type:

Linear arrangement of spheres in one direction is repeated in two dimension i.e., more number of rows can be generated identical to the one dimensional arrangement such that all spheres of different rows align vertically as well as horizontally as shown in the fig. If we denote the first row as A type arrangement, then the above mentioned packing is called AAA type, because all rows are identical as the first one. In this arrangement each sphere is in contact with four of its neighbours.

(i) ABAB.. Type:

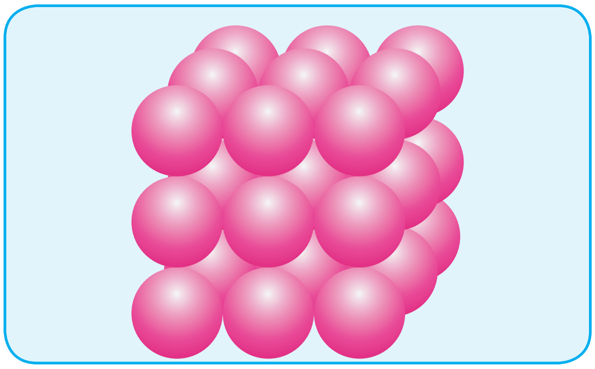
In this type, the second row spheres are arranged in such a way that they fit in the depression of the first row as shown in the figure. The second row is denoted as B type. The third row is arranged similar to the first row A, and the fourth one is arranged similar to second one. i.e., the pattern is repeated as ABAB….In this arrangement each sphere is in contact with 6 of its neighbouring spheres.



On comparing these two arrangements (AAAA...type and ABAB….type) we found that the closest arrangement is ABAB…type.

6.6.3 Simple cubic arrangement:

This type of three dimensional packing arrangements can be obtained by repeating the AAAA type two dimensional arrangements in three dimensions. i.e., spheres in one layer sitting directly on the top of those in the previous layer so that all layers are identical. All spheres of different layers of crystal are perfectly aligned horizontally and also vertically, so that any unit cell of such arrangement as simple cubic structure as shown in fig.



Simple Cubic (SC)

In simple cubic packing, each sphere is in contact with 6 neighbouring spheres - Four in its own layer, one above and one below and hence the coordination number of the sphere in simple cubic arrangement is 6.

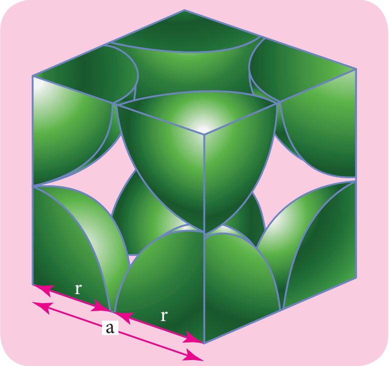
Packing efficiency:

There is some free space between the spheres of a single layer and the spheres of successive layers. The percentage of total volume occupied by these constituent spheres gives the packing efficiency of an arrangement. Let us calculate the packing efficiency in simple cubic arrangement,

$$\left\{\begin{array}{l}\text{Packing fraction}\\\text{(or) efficiency}\end{array}\right\} = \frac{\left\{\begin{array}{l}\text{Total volume occupied by}\\\text{spheres in a unit cell}\end{array}\right\}}{\text{Volume of the unit cell}} \times 100$$

Let us consider a cube with an edge length ‘a’ as shown in fig.

Volume of the cube with edge length a is = a × a × a = a^3



Let ‘r’ is the radius of the sphere. From the figure, a=2r $\Rightarrow r = \frac{a}{2}$

∴ Volume of the sphere with radius 'r'

$$= \frac{4}{3}\pi r^3$$

$$= \frac{4}{3}\pi\left(\frac{a}{2}\right)^3$$

$$= \frac{4}{3}\pi\left(\frac{a^3}{8}\right)$$

$$= \frac{\pi a^3}{6} \qquad \ldots (1)$$

In a simple cubic arrangement, number of spheres belongs to a unit cell is equal to one

$$\therefore \text{Total volume occupied by the spheres in sc unit cell} = 1 \times \left(\frac{\pi a^3}{6}\right) \qquad \ldots (2)$$

Dividing (2) by (3)

$$\text{Packing fraction} = \frac{\left(\frac{\pi a^3}{6}\right)}{\left(a^3\right)} \times 100 = \frac{100\,\pi}{6}$$

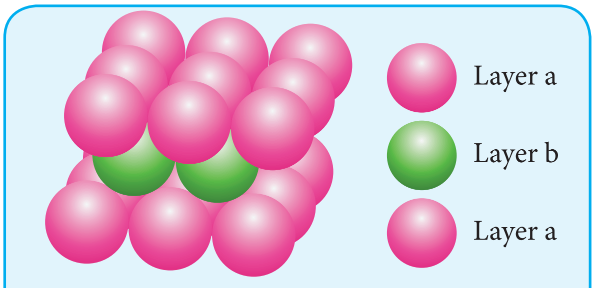
$$= 52.31\%$$

i.e., only 52.31% of the available volume is occupied by the spheres in simple cubic packing, making inefficient use of available space and hence minimizing the attractive forces.

More to know Of all the metals in the periodic table, only polonium crystallizes in simple cubic pattern.

6.6.4 Body centered cubic arrangement

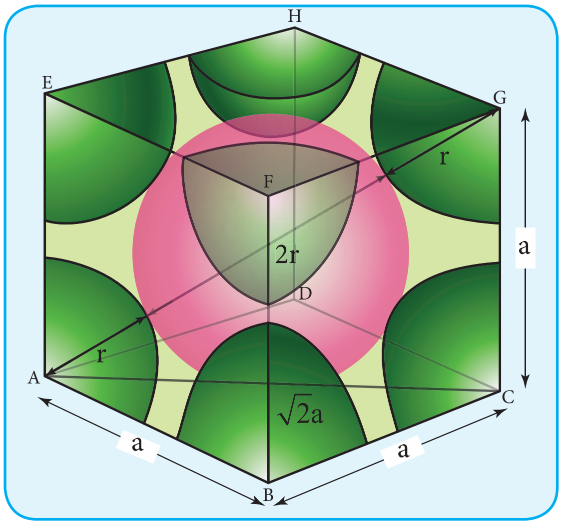
In this arrangement, the spheres in the first layer (A type) are slightly separated and the second layer is formed by arranging the spheres in the depressions between the spheres in layer A as shown in figure. The third layer is a repeat of the first. This pattern ABABAB is repeated throughout the crystal. In this arrangement, each sphere has a coordination number of 8, four neighbors in the layer above and four in the layer below.



Body Certered Cubic (BCC)

Packing efficiency:

Here, the spheres are touching along the leading diagonal of the cube as shown in the fig.



In ΔABC

$$AC^2 = AB^2 + BC^2$$

$$AC = \sqrt{AB^2 + BC^2}$$

$$AC = \sqrt{a^2 + a^2} = \sqrt{2a^2} = \sqrt{2}\,a$$

In ΔACG

$$AG^2 = AC^2 + CG^2$$

$$AG = \sqrt{AC^2 + CG^2}$$

$$AG = \sqrt{\left(\sqrt{2}a\right)^2 + a^2}$$

$$AG = \sqrt{2a^2 + a^2} = \sqrt{3a^2}$$

$$AG = \sqrt{3}\,a$$

i.e., $\sqrt{3}a = 4r$

$$r = \frac{\sqrt{3}}{4}a$$

∴ Volume of the sphere with radius 'r'

$$= \frac{4}{3}\pi r^3$$

$$= \frac{4}{3}\pi\left(\frac{\sqrt{3}}{4}a\right)^3$$

$$= \frac{\sqrt{3}}{16}\pi a^3 \qquad ...(1)$$

Number of spheres belong to a unit cell in bcc arrangement is equal to two and hence the total volume of all spheres

$$= 2 \times \left(\frac{\sqrt{3}\,\pi\, a^3}{16}\right) = \frac{\sqrt{3}\,\pi\, a^3}{8}$$

Dividing (2) by (3)

$$\text{Packing fraction} = \frac{\left(\frac{\sqrt{3}\,\pi\, a^3}{8}\right)}{\left(a^3\right)} \times 100$$

$$= \frac{\sqrt{3}\,\pi}{8} \times 100$$

$$= \sqrt{3}\,\pi \times 12.5$$

$$= 1.732 \times 3.14 \times 12.5$$

$$= 68\ \%$$

i.e., 68 % of the available volume is occupied. The available space is used more efficiently than in simple cubic packing.

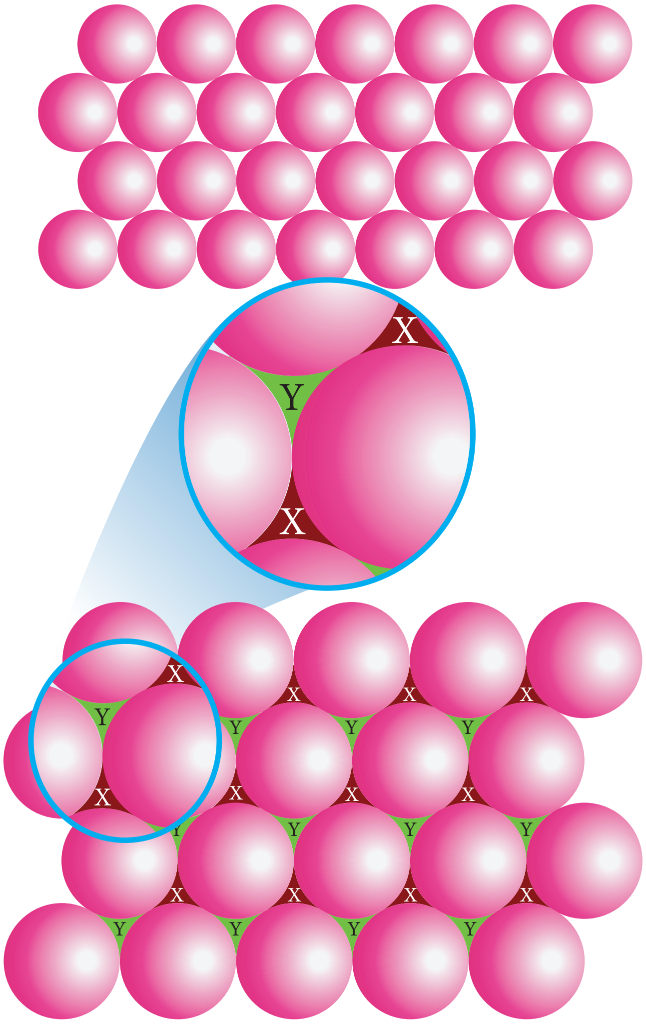
6.6.5 The hexagonal and face centered cubic arrangement:

Formation of first layer:

In this arrangement, the first layer is formed by arranging the spheres as in the case of two dimensional ABAB arrangements i.e. the spheres of second row fit into the depression of first row. Now designate this first layer as 'a'. The next layer is formed by placing the spheres in the depressions of the first layer. Let the second layer be 'b'.

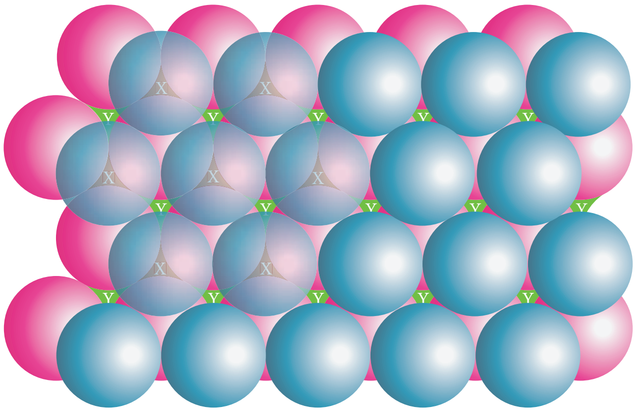
Formation of second layer:

In the first layer (a) there are two types of voids (or holes) and they are designated as x and y. The second layer (b) can be formed by placing the spheres either on the depression (voids/holes) x (or) on y. let us consider the formation of second layer by placing the spheres on the depression (x).



Wherever a sphere of second layer (b) is above the void (x) of the first layer (a), a tetrahedral void is formed. This constitutes four spheres – three in the lower (a) and one in the upper layer (b). When the centers of these four spheres are joined, a tetrahedron is formed.

At the same time, the voids (y) in the first layer (a) are partially covered by the spheres of layer (b), now such a void in (a) is called a octahedral void. This constitutes six spheres – three in the lower layer (a) and three in the upper layer (b). When the centers of these six spheres are joined, an octahedron is formed. Simultaneously new tetrahedral voids (or holes) are also created by three spheres in second layer (b) and one sphere of first layer (a)



The number of voids depends on the number of close packed spheres. If the number of close packed spheres be 'n' then, the number of octahedral voids generated is equal to n and the number of tetrahedral voids generated is equal to 2n.

Formation of third layer:

The third layer of spheres can be formed in two ways to achieve closest packing

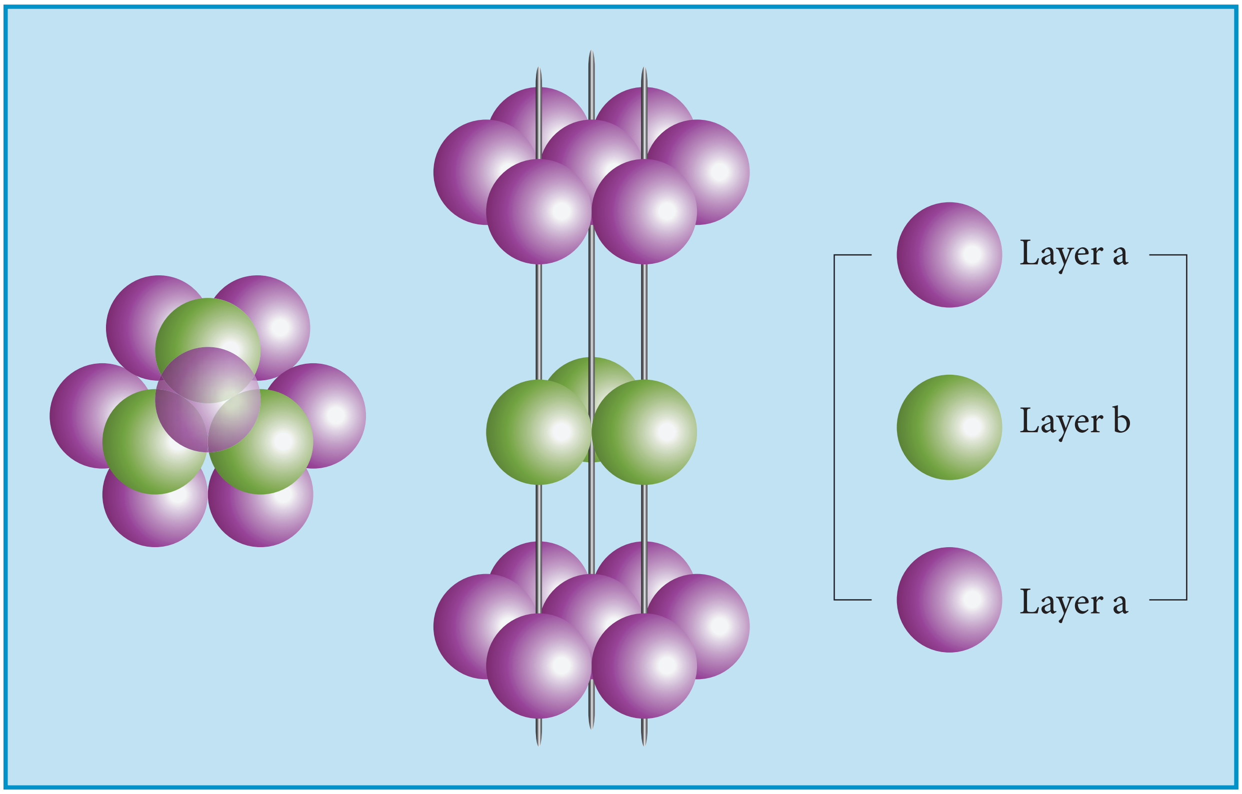
(i) aba arrangement - hcp structure

(ii) abc arrangement – ccp structure

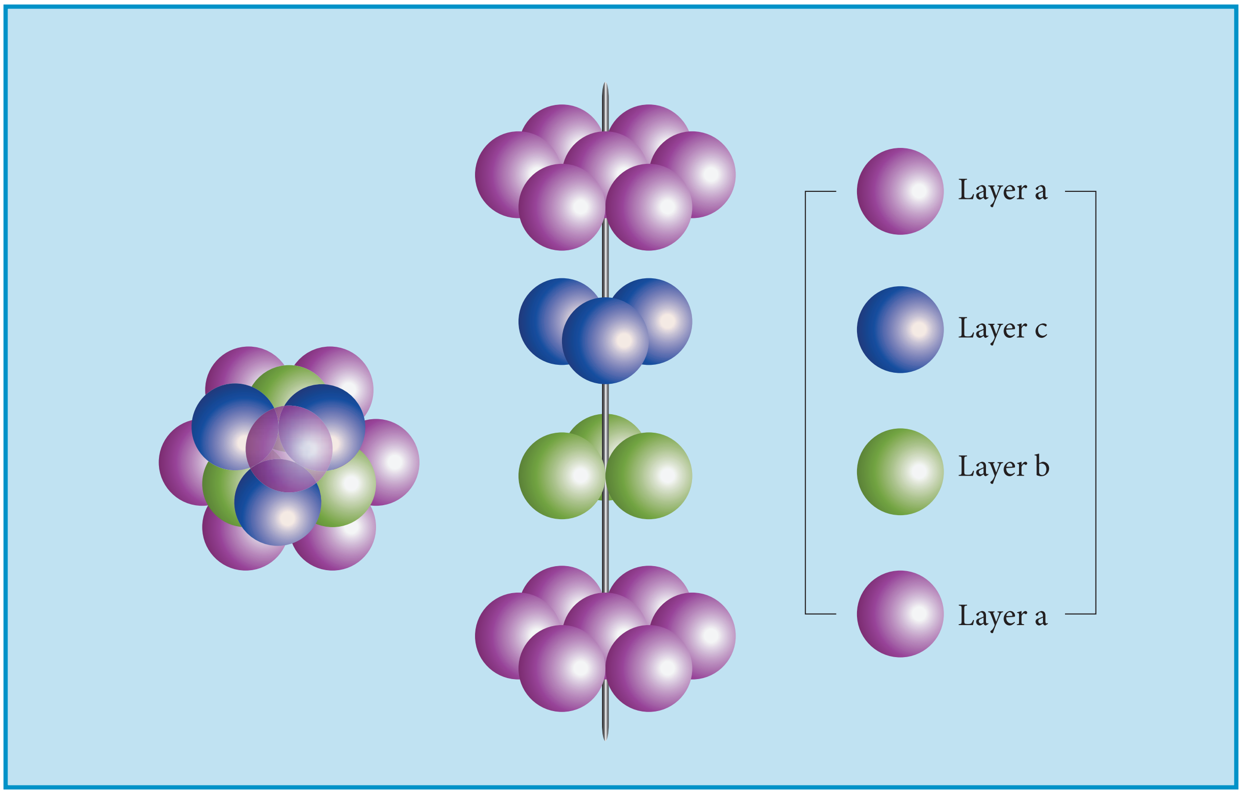
The spheres can be arranged so as to fit into the depression in such a way that the third layer is directly over a first layer as shown in the figure. This "aba" arrangement is known as the hexagonal close packed (hcp) arrangement. In this arrangement, the tetrahedral voids of the second layer are covered by the spheres of the third layer.

Alternatively, the third layer may be placed over the second layer in such a way that all the spheres of the third layer fit in octahedral voids. This arrangement of the third layer is different from other two layers (a) and (b), and hence, the third layer is designated (c). If the stacking of layers is continued in abcabcabc… pattern, then the arrangement is called cubic close packed (ccp) structure.

In both hcp and ccp arrangements, the coordination number of each sphere is 12 – six neighbouring spheres in its own layer, three spheres in the layer above and three sphere in the layer below. This is the most efficient packing.

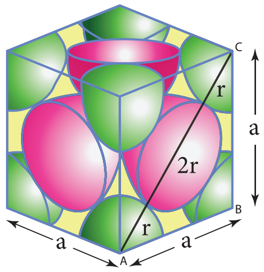


aba arrangement - hcp structure



abc arrangement – ccp structure

The cubic close packing is based on the face centered cubic unit cell. Let us calculate the packing efficiency in fcc unit cell.



From the figure

$AC = 4r$

$4r = a\sqrt{2}$

$r = \dfrac{a\sqrt{2}}{4}$

In ΔABC

$AC^2 = AB^2 + BC^2$

$AC = \sqrt{AB^2 + BC^2}$

$AC = \sqrt{a^2 + a^2} = \sqrt{2a^2} = \sqrt{2}\, a$

Volume of the sphere with radius r is

$$= \frac{4}{3}\pi\left(\frac{\sqrt{2}a}{4}\right)^3$$

$$= \frac{4}{3}\pi\left(\frac{2\sqrt{2}a^3}{64}\right)$$

$$= \frac{\sqrt{2}\,\pi a^3}{24}$$

Total number of spheres belongs to a single fcc unit cell is 4

∴ the volume of all spheres in a fcc unit cell

$$= 4\times\left(\frac{\sqrt{2}\,\pi a^3}{24}\right)$$

$$= \left(\frac{\sqrt{2}\,\pi a^3}{6}\right)$$

$$\text{packing efficiency} = \frac{\left(\frac{\sqrt{2}\,\pi\, a^3}{6}\right)}{\left(a^3\right)}\times 100$$

$$= \frac{\sqrt{2}\,\pi}{6}\times 100$$

$$= \frac{1.414\times 3.14\times 100}{6}$$

$$= 74\%$$

Radius ratio:

The structure of an ionic compound depends upon the stoichiometry and the size of the ions.generally in ionic crystals the bigger anions are present in the close packed arrangements and the cations occupy the voids. The ratio of radius of cation and anion $\left(\frac{r_{C^+}}{r_{A^-}}\right)$ plays an important role in determining the structure. The following table shows the rleation between the radius ratio and the structural arrangement in ionic solids.

$\left(\frac{r_{C^+}}{r_{A^-}}\right)$	Coordination number	Structure	Example
0.155 – 0.225	3	Trigonal planar	B_2O_3
0.225 – 0.414	4	Tetrahedral	ZnS
0.414 – 0.732	6	Octahedral	NaCl
0.732 – 1.0	8	Cubic	CsCl

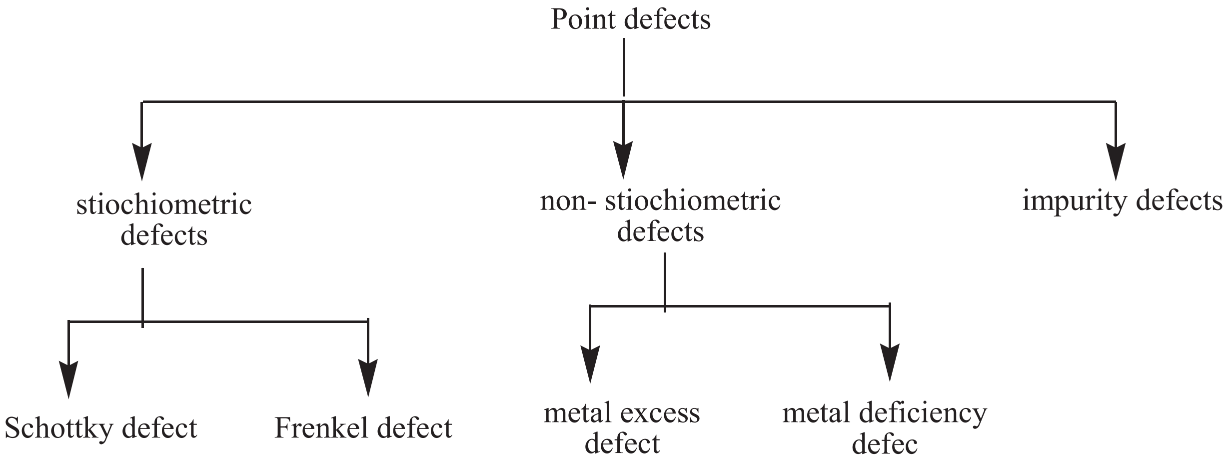
Table 6.3 Radius ratio

6.7 Imperfection in solids:

According to the law of nature nothing is perfect, and so crystals need not be perfect. They always found to have some defects in the arrangement of their constituent particles. These defects affect the physical and chemical properties of the solid and also play an important role in various processes. For example, a process called doping leads to a crystal imperfection and it increases the electrical conductivity of a semiconductor material such as silicon. The ability of ferromagnetic material such as iron, nickel etc., to be magnetized and demagnetized depends on the presence of imperfections. Crystal defects are classified as follows

1) Point defects
2) Line defects
3) Interstitial defects
4) Volume defects

In this portion, we concentrate on point defects, more specifically in ionic solids. Point defects are further classified as follows



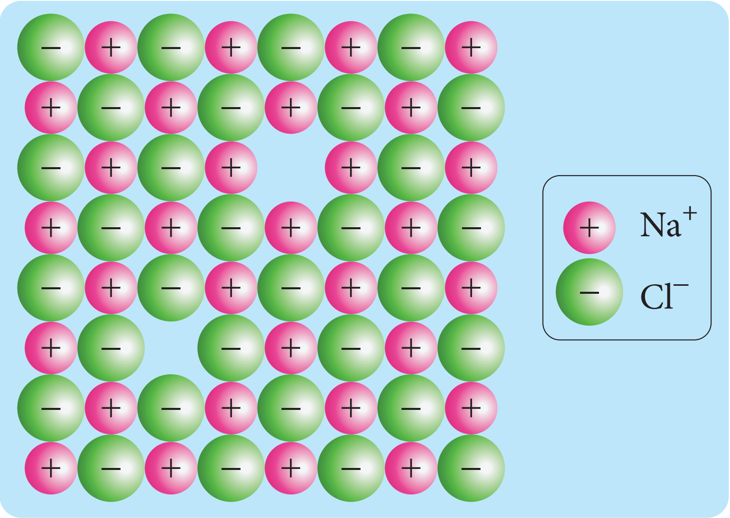
Stoichiometric defects in ionic solid:

This defect is also called intrinsic (or) thermodynamic defect. In stoichiometric ionic crystals, a vacancy of one ion must always be associated with either by the absence of another oppositely charged ion (or) the presence of same charged ion in the interstitial position so as to maintain the electrical neutrality.

6.7.1 Schottky defect:

Schottky defect arises due to the missing of equal number of cations and anions from the crystal lattice. This effect does not change the stoichiometry of the crystal. Ionic solids in which the cation and anion are of almost of similar size show schottky defect. Example: NaCl.

Presence of large number of schottky defects in a crystal, lowers

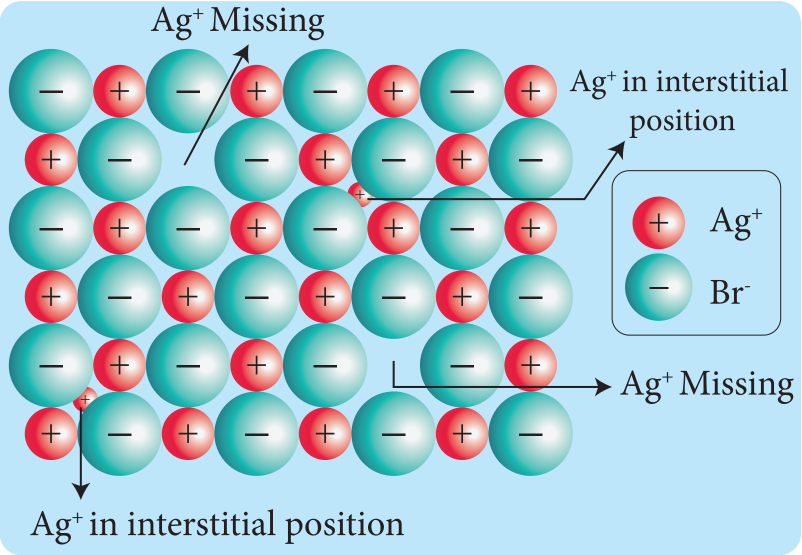


Schottky Defect

its density. For example, the theoretical density of vanadium monoxide (VO) calculated using the edge length of the unit cell is 6.5 g cm^{-3}, but the actual experimental density is 5.6 g cm^{-3}. It indicates that there is approximately 14% Schottky defect in VO crystal. Presence of Schottky defect in the crystal provides a simple way by which atoms or ions can move within the crystal lattice.

6.7.2 Frenkel defect:

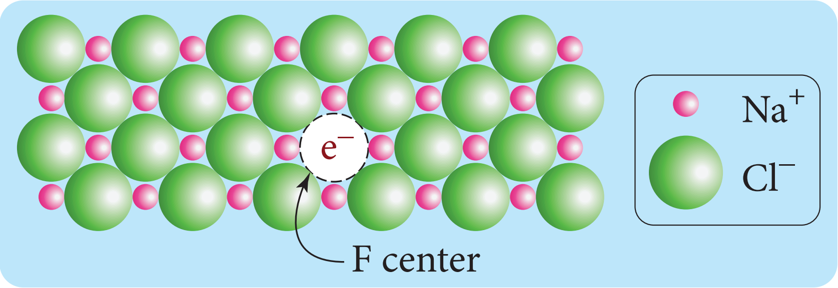
Frenkel defect arises due to the dislocation of ions from its crystal lattice. The ion which is missing from the lattice point occupies an interstitial position. This defect is shown by ionic solids in which cation and anion differ in size. Unlike Schottky defect, this defect does not affect the density of the crystal. For example AgBr, in this case, small Ag^+ ion leaves its normal site and occupies an interstitial position as shown in the figure.



Frenkel Defect

6.7.3 Metal excess defect:

Metal excess defect arises due to the presence of more number of metal ions as compared to anions. Alkali metal halides NaCl, KCl show this type of defect. The electrical neutrality of the crystal can be maintained by the presence of anionic vacancies equal to the excess metal ions (or) by the presence of extra cation and electron present in interstitial position.



Metal Excess Defect

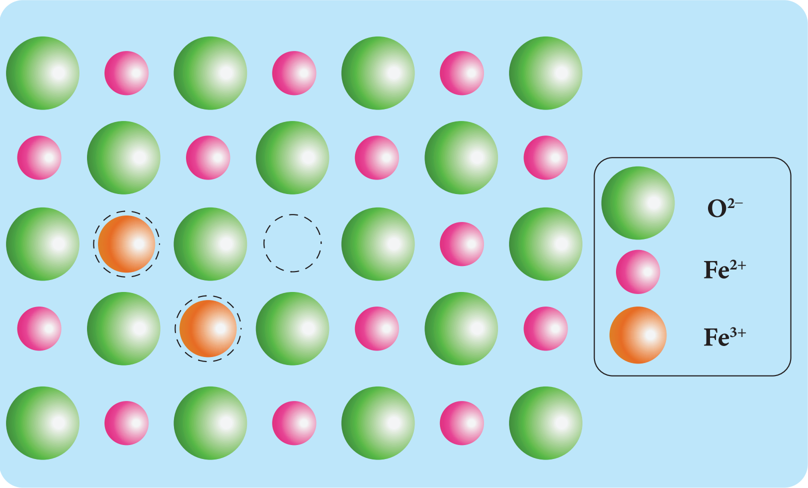
For example, when NaCl crystals are heated in the presence of sodium vapour, Na^+ ions are formed and are deposited on the surface of the crystal. Chloride ions (Cl^-) diffuse to the surface from the lattice point and combines with Na^+ ion. The electron lost by the sodium vapour diffuse into the crystal lattice and occupies the vacancy created by the Cl^- ions. Such anionic vacancies which are occupied by unpaired electrons are called F centers. Hence, the formula of NaCl which contains excess Na^+ ions can be written as $Na_{1+x}Cl$.

ZnO is colourless at room temperature. When it is heated, it becomes yellow in colour. On heating, it loses oxygen and thereby forming free Zn^{2+} ions. The excess Zn^{2+} ions move to interstitial sites and the electrons also occupy the interstitial positions.

6.7.4 Metal deficiency defect:

Metal deficiency defect arises due to the presence of less number of cations than the anions. This defect is observed in a crystal in which, the cations have variable oxidation states.

For example, in FeO crystal, some of the Fe^{2+} ions are missing from the crystal lattice. To maintain the electrical neutrality, twice the number of other Fe^{2+} ions in the crystal is oxidized to Fe^{3+} ions. In such cases, overall number of Fe^{2+} and Fe^{3+} ions is less than the O^{2-} ions. It was experimentally found that the general formula of ferrous oxide is Fe_xO, where x ranges from 0.93 to 0.98.



Metal Deficiency Defect

6.7.5 Impurity defect:

A general method of introducing defects in ionic solids is by adding impurity ions. If the impurity ions are in different valance state from that of host, vacancies are created in the crystal lattice of the host. For example, addition of $CdCl_2$ to silver chloride yields solid solutions where the divalent cation Cd^{2+} occupies the position of Ag^+. This will disturb the electrical neutrality of the crystal. In order to maintain the same, proportional number of Ag^+ ions leaves the lattice. This produces a cation vacancy in the lattice, such kind of crystal defects are called impurity defects.

DO YOU KNOW?

Energy harvesting by piezoelectric crystals:

Piezoelectricity (also called the piezoelectric effect) is the appearance of an electrical potential across the sides of a crystal when you subject it to mechanical stress. The word piezoelectricity means electricity resulting from pressure and latent heat. Even the inverse is possible which is known as inverse piezoelectric effect.

If you can make a little amount of electricity by pressing one piezoelectric crystal once, could youmake a significant amount by pressing many crystals over and over again? What happens if we bury piezoelectric crystals under streets to capture energy as vehicles pass by?

This idea, known as energy harvesting, has caught many people's interest. Even though there are limitations for the large-scale applications, you can produce electricity that is enough to charge your mobile phones by just walking. There are power generating footwears that has a slip-on insole with piezoelectric crystals that can produce enough electricity to charge batteries/ USB devices.`

Summary

- Solids have definite volume and shape.
- solids can be classified into the following two major types based on the arrangement of their constituents. (i) Crystalline solids (ii)Amorphous solids.
- A crystalline solid is one in which its constituents (atoms, ions or molecules), have an orderly arrangement extending over a long range.
- In contrast, in amorphous solids (In Greek, amorphous means no form) the constituents are randomly arranged.
- Crystalline solid is characterised by a definite orientation of atoms, ions or molecules, relative to one another in a three dimensional pattern. The regular arrangement of these species throughout the crystal is called a crystal lattice.
- A crystal may be considered to consist of large number of unit cells, each one in direct contact with its nearer neighbour and all similarly oriented in space.
- A unit cell is characterised by the three edge lengths or lattice constants a ,b and c and the angle between the edges α, β and γ
- There are seven primitive crystal systems; cubic, tetragonal, orthorhombic, hexagonal, monoclinic, triclinic and rhombohedral. They differ in the arrangement of their crystallographic axes and angles. Corresponding to the above seven, Bravis defined 14 possible crystal systems
- In the simple cubic unit cell, each corner is occupied by an identical atoms or ions or molecules. And they touch along the edges of the cube, do not touch diagonally. The coordination number of each atom is 6.
- In a body centered cubic unit cell, each corner is occupied by an identical particle and in addition to that one atom occupies the body centre. Those atoms which occupy the corners do not touch each other, however they all touch the one that occupies the body centre. Hence, each atom is surrounded by eight nearest neighbours and coordination number is 8.
- In a face centered cubic unit cell, identical atoms lie at each corner as well as in the centre of each face. Those atoms in the corners touch those in the faces but

not each other.The coordination number is 2.

- X-Ray diffraction analysis is the most powerful tool for the determination of crystal structure. The inter planar distance (d) between two successive planes of atoms can be calculated using the following equation form the X-Ray diffraction data $2d\sin\theta = n\lambda$
- The structure of an ionic compound depends upon the stoichiometry and the size of the ions.generally in ionic crystals the bigger anions are present in the close packed arrangements and the cations occupy the voids. The ratio of radius of cation and anion $\left(\frac{r_{C^+}}{r_{A^-}}\right)$ plays an important role in determining the structure
- Crystals always found to have some defects in the arrangement of their constituent particles.
- Schottky defect arises due to the missing of equal number of cations and anions from the crystal lattice.
- Frenkel defect arises due to the dislocation of ions from its crystal lattice. The ion which is missing from the lattice point occupies an interstitial position.
- Metal excess defect arises due to the presence of more number of metal ions as compared to anions.
- Metal deficiency defect arises due to the presence of less number of cations than the anions.

EVALUATION

JN28IA

Choose the best answer:

1. Graphite and diamond are

   a) Covalent and molecular crystals b) ionic and covalent crystals

   c) both covalent crystals d) both molecular crystals

2. An ionic compound A_xB_y crystallizes in fcc type crystal structure with B ions at the centre of each face and A ion occupying entre of the cube. the correct formula of AxBy is

   a) AB b) AB_3

   c) A_3B d) A_8B_6

3. The ratio of close packed atoms to tetrahedral hole in cubic packing is

   a) 1:1 b) 1:2

   c) 2:1 d) 1:4

4. Solid CO_2 is an example of

   a) Covalent solid b) metallic solid

   c) molecular solid d) ionic solid

5. Assertion : monoclinic sulphur is an example of monoclinic crystal system

   Reason: for a monoclinic system, $a \neq b \neq c$ and $\alpha = \gamma = 90^0, \beta \neq 90^0$

   a) Both assertion and reason are true and reason is the correct explanation of assertion.

   b) Both assertion and reason are true but reason is not the correct explanation of assertion.

   c) Assertion is true but reason is false.

   d) Both assertion and reason are false.

6. In calcium fluoride, having the flurite structure the coordination number of Ca^{2+} ion and F^- Ion are (NEET)

   a) 4 and 2 b) 6 and 6

   c) 8 and 4 d) 4 and 8

7. The number of unit cells in 8 gm of an element X (atomic mass 40) which crystallizes in bcc pattern is (N_A is the Avogadro number)

   a) $6.023 \text{ X } 10^{23}$ b) $6.023 \text{ X } 10^{22}$

   c) $60.23 \text{ X } 10^{23}$ d) $\left(\frac{6.023 \times 10^{23}}{8 \times 40}\right)$

8. The number of carbon atoms per unit cell of diamond is

   a) 8 b) 6 c) 1 d) 4

9. In a solid atom M occupies ccp lattice and $\left(\frac{1}{3}\right)$ of tetrahedral voids are occupied by atom N. find the formula of solid formed by M and N.

   a) MN b) M_3N c) MN_3 d) M_3N_2

10. The composition of a sample of wurtzite is $Fe_{0.93}O_{1.00}$ what % of Iron present in the form of Fe^{3+}?

    a) 16.05% b) 15.05% c) 18.05% d) 17.05%

11. The ionic radii of A^+ and B^- are 0.98×10^{-10} m and 1.81×10^{-10} m . the coordination number of each ion in AB is

    a) 8 b) 2 c) 6 d) 4

12. CsCl has bcc arrangement, its unit cell edge length is 400pm, its inter atomic distance is

    a) 400pm b) 800pm c) $\sqrt{3} \times 100$pm d) $\left(\frac{\sqrt{3}}{2}\right) \times 400$pm

13. A solid compound XY has NaCl structure. if the radius of the cation is 100pm , the radius of the anion will be

a) $\left(\frac{100}{0.414}\right)$ b) $\left(\frac{0.732}{100}\right)$ c) 100×0.414 d) $\left(\frac{0.414}{100}\right)$

14. The vacant space in bcc lattice unit cell is

a) 48%   b) 23%   c) 32%   d) 26%

15. The radius of an atom is 300pm, if it crystallizes in a face centered cubic lattice, the length oif the edge of the unit cell is

a) 488.5pm   b) 848.5pm   c) 884.5pm   d) 484.5pm

16. The fraction of total volume occupied by the atoms in a simple cubic is

a) $\left(\frac{\pi}{4\sqrt{2}}\right)$ b) $\left(\frac{\pi}{6}\right)$ c) $\left(\frac{\pi}{4}\right)$ d) $\left(\frac{\pi}{3\sqrt{2}}\right)$

17. The yellow colour in NaCl crystal is due to

a) excitation of electrons in F centers

b) reflection of light from Cl^- ion on the surface

c) refraction of light from Na^+ ion

d) all of the above

18. if 'a' stands for the edge length of the cubic system ; sc , bcc, and fcc. Then the ratio of radii of spheres in these systems will be respectively.

a) $\left(\frac{1}{2}a:\frac{\sqrt{3}}{2}a:\frac{\sqrt{2}}{2}a\right)$ b) $\left(\sqrt{1}a:\sqrt{3}a:\sqrt{2}a\right)$

c) $\left(\frac{1}{2}a:\frac{\sqrt{3}}{4}a:\frac{1}{2\sqrt{2}}a\right)$ d) $\left(\frac{1}{2}a:\sqrt{3}a:\frac{1}{\sqrt{2}}a\right)$

19. If 'a' is the length of the side of the cube, the distance between the body centered atom and one corner atom in the cube will be

a) $\left(\frac{2}{\sqrt{3}}\right)a$ b) $\left(\frac{4}{\sqrt{3}}\right)a$

c) $\left(\frac{\sqrt{3}}{4}\right)a$ d) $\left(\frac{\sqrt{3}}{2}\right)a$

20. Potassium has a bcc structure with nearest neighbor distance 4.52 A^0 . its atomic weight is 39. its density will be

a) 915 kg m^{-3} b) 2142 kg m^{-3} c) 452 kg m^{-3} d) 390 kg m^{-3}

21. Schottky defect in a crystal is observed when

a) unequal number of anions and anions are missing from the lattice

b) equal number of anions and anions are missing from the lattice

c) an ion leaves its normal site and occupies an interstitial site

d) no ion is missing from its lattice.

22. The cation leaves its normal position in the crystal and moves to some interstitial position, the defect in the crystal is known as

a) Schottky defect	b) F center
c) Frenkel defect	d) non-stoichiometric defect

23. Assertion: due to Frenkel defect, density of the crystalline solid decreases.

Reason: in Frenkel defect cation and anion leaves the crystal.

a) Both assertion and reason are true and reason is the correct explanation of assertion.

b) Both assertion and reason are true but reason is not the correct explanation of assertion.

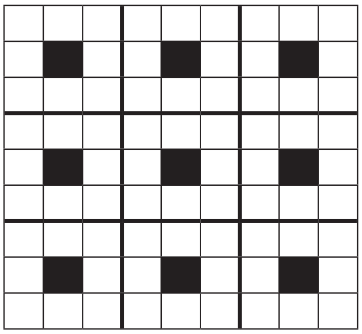
c) Assertion is true but reason is false.

d) Both assertion and reason are false

24. The crystal with a metal deficiency defect is

a) NaCl	b) FeO
c) ZnO	d) KCl

25. A two dimensional solid pattern formed by two different atoms X and Y is shown below. The black and white squares represent atoms X and Y respectively. the simplest formula for the compound based on the unit cell from the pattern is



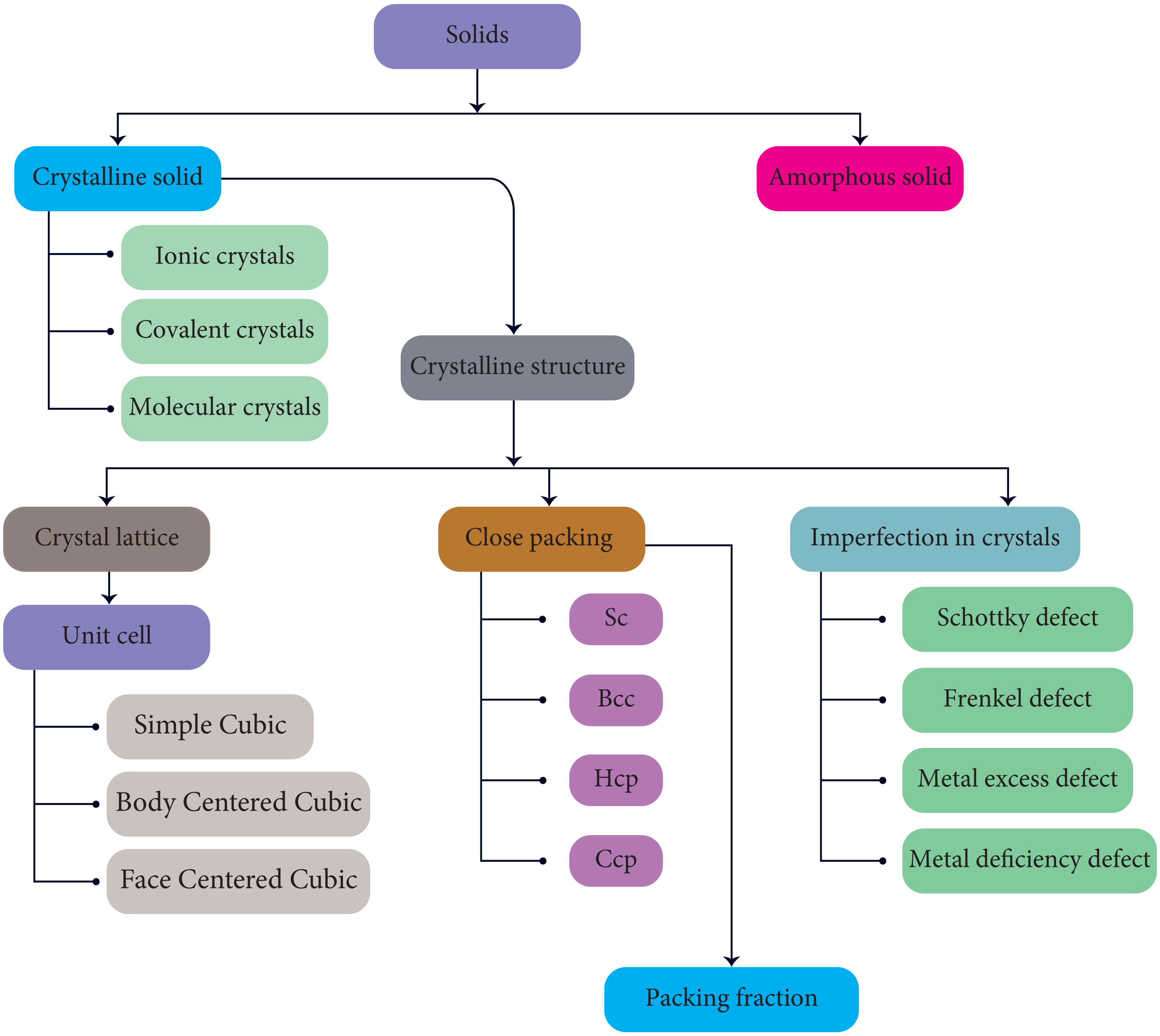
a) XY_8	b) X_4Y_9
c) XY_2	d) XY_4

Answer the following questions:

1. Define unit cell.
2. Give any three characteristics of ionic crystals.
3. Differentiate crystalline solids and amorphous solids.
4. Classify the following solids

a. P_4 b. Brass c. diamond d. NaCl e. Iodine

5. Explain briefly seven types of unit cell.
6. Distinguish between hexagonal close packing and cubic close packing.
7. Distinguish tetrahedral and octahedral voids.
8. What are point defects?
9. Explain Schottky defect.
10. Write short note on metal excess and metal deficiency defect with an example.
11. Calculate the number of atoms in a fcc unit cell.
12. Explain AAAA and ABABA and ABCABC type of three dimensional packing with the help of neat diagram.
13. Why ionic crystals are hard and brittle?
14. Calculate the percentage efficiency of packing in case of body centered cubic crystal.
15. What is the two dimensional coordination number of a molecule in square close packed layer?
16. Experiment shows that Nickel oxide has the formula $Ni_{0.96}O_{1.00}$. What fraction of Nickel exists as of Ni^{2+} and Ni^{3+} ions?
17. What is meant by the term "coordination number"? What is the coordination number of atoms in a bcc structure?
18. An element has bcc structure with a cell edge of 288 pm. the density of the element is 7.2 gcm^{-3}. how many atoms are present in 208g of the element.
19. Aluminium crystallizes in a cubic close packed structure. Its metallic radius is 125pm. calculate the edge length of unit cell.
20. if NaCl is doped with 10^{-2} mol percentage of strontium chloride, what is the concentration of cation vacancy?
21. KF crystallizes in fcc structure like sodium chloride. calculate the distance between K^{+} and F^{-} in KF.(given : density of KF is $2.48\ g\ cm^{-3}$)
22. An atom crystallizes in fcc crystal lattice and has a density of $10\ gcm^{-3}$ with unit cell edge length of 100pm. calculate the number of atoms present in 1 g of crystal.
23. Atoms X and Y form bcc crystalline structure. Atom X is present at the corners of the cube and Y is at the centre of the cube. What is the formula of the compound?
24. Sodium metal crystallizes in bcc structure with the edge length of the unit cell $4.3\times10^{-8}\,cm$. calculate the radius of sodium atom.
25. Write a note on Frenkel defect.


Solids
Crystalline solid
Amorphous solid
Ionic crystals
Covalent crystals
Molecular crystals
Crystalline structure
Crystal lattice
Close packing
Imperfection in crystals
Unit cell
Simple Cubic
Body Centered Cubic
Face Centered Cubic
Sc
Bcc
Hcp
Ccp
Schottky defect
Frenkel defect
Metal excess defect
Metal deficiency defect
Packing fraction

ICT Corner

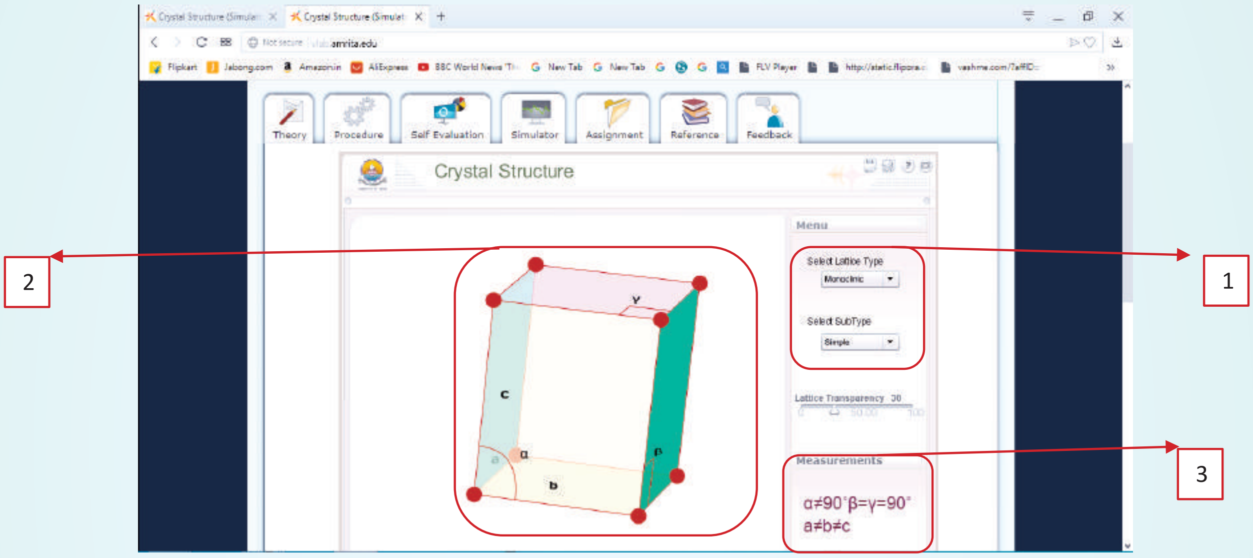
CRYSTAL SYSTEMS

By using this tool, you will be able to visualize different crystal systems and know their unit cell parameters.

Please go to the URL
http://vlab.amrita.edu
(or) Scan the QR code on the right side

Steps

- Open the Browser and type the URL given (or) Scan the QR Code. In the webpage click physical science tab and then click solid state virtual lab. Then go to crystal structure and then click simulator.
  Note: *One time sign up is needed to access this webpage. Login using your username and password. Once logged in click the simulator tab.*
- Now the using the menu (box 1) select any one of the seven crystal systems and the lattice type. Now the unit cell of the selected crystal system will appear on screen (box 2) and the unit cell parameters will also be displayed in the measurement tab (box 3)



Select Lattice Type: Monoclinic

Select SubType: Simple

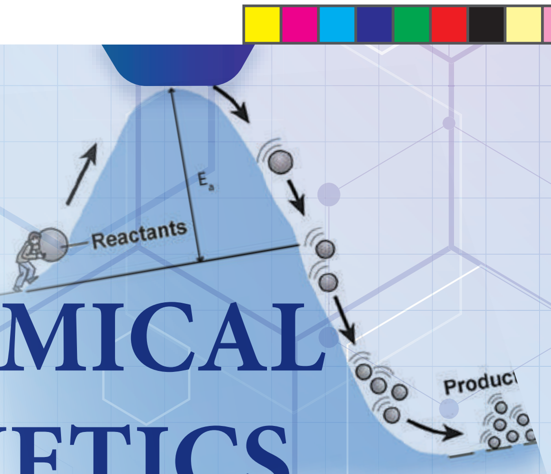
Lattice Transparency 30

$\alpha \neq 90^\circ$ $\beta = \gamma = 90^\circ$
$a \neq b \neq c$

B264_12_CHEMISTRY_EM

UNIT 7

CHEMICAL KINETICS



Svante August Arrhenius
(1859 –1927)

Svante August Arrhenius was a Swedish scientist. Arrhenius was one of the founders of the science of physical chemistry. He focused his attention on the conductivities of electrolytes. He proposed that crystalline salts dissociate into paired charged ions when dissolved in water, for which he received the Nobel Prize for Chemistry in 1903. He also proposed definitions for acids and bases. He formulated the concept of activation energy.

WJN386

Learning Objectives

After studying this unit, the students will be able to

- define the rate and order of a reaction,
- derive the integrated rate equations for zero and first order reactions,
- describe the half life period,
- describe the collision theory,
- discuss the temperature dependence of the rate of a reaction, and
- explain various factors which affect the rate of a reaction.

INTRODUCTION

We have already learnt in XI standard that the feasibility of a chemical reaction under a given set of conditions can be predicted, using the principles of thermodynamics. However, thermodynamics does not provide an answer to a very important question of how fast a chemical reaction takes place. We know from our practical experience that all chemical reactions take some time for completion. Reaction speeds ranging from extremely fast (in femto seconds) to extremely slow (in years). For example, when the reactants $BaCl_2$ solution and dilute H_2SO_4 are just mixed, a white precipitate of $BaSO_4$ is immediately formed; on the other hand reactions such as rusting of Iron take many years to complete. The answers to the questions such as (i) how fast a chemical change can occur and (ii) What happens in a chemical reaction during the period between the initial stage and final stage are provided by the chemical kinetics. The word kinetics is derived from the Greek word "kinesis" meaning movement.

Chemical kinetics is the study of the rate and the mechanism of chemical reactions, proceeding under given conditions of temperature, pressure, concentration etc.

The study of chemical kinetics not only help us to determine the rate of a chemical reaction, but also useful in optimizing the process conditions of industrial manufacturing processes, organic and inorganic synthesis etc.

In this unit, we discuss the rate of a chemical reaction and the factors affecting it. We also discuss the theories of the reaction rate and temperature dependence of a chemical reaction.

7.1 Rate of a chemical reaction:

A rate is a change in a particular variable per unit time. You have already learnt in physics that change in the displacement of a particle per unit time gives its velocity. Similarly in a chemical reaction, the change in the concentration of the species involved in a chemical reaction per unit time gives the rate of a reaction.

Let us consider a simple general reaction

$$A \longrightarrow B$$

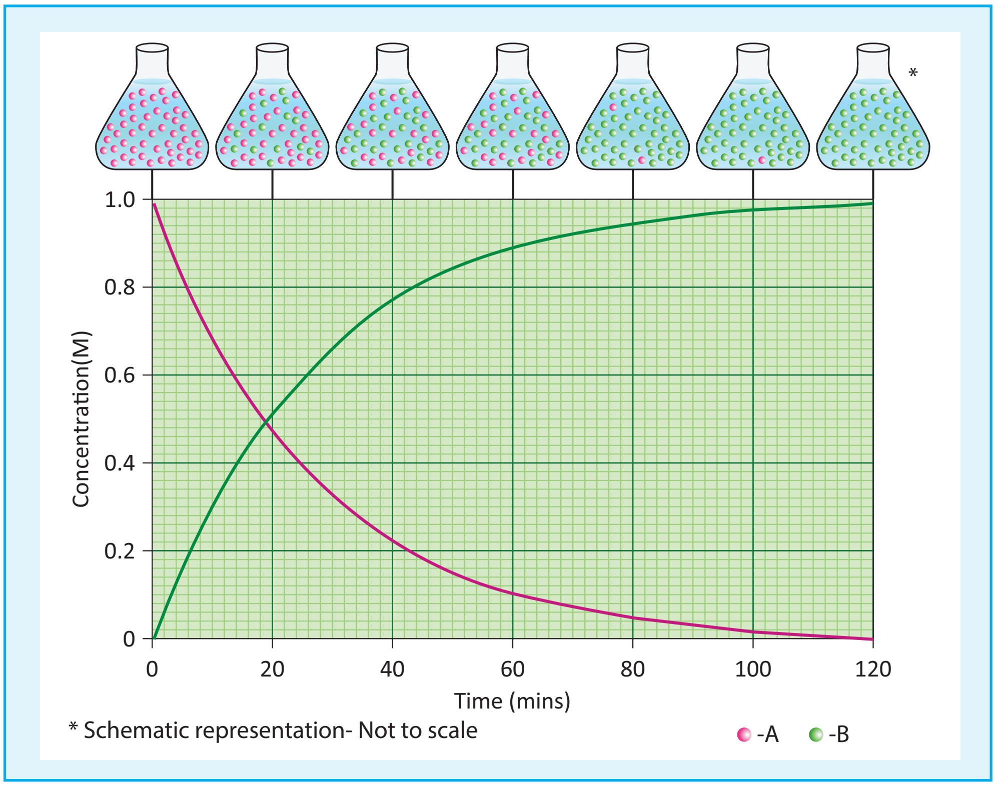
The concentration of the reactant ([A]) can be measured at different time intervals. Let the concentration of A at two different times t_2 and t_2 , (t_2>t_1) be [A_1] and [A_2] respectively. The rate of the reaction can be expressed as

$$\text{Rate} = \frac{-\,[\text{Change in the concentration of the reactants}]}{(\text{Change in time})}$$

$$\text{i.e., Rate} = \frac{-([A_2]-[A_1])}{(t_2-t_1)} = -\left(\frac{\Delta[A]}{\Delta t}\right) \quad ...(7.1)$$

During the reaction, the concentration of the reactant decreases i.e. $[A_2]<[A_1]$ and hence the change in concentration $[A_2]-[A_1]$ gives a negative value. By convention the reaction rate is a positive one and hence a negative sign is introduced in the rate expression (equation 7.1)

If the reaction is followed by measuring the product concentration, the rate is given by $\left(\frac{\Delta[B]}{\Delta t}\right)$ since $[B_2]>[B_1]$, no minus sign is required here.



* Schematic representation- Not to scale

Fig 7.1 change in concentration of A and B for the reaction $A \longrightarrow B$

Unit of rate of a reaction:

$$\text{unit of rate} = \frac{\text{unit of concentration}}{\text{unit of time}}$$

Usually, concentration is expressed in number of moles per litre and time is expressed in seconds and therefore the unit of the rate of a reaction is $\text{mol L}^{-1}\text{s}^{-1}$. Depending upon the nature of the reaction, minute, hour, year etc can also be used.

For a gas phase reaction, the concentration of the gaseous species is usually expressed in terms of their partial pressures and in such cases the unit of reaction rate is atm s^{-1}.

7.1.1 Stoichiometry and rate of a reaction:

In a reaction $A \longrightarrow B$, the stoichiometry of both reactant and product are same, and hence the rate of disappearance of reactant (A) and the rate of appearance of product (B) are same.

Now, let us consider a different reaction

$$A \longrightarrow 2B$$

In this case, for every mole of A, that disappears two moles of B appear, i.e., the rate of formation of B is twice as fast as the rate of disappearance of A. therefore, the rate of the reaction can be expressed as below

$$\text{Rate} = \frac{+\,d[B]}{dt} = 2\left(\frac{-d[A]}{dt}\right)$$

In other words,

$$\text{Rate} = \frac{-d[A]}{dt} = \frac{1}{2}\frac{d[B]}{dt}$$

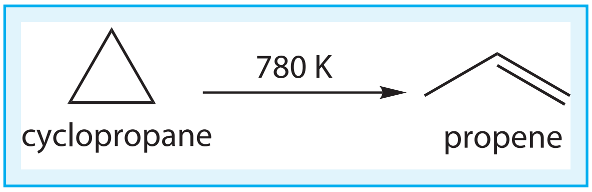
For a general reaction, the rate of the reaction is equal to the rate of consumption of a reactant (or formation of a product) divided by its coefficient in the balanced equation

$$xA + yB \longrightarrow lC + mD$$

$$\text{Rate} = \frac{-1}{x}\frac{d[A]}{dt} = \frac{-1}{y}\frac{d[B]}{dt} = \frac{1}{l}\frac{d[C]}{dt} = \frac{1}{m}\frac{d[D]}{dt}$$

7.1.2 Average and instantaneous rate:

Let us understand the average rate and instantaneous rate by considering the isomerisation of cyclopropane.



The kinetics of the above reaction is followed by measuring the concentration of cyclopropane at regular intervals and the observations are shown below. (Table 7.1)

Table 7.1 Concentration of cyclopropane at various times during its isomerisation at 780K

Time (min)	[cyclopropane] (mol L^{-1})
0	2.00
5	1.67
10	1.40
15	1.17
20	0.98
25	0.82
30	0.69

$$\text{Rate of the reaction} = \frac{-\Delta\,[\text{cyclopropane}]}{\Delta t}$$

$$\text{The rate over the entire 30 min} = \frac{-(0.69-2)\ \text{molL}^{-1}}{(30-0)\ \text{min}}$$

$$= \frac{1.31}{30} = 4.36 \times 10^{-2}\ \text{molL}^{-1}\text{min}^{-1}$$

It means that during the first 30 minutes of the reaction, the concentration of the reactant (cyclo propane) decreases as an average of 4.36 × 10^{-2} mol L^{-1}each minute.

Let us calculate the average rate for an initial and later stage over a short period.

$$(\text{Rate})_{\substack{\text{initial}\\ \text{stage}}} = \frac{-(2.0-1.4\,)}{(10-0)}$$

$$= \frac{0.6}{10} = 6 \text{ x } 10^{-2}\ \text{mol L}^{-1}\ \text{min}^{-1}$$

$$(\text{Rate})_{\substack{\text{later}\\ \text{stage}}} = \frac{-(\,0.69 - 0.98)}{(30\text{-}20)}$$

$$= \frac{0.29}{10} = 2.9 \text{ x } 10^{-2}\ \text{mol L}^{-1}\text{min}^{-1}$$

From the above calculations, we come to know that the rate decreases with time as the reaction proceeds and the average rate cannot be used to predict the rate of the reaction at any instant. The rate of the reaction, at a particular instant during the reaction is called the instantaneous rate. The shorter the time period, we choose, the closer we approach to the instantaneous rate,

As $\Delta t \rightarrow 0$;

$$\frac{-\Delta[\text{cyclopropane}]}{\Delta t} = \frac{-d[\text{cyclopropane}]}{dt}$$

A plot of [cyclopropane] Vs (time) gives a curve as shown in the figure 7.2.

Instantaneous rate at a particular instant 't ' $\frac{-d\,[\text{cyclopropane}]}{dt}$ is obtained by calculating the slope of a tangent drawn to the curve at that instant.

In general, the instantaneous reaction rate at a moment of mixing the reactants is calculated from the slope of the tangent drawn to the curve at mol L^{-1}, the rate calculated by this method is called initial rate of a reaction.

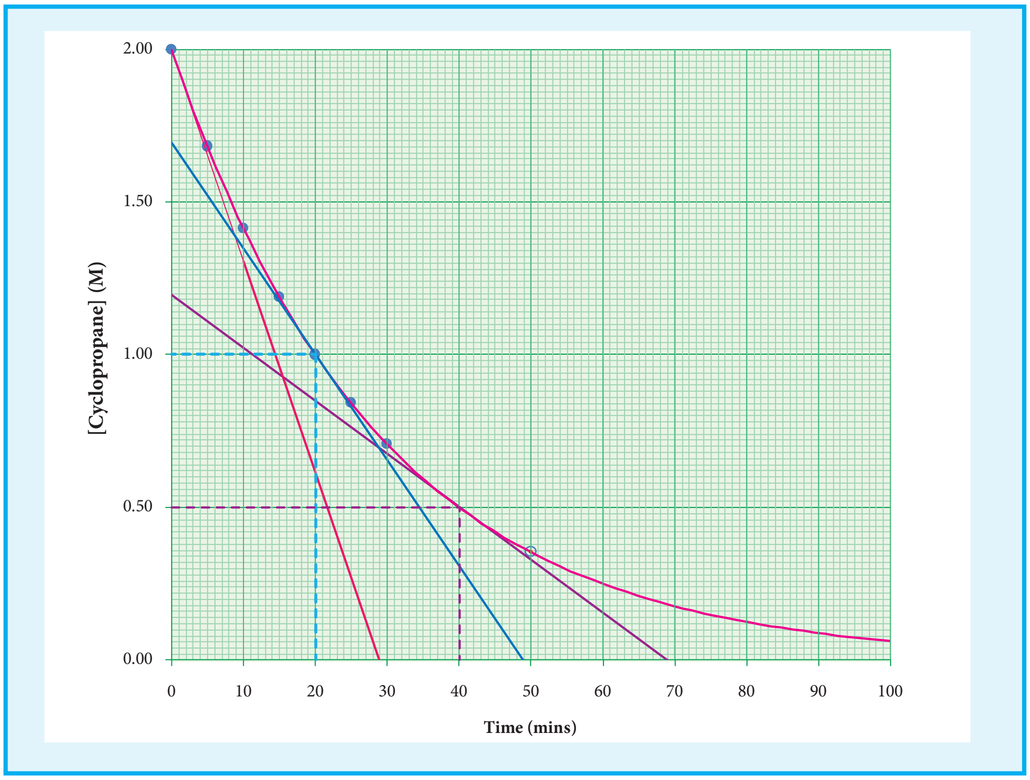


Fig 7.2 Concentration of cyclopropane vs time - graph

Let us calculate the instantaneous rate of isomerisation cyclopropane at different concentrations: 2 M, 1M and 0.5 M from the graph shown in fig 7.2, the results obtained are tabulated below.

[cyclopropane] mol L^{-1}	Rate mol $L^{-1}min^{-1}$
2	6.92×10^{-2}
1	3.46×10^{-2}
0.5	1.73×10^{-2}

Table 7.2 Rate of isomerisation

7.3 Rate law and rate constant:

We have just learnt that, the rate of the reaction depends upon the concentration of the reactant. Now let us understand how the reaction rate is related to concentration by considering the following general reaction.

$$xA + yB \longrightarrow \text{products}$$

The rate law for the above reaction is generally expressed as

Rate = k $[A]^m[B]^n$

Where k is proportionality constant called the rate constant. The values of m and n represent the reaction order with respect to A and B respectively. The overall order of the reaction is given by (m+n). The values of the exponents (m and n) in the rate law must be determined by experiment. They cannot be deduced from the Stoichiometry of the reaction. For example, consider the isomerisation of cyclopropane, that we discussed earlier.

The results shown in table 7.2 indicate that if the concentration of cyclopropane is reduced to half, the rate also reduced to half. It means that the rate depends upon [cyclopropane] raised to the first power

i.e., Rate = k$[\text{cyclopropane}]^1$

$$\Rightarrow \frac{\text{Rate}}{[\text{cyclopropane}]} = k$$

Table 7.3 Rate constant for isomerisation

Rate mol $L^{-1}min^{-1}$	[cyclopropane] mol L^{-1}	$k = \frac{\text{Rate}}{[\text{cyclopropane}]}$
6.92×10^{-2}	2	3.46×10^{-2}
3.46×10^{-2}	1	3.46×10^{-2}
1.73×10^{-2}	0.5	3.46×10^{-2}

Let us consider an another example, the oxidation of nitric oxide (NO)

$$2NO(g) + O_2(g) \longrightarrow 2NO_2\ (g)$$

Series of experiments are conducted by keeping the concentration of one of the reactants constant and the changing the concentration of the others.

Experiment	[NO] X 10^{-2} (mol L^{-1})	[O_2] X 10^{-2} (mol L^{-1})	Initial rate x 10^{-2} (mol $L^{-1}min^{-1}$)
1	1.3	1.1	19.26
2	1.3	2.2	38.40
3	2.6	1.1	76.80

$$Rate = k\ [NO]^m[O_2]^n$$

For experiment 1, the rate law is

$$Rate_1 = k\ [NO]^m[O_2]^n$$

$$19.26\ X10^{-2} = k\ [1.3]^m[1.1]^n \quad ...(1)$$

Similarly for experiment 2

$$Rate_2 = k\ [NO]^m[O_2]^n$$

$$38.40\ X10^{-2} = k\ [1.3]^m[2.2]^n \quad ...(2)$$

For experiment 3

$$Rate_3 = k\ [NO]^m[O_2]^n$$

$$76.8 \times 10^{-2} = k\ [2.6]^m[1.1]^n \quad ...(3)$$

$$\frac{(2)}{(1)} \Rightarrow \frac{38.40 \text{ x } 10^{-2}}{19.26 \text{ x } 10^{-2}} = \frac{k\ [1.3]^m[2.2]^n}{k\ [1.3]^m[1.1]^n}$$

$$2 = \left(\frac{2.2}{1.1}\right)^n$$

$2=2^n$ i.e., n=1

Therefore the reaction is first order with respect to O_2

$$\frac{(3)}{(1)} \Rightarrow \frac{76.8 \text{ x } 10^{-2}}{19.26 \text{ x } 10^{-2}} = \frac{k\ [2.6]^m[1.1]^n}{k\ [1.3]^m[1.1]^n}$$

$$4 = \left(\frac{2.6}{1.3}\right)^m$$

$4=2^m$ i.e., m=2

Therefore the reaction is second order with respect to NO

The rate law is $Rate_1 = k\ [NO]^2[O_2]^1$

The overall order of the reaction = (2 + 1) = 3

Differences between rate and rate constant of a reaction:

S.no	Rate of a reaction	Rate constant of a reaction
1	It represents the speed at which the reactants are converted into products at any instant.	It is a proportionality constant

s.no	Rate of a reaction	Rate constant of a reaction
2	It is measured as decrease in the concentration of the reactants or increase in the concentration of products.	It is equal to the rate of reaction, when the concentration of each of the reactants in unity
3	It depends on the initial concentration of reactants.	It does not depend on the initial concentration of reactants.

7.4 Molecularity:

Kinetic studies involve not only measurement of a rate of reaction but also proposal of a reasonable reaction mechanism. Each and every single step in a reaction mechanism is called an elementary reaction.

An elementary step is characterized by its molecularity. The total number of reactant species that are involved in an elementary step is called molecularity of that particular step. Let us recall the hydrolysis of t-butyl bromide studied in XI standard. Since the rate determining elementary step involves only t-butyl bromide, the reaction is called a Unimolecular Nucleophilic substitution $(S_N{}^1)$ reaction.

Let us understand the elementary reactions by considering another reaction, the decomposition of hydrogen peroxide catalysed by I^-.

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

It is experimentally found that the reaction is first order with respect to both H_2O_2 and I^-, which indicates that I^- is also involved in the reaction. The mechanism involves the following steps.

Step:1

$$H_2O_2(aq) + I^-(aq) \longrightarrow H_2O(l) + OI^-(aq)$$

Step : 2

$$H_2O_2(aq) + OI^-(aq) \rightarrow H_2O(l) + I^-(aq) + O_2(g)$$

Overall reaction is

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

These two reactions are elementary reactions. Adding equ (1) and (2) gives the overall reaction. Step 1 is the rate determining step, since it involves both H_2O_2 and I^-, the overall reaction is bimolecular.

Differences between order and molecularity:

s.no	Order of a reaction	Molecularity of a reaction
1	It is the sum of the powers of concentration terms involved in the experimentally determined rate law.	It is the total number of reactant species that are involved in an elementary step.
2	It can be zero (or) fractional (or) integer	It is always a whole number, cannot be zero or a fractional number.
3	It is assigned for a overall reaction.	It is assigned for each elementary step of mechanism.

Example 1

Consider the oxidation of nitric oxide to form NO_2

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

(a). Express the rate of the reaction in terms of changes in the concentration of NO, O_2 and NO_2.

(b). At a particular instant, when $[O_2]$ is decreasing at 0.2 mol $L^{-1}s^{-1}$ at what rate is $[NO_2]$ increasing at that instant?

Solution:

a) $\text{Rate} = \frac{-1}{2}\frac{d[NO]}{dt} = \frac{-d[O_2]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt}$

b) $\frac{-d[O_2]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt}$

$$\frac{d[NO_2]}{dt} = 2x\left(\frac{-d[O_2]}{dt}\right) = 2\ x0.2\ \text{mol}\ L^{-1}s^{-1}$$

$$= 0.4\ \text{mol}\ L^{-1}s^{-1}$$

Evaluate yourself 1

1). Write the rate expression for the following reactions, assuming them as elementary reactions.

i) $3A + 5B_2 \longrightarrow 4CD$

ii) $X_2 + Y_2 \longrightarrow 2XY$

2). Consider the decomposition of $N_2O_5(g)$ to form $NO_2(g)$ and $O_2(g)$. At a particular instant N_2O_5 disappears at a rate of 2.5×10^{-2} mol $dm^{-3}s^{-1}$ At what rates are NO_2 and O_2 formed? What is the rate of the reaction?

Example 2

1. What is the order with respect to each of the reactant and overall order of the following reactions?

(a). $5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq)$ $\longrightarrow 3Br_2(l) + 3H_2O(l)$

The experimental rate law is

$\text{Rate} = k\,[Br^-][BrO_3^-][H^+]^2$

(b). $CH_3CHO(g) \xrightarrow{\Delta} CH_4(g) + CO(g)$

the experimental rate law is

$\text{Rate} = k\,[CH_3CHO]^{\frac{3}{2}}$

Solution:

a) First order with respect to Br^-, first order with respect to BrO_3^- and second order with respect to H^+. Hence the overall order of the reaction is equal to $1 + 1 + 2 = 4$

b) Order of the reaction with respect to acetaldehyde is $\frac{3}{2}$ and overall order is also $\frac{3}{2}$

Example 3

2. The rate of the reaction $x + 2y \rightarrow$ product is 4×10^{-3} mol $L^{-1}s^{-1}$, if [x]=[y]=0.2 M and rate constant at 400K is $2 \times 10^{-2} s^{-1}$, What is the overall order of the reaction.

Solution :

$\text{Rate} = k\,[x]^n[y]^m$

$$4 \times 10^{-3}\ \text{mol}\ L^{-1}s^{-1} = 2 \times 10^{-2}\ s^{-1}(0.2\text{mol}\ L^{-1})^n(0.2\text{mol}\ L^{-1})^m$$

$$\frac{4 \times 10^{-3}\ \text{mol}\ L^{-1}s^{-1}}{2 \times 10^{-2}\ s^{-1}} = (0.2)^{n+m}\left(\text{mol}\ L^{-1}\right)^{n+m}$$

$$0.2\left(\text{mol}\ L^{-1}\right) = (0.2)^{n+m}\left(\text{mol}\ L^{-1}\right)^{n+m}$$

Comparing the powers on both sides

The overall order of the reaction $n + m = 1$

Evaluate yourself 2

1). For a reaction, $X + Y \longrightarrow$ product ; quadrupling [x] , increases the rate by a factor of 8. Quadrupling both [x] and [y], increases the rate by a factor of 16. Find the order of the reaction with respect to x and y. what is the overall order of the reaction?

2). Find the individual and overall order of the following reaction using the given data.

$$2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$$

Experiment number	Initial concentration		Initial rate
	NO		NOCl mol $L^{-1}s^{-1}$
1	0.1	0.1	7.8×10^{-5}
2	0.2	0.1	3.12×10^{-4}
3	0.2	0.3	9.36×10^{-4}

7.5 The integrated rate equation:

We have just learnt that the rate of change of concentration of the reactant is directly proportional to that of concentration of the reactant. For a general reaction,

$$A \longrightarrow \text{product}$$

The rate law is

$$\text{Rate} = \frac{-d[A]}{dt} = k\,[A]^x$$

Where k is the rate constant, and x is the order of the reaction. The above equation is a differential equation, $\frac{-d[A]}{dt}$, so it gives the rate at any instant. However, using the above expression, we cannot answer questions such as how long will it take for a specific concentration of A to be used up in the reaction? What will be the concentration of reactant after a time ' t '?. To answer such questions, we need the integrated form of the above rate law which contains time as a variable.

7.5.1 Integrated rate law for a first order reaction

A reaction whose rate depends on the reactant concentration raised to the first power is called a first order reaction. Let us consider the following Cl_2 first order reaction,

$$A \longrightarrow \text{product}$$

Rate law can be expressed as

$$\text{Rate} = k\,[A]^1$$

Where, k is the first order rate constant.

$$\frac{-d[A]}{dt} = k\,[A]^1$$

$$\Rightarrow \frac{-d[A]}{[A]} = k\,dt \qquad ...(1)$$

Integrate the above equation between the limits of time t = 0 and time equal to t, while the concentration varies from the initial concentration $[A_0]$ to [A] at the later time.

$$\int_{[A_0]}^{[A]} \frac{-d[A]}{[A]} = k\int_0^t dt$$

$$\left(-\ln[A]\right)_{[A_0]}^{[A]} = k\left(t\right)_0^t$$

$$-\ln[A] - \left(-\ln[A_0]\right) = k\,(t-0)$$

$$-\ln[A] + \ln[A_0] = kt$$

$$\ln\left(\frac{[A_0]}{[A]}\right) = kt \qquad ...(2)$$

This equation is in natural logarithm. To convert it into usual logarithm with base 10, we have to multiply the term by 2.303.

$$2.303\log\left(\frac{[A_0]}{[A]}\right) = kt$$

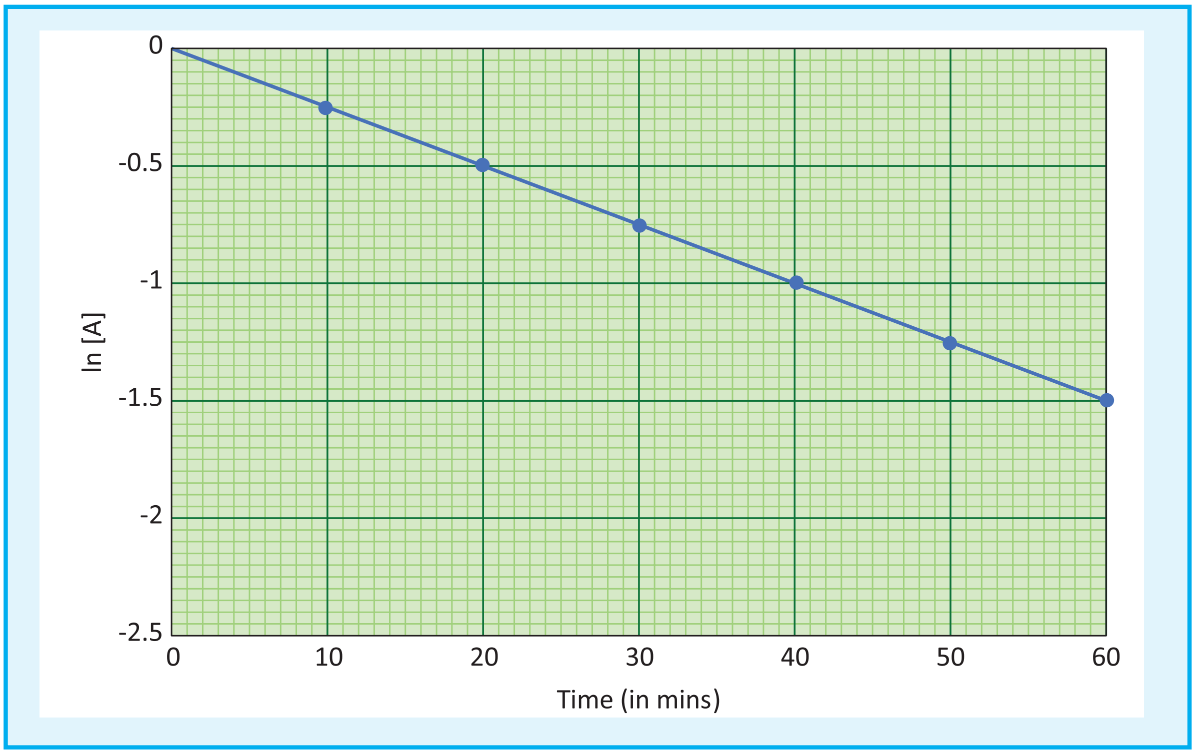


Fig: 7.3 A plot of ln[A] Vs t for a first order reaction, $A \longrightarrow$ product with initial concentration of [A] = 1.00 M and $k = 2.5 \times 10^{-2} \text{min}^{-1}$.

$$k = \frac{2.303}{t} \log\left(\frac{[A_0]}{[A]}\right) \text{ ------ (3)}$$

Equation (2) can be written in the form $y = mx + c$ as below

$\ln[A_0] - \ln[A] = kt$

$\ln[A] = \ln[A_0] - kt$

$\Rightarrow y = c + mx$

If we follow the reaction by measuring the concentration of the reactants at regular time interval't', a plot of ln[A] against 't' yields a straight line with a negative slope.From this, the rate constant is calculated.

Examples for the first order reaction

(i) Decomposition of dinitrogen pentoxide

$$N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$$

(ii) Decomposition of thionylchloride; $SO_2Cl_2(l) \longrightarrow SO_2(g) + Cl_2(g)$

(iii) Decomposition of the H_2O_2 in aqueous solution; $H_2O_2(aq) \longrightarrow H_2O(l) + \frac{1}{2}O_2(g)$

(iv) Isomerisation of cyclopropane to propene.

Pseudo first order reaction:

Kinetic study of a higher order reaction is difficult to follow, for example, in a study of a second order reaction involving two different reactants; the simultaneous measurement of change in the concentration of both the reactants is very difficult. To overcome such difficulties, A second order reaction can be altered to a first order reaction by taking one of the reactant in large excess, such reaction is called pseudo first order reaction. Let us consider the acid hydrolysis of an ester,

$$CH_3COOCH_3\ (aq) + H_2O\ (l) \xrightarrow{H^+} CH_3COOH\ (aq) + CH_3OH\ (aq)$$

$$\text{Rate} = k\,[CH_3COOCH_3]\,[H_2O]$$

If the reaction is carried out with the large excess of water, there is no significant change in the concentration of water during hydrolysis. i.e.,concentration of water remains almost a constant.

Now, we can define $k\,[H_2O] = k'$; Therefore the above rate equation becomes

$$\text{Rate} = k'\,[CH_3COOCH_3]$$

Thus it follows first order kinetics.

7.5.2 Integrated rate law for a zero order reaction:

A reaction in which the rate is independent of the concentration of the reactant over a wide range of concentrations is called as zero order reactions. Such reactions are rare. Let us consider the following hypothetical zero order reaction.

$A \longrightarrow \text{product}$

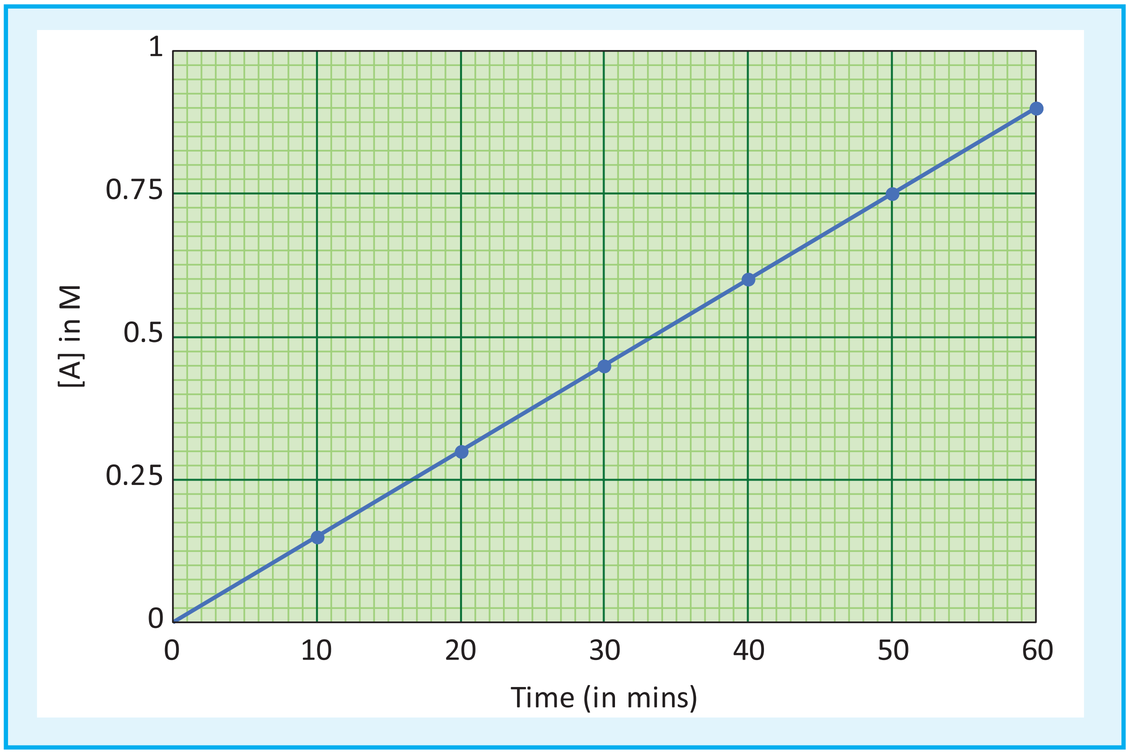


Fig 7.4 : A plot of [A] Vs time for a zero order reaction $A \longrightarrow \text{product}$ with initial concentration of $[A] = 0.5M$ and $k = 1.5\text{x}10^{-2}\,mol^{-1}L^{-1}min^{-1}$

The rate law can be written as,

$$\text{Rate} = k\,[A]^0$$

$$\frac{-d[A]}{dt} = k\,(1) \qquad \left(\therefore [A]^0 = 1\right)$$

$$\Rightarrow \quad -d[A] = k\,dt$$

Integrate the above equation between the limits of $[A_0]$ at zero time and $[A]$ at some later time 't',

$$-\int_{[A_0]}^{[A]} d[A] = k\int_0^t dt$$

$$-\left([A]\right)_{[A_0]}^{[A]} = k\left(t\right)_0^t$$

$$[A_0]-[A] = kt$$

$$k = \frac{[A_0]-[A]}{t}$$

Equation (2) is in the form of a straight line $y = mx + c$

$$\text{Ie., } [A] = -kt + [A_0]$$

$$\Rightarrow y = c + mx$$

A plot of $[A]$ Vs time gives a straight line with a slope of $-k$ and y - intercept of $[A_0]$.

Examples for a zero order reaction:

1. Photochemical reaction between H_2 and I_2

   $$H_2(g)+Cl_2(g) \xrightarrow{h\nu} 2HCl(g)$$

2. Decomposition of N_2O on hot platinum surface

   $$N_2O(g) \rightleftharpoons N_2(g) + \frac{1}{2}O_2(g)$$

3. Iodination of acetone in acid medium is zero order with respect to iodine.

   $$CH_3COCH_3 + I_2 \xrightarrow{H^+} ICH_2COCH_3 + HI$$

   $$\text{Rate} = k\,[CH_3COCH_3]\,[H^+]$$

General rate equation for a nth order reaction involving one reactant [A].

$$A \longrightarrow \text{product}$$

$$\text{Rate law } \frac{-d[A]}{dt} = k[A]^n$$

Consider the case in which $n \neq 1$, integration of above equation between $[A_0]$ and $[A]$ at time $t = 0$ and $t = t$ respectively gives $\dfrac{1}{[A]^{n-1}} - \dfrac{1}{[A_0]^{n-1}} = (n-1)kt$

7.6 Half life period of a reaction:

The half life of a reaction is defined as the time required for the reactant concentration to reach one half its initial value. For a first order reaction, the half life is a constant i.e., it does not depend on the initial concentration.

The rate constant for a first order reaction is given by

$$k = \frac{2.303}{t}\log\frac{[A_0]}{[A]}$$

$$\text{at } t = t_{1/2} \;;\; [A] = [A_0]/2$$

$$k = \frac{2.303}{t_{1/2}}\log\frac{[A_0]}{[A_0]/2}$$

$$k = \frac{2.303}{t_{1/2}}\log 2$$

$$k = \frac{2.303\text{x}0.3010}{t_{1/2}} = \frac{0.6932}{t_{1/2}}$$

$$t_{1/2} = \frac{0.6932}{k}$$

Let us calculate the half life period for a zero order reaction.

Rate constant, $k = \frac{[A_0]-[A]}{t}$

at $t = t_{1/2}$; $[A] = [A_0]/2$

$$k = \frac{[A_0] - [A_0]/2}{t_{1/2}}$$

$$k = \frac{[A_0]}{2t_{1/2}}$$

$$t_{1/2} = \frac{[A_0]}{2k}$$

Hence, in contrast to the half life of a first order reaction, the half life of a zero order reaction is directly proportional to the initial concentration of the reactant.

More to know

Half life for an n^th^ order reaction involving reactant A and $n \neq 1$

$$t_{1/2} = \frac{2^{n-1}-1}{(n-1)k\,[A_0]^{n-1}}$$

Example 4

(i) A first order reaction takes 8 hours for 90% completion. Calculate the time required for 80% completion. (log 5 = 0.6989 ; log10 = 1)

Solution:

For a first order reaction,

$$k = \frac{2.303}{t}\log\left(\frac{[A_0]}{[A]}\right) \qquad ....(1)$$

Let $[A_0] = 100M$

When

$t = t_{90\%}$; $[A]=10M$ (given that $t_{90\,\%}$ =8hours)

$t = t_{80\%}$; $[A]=20M$

$$k = \frac{2.303}{t_{80\%}}\log\left(\frac{100}{20}\right)$$

$$t_{80\%} = \frac{2.303}{k}\log(5) \text{———}(2)$$

Find the value of k using the given data

$$k = \frac{2.303}{t_{90\%}}\log\left(\frac{100}{10}\right)$$

$$k = \frac{2.303}{8\text{ hours}}\log 10$$

$$k = \frac{2.303}{8\text{ hours}}(1)$$

Substitute the value of k in equation (2)

$$t_{80\%} = \frac{2.303}{2.303/8\text{ hours}}\log(5)$$

$$t_{80\%} = 8\text{hours x } 0.6989$$

$$t_{80\%} = 5.59\text{hours}$$

Example 5

(ii) The half life of a first order reaction $x \longrightarrow$ products is $6.932 \text{ x } 10^4$s at 500K . What percentage of x would be decomposed on heating at 500K for 100 min. ($e^{0.06} = 1.06$)

Solution:

Given $t_{1/2} = 0.6932 \text{ x } 10^4\, s$

To solve : when t=100 min,

$$\frac{[A_0]-[A]}{[A_0]} \text{ x } 100 = ?$$

We know that

For a first order reaction, $t_{1/2} = \frac{0.6932}{k}$

$$k = \frac{0.6932}{6.932 \text{ x } 10^4}$$

$$k = 10^{-5}\,s^{-1}$$

$$k = \left(\frac{1}{t}\right) \ln \left(\frac{[A_0]}{[A]}\right)$$

$$10^{-5} s^{-1} \text{ x } 100 \text{ x } 60 \text{ s} = \ln \left(\frac{[A_0]}{[A]}\right)$$

$$0.06 = \ln \left(\frac{[A_0]}{[A]}\right)$$

$$\frac{[A_0]}{[A]} = e^{0.06}$$

$$\frac{[A_0]}{[A]} = 1.06$$

$$\therefore \frac{[A_0]-[A]}{[A_0]} \times 100 \%$$

$$= \left(1 - \frac{[A]}{[A_0]}\right) \times 100 \%$$

$$= \left(1 - \frac{1}{1.06}\right) \times 100 \%$$

$$= 5.6 \%$$

Example 6

Show that in case of first order reaction, the time required for 99.9% completion is nearly ten times the time required for half completion of the reaction.

Let

$[A_0] = 100;$

when $t = t_{99.9\%}$; $[A] = (100-99.9) = 0.1$

$$k = \frac{2.303}{t} \log \left(\frac{[A_0]}{[A]}\right)$$

$$t_{99.9\%} = \frac{2.303}{k} \log \left(\frac{100}{0.1}\right)$$

$$t_{99.9\%} = \frac{2.303}{k} \log 1000$$

$$t_{99.9\%} = \frac{2.303}{k} (3)$$

$$t_{99.9\%} = \frac{6.909}{k}$$

$$t_{99.9\%} \simeq 10 \text{ x } \frac{0.69}{k}$$

$$t_{99.9\%} \simeq 10\, t_{1/2}$$

Evaluate yourself:

(1) In a first order reaction $A \longrightarrow products$ 60% of the given sample of A decomposes in 40 min. what is the half life of the reaction?

(2) The rate constant for a first order reaction is $2.3 \text{ X } 10^{-4} s^{-1}$ If the initial concentration of the reactant is 0.01M . What concentration will remain after 1 hour?

(3) Hydrolysis of an ester in an aqueous solution was studied by titrating the liberated carboxylic acid against sodium hydroxide solution. The concentrations of the ester at different time intervals are given below.

Time (min)	0	30	60	90
Ester concentration mol L^{-1}	0.85	0.80	0.754	0.71

Show that, the reaction follows first order kinetics.

7.7 Collision theory :

Collision Theory was proposed independently by Max Trautz in 1916 and William Lewis in 1918. This theory is based on the kinetic theory of gases. According to this theory, chemical reactions occur as a result of collisions between the reacting molecules. Let us understand this theory by considering the following reaction.

$$A_2(g) + B_2(g) \longrightarrow 2AB(g)$$

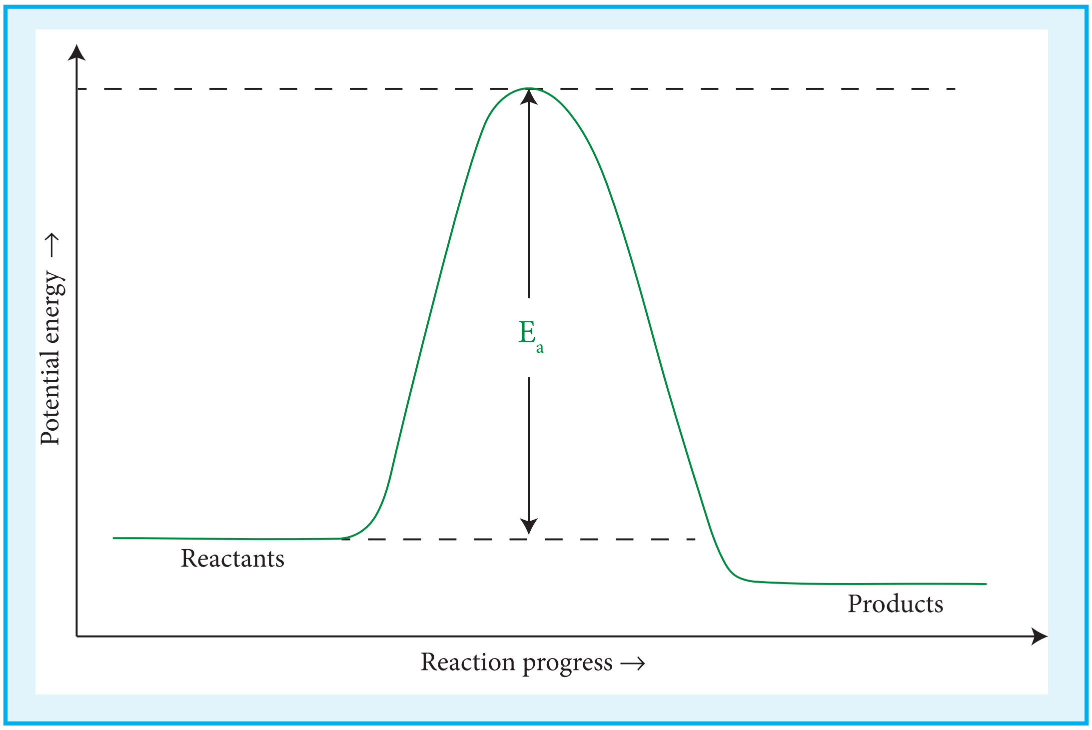


Fig 7.5 progress of the reaction

If we consider that, the reaction between A_2 and B_2 molecules proceeds through collisions between them, then the rate would be proportional to the number of collisions per second.

Rate $\propto$ number of molecules colliding per litre per second (collision rate)

The number of collisions is directly proportional to the concentration of both A_2 and B_2.

$$\text{Collision rate} \propto [A_2][B_2]$$

$$\text{Collision rate} = Z\,[A_2][B_2]$$

Where, Z is a constant.

The collision rate in gases can be calculated from kinetic theory of gases. For a gas at room temperature (298K) and 1 atm pressure, each molecule undergoes approximately 10^9 collisions per second, i.e., 1 collision in 10^{-9} second. Thus, if every collision resulted in reaction, the reaction would be complete in 10^{-9} second. In actual practice this does not happen. It implies that all collisions are not effective to lead to the reaction. In order to react, the colliding molecules must possess a minimum energy called activation energy. The molecules that collide with less energy than activation energy will remain intact and no reaction occurs.

Fraction of effective collisions (f) is given by the following expression

$$f = e^{\frac{-E_a}{RT}}$$

To understand the magnitude of collision factor (f), Let us calculate the collision factor (f) for a reaction having activation energy of $100\ \text{kJ mol}^{-1}$ at 300K.

$$f = e^{-\left(\frac{100\times 10^{3}\ \text{J mol}^{-1}}{8.314\text{J K}^{-1}\ \text{mol}^{-1}\ \times\ 300K}\right)}$$

$$f = e^{-40} \approx 4 \text{ x } 10^{-18}$$

Thus, out of 10^{18} collisions only four collisions are sufficiently energetic to convert reactants to products. This fraction of collisions is further reduced due to

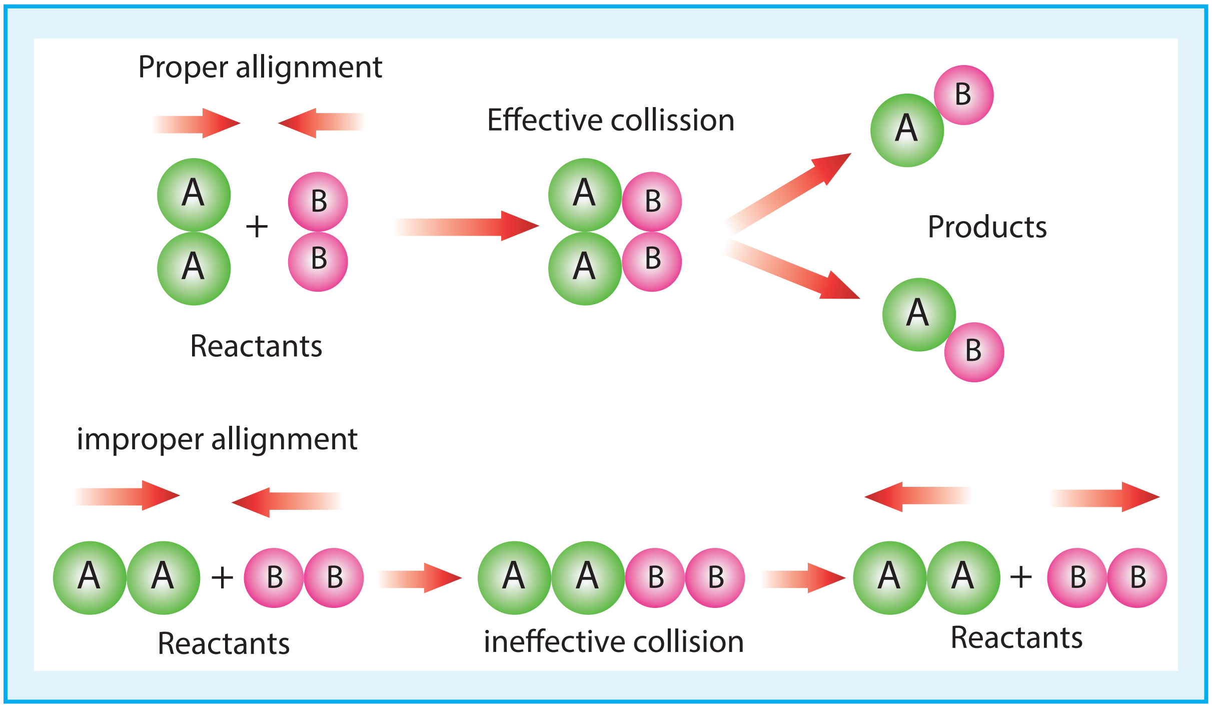


Fig 7.6 - Orientation of reactants - schematic representation

orientation factor i.e., even if the reactant collide with sufficient energy, they will not react unless the orientation of the reactant molecules is suitable for the formation of the transition state.

The figure 7. 6 illustrates the importance of proper alignment of molecules which leads to reaction.

The fraction of effective collisions (f) having proper orientation is given by the steric factor p.

$\Rightarrow$ Rate = p x f x collision rate

i.e., $\text{Rate} = p \text{ x } e^{\frac{-E_a}{RT}} \text{ x } Z\ [A_2][B_2]$ ...(1)

As per the rate law,

$\text{Rate} = k\ [A_2]\ [B_2]$ ...(2)

Where k is the rate constant

On comparing equation (1) and (2), the rate constant k is ‘

$$k = p\,Z\,e^{\frac{-Ea}{RT}}$$

7.8 Arrhenius equation – The effect of temperature on reaction rate

Generally, the rate of a reaction increase with increasing temperature. However, there are very few exceptions. The magnitude of this increase in rate is different for different reactions. As a rough rule, for many reactions near room temperature, reaction rate tends to double when the temperature is increased by 10^0C .

Activity

Let us understand the effect of temperature on reaction rate by doing this activity.

i. Take two test tubes, label them as A and B

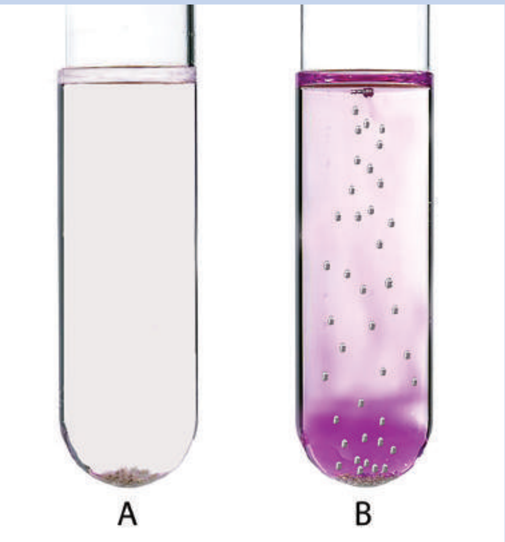
ii. Take 5 ml of cold water in A, add a drop of phenolphthalein indicator and then add Magnesium granules.

iii. Repeat the above with 5 ml of hot water in test tube B.

iv. Observe the two test tubes.

v. The observation shows that the solution in test tube B changes to pink colour and there is no such colour change in test tube A. That is, hot water reacts with magnesium according to the following reaction and there is no such reaction in cold water.

$$Mg + 2H_2O \longrightarrow Mg^{2+} + 2OH^- + H_2 \uparrow$$



vi. The resultant solution is basic and it is indicated by phenolphthalein.

A large number of reactions are known which do not take place at room temperature but occur readily at higher temperatures. Example: Reaction between H_2 and O_2 to form H_2O takes place only when an electric spark is passed.

Arrhenius suggested that the rates of most reactions vary with temperature in such a way that the rate constant is directly proportional to $e^{-\left(\frac{E_a}{RT}\right)}$ and he proposed a relation between the rate constant and temperature.

$$k = Ae^{-\left(\frac{E_a}{RT}\right)} \qquad \text{....(1)}$$

Where A the frequency factor,

R the gas constant,

E_a the activation energy of the reaction and,

T the absolute temperature (in K)

The frequency factor (A) is related to the frequency of collisions (number of collisions per second) between the reactant molecules. The factor A does not vary significantly with temperature and hence it may be taken as a constant.

E_a is the activation energy of the reaction, which Arrhenius considered as the minimum energy that a molecule must have to posses to react.

Taking logarithm on both side of the equation (1)

$$\ln k = \ln A + \ln e^{-\left(\frac{E_a}{RT}\right)}$$

$$\ln k = \ln A - \left(\frac{E_a}{RT}\right) \qquad (\because \ln e = 1)$$

$$\ln k = \ln A - \left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) \qquad \text{....(2)}$$

$$y = c + m\,x$$

The above equation is of the form of a straight line $y = mx + c$.

A plot of $\ln k$ Vs $1/T$ gives a straight line with a negative slope $-\frac{E_a}{R}$. If the rate constant for a reaction at two different temperatures is known, we can calculate the activation energy as follows.

At temperature $T = T_1$; the rate constant $k = k_1$

$$\ln k_1 = \ln A - \left(\frac{E_a}{RT_1}\right) \qquad \text{....(3)}$$

At temperature $T = T_2$; the rate constant $k = k_2$

$$\ln k_2 = \ln A - \left(\frac{E_a}{RT_2}\right) \qquad ....(4)$$

(4) −(3)

$$\ln k_2 - \ln k_1 = -\left(\frac{E_a}{RT_2}\right) + \left(\frac{E_a}{RT_1}\right)$$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$2.303\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

$$\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

$$\ln k_2 - \ln k_1 = -\left(\frac{E_a}{RT_2}\right) + \left(\frac{E_a}{RT_1}\right)$$

This equation can be used to calculate E_a from rate constants k_1 and k_2 at temperatures T_1 and T_2.

Example 7

The rate constant of a reaction at 400 and 200K are 0.04 and 0.02 s^{-1} respectively. Calculate the value of activation energy.

Solution

According to Arrhenius equation

$$\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

$T_2 = 400K$; $k_2 = 0.04\ s^{-1}$

$T_1 = 200K$; $k_1 = 0.02\ s^{-1}$

$$\log\left(\frac{0.04\ s^{-1}}{0.02\ s^{-1}}\right) = \frac{E_a}{2.303 \text{ x } 8.314\ JK^{-1}mol^{-1}}\left(\frac{400K - 200K}{200K \text{ x } 400K}\right)$$

$$\log(2) = \frac{E_a}{2.303 \text{ x } 8.314\ JK^{-1}mol^{-1}}\left(\frac{1}{400K}\right)$$

$$E_a = \log(2) \text{ x } 2.303 \text{ x } 8.314\ JK^{-1}mol^{-1} \text{ x } 400K$$

$$E_a = 2305\ J\ mol^{-1}$$

Example 8

Rate constant k of a reaction varies with temperature T according to the following Arrhenius equation

$$\log k = \log A - \frac{E_a}{2.303R}\left(\frac{1}{T}\right)$$

Where E_a is the activation energy. When a graph is plotted for $\log k$ Vs $\frac{1}{T}$ a straight line with a slope of -4000K is obtained. Calculate the activation energy

Solution

$$\log k = \log A - \frac{E_a}{2.303R}\left(\frac{1}{T}\right)$$

$$y = c + mx$$

$$m = -\frac{E_a}{2.303R}$$

$$E_a = -2.303\ R\ m$$

$$E_a = -2.303 \text{ x } 8.314\ J\ K^{-1}\ mol^{-1} \text{ x } (-4000K)$$

$$E_a = 76{,}589 J\ mol^{-1}$$

$$E_a = 76.589\ kJ\ mol^{-1}$$

Evaluate yourself

For a first order reaction the rate constant at 500K is $8 \text{ X } 10^{-4} s^{-1}$. Calculate the frequency factor, if the energy of activation for the reaction is 190 kJ mol^{-1}.

7.9 Factors affecting the reaction rate:

The rate of a reaction is affected by the following factors.

1. Nature and state of the reactant
2. Concentration of the reactant
3. Surface area of the reactant
4. Temperature of the reaction
5. Presence of a catalyst

7.9.1 Nature and state of the reactant:

We know that a chemical reaction involves breaking of certain existing bonds of the reactant and forming new bonds which lead to the product. The net energy involved in this process is dependent on the nature of the reactant and hence the rates are different for different reactants.

Let us compare the following two reactions that you carried out in volumetric analysis.

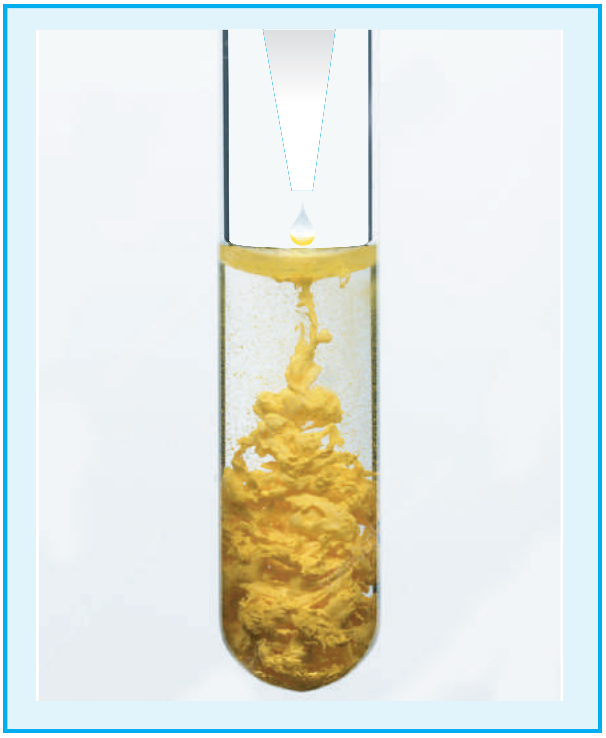
1). Redox reaction between ferrous ammonium sulphate (FAS) and $KMnO_4$

2). Redox reaction between oxalic acid and $KMnO_4$

The oxidation of oxalate ion by $KMnO_4$ is relatively slow compared to the reaction between $KMnO_4$ and Fe^{2+}. In fact heating is required for the reaction between $KMnO_4$ and Oxalate ion and is carried out at around 60^0C.

The physical state of the reactant also plays an important role to influence the rate of reactions. Gas phase reactions are faster as compared to the reactions involving solid or liquid reactants. For example, reaction of sodium metal with iodine vapours is faster than the reaction between solid sodium and solid iodine.

Let us consider another example that you carried out in inorganic qualitative analysis of lead salts. If you mix the aqueous solution of colorless potassium iodide with the colorless solution of lead nitrate, precipitation of yellow lead iodide take place instantaneously, whereas if you mix the solid lead nitrate with solid potassium iodide, yellow coloration will appear slowly.



7.9.2 Concentration of the reactants:

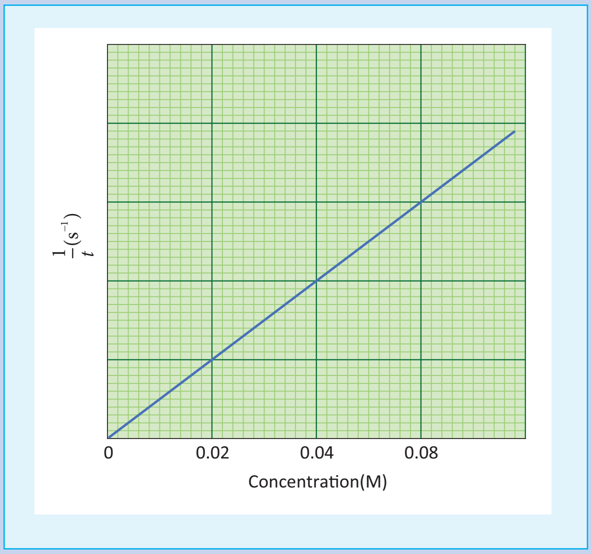
The rate of a reaction increases with the increase in the concentration of the reactants. The effect of concentration is explained on the basis of collision theory of reaction rates. According to this theory, the rate of a reaction depends upon the number of collisions between the reacting molecules. Higher the concentration, greater is the possibility for collision and hence the rate.

Activity

1. Take three conical flasks and label them as A, B, and C.
2. using a burette, add 10, 20 and 40 ml of 0.1M sodium thiosulphate solution to the flask A, B and C respectively. And then add 40, 30 and 10 ml of distilled water to the respective flasks so that the volume of solution in each flask is 50ml.
3. Add 10 ml of 1M HCl to the conical flask A. Start the stop watch when half of the HCl has been added. Shake the contents carefully and place it on the tile with a cross mark as shown in the figure. Observe the conical flask from top and stop the stops watch when the cross mark just becomes invisible. Note the time.
4. Repeat the experiment with the contents on B and C. Record the observation.

Flask	Volume of $Na_2S_2O_3$	Volume of water	Strength of $Na_2S_2O_3$	Time taken (t)
A	10	40	0.02	
B	20	30	0.04	
C	40	10	0.08	

Draw a graph between $\frac{1}{t}$ Vs concentration of sodium thiosulphate. A graph like the following one is obtained.



$\frac{1}{t}$ is a direct measure of rate of reaction and therefore, the increase in the concentration of reactants i.e $Na_2S_2O_3$, increases the rate.

7.9.3 Effect of surface area of the reactant:

In heterogeneous reactions, the surface areas of the solid reactants play an important role in deciding the rate. For a given mass of a reactant, when the particle size decreases surface area increases. Increase in surface area of reactant leads to more collisions per litre per second, and hence the rate of reaction is increased.For example, powdered calcium carbonate reacts much faster with dilute HCl than with the same mass of $CaCO_3$ as marble

Activity

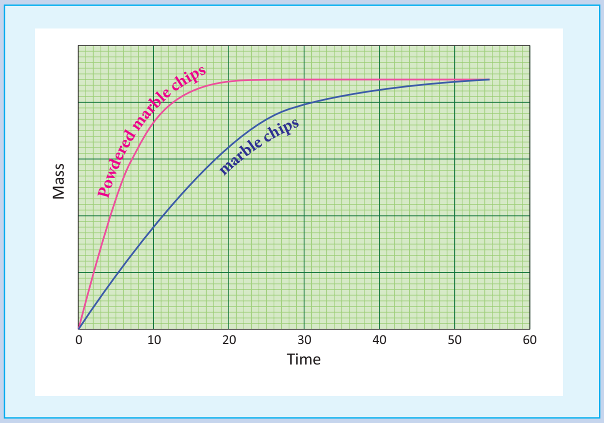
A Known mass of marble chips are taken in a flask and a known volume of dilute HCl is added to the content, a stop clock is started when half the volume of HCl is added. The mass is noted at regular intervals until the reaction is complete. Same experiment is repeated with the same mass of powdered marble chips and the observations are recorded.

Reaction

$$CaCO_3(s) + 2HCl\,(aq) \longrightarrow CaCl_2(aq) + H_2O\,(l) + CO_2(g)$$

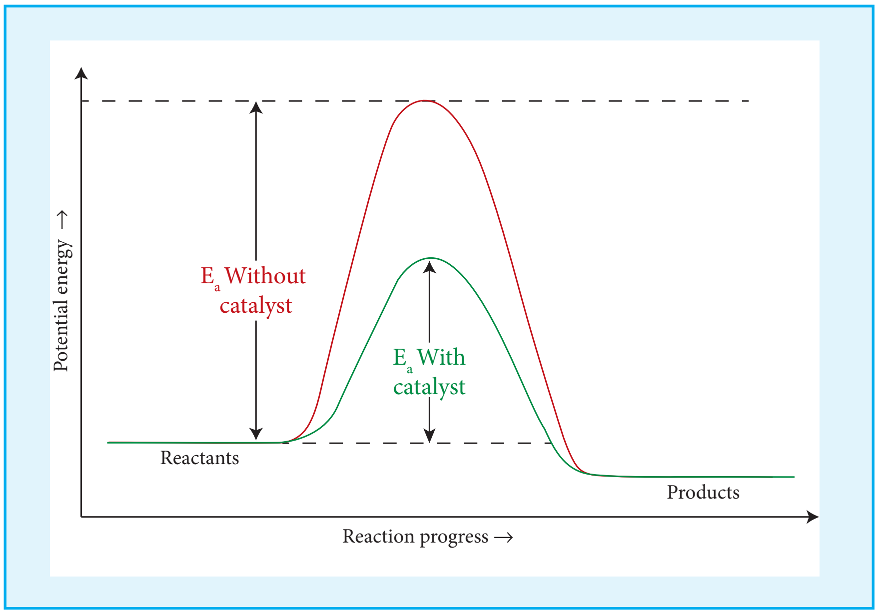
Since, carbon dioxide escapes during reaction, the mass of the flask gets lighter as the reaction proceeds. So, by measuring the flask, we can follow the rate of the reaction. A plot of loss in mass Vs time is drawn and it looks like the one as shown below.

For the powdered marble chips, the reaction is completed in less time. i.e., rate of a reaction increases when the surface area of a solid reactant is increased.



7.9.4 Effect of presence of catalyst:

So far we have learnt, that rate of reaction can be increased to certain extent by increasing the concentration, temperature and surface area of the reactant. However significant changes in the reaction can be brought out by the addition of a substance called catalyst. A catalyst is substance which alters the rate of a reaction without itself undergoing any permanent chemical change. They may participate in the reaction, but again regenerated and the end of the reaction. In the presence of a catalyst, the energy of activation is lowered and hence, greater number of molecules can cross the energy barrier and change over to products, thereby increasing the rate of the reaction.



Activity

Take two test tubes and label them as A and B. Add 7 ml of 0.1N oxalic acid solution, 5 ml of 0.1N $KMnO_4$ solution and 5 ml of 2N dilute H_2SO_4 in both the test tubes. The colour of the solution is pink in both the test tubes.

Now add few crystals of manganese sulphate to the content in test tube A. the pink colour fades up and disappears. In this case, $MnSO_4$ acts as a catalyst and increases the rate of oxidation of $C_2O_4^{2-}$ by MnO_4^-

Chemical kinetics in pharmaceuticals

Chemical kinetics has many applications in the field of pharmaceuticals. It is used to study the lifetimes and bioavailability of drugs within the body and this branch of study is called **pharmacokinetics** Doctors usually prescribe drugs to be taken at different times of the day. i.e.some drugs are to be taken twice a day, while others are taken three times a day, or just once a day. Pharmacokinetic studies is used to determine the prescription (dosage and frequency). For example, Paracetamol is a well known anti-pyretic and analgesic that is prescribed in cases of fever and body pain. Pharmacokinetic studies showed that Paracetamol has a half-life of 2.5 hours within the body i.e.the plasma concentration of a drug is halved after 2.5 hrs. After 10 hours (4 half-lives)only 6.25 % of drug remains. Based on such studies the dosage and frequency will be decided. In case of paracetamol, it is usually prescribed to take once in 6 hours depending upon the conditions.

Summary

- Chemical kinetics is the study of the rate and the mechanism of chemical reactions, proceeding under given conditions of temperature, pressure, concentration etc.
- The change in the concentration of the species involved in a chemical reaction per unit time gives the rate of a reaction.
- The rate of the reaction, at a particular instant during the reaction is called the instantaneous rate. The shorter the time period, we choose, the closer we approach to the instantaneous rate,
- The rate represents the speed at which the reactants are converted into products at any instant.
- The rate constant is a proportionality constant and It is equal to the rate of reaction, when the concentration of each of the reactants in unity
- Molecularity of a reaction is the total number of reactant species that are involved in an elementary step.
- The half life of a reaction is defined as the time required for the reactant concentration to reach one half its initial value. For a first order reaction, the half life is a constant

i.e., it does not depend on the initial concentration.

- According to collision theory, chemical reactions occur as a result of collisions between the reacting molecules.
- Generally, the rate of a reaction increase with increasing temperature. However, there are very few exceptions. The magnitude of this increase in rate is different for different reactions. As a rough rule, for many reactions near room temperature, reaction rate tends to double when the temperature is increased by 10^0C .
- According to Arrhenius, activation energy of the reaction is the minimum energy that a molecule must have to posses to react.
- The rate of a reaction is affected by the following factors.
    1. Nature and state of the reactant
    2. Concentration of the reactant
    3. Surface area of the reactant
    4. Temperature of the reaction
    5. Presence of a catalyst

9G9WX2

EVALUATION

1. For a first order reaction $A \longrightarrow B$ the rate constant is x min^{-1}. If the initial concentration of A is 0.01M , the concentration of A after one hour is given by the expression.

   a) $0.01\, e^{-x}$ b) $1\times10^{-2}\left(1-e^{-60x}\right)$

   c) $\left(1\times10^{-2}\right)e^{-60x}$ d) none of these

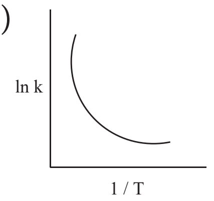
2. A zero order reaction $X \longrightarrow$ Product, with an initial concentration 0.02M has a half life of 10 min. if one starts with concentration 0.04M, then the half life is

   a) 10 s b) 5 min c) 20 min

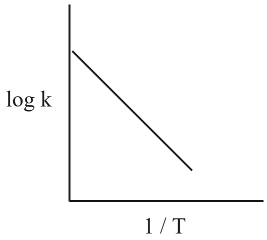
   d) cannot be predicted using the given information

3. Among the following graphs showing variation of rate constant with temperature (T) for a reaction, the one that exhibits Arrhenius behavior over the entire temperature range is

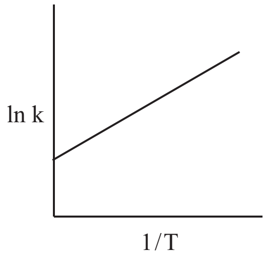
   a)



   b)



   c)



   d) both (b) and (c)

4. For a first order reaction $A \longrightarrow$ product with initial concentration x mol L^{-1} , has a half life period of 2.5 hours. For the same reaction with initial concentration $\left(\frac{x}{2}\right)$ mol L^{-1} the half life is

a) (2.5×2) hours

b) $\left(\frac{2.5}{2}\right)$ hours

c) 2.5 hours

d) Without knowing the rate constant, $t_{1/2}$ cannot be determined from the given data

5. For the reaction, $2NH_3 \longrightarrow N_2 + 3H_2$, if $\frac{-d[NH_3]}{dt} = k_1[NH_3]$, $\frac{d[N_2]}{dt} = k_2[NH_3]$, $\frac{d[H_2]}{dt} = k_3[NH_3]$ then the relation between k_1, k_2 and k_3 is

a) $k_1 = k_2 = k_3$

b) $k_1 = 3\,k_2 = 2\,k_3$

c) $1.5\,k_1 = 3\,k_2 = k_3$

d) $2k_1 = k_2 = 3\,k_3$

6. The decomposition of phosphine (PH_3) on tungsten at low pressure is a first order reaction. It is because the (NEET)

a) rate is proportional to the surface coverage

b) rate is inversely proportional to the surface coverage

c) rate is independent of the surface coverage

d) rate of decomposition is slow

7. For a reaction Rate $= k[\text{acetone}]^{3/2}$ then unit of rate constant and rate of reaction respectively is

a) $(\text{mol L}^{-1}\text{s}^{-1}),(\text{mol}^{-1/2}\ \text{L}^{1/2}\ \text{s}^{-1})$

b) $(\text{mol}^{-1/2}\ \text{L}^{1/2}\ \text{s}^{-1}),(\text{mol L}^{-1}\text{s}^{-1})$

c) $(\text{mol}^{1/2}\ \text{L}^{1/2}\ \text{s}^{-1}),(\text{mol L}^{-1}\text{s}^{-1})$

d) $(\text{mol L s}^{-1}),(\text{mol}^{1/2}\ \text{L}^{1/2}\text{s})$

8. The addition of a catalyst during a chemical reaction alters which of the following quantities? (NEET)

a) Enthalpy

b) Activation energy

c) Entropy

d) Internal energy

9. Consider the following statements :

(i) increase in concentration of the reactant increases the rate of a zero order reaction.

(ii) rate constant k is equal to collision frequency A if $E_a = 0$

(iii) rate constant k is equal to collision frequency A if $E_a = \circ$

(iv) a plot of $\ln(k)$ vs T is a straight line.

(v) a plot of $\ln(k)$ vs $\left(\frac{1}{T}\right)$ is a straight line with a positive slope.

Correct statements are

a) (ii) only

b) (ii) and (iv)

c) (ii) and (v)

d) (i), (ii) and (v)

10. In a reversible reaction, the enthalpy change and the activation energy in the forward direction are respectively $-x$ kJ mol^{-1} and y kJ mol^{-1}. Therefore , the energy of activation in the backward direction is

a) $(y-x)$ kJ mol^{-1}

b) $(x+y)$ J mol^{-1}

c) $(x-y)$ kJ mol^{-1}

d) $(x+y)\times 10^3$ J mol^{-1}

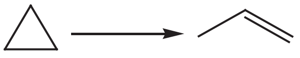
11. What is the activation energy for a reaction if its rate doubles when the temperature is raised from 200K to 400K? (R = 8.314 $JK^{-1}mol^{-1}$)

a) 234.65 kJ $mol^{-1}K^{-1}$

b) 434.65 kJ $mol^{-1}K^{-1}$

c) 434.65 J $mol^{-1}K^{-1}$

d) 334.65 J $mol^{-1}K^{-1}$

12.  ; This reaction follows first order kinetics. The rate constant at particular temperature is 2.303×10^{-2} $hour^{-1}$. The initial concentration of cyclopropane is 0.25 M. What will be the concentration of cyclopropane after 1806 minutes? $(\log 2 = 0.3010)$

a) 0.125M b) 0.215M

c) 0.25×2.303M d) 0.05M

13. For a first order reaction, the rate constant is 6.909 min^{-1}.the time taken for 75% conversion in minutes is

a) $\left(\frac{3}{2}\right)\log 2$ b) $\left(\frac{2}{3}\right)\log 2$

c) $\left(\frac{3}{2}\right)\log\left(\frac{3}{4}\right)$ d) $\left(\frac{2}{3}\right)\log\left(\frac{4}{3}\right)$

14. In a first order reaction $x \longrightarrow y$; if k is the rate constant and the initial concentration of the reactant x is 0.1M, then, the half life is

a) $\left(\frac{\log 2}{k}\right)$ b) $\left(\frac{0.693}{(0.1)\,k}\right)$

c) $\left(\frac{\ln 2}{k}\right)$ d) none of these

15. Predict the rate law of the following reaction based on the data given below

$$2A + B \longrightarrow C + 3D$$

Reaction number	[A] (min)	[B] (min)	Initial rate ($M\ s^{-1}$)
1	0.1	0.1	x
2	0.2	0.1	$2x$
3	0.1	0.2	$4x$
4	0.2	0.2	$8x$

a) $rate = k[A]^2[B]$ b) $rate = k[A][B]^2$

c) $rate = k[A][B]$

d) $rate = k[A]^{1/2}[B]^{3/2}$

16. Assertion: rate of reaction doubles when the concentration of the reactant is doubles if it is a first order reaction.

Reason: rate constant also doubles

a) Both assertion and reason are true and reason is the correct explanation of assertion.

b) Both assertion and reason are true but reason is not the correct explanation of assertion.

c) Assertion is true but reason is false.

d) Both assertion and reason are false.

17. The rate constant of a reaction is $5.8 \times 10^{-2}\ s^{-1}$. The order of the reaction is

a) First order b) zero order

c) Second order d) Third order

18. For the reaction $N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$, the value of rate of disappearance of N_2O_5 is given as 6.5×10^{-2} mol $L^{-1}s^{-1}$. The rate of formation of NO_2 and O_2 is given

respectively as

a) $\left(3.25 \times 10^{-2} \text{ mol L}^{-1}\text{s}^{-1}\right)$ and $\left(1.3 \times 10^{-2} \text{ mol L}^{-1}\text{s}^{-1}\right)$

b) $\left(1.3\times 10^{-2} \text{ mol L}^{-1}\text{s}^{-1}\right)$ and $\left(3.25 \times 10^{-2} \text{ mol L}^{-1}\text{s}^{-1}\right)$

c) $\left(1.3 \times 10^{-1} \text{ mol L}^{-1}\text{s}^{-1}\right)$ and $\left(3.25 \times 10^{-2} \text{ mol L}^{-1}\text{s}^{-1}\right)$

d) None of these

19. During the decomposition of H_2O_2 to give dioxygen, 48 g O_2 is formed per minute at certain point of time. The rate of formation of water at this point is

a) 0.75 mol min^{-1}

b) 1.5 mol min^{-1}

c) 2.25 mol min^{-1}

d) 3.0 mol min^{-1}

20. If the initial concentration of the reactant is doubled, the time for half reaction is also doubled. Then the order of the reaction is

a) Zero b) one

c) Fraction d) none

21. In a homogeneous reaction $A \longrightarrow B + C + D$, the initial pressure was P_0 and after time t it was P. expression for rate constant in terms of P_0, P and t will be

a) $k = \left(\dfrac{2.303}{t}\right)\log\left(\dfrac{2P_0}{3P_0 - P}\right)$

b) $k = \left(\dfrac{2.303}{t}\right)\log\left(\dfrac{2P_0}{P_0 - P}\right)$

c) $k = \left(\dfrac{2.303}{t}\right)\log\left(\dfrac{3P_0 - P}{2P_0}\right)$

d) $k = \left(\dfrac{2.303}{t}\right)\log\left(\dfrac{2P_0}{3P_0 - 2P}\right)$

22. If 75% of a first order reaction was completed in 60 minutes , 50% of the same reaction under the same conditions would be completed in

a) 20 minutes b) 30 minutes

c) 35 minutes d) 75 minutes

23. The half life period of a radioactive element is 140 days. After 560 days , 1 g of element will be reduced to

a) $\left(\dfrac{1}{2}\right)g$ b) $\left(\dfrac{1}{4}\right)g$

c) $\left(\dfrac{1}{8}\right)g$ d) $\left(\dfrac{1}{16}\right)g$

24. The correct difference between first and second order reactions is that (NEET)

a) A first order reaction can be catalysed; a second order reaction cannot be catalysed.

b) The half life of a first order reaction does not depend on $[A_0]$; the half life of a second order reaction does depend on $[A_0]$.

c) The rate of a first order reaction does not depend on reactant concentrations; the rate of a second order reaction does depend on reactant concentrations.

d) The rate of a first order reaction does depend on reactant concentrations; the rate of a second order reaction does not depend on reactant concentrations.

25. After 2 hours, a radioactive substance becomes $\left(\dfrac{1}{16}\right)^{\text{th}}$ of original amount.

Then the half life (in min) is

a) 60 minutes b) 120 minutes

c) 30 minutes d) 15 minutes

Answer the following questions:

1. Define average rate and instantaneous rate.
2. Define rate law and rate constant.
3. Derive integrated rate law for a zero order reaction $A \longrightarrow \text{product}$.
4. Define half life of a reaction. Show that for a first order reaction half life is independent of initial concentration.
5. What is an elementary reaction? Give the differences between order and molecularity of a reaction.
6. Explain the rate determining step with an example.
7. Describe the graphical representation of first order reaction.
8. Write the rate law for the following reactions.
   (a) A reaction that is 3/2 order in x and zero order in y.
   (b) A reaction that is second order in NO and first order in Br_2.
9. Explain the effect of catalyst on reaction rate with an example.
10. The rate law for a reaction of A, B and C has been found to be $\text{rate} = k[A]^2[B][L]^{3/2}$. How would the rate of reaction change when
    (i) Concentration of [L] is quadrupled
    (ii) Concentration of both [A] and [B] are doubled
    (iii) Concentration of [A] is halved
    (iv) Concentration of [A] is reduced to $\left(1/3\right)$ and concentration of [L] is quadrupled.
11. The rate of formation of a dimer in a second order reaction is 7.5×10^{-3} mol $L^{-1}s^{-1}$ at 0.05 mol L^{-1} monomer concentration. Calculate the rate constant.
12. For a reaction $x + y + z \longrightarrow \text{products}$ the rate law is given by $\text{rate} = k[x]^{3/2}[y]^{1/2}$ what is the overall order of the reaction and what is the order of the reaction with respect to z.
13. Explain briefly the collision theory of bimolecular reactions.
14. Write Arrhenius equation and explains the terms involved.
15. The decomposition of Cl_2O_7 at 500K in the gas phase to Cl_2 and O_2 is a first order reaction. After 1 minute at 500K, the pressure of Cl_2O_7 falls from 0.08 to 0.04 atm. Calculate the rate constant in s^{-1}.
16. Hydrolysis of methyl acetate in aqueous solution has been studied by titrating the liberated acetic acid against sodium hydroxide. The concentration of an ester at different temperatures is given below.
17. Explain pseudo first order reaction with an example.
18. Identify the order for the following reactions

(i) Rusting of Iron

(ii) Radioactive disintegration of ${}_{92}U^{238}$

(iii) $2A + 3B \longrightarrow \text{products}\ ;\ \text{rate} = k[A]^{1/2}[B]^2$

19. A gas phase reaction has energy of activation 200 kJ mol^{-1}. If the frequency factor of the reaction is $1.6 \times 10^{13}\ s^{-1}$

. Calculate the rate constant at 600 K. $\left(e^{-40.09} = 3.8\times10^{-18}\right)$

20. For the reaction $2x + y \longrightarrow L$ find the rate law from the following data.

[x] (min)	[y] (min)	rate (M s^{-1})
0.2	0.02	0.15
0.4	0.02	0.30
0.4	0.08	1.20

21. How do concentrations of the reactant influence the rate of reaction?
22. How do nature of the reactant influence rate of reaction.
23. The rate constant for a first order reaction is $1.54\times10^{-3}\,s^{-1}$. Calculate its half life time.
24. The half life of the homogeneous gaseous reaction $SO_2Cl_2 \rightarrow SO_2 + Cl_2$ which obeys first order kinetics is 8.0 minutes. How long will it take for the concentration of SO_2Cl_2 to be reduced to 1% of the initial value?
25. The time for half change in a first order decomposition of a substance A is 60 seconds. Calculate the rate constant. How much of A will be left after 180 seconds?
26. A zero order reaction is 20% complete in 20 minutes. Calculate the value of the rate constant. In what time will the reaction be 80% complete?
27. The activation energy of a reaction is 225 k Cal mol^{-1} and the value of rate constant at 40°C is $1.8\times10^{-5}\ s^{-1}$. Calculate the frequency factor, A.
28. Benzene diazonium chloride in aqueous solution decomposes according to the equation $C_6H_5N_2Cl \longrightarrow C_6H_5Cl + N_2$. Starting with an initial concentration of 10 g L^{-1}, the volume of N_2 gas obtained at 50 °C at different intervals of time was found to be as under:

t (min):	6	12	18	24	30	∞
Vol. of N_2 (ml):	19.3	32.6	41.3	46.5	50.4	58.3

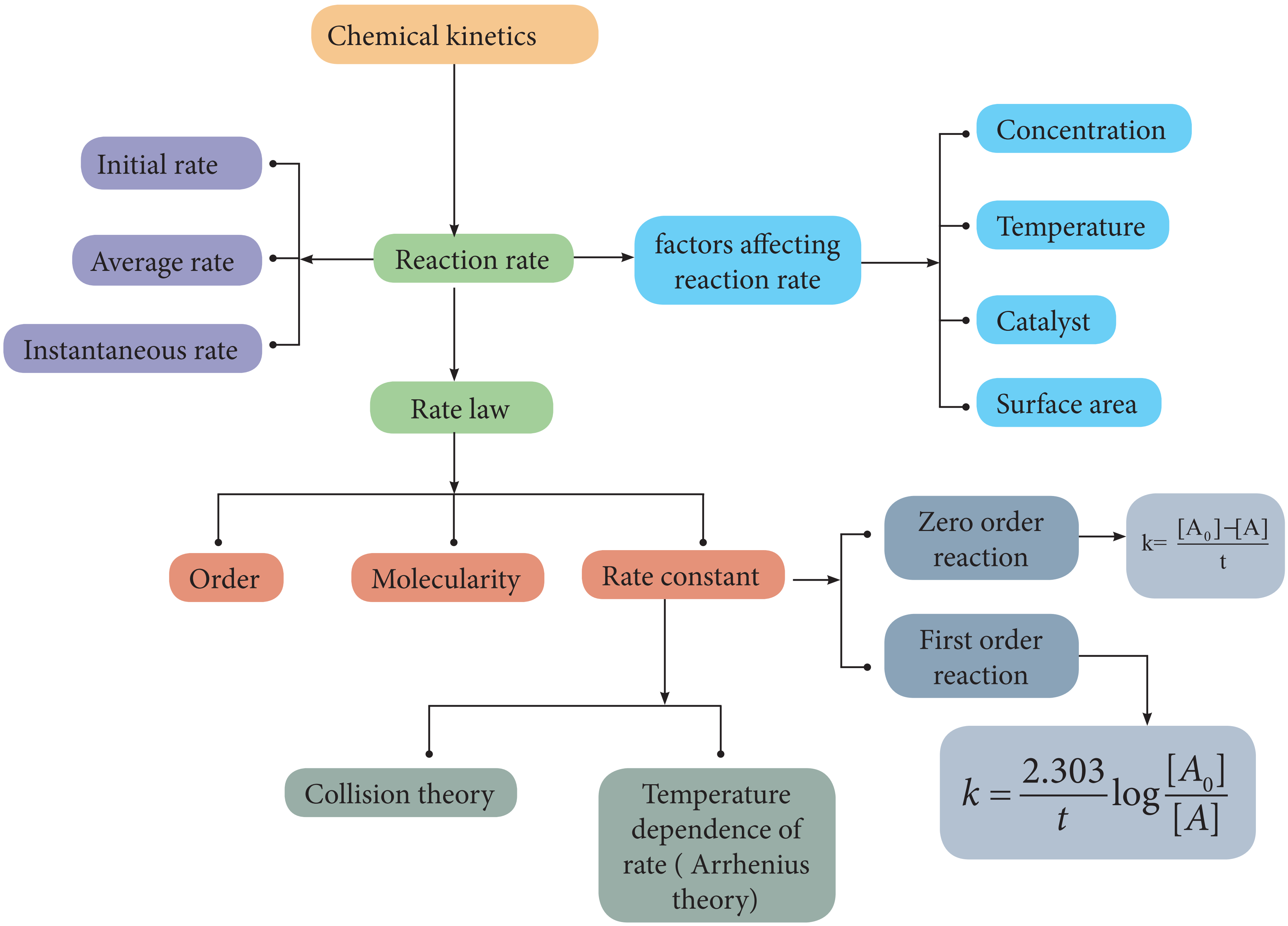
Show that the above reaction follows the first order kinetics. What is the value of the rate constant?

29. From the following data, show that the decomposition of hydrogen peroxide is a reaction of the first order:

t (min)	0	10	20
V (ml)	46.1	29.8	19.3

Where *t* is the time in minutes and V is the volume of standard $KMnO_4$ solution required for titrating the same volume of the reaction mixture.

30. A first order reaction is 40% complete in 50 minutes. Calculate the value of the rate constant. In what time will the reaction be 80% complete?


Chemical kinetics
Reaction rate
Initial rate
Average rate
Instantaneous rate
factors affecting reaction rate
Concentration
Temperature
Catalyst
Surface area
Rate law
Order
Molecularity
Rate constant
Zero order reaction
$k = \frac{[A_0]-[A]}{t}$
First order reaction
$k = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$
Collision theory
Temperature dependence of rate (Arrhenius theory)

ICT Corner

CHEMICAL KINETICS

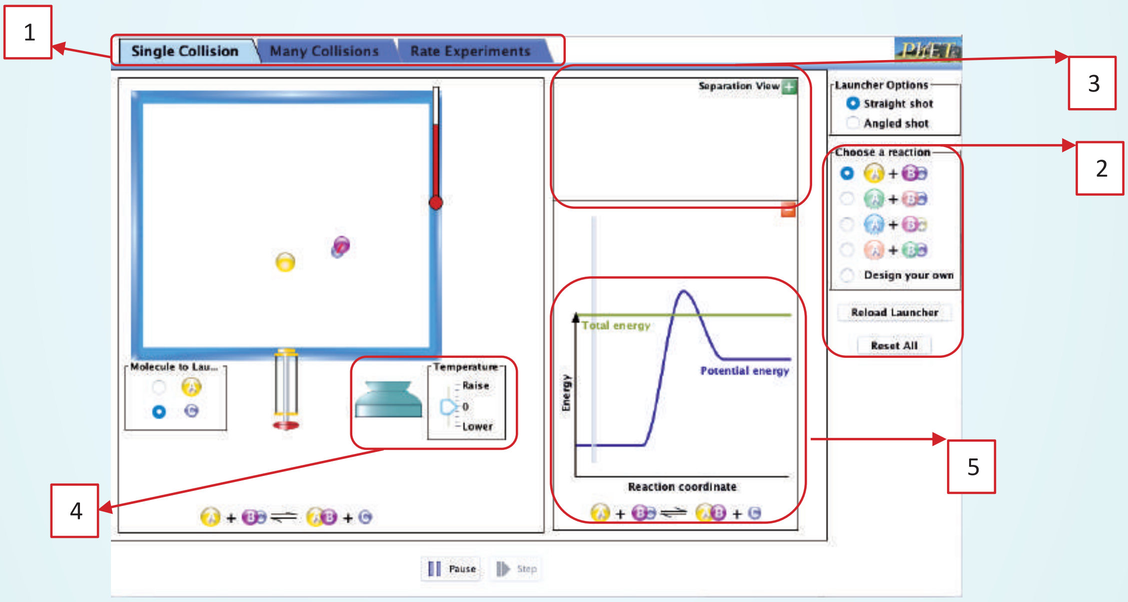
By using this tool you can understand collision and the activation energy. You can also perform virtual kinetic experiment to understand the effect of temperature on reaction rate.

Please go to the URL https://phet.colorado.edu/en/simulation/legacy/reactions-and-rates
(or) Scan the QR code on the right side

B264_12_CHEMISTRY_EM

Steps

- Open the Browser and type the URL given (or) Scan the QR Code. You can see a webpage which displays the java applet called reactions and rates. You can click it and you will get a window as shown in the figure. This applet contains three modules which can be selected by clicking the appropriate tab (box1).
- Select single collision tab (tab 1) to visualise collision between two molecules. You can visualise the progress of the reaction (box 5) by varying the temperature using the slider (box 2). You can visualise that the raise in temperature, will raise the energy of the system and allows the reactants to cross the energy barrier to form products. You can repeat this simulation with more molecules in the many collisions tab (box 1).
- You can also perform virtual kinetic experiment, using rate experiments mode. Choose the types reacting molecules and their stoichiometry using the options provided (box 2). The number of reactant and product molecules at a given time will be displayed in panel (box-3). You can see the effect of temperature on reaction rate by varying the temperature (box 4).



VOLUME I

ANSWERS

UNIT-I

Choose the correct answer

1. b) $Al_2O_3.nH_2O$ 2. c) SO_2 3. c) $MgCO_3 \longrightarrow MgO + CO_2$

4. b) Al_2O_3 5. a) Al

6. d) Carbon and hydrogen are suitable reducing agents for metal sulphides.

7. c) A-iv , B-ii , C-iii , D-i

8. d)Electromagnetic separation

9. b) $Cu(s) + Zn^{2+}(aq) \longrightarrow Zn(s) + Cu^{2+}(aq)$

10. c) sodium 11. b) Infusible impurities to soluble impurities

12. c) Galena 13. a) Lower the melting point of alumina

14. a) Carbon reduction 15. a) Silver

16. c) Displacement with zinc 17. c) Mg

18. b) van Arkel process 19. d) Both (a) and (c)

20. d) In the metallurgy of gold, the metal is leached with dilute sodium chloride solution

21. b) Impure copper 22. b) ΔG^0 Vs T

23. c) $\left(\frac{\Delta G^0}{\Delta T}\right)$ is negative 24. b) $Al_2O_3 + 2Cr \longrightarrow Cr_2O_3 + 2Al$

25. b) The graph for the formation of CO_2 is a straight line almost parallel to free energy axis.

UNIT-2

Choose the correct answer:

1. c) basic

$$Na_2B_4O_7 + 7H_2O \rightleftharpoons \underset{\text{Strong base}}{2NaOH} + \underset{\text{Weak acid}}{4H_3BO_3}$$

2. d) accepts OH^- from water ,releasing proton.

$$B(OH)_3 + H_2O \rightleftharpoons [B(OH)_4]^- + H^+$$

3. b) B_3H_6

nido borane : B_nH_{4+n}
aracno borane : B_nH_{6+n}
B_3H_6 is not a borane

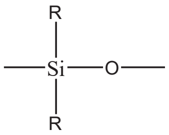
4. a) Aluminium
5. c) four

There are two $3c - 2e^-$ bonds i.e., the bonding in the bridges account for 4 electrons.

6. c) Lead
7. c) sp^2 hybridised
8. a) +4

Example : CH_{4+} in which the oxidation state of carbon is +4

9. d) $(SiO_4)^{4-}$
10. b)



11. a) Me_3SiCl
12. d) dry ice

dry ice – solid CO_2 in which carbon is in sp hybridized state

13. a) Tetrahedral
14. d) Feldspar is a three dimensional silicate
15. b) $K_3[AlF_6]$

$$AlF_3 + 3KF \longrightarrow K_3[AlF_6]$$

16. a) A-b , B-1 , C-4 , D-3
17. d) Al,Cu,Mn,Mg

Al-95% , Cu-4% , Mn-0.5% , Mn-0.5%

18. b) graphite
19. a) Metal borides
20. a) Al < Ga < In < Tl

stability of +1 oxidation state decreases down the group due to inert pair effect

UNIT-3

Choose the correct answer:

1. a) Nessler's reagent
2. d) ability to form $p\pi - p\pi$ bonds with itself
3. d) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$
4. b) P_4(white) and PH_3
5. b) Nitroso ferrous sulphate
6. a) H_3PO_3
7. a) H_3PO_3
8. b) 2
9. a) 6N
10. d) Both assertion and reason are wrong. The converse is true.
11. b) F_2
12. b) HF > HCl > HBr > HI
13. d) NeF_2
14. c) He
15. c) XeO_3
16. c) SO_4^{2-}
17. a) HI
18. d) $Cl_2 > Br_2 > F_2 > I_2$
19. d) $HClO < HClO_2 < HClO_3 < HClO_4$
20. c) $Cu(NO_3)_2$ and NO_2

UNIT-4

Choose the correct answer:

1. b) in case of Sc, 3d orbital are partially filled but in Zn these are completely filled

2. a) Cr

   $Cr \Rightarrow [Ar]3d^5 4s^1$

3. a) Ti

4. c) Ni^{2+}

5. a) 5.92BM

   $Mn^{2+} \Rightarrow 3d^5$ contains 5 unpaired electrons

   $n=5 ;\ \ldots = \sqrt{n(n+2)}BM$

   $\ldots = \sqrt{5(5+2)} = \sqrt{35} = 5.92BM$

6. b) Ti^{4+}

   Ti^{4+} contains no unpaired electrons in d orbital, hence no d-d transition.

7. c) their ability to adopt variable oxidation states

8. a) $VO_2^{\ +} < Cr_2O_7^{\ 2-} < MnO_4^{\ -}$

   $\overset{+5}{V}O_2^{\ +} < \overset{+6}{Cr_2}O_7^{\ 2-} < \overset{+7}{Mn}O_4^{\ -}$ greater the oxidation state, higher is the oxidising power

9. d) brass

   Brass contains 70% Cu + 30% Zn

10. b) $(NH_4)_2Cr_2O_7$

    $$2K_2Cr_2O_7 \longrightarrow 2K_2CrO_4 + Cr_2O_3 + \left(\frac{3}{2}\right)O_2$$

    $$(NH_4)_2Cr_2O_7 \longrightarrow Cr_2O_3 + 4H_2O + N_2$$

    $$KClO_3 \longrightarrow KCl + \left(\frac{3}{2}\right)O_2$$

    $$Zn(ClO_3)_2 \longrightarrow ZnCl_2 + 3O_2$$

11. b) Carbon dioxide

    $$5(COO)_2^{\ 2-} + 2MnO_4^{\ -} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2\uparrow + 8H_2O$$

12. b) $Na_2Cr_2O_7$ is preferred over $K_2Cr_2O_7$ in volumetric analysis

13. b) Mn^{2+}

    $$MnO_4^{\ -} + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

14. a) Na_2SO_3 , SO_2 , $Cr_2(SO_4)_3$

$$\underset{(A)}{Na_2S_2O_3} + 2HCl \longrightarrow 2NaCl + \underset{(B)}{SO_2}\uparrow + \underset{\text{yellow ppt}}{S}\downarrow + H_2O$$

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + \underset{(C)}{Cr_2(SO_4)_3} + H_2O$$

15. a) BrO_3^- , MnO_2

$$2MnO_4^- + Br^- + H_2O \longrightarrow 2OH^- + 2MnO_2 + BrO_3^-$$

16. c) 3

$$K_2Cr_2O_7 + 6KI + 7H_2SO_4 \longrightarrow 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3I_2$$

17. c) 0.6

$$\overset{7+}{Mn}O_4^- + \overset{+2}{Fe}\overset{+3}{C_2}O_4 \longrightarrow Mn^{2+} + Fe^{3+} + 2\overset{+4}{C}O_2$$

$5e^-$ acception $3e^-$ release

5 moles of $FeC_2O_4 \equiv$ 3 moles of $KMnO_4$

1 mole of $FeC_2O_4 \equiv \left(\frac{3}{5}\right)$ moles of $KMnO_4$

1 mole of $FeC_2O_4 \equiv$ 0.6 moles of $KMnO_4$

18. a) MnO_2, Cl_2 , NCl_3

$$\underset{(A)}{MnO_2} + 4HCl \longrightarrow MnCl_2 + \underset{(B)}{Cl_2}\uparrow + H_2O$$

$$NH_3 + 3Cl_2 \longrightarrow \underset{(C)}{NCl_3} + 3HCl$$

19. c) All the lanthanons are much more reactive than aluminium.

As we move from La to Lu , their metallic behaviour because almost similar to that of aluminium.

20. b) Yb^{2+}

Yb^{2+} - $4f^{14}$ –no unpaired electrons - diamagnetic

21. d) 3

22. a) Both assertion and reason are true and reason is the correct explanation of assertion.

23. c) +4

24. a) Np, Pu ,Am

25. a) $La(OH)_2$ is less basic than $Lu(OH)_3$

UNIT-5

Choose the correct answer:

1. In the complex $\left[\mathrm{M}(\mathrm{en})_2(\mathrm{Ox})\right]\mathrm{Cl}$ For the central metal ion M^{3+}

   The primary valance is $=+3$

   The secondary valance $=6$

   sum of primary valance and secondary valance = 3+6 = 9

   Answer : option (d)

2. The complex is $\left[\mathrm{M}(\mathrm{H_2O})_5 Cl\right]\mathrm{Cl}_2$

   1000 ml of 1M solution of the complex gives 2 moles of Cl^- ions

   1000 ml of 0.01M solution of the complex will give

   $$\frac{100\text{ ml} \times 0.01\text{M} \times 2Cl^-}{1000\text{ ml} \times 1\text{M}} = 0.002 \text{ moles of } Cl^- ions$$

   Answer : option (b)

3. Molecular formula: $\mathrm{MSO_4Cl.\ 6H_2O}$.

   Formation of white precipitate with Barium chloride indicates that $\mathrm{SO_4}^{2-}$ ions are outside the coordination sphere, and no precipitate with $\mathrm{AgNO_3}$ solution indicates that the Cl^- ions are inside the coordination sphere.Since the coordination number of M is 6, Cl^- and 5 $\mathrm{H_2O}$ are ligands, remaining 1 $\mathrm{H_2O}$ molecular and $\mathrm{SO_4}^{2-}$ are in the outer coordination sphere.

   Answer : option (c)

4. $\left[\overset{+}{\mathrm{Fe}}(\mathrm{H_2O})_5\overset{+}{\mathrm{NO}}\right]^{2+}\mathrm{SO_4}^{2-}$

   +1 and +1 respectively

   Answer : option(d)

5. Answer : option(d)

6. Answer : option(d)

7. Answer : option(c)

   $\mathrm{Ti}^{4+}\left(\mathrm{d}^0 \Rightarrow 0\mathrm{BM}\right)$

   $\mathrm{Co}^{2+}\left(\mathrm{d}^7\text{spin free} \Rightarrow t_{2g}{}^5, e_g{}^2\ ;\ n=3\ ;\ \mu=3.9BM\right)$

   $\mathrm{Cu}^{2+}\left(\mathrm{d}^9\text{Low spin} \Rightarrow t_{2g}{}^6, e_g{}^3\ ;\ n=1\ ;\ \mu=1.732BM\right)$

   $\mathrm{Ni}^{2+}\left(\mathrm{d}^8\text{Low spin} \Rightarrow t_{2g}{}^6, e_g{}^2\ ;\ n=2\ ;\ \mu=2.44BM\right)$

8. Answer : option(b)

   The electronic configuration $\mathrm{t}_{2g}{}^3, e_g{}^2$

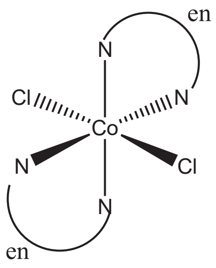
   $\left[3\times(-0.4)+2(0.6)\right]\Delta_0$

$[-1.2+1.2]\Delta_0 = 0$

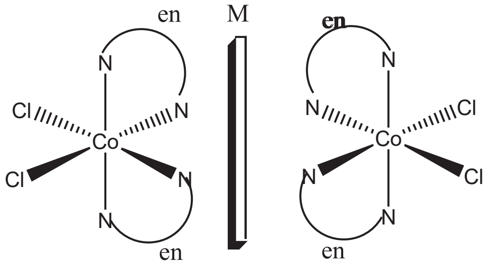
9. Answer : option(a)

In all the complexes, the central metal ion is Co^{3+}, among the given ligands CN^- is the strongest ligand, which causes large crystal field splitting i.e maximum $\varnothing_0$

10. Answer : option(b)



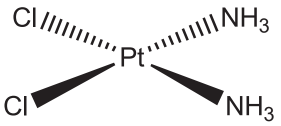
inactive

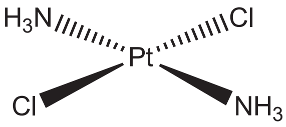


Active forms (enantiomorphs)

Complexes given in other options (a), (c) and (d) have symmetry elements and hence they are optically inactive.

11. Answer : option(d)





12. Three isomers. If we consider any one of the ligands as reference (say Py), the arrangement of other three ligands (NH_3, Br^- and Cl^-) with respect to (Py) gives three geometrical isomers.

13. Answer : option(c)

(a)coordination isomers

(b) no isomerism (different molecular formula)

(c) $\leftarrow NCS$, $\leftarrow SCN$ coordinating atom differs : linkage isomers

14. Answer : option(a)

For $[MA_4B_2]^{n+}$ complexes-geometrical isomerism is possible

$$\left.\begin{cases}\left[Co(NH_3)_4Br_2\right]Cl \\ \left[Co(NH_3)_4Br\,Cl\right]Br\end{cases}\right\}\rightarrow \text{ionisation isomers}$$

15. Answer : option(d)

Option (a) and (b) – geometrical isomerism is possible

Option (c) – ionization isomerism is possible

Option (d) – no possibility to show either constitutional isomerism or stereo isomerism

16. Answer : option(c)

(a) Fe^{2+} (b) Fe^{3+} (c) Fe^0

17. Answer : option(d)

$\left[\mathrm{Fe}(\mathrm{en})_3\right]^{2+}\left(\mathrm{PO_4}^{3-}\right)$

18. Answer : option(c)

(a) $\mathrm{Zn}^{2+}\left(\mathrm{d}^{10} \Rightarrow \text{diamagnetic}\right)$

(b) $\mathrm{Co}^{3+}\left(\mathrm{d}^6\text{Low spin} \Rightarrow t_{2g}{}^{6}, e_g{}^{0}\ ;\ \text{diamagnetic}\right)$

(c) $\mathrm{Ni}^{2+}\left(\mathrm{d}^8\text{Low spin} \Rightarrow t_{2g}{}^{6}, e_g{}^{2}\ ;\ \text{paramagnetic}\right)$

(d) $[\mathrm{Ni(CN)_4}]^{2-}\left(\mathrm{dsp}^2\ ;\ \text{square planar, diamagnetic}\right)$

19. Answer : option(c)

$\left[\mathrm{Co}(\mathrm{NH_3})_3(Cl)_3\right]$

20. Answer : option(d)

$\mathrm{V}^{2+}\left(t_{2g}{}^{3}, e_g{}^{0}\ ;\ \mathrm{CFSE} = 3 \times (-0.4)\Delta_0 = -1.2\Delta_0\right)$

$\mathrm{Ti}^{2+}\left(t_{2g}{}^{2}, e_g{}^{0}\ ;\ \mathrm{CFSE} = 2 \times (-0.4)\Delta_0 = -0.8\Delta_0\right)$

Statements given in option (a) ,(b), and (c) are wrong.

The current statements are

(a) since, the crystal field stabilization is more in octahedral field , octahedral complexes are more stable than square planar complexes.

(b)

$$[\mathrm{FeF_6}]^{4-} - \left(\begin{array}{l} \mathrm{Fe}^{2+} - \mathrm{d}^6\text{High Spin} - t_{2g}{}^{4}, e_g{}^{2}\ ) \\ \mathrm{CFSE} = 4 \times (-0.4) + (0.6) \times 2 + \mathrm{P} \end{array}\right)$$

$$\left[\mathrm{Fe}(\mathrm{CN})_6\right]^{4-} - \left(\begin{array}{l} \mathrm{Fe}^{2+} - \mathrm{d}^6\ \text{Low Spin} - t_{2g}{}^{6}, e_g{}^{0}\ ) \\ \mathrm{CFSE} = 6 \times (-0.4) + 3\mathrm{P} \end{array}\right)$$

UNIT-6

Choose the correct answer:

1. c) both covalent crystals

2. b) $\mathrm{AB_3}$

number of A ions $= \left(\frac{N_c}{8}\right) = \left(\frac{8}{8}\right) = 1$

number of B ions $= \left(\frac{N_f}{2}\right) = \left(\frac{6}{2}\right) = 3$

simplest formula $\mathrm{AB_3}$

3. b) 1:2

if number of close packed atoms =N; then,

The number of Tetrahedral holes formed = 2N

number of Octahedral holes formed = N

therefore N:2N = 1:2

4. c) molecular solid

lattice points are occupied by CO_2 molecules

5. a) Both assertion and reason are true and reason is the correct explanation of assertion.

6. c) 8 and 4

CaF_2 has cubical close packed arrangement

Ca^{2+} ions are in face centered cubic arrangement, each Ca^{2+} ions is surrounded by 8 F^- ions and each F^- ion is surrounded by 4 Ca^{2+} ions.

Therefore coordination number of Ca^{2+} is 8 and of F^- is 4

7. b) 6.023×10^{22}

in bcc unit cell,

2 atoms $\equiv$ 1 unit cell

Number of atoms in 8g of element is ,

$$\text{Number of moles} = \frac{8g}{40\text{ g mol}^{-1}} = 0.2\text{ mol}$$

1 mole contains 6.023×10^{23} atoms

0.2 mole contains $0.2 \times 6.023 \times 10^{23}$ atoms

$$\left(\frac{1\text{unit cell}}{2\text{ atoms}}\right) \times 0.2 \times 6.023 \times 10^{23}$$

6.023×10^{22} unit cells

8. a) 8

in diamond carbon forming fcc. Carbon occupies corners and face centres and also occupying half of the tetrahedral voids.

$$\left(\frac{N_c}{8}\right) + \left(\frac{N_f}{2}\right) + 4\text{ C atoms inTd voids}$$

$$\left(\frac{8}{8}\right) + \left(\frac{6}{2}\right) + 4 = 8$$

9. d) M_3N_2

if the total number of M atoms is n, then the number of tetrahedral voids =2n

given that $\left(\frac{1}{3}\right)^{rd}$ of tetrahedral voids are occupied i.e., $\left(\frac{1}{3}\right) \times 2n$ are occupied by N atoms

$$\therefore \text{M:N} \Rightarrow n : \left(\frac{2}{3}\right) n$$

$$1 : \left(\frac{2}{3}\right)$$

$$3 : 2 \Rightarrow M_3N_2$$

10. b) 15.05%

let

the number of Fe^{2+} ions in the crystal be x

the number of Fe^{3+} ions in the crystal be y

total number of Fe^{2+} and Fe^{3+} ions is $x + y$

given that $x + y = 0.93$

the total charge =0

$$x(2+) + (0.93 - x)(+3) - 2 = 0$$

$$2x + 2.97 - 3x - 2 = 0$$

$$x = 0.79$$

Percentage of Fe^{3+}

$$= \left(\frac{(0.93 - 0.79)}{(0.93)}\right) 100 = 15.05\%$$

11. c) 6

$$\frac{r_{C^+}}{r_{A^-}} = \frac{0.98 \times 10^{-10}}{1.81 \times 10^{-10}} = 0.54$$

it is in the range of 0.414 - 0.732, hence the coordination number of each ion is 6

12. d) $\left(\frac{\sqrt{3}}{2}\right) \times 400\text{pm}$

$$\sqrt{3}\,a = r_{Cs^+} + 2r_{Cl^-} + r_{Cs^+}$$

$$\left(\frac{\sqrt{3}}{2}\right)a = \left(r_{Cs^+} + r_{Cl^-}\right)$$

$$\left(\frac{\sqrt{3}}{2}\right)400 = \text{inter ionic distance}$$

13. a) $\left(\frac{100}{0.414}\right)$

for an fcc structure $\frac{r_{X^+}}{r_{y^-}} = 0.414$

given that $r_{X^+} = 100\,pm$

$$r_{y^-} = \frac{100\,pm}{0.414}$$

14. c) 32%

packing efficiency = 68%

therefore empty space percentage = (100-68) = 32%

15. b) 848.5pm

let edge length =a

$$\sqrt{2}a = 4r$$

$$a = \frac{4\times 300}{\sqrt{2}}$$

$$a = 600\times 1.414$$

$$a = 848.4 \text{ pm}$$

16. b) $\left(\frac{\pi}{6}\right)$

$$\left(\frac{\frac{4}{3}\pi r^3}{a^3}\right) = \left(\frac{\frac{4}{3}\pi\left(\frac{a}{2}\right)^3}{a^3}\right) = \left(\frac{\pi}{6}\right)$$

17. a) excitation of electrons in F centers

18. c) $\left(\frac{1}{2}a : \frac{\sqrt{3}}{4}a : \frac{1}{2\sqrt{2}}a\right)$

$$sc \Rightarrow 2r = a \Rightarrow r = \frac{a}{2}$$

$$bcc \Rightarrow 4r = \sqrt{3}a \Rightarrow r = \frac{\sqrt{3}a}{4}$$

$$fcc \Rightarrow 4r = \sqrt{2}a \Rightarrow r = \frac{\sqrt{2}a}{4} = \frac{a}{2\sqrt{2}}$$

$$\left(\frac{a}{2}\right) : \left(\frac{\sqrt{3}a}{4}\right) : \left(\frac{a}{2\sqrt{2}}\right)$$

19. d) $\left(\frac{\sqrt{3}}{2}\right)a$

if a is the length of the side, then the length of the leading diagonal passing through the body centered atom is $\sqrt{3}a$

$$\text{Required distance} = \left(\frac{\sqrt{3}}{2}\right)a$$

20. a) 915 kg m-3

$$\rho = \frac{n \times M}{a^3 N_A}$$

for bcc

$n = 2$

M=39

nearest distance 2r = 4.52

$$a = \frac{4r}{\sqrt{3}} = \frac{2\times 4.52\times 10^{-10}}{\sqrt{3}} = 5.21\times 10^{-10}$$

$$\rho = \frac{2\times 39}{\left(5.21\times 10^{-10}\right)^3 \times \left(6.023\times 10^{23}\right)}$$

$$\rho = 915 \text{ Kg m}^{-3}$$

N_A

21. b) equal number of anions and anions are missing from the lattice

22. c) Frenkel defect

23. d) Both assertion and reason are false

24. b) FeO

25. a) XY_8

UNIT-7

Choose the correct answer:

1. option (c)

$$k = \left(\frac{2.303}{t}\right)\log\left(\frac{[A_0]}{[A]}\right)$$

$$k = \left(\frac{1}{t}\right)\ln\left(\frac{[A_0]}{[A]}\right)$$

$$e^{kt} = \left(\frac{[A_0]}{[A]}\right)$$

$$[A] = [A_0]e^{-kt}$$

In this case

$k = x\,\text{min}^{-1}$ and $[A_0] = 0.01M = 1 \times 10^{-2}M$

$t = 1$ hour $= 60$ min

$$[A] = 1 \times 10^{-2}\ \left(e^{-60x}\right)$$

2. option (c)

$$\text{for } n \neq 1 \qquad t_{1/2} = \frac{2^{n-1}-1}{(n\text{-}1)\,k\,[A_0]^{n-1}}$$

$$\text{for } n = 0 \qquad t_{1/2} = \frac{1}{2\,k\,[A_0]^{-1}}$$

$$t_{1/2} = \frac{[A_0]}{2\,k}$$

$$t_{1/2}\ \alpha\ [A_0] \text{———} (1)$$

given

$[A_0] = 0.02M$; $t_{1/2} = 10\,\text{min}$

$[A_0] = 0.04M$; $t_{1/2} = ?$

substitute in (1)

$10 \text{ min}\ \alpha\ 0.02M$ ——— (2)

$t_{1/2}\ \alpha\ 0.04M$ ——— (3)

$$(3)/(2)$$

$$\Rightarrow \frac{t_{1/2}}{10\,\text{min}} = \frac{0.04\text{ M}}{0.02\text{ M}}$$

$$t_{1/2} = 2 \times 10\,\text{min} = 20\,\text{min}$$

3. option (b)

$$k = A\,e^{-\left(\frac{E_a}{RT}\right)}$$

$$\ln k = \ln A - \left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right)$$

this equation is in the form of a straight line equatoion

$y = c + m\,x$

a plot of $\ln k$ vs $\left(\frac{1}{T}\right)$ is a straight line with negative slope

4. option(d)

For a first order reaction

$$t_{1/2} = \frac{0.693}{k}$$

$t_{1/2}$ does not depend on the initial concentration and it remains constant (whatever may be the initial concentration)

$t_{1/2} = 2.5$ hrs

5. option(c)

$$Rate = \left(\frac{-1}{2}\right)\frac{d[NH_3]}{dt} = \frac{d[N_2]}{dt} = \left(\frac{1}{3}\right)\frac{d[H_2]}{dt}$$

$$\left(\frac{1}{2}\right)k_1[NH_3] = k_2[NH_3] = \left(\frac{1}{3}\right)k_3[NH_3]$$

$$\left(\frac{3}{2}\right)k_1 = 3k_2 = k_3$$

$$1.5\,k_1 = 3k_2 = k_3$$

6. option(c)

Given :

At low pressure the reaction follows first order, therefore

$$Rate\ \alpha[\text{reactant}]^1$$

$$Rate\ \alpha\ (\text{surface area})$$

At high pressure due to the complete coverage of surface area, the reaction follows zero order.

$$Rate\ \alpha[\text{reactant}]^0$$

Therefore the rate is independent of surface area.

7. option(b)

$$\text{rate} = k[A]^n$$

$$\text{rate} = \frac{-d[A]}{dt}$$

$$\text{unit of rate} = \frac{\text{mol L}^{-1}}{s} = \text{mol L}^{-1}s^{-1}$$

$$\text{unit of rate constant} = \frac{(\text{mol L}^{-1}s^{-1})}{(\text{mol L}^{-1})^n} = \text{mol}^{1-n}\ \text{L}^{n-1}s^{-1}$$

in this case

$$\text{rate} = k[\text{Acetone}]^{3/2}$$

$$n = 3/2$$

$$\text{mol}^{1-(3/2)}\ \text{L}^{(3/2)-1}s^{-1}$$

$$\text{mol}^{-(1/2)}\ \text{L}^{(1/2)}s^{-1}$$

8. option(b)

A catalyst provides a new path to the reaction with low activation energy. i.e., it lowers the activation energy.

9. option(a)

In zero order reactions, increase in the concentration of reactant does not alter the rate. So statement (i) is wrong.

$$k = A\,e^{-\left(\frac{E_a}{RT}\right)}$$

if $E_a = 0$ so, statement (ii) is correct, and statement (iii) is wrong

$$k = A\,e^0$$

$$k = A$$

$$\ln k = \ln A - \left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right)$$

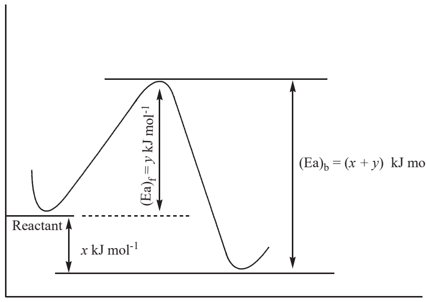
this equation is in the form of a straight line equatoion

$$y = c + m\,x$$

a plot of lnk vs $\left(\frac{1}{T}\right)$ is a straight line with negative slope

so statements (iv) and (v) are wrong.

10. option(d)



$$(x+y)\,\text{kJmol}^{-1}$$
$$(x+y)\times 10^{3}\ \text{Jmol}^{-1}$$

11. option(c)

$T_1 = 200\text{K}\ ;\ k = k_1$

$T_2 = 400\text{K}\ ;\ k = k_2 = 2k_1$

$$\log\left(\frac{k_2}{k_1}\right) = \frac{2.303\ E_a}{R}\left(\frac{T_2 - T_1}{T_1\ T_2}\right)$$

$$\log\left(\frac{2\ k_1}{k_1}\right) = \frac{2.303\ E_a}{8.314\ \text{J K}^{-1}\text{mol}^{-1}}\left(\frac{400\ \text{K} - 200\text{K}}{200\text{K}\ \times\ 400\text{K}}\right)$$

$$E_a = \frac{0.3010\ \times\ 8.314\ \text{J mol}^{-1}\times\ 200\ \times\ 400}{2.303\ \times\ 200}$$

$$E_a = 434.65\ \text{J mol}^{-1}$$

12. option(b)

$$k = \left(\frac{2.303}{t}\right)\log\left(\frac{[A_0]}{[A]}\right)$$

$$2.303\ \times\ 10^{-2}\ \text{hour}^{-1} = \left(\frac{2.303}{1806\ \text{min}}\right)\log\left(\frac{0.25}{[A]}\right)$$

$$\left(\frac{2.303\ \times\ 10^{-2}\ \text{hour}^{-1}\times 1806\ \text{min}}{2.303}\right) = \log\left(\frac{0.25}{[A]}\right)$$

$$\left(\frac{1806 \ \times 10^{-2}}{60}\right) = \log\left(\frac{0.25}{[A]}\right)$$

$$0.301 = \log\left(\frac{0.25}{[A]}\right)$$

$$\log 2 = \log\left(\frac{0.25}{[A]}\right)$$

$$2 = \left(\frac{0.25}{[A]}\right)$$

$$[A] = \left(\frac{0.25}{2}\right) = 0.125\text{M}$$

13. option(b)

$$k = \left(\frac{2.303}{t}\right)\log\left(\frac{[A_0]}{[A]}\right)$$

$$[A_0] = 100 \ ; \ [A] = 25$$

$$6.909 = \left(\frac{2.303}{t}\right)\log\left(\frac{100}{25}\right)$$

$$t = \left(\frac{2.303}{6.909}\right)\log(4)$$

$$t = \left(\frac{1}{3}\right)\log 2^2$$

$$t = \left(\frac{2}{3}\right)\log 2$$

14. option(c)

$$k = \left(\frac{1}{t}\right)\ln\left(\frac{[A_0]}{[A]}\right)$$

$$[A_0] = 0.1 \ ; \ [A] = 0.05$$

$$k = \left(\frac{1}{t_{1/2}}\right)\ln\left(\frac{0.1}{0.05}\right)$$

$$k = \left(\frac{1}{t_{1/2}}\right)\ln(2)$$

$$t_{1/2} = \frac{\ln(2)}{k}$$

15. option(b)

$$\text{rate}_1 = k[0.1]^n[0.1]^m \text{———}(1)$$

$$\text{rate}_2 = k[0.2]^n[0.1]^m \text{———}(2)$$

$$^{(2)}/_{(1)}$$

$$\frac{2x}{x} = \frac{k[0.2]^n[0.1]^m}{k[0.1]^n[0.1]^m}$$

$$\frac{2x}{x} = 2^n \quad \therefore\ n = 1$$

$$\text{rate}_3 = k[0.1]^n[0.2]^m \text{———}(3)$$

$$\text{rate}_4 = k[0.2]^n[0.2]^m \text{———}(4)$$

$$^{(4)}/_{(2)}$$

$$\frac{8x}{2x} = \frac{k[0.2]^n[0.2]^m}{k[0.2]^n[0.1]^m}$$

$$\frac{8}{2} = 2^m \quad \therefore\ m = 2$$

$$\therefore\ \text{rate} = k[A]^1[B]^2$$

16. option(c)

For a first reaction, If the concentration of reactant is doubled, then the rate of reaction also doubled.

Rate constant is independent of concentration and is a constant at a constant temperature,

17. option(a)

The unit of rate constant is s^{-1} and it indicates that the reaction is first order.

18. option(c)

$$Rate = \frac{d[N_2O_5]}{dt} = \left(\frac{1}{2}\right)\frac{d[NO_2]}{dt} = \frac{2\,d[O_2]}{dt}$$

Given that

$$\frac{d[N_2O_5]}{dt} = 6.5 \times 10^{-2}\ \text{mol L}^{-1}\text{s}^{-1}$$

$$\frac{d[NO_2]}{dt} = 2 \times 6.5 \times 10^{-2} = 1.3 \times 10^{-1}\ \text{mol L}^{-1}\text{s}^{-1}$$

$$\frac{d[O_2]}{dt} = \frac{6.5 \times 10^{-2}}{2} = 3.25 \times 10^{-2}\ \text{mol L}^{-1}\text{s}^{-1}$$

19. option(d)

$$H_2O_2 \longrightarrow H_2O + \tfrac{1}{2}O_2$$

$$Rate = \frac{-d[H_2O_2]}{dt} = \frac{d[H_2O]}{dt} = \frac{2d[O_2]}{dt}$$

no of moles of oxygen $= \left(\frac{48}{32}\right) = 1.5$ mol

$\therefore$ rate of formation of oxygen $= 2 \times 1.5 = 3$ mol min^{-1}

20. option(a)

For a first order reaction $t_{1/2}$ is independent of initial concentration .i.e., $\therefore\ n \neq 1$; for such cases

$$t_{1/2}\ \alpha\ \frac{1}{[A_0]^{n-1}} \quad \text{-------}\ (1)$$

If $[A_0] = 2[A_0]$; then $t_{1/2} = 2t_{1/2}$

$$2\,t_{1/2}\ \alpha\ \frac{1}{[2\,A_0]^{n-1}} \quad \text{------}\ (2)$$

$$\frac{(2)}{(1)} \Rightarrow$$

$$2 = \frac{1}{[2A_0]^{n-1}} \times \frac{[A_0]^{n-1}}{1}$$

$$2 = \frac{[A_0]^{n-1}}{[2A_0]^{n-1}}$$

$$2 = \left(\frac{1}{2}\right)^{n-1}$$

$$2 = \left(2^{-1}\right)^{n-1}$$

$$2^{1} = \left(2^{-n+1}\right)$$

$$n = 0$$

21. Answer : option(a)

	A	$\longrightarrow$	B	C	D
Initial	a		0	0	0
Reacted at time t	x		x	x	x
After time t	$(a-x)$		x	x	x
Total number of moles		$=(a+2x)$			

$$\mathrm{a} \propto \mathrm{P_0}$$

$$(a+2x) \propto \mathrm{P}$$

$$\frac{\mathrm{a}}{(a+2x)} = \frac{\mathrm{P_0}}{\mathrm{P}}$$

$$x = \frac{(\mathrm{P}-\mathrm{P_0})\mathrm{a}}{2\mathrm{P_0}}$$

$$(a-x) = a - \left(\frac{(\mathrm{P}-\mathrm{P_0})\mathrm{a}}{2\mathrm{P_0}}\right)$$

$$(a-x) = a\left\{\frac{3\mathrm{P_0}-\mathrm{P}}{2\mathrm{P_0}}\right\}$$

$$\mathrm{k} = \left(\frac{2.303}{\mathrm{t}}\right)\log\frac{[\mathrm{A_0}]}{[\mathrm{A}]}$$

$$\mathrm{k} = \left(\frac{2.303}{\mathrm{t}}\right)\log\left(\frac{\mathrm{a}}{\mathrm{a}-x}\right)$$

$$\mathrm{k} = \left(\frac{2.303}{\mathrm{t}}\right)\log\left(\frac{\mathrm{a}}{a\left\{\frac{3\mathrm{P_0}-\mathrm{P}}{2\mathrm{P_0}}\right\}}\right)$$

$$\mathrm{k} = \left(\frac{2.303}{\mathrm{t}}\right)\log\left(\frac{2\mathrm{P_0}}{3\mathrm{P_0}-\mathrm{P}}\right)$$

22. Answer : option(d)5

$$t_{75\%} = 2t_{50\%}$$

$$t_{50\%} = \left(\frac{t_{75\%}}{2}\right) = \left(\frac{60}{2}\right) = 30\,\text{min}$$

23. Answer : option(d)

$$\text{in140 days} \Rightarrow \text{ initial concentration reduced to } \left(\frac{1}{2}\right)g$$

$$\text{in 280 days} \Rightarrow \text{ initial concentration reduced to } \left(\frac{1}{4}\right)g$$

$$\text{in 420 days} \Rightarrow \text{ initial concentration reduced to } \left(\frac{1}{8}\right)g$$

$$\text{in 560 days} \Rightarrow \text{ initial concentration reduced to } \left(\frac{1}{16}\right)g$$

24. Answer : option(b)

For a first order reaction

$$t_{1/2} = \frac{0.6932}{k}$$

For a second order reaction

$$t_{1/2} = \frac{2^{n-1}-1}{(n-1)\,k\,[A_0]^{n-1}}$$

$$n = 2$$

$$t_{1/2} = \frac{2^{2-1}-1}{(2-1)\,k\,[A_0]^{2-1}}$$

$$t_{1/2} = \frac{1}{k\,[A_0]}$$

25. Answer : option(c)

$$1 \xrightarrow{t_{1/2}} \left(\frac{1}{2}\right) \xrightarrow{t_{1/2}} \left(\frac{1}{4}\right) \xrightarrow{t_{1/2}} \left(\frac{1}{8}\right) \xrightarrow{t_{1/2}} \left(\frac{1}{16}\right)$$

$$\therefore\ 4\,t_{1/2} = 2 \text{ hours}$$

$$t_{1/2} = 30 \text{ min}$$

Answer the following:

10 solution

$$\text{Rate} = k[A]^2[B][L]^{3/2} \text{ -----(1)}$$

(i) when $[L] = [4L]$

$$\text{Rate} = k[A]^2[B][4L]^{3/2}$$

$$\text{Rate} = 8\left(k[A]^2[B][L]^{3/2}\right)\text{-----(2)}$$

Comparing (1) and (2) ; rate is increased by 8 times.

(ii) when $[A] = [2A] \, and \, [B] = [2B]$

$$\text{Rate} = k[2A]^2[2B][L]^{3/2}$$

$$\text{Rate} = 8\left(k[A]^2[B][L]^{3/2}\right)\text{-----(3)}$$

Comparing (1) and (3) ; rate is increased by 8 times.

(iii) when $[A] = \left[\frac{A}{2}\right]$

$$\text{Rate} = k\left[\frac{A}{2}\right]^2[B][L]^{3/2}$$

$$\text{Rate} = \left(\frac{1}{4}\right)\left(k[A]^2[B][L]^{3/2}\right)\text{-----(4)}$$

Comparing (1) and (4) ; rate is reduced to ¼ times.

(iv) when $[A] = \left[\frac{A}{3}\right] and [L] = [4L]$

$$\text{Rate} = k\left[\frac{A}{3}\right]^2[B][4L]^{3/2}$$

$$\text{Rate} = \left(\frac{8}{9}\right)\left(k[A]^2[B][L]^{3/2}\right)\text{-----(5)}$$

Comparing (1) and (5) ; rate is reduced to 8/9 times.

11. solution

Let us consider the dimerisation of a monomer M

$$2M \longrightarrow (M)_2$$

$$\text{Rate} = k[M]^n$$

Given that n=2 and [M] = 0.05 mol L^{-1}

Rate = 7.5 X 10^{-3} mol $L^{-1}s^{-1}$

$$k=\frac{\text{Rate}}{[M]^n}$$

$$k=\frac{7.5\times10^{-3}}{(0.05)^2}=3\ \text{mol}^{-1}\text{Ls}^{-1}$$

12. Solution

$$\text{rate}=k[x]^{\left(\frac{3}{2}\right)}[y]^{\left(\frac{1}{2}\right)}$$

$$\text{overall order}=\left(\frac{3}{2}+\frac{1}{2}\right)=2$$

i.e., second order reaction.

Since the rate expression does not contain the concentration of z , the reaction is zero order with respect to z.

15. Solution:

$$k=\frac{2.303}{t}\log\frac{[A_0]}{[A]}$$

$$k=\frac{2.303}{1\,\text{min}}\log\frac{[0.08]}{[0.04]}$$

$$k=2.303\log 2$$

$$k=2.303\times0.3010$$

$$k=0.6932\,\text{min}^{-1}$$

$$k=\left(\frac{0.6932}{60}\right)s^{-1}$$

$$k=1.153\times10^{-2}\ s^{-1}$$

19. Solution

$$k=A\,e^{-\left(\frac{E_a}{RT}\right)}$$

$$k=1.6\ \times10^{13}\text{s}^{-1}e^{-\left(\frac{200\times103\ \text{J mol}^{-1}}{8.314\,\text{JK}^{-1}\text{mol}^{-1}\times600\,\text{K}}\right)}$$

$$k=1.6\ \times10^{13}\text{s}^{-1}\ e^{-(40.1)}$$

$$k=1.6\ \times10^{13}\text{s}^{-1}\times3.8\times10^{-18}$$

$$k=6.21\times10^{-5}\text{s}^{-1}$$

20. Solution

$$\text{rate} = k[x]^n[y]^m$$

$$0.15 = k[0.2]^n[0.02]^m \text{ ———(1)}$$

$$0.30 = k[0.4]^n[0.02]^m \text{ ———(2)}$$

$$1.20 = k[0.4]^n[0.08]^m \text{ ———(3)}$$

$$(3)/(2)$$

$$\frac{1.2}{0.3} = \frac{k[0.4]^n[0.08]^m}{k[0.4]^n[0.02]^m}$$

$$4 = \left(\frac{[0.08]}{[0.02]}\right)^m$$

$$4 = (4)^m$$

$$\therefore\ m = 1$$

$$(2)/(1)$$

$$\frac{0.30}{0.15} = \frac{k[0.4]^n[0.02]^m}{k[0.2]^n[0.02]^m}$$

$$2 = \left(\frac{[0.4]}{[0.2]}\right)^n$$

$$2 = (2)^n$$

$$\therefore\ n = 1$$

$$\text{Rate} = k\,[x]^1[y]^1$$

$$0.15 = k\,[0.2]^1[0.02]^1$$

$$\frac{0.15}{[0.2]^1[0.02]^1} = k$$

$$k = 37.5\ \text{mol}^{-1}\text{L}\ s^{-1}$$

23**Solution:**

We know that, $t_{1/2} = 0.693/\ k$

$t_{1/2} = 0.693/1.54\text{x}\ 10^{-3}\ \text{s}^{-1}$ = **450 s**

24.**Solution:**

We know that, $k = 0.693/\ t_{1/2}$

$k = 0.693/\ 8.0$ minutes $= 0.087$ minutes^{-1}

For a first order reaction,

$$t = \frac{2.303}{k}\log\frac{[A_0]}{[A]}$$

$$t = \frac{2.303}{0.087\ \text{min}^{-1}}\log\left(\frac{100}{1}\right)$$

$$t = 52.93\,\text{min}$$

25 **Solution:**

i) Order of a reaction = 1; $t_{1/2}$ = 60 ; seconds, k = ?

We know that, $k = \dfrac{2.303}{t_{1/2}}$

$$k = \frac{2.303}{60} = 0.01155\ s^{-1}$$

ii) $[A_0] = 100\%$ t = 180 s , k = 0.01155 seconds^{-1}, $[A]$ = ?

For the first order reaction

$$k = \frac{2.303}{t}\log\frac{[A_0]}{[A]}$$

$$0.01155 = \frac{2.303}{180}\log\left(\frac{100}{[A]}\right)$$

$$\frac{0.01155\times180}{2.303} = \log\left(\frac{100}{[A]}\right)$$

$$0.9207 = \log100 - \log[A]$$

$$\log[A] = \log100 - 0.9207$$

$$\log[A] = 2 - 0.9207$$

$$\log[A] = 1.0973$$

$$[A] = \text{antilog of }(1.0973)$$

$$[A] = 12.5\%$$

26 **Solution:**

i) Let A = 100M, $[A_0]-[A]$ = 20M,

For the zero order reaction

$$k = \left(\frac{[A_0]-[A]}{t}\right)$$

$$k=\left(\frac{20\text{M}}{20\text{min}}\right)=1\,\text{Mmin}^{-1}$$

Rate constant for a reaction = 1Mmin^{-1}

ii) To calculate the time for 80% of completion

k = 1Mmin^{-1}, $[A_0]$ = 100M, $[A_0]$-[A] = 80M, t = ?

Therefore,

$$t=\left(\frac{[A_0]-[A]}{k}\right)=\left(\frac{80\text{M}}{1\text{Mmin}^{-1}}\right)=80\,\text{min}$$

27 Solution:

Here, we are given that

E_a = 22.5 kcal mol^{-1} = 22500 cal mol^{-1}

T = 40°C = 40 + 273 = 313 K

k = 1.8 × 10^{-5} sec^{-1}

Substituting the values in the equation

$$\log A=\log k+\left(\frac{E_a}{2.303RT}\right)$$

$$\log A=\log\left(1.8\times10^{-5}\right)+\left(\frac{22500}{2.303\times1.987\times313}\right)$$

$$\log A=\log\left(1.8\right)-5+\left(15.7089\right)$$

$$\log A=10.9642$$

$$A=\text{antilog}\left(10.9642\right)$$

$$A=\ 9.208\times10^{10}\text{collisions s}^{-1}$$

28.**Solution:**

For a first order reaction

$$k=\frac{2.303}{t}\log\frac{[A_0]}{[A]}$$

$$k=\frac{2.303}{t}\log\frac{V_\infty}{V_\infty-V_t}$$

In the present case, V_∞ = 58.3 ml.

The value of *k* at different time can be calculated as follows:

t (*min*)	V_t	$V_\infty - V_t$	$\frac{2.303}{t}\log\frac{V_\circ}{V_\circ - V_t}$
6	19.3	58.3-19.3 = 39.0	$k=\frac{2.303}{6}\log\left(\frac{58.3}{39}\right)$ = 0.0670 min^{-1}
12	32.6	58.3-32.6 = 25.7	$k=\frac{2.303}{12}\log\left(\frac{58.3}{25.7}\right)$ = 0.0683 min^{-1}
18	41.3	58.3-41.3 = 17.0	$k=\frac{2.303}{18}\log\left(\frac{58.3}{17}\right)$ = 0.0685 min^{-1}
24	46.5	58.3-46.5 = 11.8	$k=\frac{2.303}{24}\log\left(\frac{58.3}{11.8}\right)$ = 0.0666 min^{-1}

Since the value of *k* comes out to be nearly constant, the given reaction is of the first order. The mean value of *k* = 0.0676 min^{-1}

29.**Solution:**

$$k = \frac{2.303}{t}\log\frac{[A_0]}{[A]}$$

$$k = \left(\frac{2.303}{t}\right)\log\left(\frac{V_0}{V_t}\right)$$

In the present case, V_o = 46.1 ml.

The value of *k* at each instant can be calculated as follows:

t (*min*)	V_t	$k = \left(\frac{2.303}{t}\right)\log\left(\frac{V_0}{V_t}\right)$
10	29.8	$k = \frac{2.303}{10}\log\left(\frac{46.1}{29.8}\right) = 0.0436\ \text{min}^{-1}$
20	19.3	$k = \frac{2.303}{20}\log\left(\frac{46.1}{19.3}\right) = 0.0435\ \text{min}^{-1}$

Thus, the value of *k* comes out to be nearly constant. Hence it is a reaction of the first order.

30. Solution:

i) For the first order reaction $k = \frac{2.303}{t}\log\frac{[A_0]}{[A]}$

Assume, $[A_0]$ = 100 %, t = 50 minutes

Therefore, [A] = 100 – 40 = 60

k = (2.303 / 50) log (100 / 60)

k = 0.010216 min^{-1}

Hence the value of the rate constant is 0.010216 min^{-1}

ii) t = ?, when the reaction is 80% completed,

[A] = 100 – 80 = 20 %

From above, k = 0.010216 min^{-1}

t = (2.303 / 0.010216) log (100 / 20)

t = 157.58 min

The time at which the reaction will be 80% complete is 157.58 min.

+2 PRACTICALS

I-ORGANIC QUALITATIVE ANALYSIS

S.no	Experiment	Observation	Inference
		Preliminary tests	
1	**Odour:** Note the Odour of the organic compound.	(i) Fish odour (ii) Bitter almond odour (iii) Phenolic odour (iv) Pleasant fruity odour	(i) May be an amine (ii) May be benzaldehyde (iii) May be phenol (iv) May be an ester
2	**Test with litmus paper:** Touch the Moist litmus paper with an organic compound.	(i) Blue litmus turns red (ii) Red litmus turns blue (iii) No colour change is noted	(i) May be a carboxylic acid or phenol (ii) May be an amine (iii) Absence of carboxylic acid , phenol and amine
3	**Action with sodium bicarbonate:** Take 2 ml of saturated sodium bi carbonate solution in a test tube. Add 2 or 3 drops (or a pinch of solid) of an organic compound to it.	(i) Brisk effervescence (ii) No brisk effervescence	(i) Presence of a carboxylic acid. (ii) Absence of a carboxylic acid.
4	**Action with Borsche's reagent:** Take a small amount of an organic compound in a test tube. Add 3 ml of Borsche's reagent, 1 ml of Conc HCl to it, then warm the mixture gently and cool it.	yellow or orange or red precipitate	Presence of an aldehyde or ketone

5	**Charring test:** Take a small amount of an organic compound in a dry test tube. Add 2 ml of conc H_2SO_4 to it, and heat the mixture.	Charring takes place with smell of burnt sugar	Presence of carbohydrate
Tests for Aliphatic or Aromatic nature:			
6	**Ignition test:** Take small amount of the organic compound in a Nickel spatula and burn it in Bunsen flame.	(i) Burn with sooty flame (ii) Burns with non sooty flame	(i) Presence of an aromatic compound (ii) Presence of an aliphatic compound
Tests for an unsaturation:			
7	**Test with bromine water:** Take small amount of the organic compound in a test tube add 2 ml of distilled water to dissolve it. To this solution add few drops of bromine water and shake it well.	(i) Orange - yellow colour of bromine water is decolourised (ii) No Decolourisation takes place (iii) Decolourisation with formation of white precipitate.	(i) Substance is unsaturated. (ii) Substance is saturated. (iii) Presence of an aromatic amine or phenol.
8	**Test with $KMnO_4$ solution:** Take small amount of the organic compound in a test tube add 2 ml of distilled water to dissolve it. To this solution add few drops of very dilute alkaline $KmnO_4$ solution and shake it well.	(i) Pink colour of $KmnO_4$ solution is decolourised (ii) No Decolourisation takes place	(i) Substance is unsaturated. (ii) Substance is unsaturated.
TEST FOR SELECTED ORGANIC FUNCTIONAL GROUPS			
Test For Phenol			
9	**Neutral $FeCl_3$ test:** Take 1 ml of neutral ferric chloride solution is taken in a dry clean test tube. Add 2 or 3 drops (or a pinch of solid) oforganic compound to it. If no colouration occurs add 3 or 4 drops of alcohol.	(i) Violet colouration is seen (ii) violet – blue colouration is seen (iii) green colouration is seen	(i) Presence of phenol. (ii) Presence of α–naphthol (iii) Presence of β– naphthol

TEST FOR CARBOXYLIC ACIDS			
10	**Esterification reaction:** Take 1 ml (or a pinch of solid) of an organic compoundin a clean test tube. Add 1 ml of ethyl alcohol and 4 to 5 drops of conc. sulphuric acid to it. Heat the reaction mixture strongly for about 5 minutes. Then pour the mixture into a beaker containing dil. Sodium carbonate solution and note the smell.	A Pleasant fruity odour is noted.	Presence of carboxylic group.
Test for aldehydes.			
11	**Tollen's reagent test:** Take 2 ml of Tollen's reagent in a clean dry test tube. Add 3-4 drops of an organic compound (or 0.2 g of solid) to it, and warm the mixture on a water bath for about 5 minutes.	Shining silver mirror is formed.	Presence of an aldehyde
12	**Fehling's test:** Take 1 ml each of Fehling's solution A and B are taken in a test tube. Add 4-5 drops of an organic compound (or 0.2g of solid) to it, and warm the mixture on a water bath for about 5 minutes.	Red precipitate is formed.	Presence of an aldehyde
Test for ketones			
13	**Legal's test:** A small amount of the substance is taken in a test tube. 1 ml sodium nitro prusside solution is added. Then sodium hydroxide solution is added dropwise.	Red colouration.	Presence of a ketone.
Test for an amine.			

14	**Dye test:** Take A small amount of an organic substance in a clean test tube, add 2 ml of HCl to dissolve it. Add few crystals of $NaNO_2$, and cool the mixture in ice bath. Then add 2 ml of ice cold solution of β-naphtholin NaOH.	Scarlet red dye is obtained.	Presence of an aromatic primary amine
	Test for diamide		
15	**Biuret test:** Take A small amount of an organic compound in a test tube. Heat strongly and then allow to cool. Dissolve the residue with 2 ml of water. To this solution Add 1 ml of dilute copper sulphate solution and few drops of 10% NaOH solution drop by drop.	Violet colour is appeared.	presence of a diamide
	Test for carbohydrates		
16	**Molisch's test:** Take A small amount of an organic compound in a test tube. It is dissolved in 2 ml of water. Add 3-4 drops of alpha naphthol to it.Then add conc H_2SO_4 through the sides of test tube carefully.	Violet or purple ring is formed at the junction of the two liquids.	Presence of carbohydrate
17	**Osazone test:** Take A small amount of an organic compound in a test tube. Add 1 ml of phenyl hydrazine solution and heat the mixture for about 5 minutes on a boiling water bath.	Yellow crystals are obtained	Presence of carbohydrate

Report:

The given organic compound contains /is

(i) Aromatic / aliphatic

(ii) Saturated / unsaturated

(iii) ___________ functional group

List of organic compounds for analysis:

1. Benzaldehyde
2. Cinnamaldehyde
3. Acetophenone
4. Benzophenone
5. Benzoic acid
6. Cinnamic acid
7. Urea
8. Glucose
9. Aniline_
10. Salicylic acid

REASONING

3. Action with sodium bicarbonate:

Carboxylic acids react with sodium bi carbonate and liberate CO_2. Evolution of carbon dioxide gives brisk effervescence.

$$2R\text{-}COOH + 2NaHCO_3 \longrightarrow 2R\text{-}COONa + CO_2\uparrow + H_2O$$

4. Action with Borsches reagent:

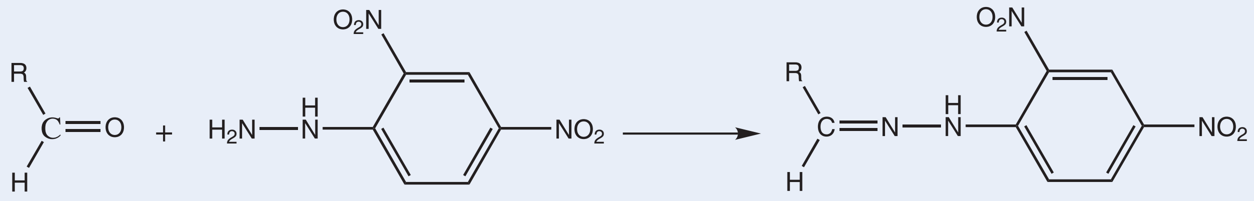
Borsches reagent is prepared by dissolving 2,4-dinitrophenylhydrazine in a solution containing methanol and little of conc sulphuric acid.

Aldehydes and ketones react with borsches reagent to form yellow, orange or red precipitate (dinitro phenylhydrazone)

Aliphatic carbonyl compounds give deep yellow precipitate.

Aromatic carbonyl compounds give red precipitate.

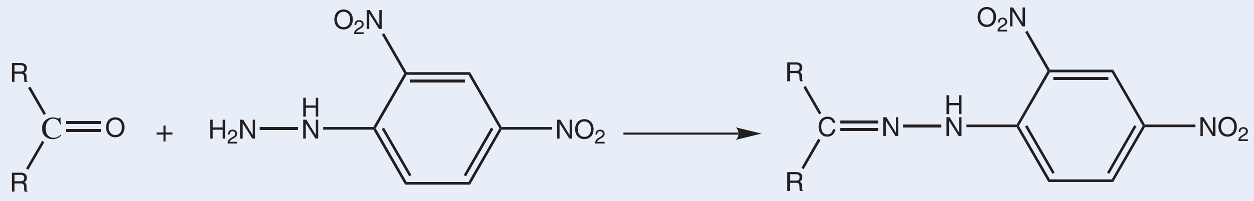
2,4-dinitrophenyl hydrazine can be used to qualitatively detect the carbonyl group of an aldehyde or ketone. A positive result is indicated by the formation of an yellow or orange-red precipitate of 2,4-dinitrophenyl hydrazone.



Aldehyde

2,4 dinitrophenylhydrazine

Aldehyde 2,4 dinitrophenylhydrazone
(Yellow or orange)



Ketone

2,4 dinitrophenylhydrazine

Ketone 2,4 dinitrophenylhydrazone
(Yellow or orange or red)

5.Charring test:

When carbohydrates are treated with concentrated sulphuric acid, dehydration of carbohydrates results in charring.

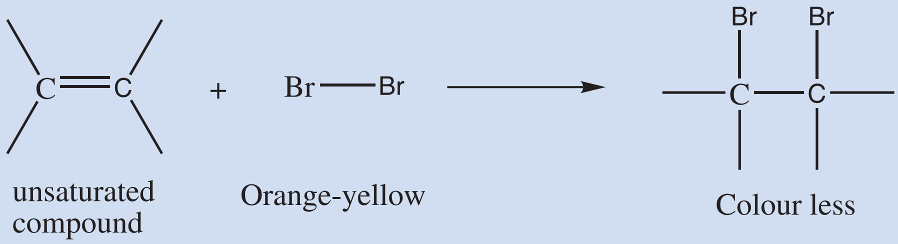
$$C_x(H_2O)_y \xrightarrow[\Delta]{H_2SO_4} x\,C + yH_2O$$

6. Ignition test

Aromatic compounds burn with a strong sooty yellow flame because of the high carbon–hydrogen ratio. Aliphatic compounds burn with non-sooty flame.

7.Test with bromine water:

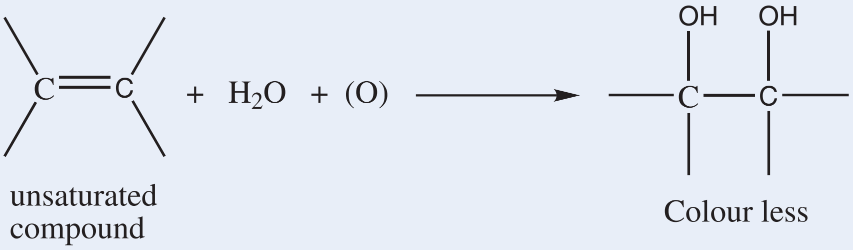
In this test, the orange-red colour of bromine solution disappears when it is added to an unsaturated organic compound.



8. Test with $KMnO_4$ (Baeyer's Test)

In this test, pink colour of $KMnO_4$ disappears, when alkaline $KMnO_4$ is added to an unsaturated hydrocarbon. The disappearance of pink colour may take place with or without the formation of brown precipitate of MnO_2.

$$2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3(O)$$



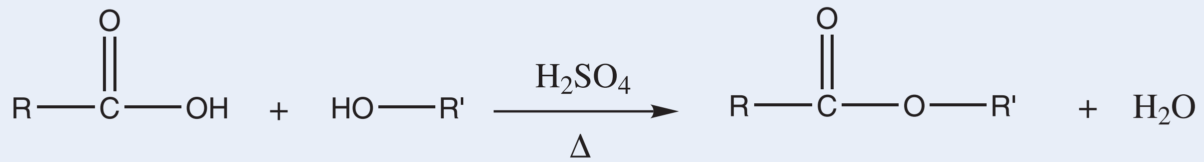
9. Neutral $FeCl_3$ test:

Phenol reacts with ferric ions to form violet coloured complex.

Aqueous solution Naphthols do not give any characteristic colour with neutral ferric chloride. But alcoholic solution of α and β naphtholsgiveblue-violet and green colouration respectively due to the formation of binaphthols.

10. Esterification test:

Alcohols react with carboxylic acids to form fruity smelling compounds called esters. This esterification is catalysed by an acid such as concentrated sulphuric acid.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + HO-R' \xrightarrow[\Delta]{H_2SO_4} R-\overset{\overset{\displaystyle O}{\|}}{C}-O-R' + H_2O$$

Carboxylic acid Alcohol Ester (pleasent fruity odour)

11. Tollen's reagent test:

Aldehydes react with Tollen's reagent to form elemental silver, accumulated onto the inner surface of the test tube. Thus silver mirror is produced on the inner walls of the test tube.

$$\underset{\text{Aldehyde}}{\text{R-CHO}} + 2\underset{\text{Tollen'sreagent}}{\left[Ag\left(NH_3\right)_2\right]OH} \longrightarrow \underset{\substack{\text{Metallic silver}\\\text{(Silver mirror)}}}{2Ag\downarrow} + R-COONH_4 + H_2O + 3NH_3$$

Tollen's reagent preparation:

Tollen's reagent is ammoniacal silver nitrate. It is prepared as follows. About 1 g of silver nitrate crystals are dissolved in distilled water in a clean dry test tube. To this aqueous solution of silver nitrate, add 2 ml of dilute NaOH solution to it. A brown precipitate of silver oxide is formed. This precipitate is dissolved by adding dilute ammonia solution drop wise.

12. Fehling's Test

Fehling's solution A is an aqueous solution of copper sulphate.

Fehling's solution B is a clear solution of sodium potassium tartrate (Rochelle salt) and strong alkali (NaOH).

The Fehling's solution is obtained by mixing equal volumes of both Fehling's solution A and Fehling's solution B that has a deep blue colour. In Fehling's solution, copper (II) ions form a complex with tartrate ions in alkali. Aldehydes reduces the Cu(II) ions in the Fehling's solution to red precipitate of cuprous oxide(copper (I) oxide).

$$\underset{\text{Aldehyde}}{RCHO} + \underbrace{2Cu^{2+} + 5OH^-}_{\downarrow\ \text{Fehling's solution}} \longrightarrow \underset{\substack{\text{(Cuprous oxide)}\\\text{(Red colour)}}}{Cu_2O\downarrow} + RCOO^- + 3H_2O$$

Note: Benzaldehyde may not give this test as the reaction is very slow.

13. Sodium nitroprusside Test

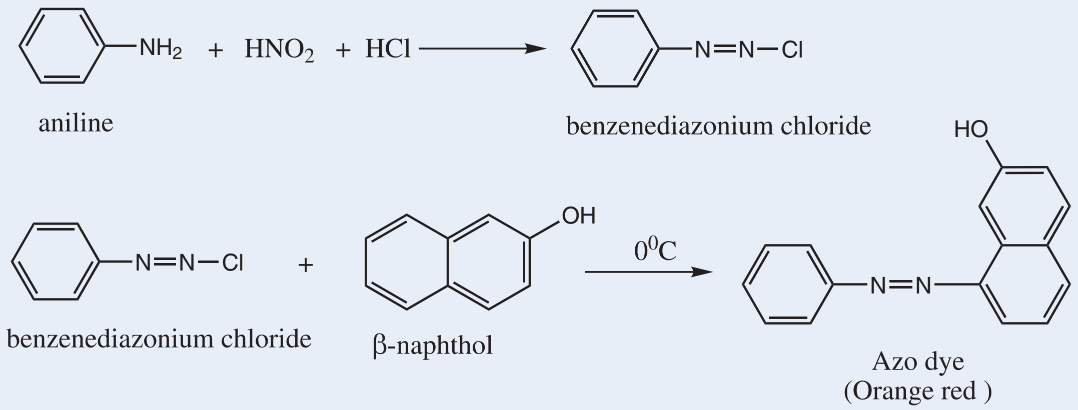
The anion of the ketone formed by a alkali reacts with nitroprusside ion to form a red coloured complex.this test is not given by aldehydes.

$$CH_3COCH_3 \xrightarrow{^-OH} CH_3COCH_2^- + H_2O$$

$$\underset{\text{sodium nitro prusside}}{[Fe(CN)_5\,NO]^{2-}} + CH_3COCH_2^- \longrightarrow \underset{\text{(Red coloured complex)}}{[Fe(CN)_5\,NO.CH_3COCH_2]^{3-}}$$

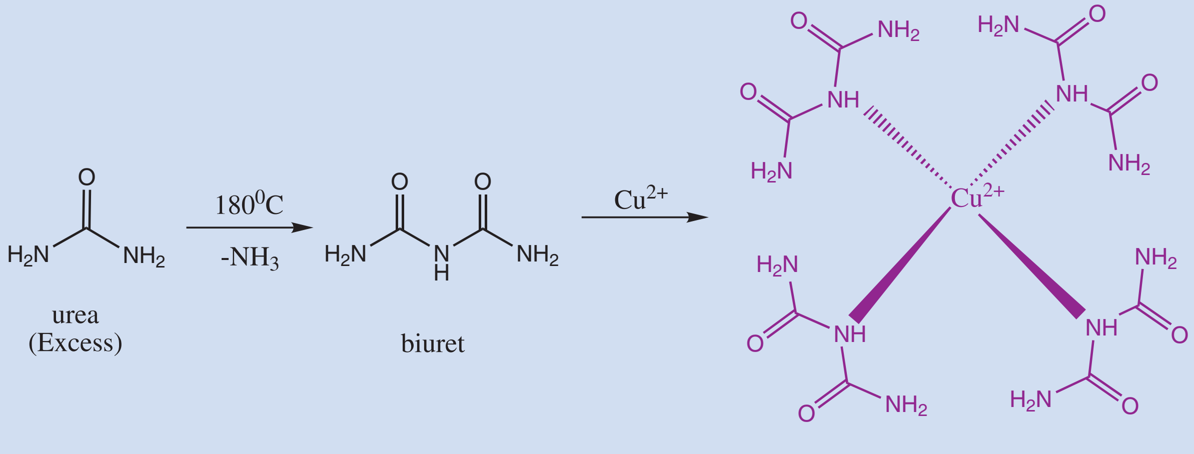
14. Azo-Dye Test

This test is given by aromatic primary amines. Aromatic primary amines react with nitrous acid to form diazonium salts. These diazonium salts undergo coupling reaction with β-naphthol to form orange coloured azo dye.



15. Biuret test

On strong heating Diamide (like urea) form biuret, which forms a copper complex with Cu^{2+} ions from copper sulphate solution. This copper –biuret complex is deep violet coloured.

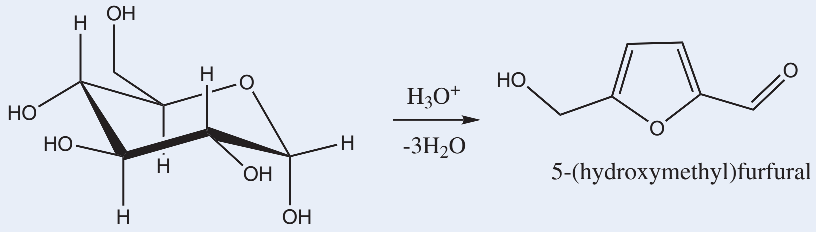


$[Cu(Biuret)_4]^{2+}$ complex

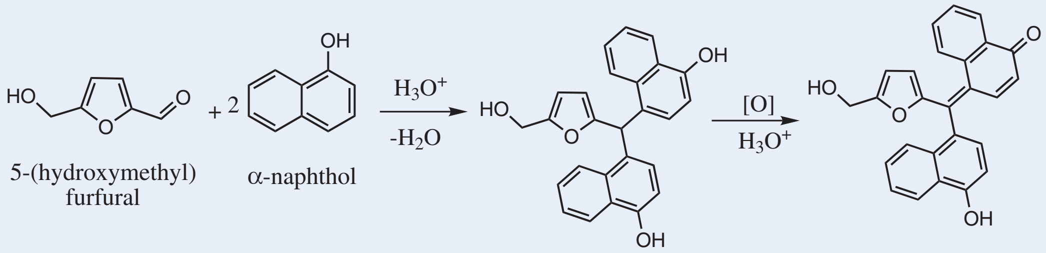
(violet colour)

16. Molisch's test:

Disaccharides, and polysaccharidesare hydrolysed to Monosaccharides by strong mineral acids. Pentoses are then dehydrated to furfural, while hexoses are dehydrated to 5-hydroxymethylfurfural. These aldehydes formed will condense with two molecules of α-Naphthol to form a purple-coloured product, as shown below.



5-(hydroxymethyl)furfural



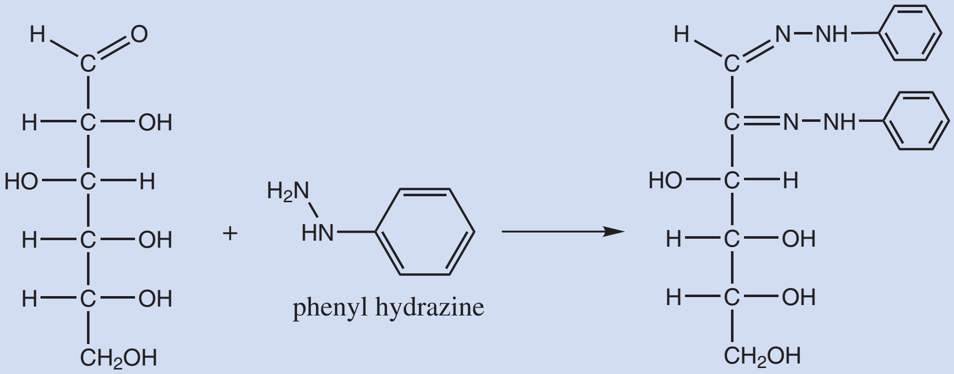
5-(hydroxymethyl) furfural

α-naphthol

A purple dye

17.Osazone test:

Phenyl hydrazine in acetic acid, when boiled with reducing sugars forms Osazone. The first two carbon atoms are involved in this reaction. The sugars that differ in their configuration on these carbon atoms give the same type of Osazone. Thus glucose, fructose and mannose give the same needle type yellow crystals.



phenyl hydrazine

Glucose

Glucosazone
(Yellow crystals)

II-VOLUMETRIC ANALYSIS

1. Estimation of Ferrous Sulphate (Fe^{2+})

Aim :

To estimate the amount of ferrous sulphate dissolved in 750 ml of the given unknown solution volumetrically. For this you are given with a standard solution of ferrous ammonium sulphate (FAS) of normality 0.1102 N and potassium permanganate solution as link solution.

Principle:

During these titrations, Fe^{2+} ions (from ferrous salts) are oxidised to MnO_4^- ions and MnO_4^- ion (from Mn^{2+}) is reduced to Mn^{2+} ion.

Oxidation : $5\,Fe^{2+} \longrightarrow 5\,Fe^{3+} + 5e^-$

Reduction : $\underset{\text{Pink}}{MnO_4^-} + 8H^+ + 5e^- \longrightarrow \underset{\text{colourless}}{Mn^{2+}} + 4H_2O$

Overall reaction : $5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

Short procedure:

S.no	Content	Titration-I	Titration-II
1	Burette solution	$KMnO_4$	$KMnO_4$
2	Pipette solution	20 ml of standard FAS	20 ml of unknown $FeSO_4$
3	Acid to be added	20ml of 2N H_2SO_4 (approx)	20ml of 2N H_2SO_4 (approx)
4	Temperature	Lab temperature	Lab temperature
5	Indicator	Self-indicator ($KMnO_4$)	Self-indicator ($KMnO_4$)
6	End point	Appearance of permanent pale pink colour	Appearance of permanent pale pink colour
7	Equivalent weight of $FeSO_4$ = 278		

Procedure :

Titration–I

(Link $KMnO_4$)Vs (Standard FAS)

Burette is washed with water, rinsed with $KMnO_4$ solution and filled with same $KMnO_4$ solution up to the zero mark. Exactly 20 ml of standard FAS solution is pipetted out into the clean, washed conical flask. To this FAS solution, approximately 20ml of 2N sulphuric acid is added. This mixture is titrated against $KMnO_4$ Link solution from the burette. $KMnO_4$ is added drop wise till the appearance of permanent pale pink colour. Burette reading is noted, and the same procedure is repeated to get concordant values.

Titration –I

(Link $KMnO_4$)Vs (Standard FAS)

S.no	Volume of standard FAS (ml)	Burette readings		Concordant value (Volume of $KMnO_4$) (ml)
		Initial (ml)	Final (ml)	
1	20			
2	20			
3	20			

Calculation :

Volume of $KMnO_4$ (link) solution (V_1) = ----------ml

Normality $KMnO_4$ (link) solution (N_1) =-----------N

Volume of standard FAS solution (V_2) = 20 ml

Normality of standard FAS solution (N_2) = 0.1102 N

According to normality equation: $V_1 \times N_1 = V_2 \times N_2$

$$N_1 = \frac{V_2 \times N_2}{V_1}$$

Normality of $KMnO_4$ (link) solution (N_1) = ________X________ N

Titration–II

(Unknown $FeSO_4$) Vs (Link $KMnO_4$)

Burette is washed with water, rinsed with $KMnO_4$ solution and filled with same $KMnO_4$ solution up to the zero mark. Exactly 20 ml of unknown $FeSO_4$ solution is pipetted out into the clean, washed conical flask. To this $FeSO_4$ solution approximately 20ml of 2N sulphuric acid is added. This mixture is titrated against $KMnO_4$ Link solution from the burette. $KMnO_4$ is added drop wise till the appearance of permanent pale pink colour. Burette reading is noted and the same procedure is repeated to get concordant values.

Titration –II

(Link $FeSO_4$)Vs (Unknown $FeSO_4$ solution)

s.no	Volume of Unknown $FeSO_4$ (ml)	Burette readings		Concordant value (Volume of $KMnO_4$) (ml)
		Initial (ml)	Final (ml)	
1	20			
2	20			
3	20			

Calculation :

Volume of Unknown $FeSO_4$ solution V_1 = 20 ml

Normality of Unknown $FeSO_4$ solution N_1 = ? N

Volume of $KMnO_4$ (link) solution V_2 = ml

Normality $KMnO_4$ (link) solution N_2 = X N

According to normality equation: $V_1 \times N_1 = V_2 \times N_2$

$$N_1 = \frac{V_2 \times N_2}{V_1}$$

$$N_1 = \_\_\_\_\_\_Y\_\_\_\_\_\_ \text{ N}$$

The normality of unknown $FeSO_4$ solution = ________________ N

Weight calculation:

The amount of $FeSO_4$ dissolved in 1 lit of the solution = (Normality) x (equivalent weight)

The amount of $FeSO_4$ dissolved in 750 ml of the solution = $\frac{\text{Normality x equivalentweight x 750}}{1000}$

$$N_1 = \frac{Y \times 278 \times 3}{4}$$

$$= \qquad g$$

Report :

The amount of $FeSO_4$ dissolved in 750 ml of the solution = g

2. Estimation of Ferrous Ammonium Sulphate (FAS)

Aim :

To estimate the amount of ferrous ammonium sulphate (FAS) dissolved in 1500 ml of the given unknown solution volumetrically. For this you are given with a standard solution of ferrous sulphate ($FeSO_4$)of normality 0.1024 N and potassium permanganate solution as link solution.

Principle:

Oxidation : $5\ Fe^{2+} \longrightarrow 5\ Fe^{3+} + 5e^-$

Reduction : $5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

Overall reaction : $5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

Short procedure:

s.no	Content	Titration-I	Titration-II
1	Burette solution	$KMnO_4$	$KMnO_4$
2	Pipette solution	20 ml of standard $FeSO_4$	20 ml of unknown FAS
3	Acid to be added	20ml of 2N H_2SO_4(approx)	20ml of 2N H_2SO_4 (approx)
4	Temperature	Lab temperature	Lab temperature
5	Indicator	Self-indicator ($KMnO_4$)	Self-indicator ($KMnO_4$)
6	End point	Appearance of permanent pale pink colour	Appearance of permanent pale pink colour
7	Equivalent weight of FAS = 392		

Procedure :

Titration–I

(Link $KMnO_4$)Vs (Standard $FeSO_4$)

Burette is washed with water, rinsed with $KMnO_4$ solution and filled with same $FeSO_4$ solution up to the zero mark. Exactly 20 ml of standard $FeSO_4$ solution is pipetted out into the clean, washed conical flask. To this solution, approximately 20ml of 2N sulphuric acid is added. This mixture is titrated against $KMnO_4$ Link solution from the burette. $KMnO_4$ is added drop wise till the appearance of permanent pale pink colour. Burette reading are noted, the same procedure is repeated to get concordant values.

Titration –I

(Link $KMnO_4$)Vs (Standard $FeSO_4$)

s.no	Volume of standard $FeSO_4$ (ml)	Burette readings		Concordant value (Volume of $KMnO_4$) (ml)
		Initial (ml)	Final (ml)	
1	20			
2	20			
3	20			

Calculation :

Volume of $KMnO_4$ (link) solution V_1 = ml

Normality $KMnO_4$ (link) solution N_1 = ?N

Volume of standard $FeSO_4$ solution V_2 = 20 ml

Normality of standard $FeSO_4$ solution N_2 = 0.1024 N

According to normality equation:

According to normality equation: $V_1 \times N_1 = V_2 \times N_2$

$$N_1 = \frac{V_2 \times N_2}{V_1}$$

Normality of $KMnO_4$ (link) solution (N_1) = ________X________ N

Titration–II

(Unknown FAS) Vs (Link $KMnO_4$)

Burette is washed with water, rinsed with $KMnO_4$ solution and filled with same $KMnO_4$ solution up to the zero mark. Exactly 20 ml of unknown FAS solution is pipetted out into the clean, washed conical flask. To this FAS solution approximately 20ml of 2N sulphuric acid is added. This mixture is titrated against $KMnO_4$ Link solution from the burette. $KMnO_4$ is added drop wise till the appearance of permanent pale pink colour. Burette reading is noted and the same procedure is repeated to get concordant values.

Titration –II

(Link $KMnO_4$)Vs (Unknown FAS)

s.no	Volume of Unknown FAS (ml)	Burette readings		Concordant value (Volume of $KMnO_4$) (ml)
		Initial (ml)	Final (ml)	
1	20			
2	20			
3	20			

Calculation :

Volume of Unknown FAS solution V_1 = 20ml

Normality of Unknown FAS solution N_1 = ? N

Volume of $KMnO_4$ (link) solution V_2 = ml

Normality $KMnO_4$ (link) solution N_2 = N

According to normality equation: $V_1 \times N_1 = V_2 \times N_2$

$$N_1 = \frac{V_2 \times N_2}{V_1}$$

N_1= ________Y_________ N

The normality of unknown FAS solution = _____Y_____ N

Weight calculation:

The amount of FAS dissolved in 1 lit of the solution = (Normality) x (equivalent weight)

The amount of FAS dissolved in 1500 ml of the solution $= \dfrac{\text{Normality} \times \text{equivalentweight} \times 1500}{1000}$

$$= \frac{Y \times 392 \times 1500}{1000}$$

= g

Report :

The amount of FAS dissolved in 1500 ml of the solution = g

3. Estimation of oxalic acid

Aim :

To estimate the amount of oxalic acid dissolved in 500 ml of the given solution volumetrically. For this you are given with a standard solution of ferrous ammonium sulphate (FAS) of normality 0.1 N and potassium permanganate solution as link solution.

Principle:

During these titrations, oxalic acid is oxidized to CO_2 and MnO_4^- ions (from $KMnO_4$) is reduced to Mn^{2+} ion.

Oxidation : $\underset{\text{Pink}}{MnO_4^-} + 8H^+ + 5e^- \longrightarrow \underset{\text{colourless}}{Mn^{2+}} + 4H_2O$

Reduction : $\underset{\text{Pink}}{MnO_4^-} + 8H^+ + 5e^- \longrightarrow \underset{\text{colourless}}{Mn^{2+}} + 4H_2O$

Overall reaction : $5(COOH)_2 + 2MnO_4^- + 6H^+ \longrightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$

Since one mole oxalic acid releases 2 moles of electrons, the equivalent weight of oxalic acid $= \frac{106}{2} = 63$ (oxalic acid is dihydrated)

Short procedure:

s.no	Content	Titration-I	Titration-II
1	Burette solution	$KMnO_4$	$KMnO_4$
2	Pipette solution	20 ml of standard FAS	20 ml of unknown oxalic acid
3	Acid to be added	20ml of 2N H_2SO_4(approx)	20ml of 2N H_2SO_4 (approx)
4	Temperature	Lab temperature	60 – 70 ^{0}C
5	Indicator	Self-indicator ($KMnO_4$)	Self-indicator ($KMnO_4$)
6	End point	Appearance of permanent pale pink colour	Appearance of permanent pale pink colour
7	Equivalent weight of oxalic acid = 63		

Procedure :

Titration–I

(Link $KMnO_4$)Vs (Standard FAS)

Burette is washed with water, rinsed with $KMnO_4$ solution and filled with same $KMnO_4$ solution up to the zero mark. Exactly 20 ml of standard FAS solution is pipetted out into the clean, washed conical flask. To this FAS solution, approximately 20ml of 2N sulphuric acid is added. This mixture is titrated against $KMnO_4$ Link solution from the burette. $KMnO_4$ is added drop wise till the appearance of permanent pale pink colour. Burette reading is noted and the same procedure is repeated to get concordant values.

Titration –I

(Link $KMnO_4$)Vs (Standard FAS solution)

s.no	Volume of standard FAS (ml)	Burette readings		Concordant value (Volume of $KMnO_4$) (ml)
		Initial (ml)	Final (ml)	
1	20			
2	20			
3	20			

Calculation :

Volume of $KMnO_4$ (link) solution V_1 = ml

Normality $KMnO_4$ (link) solution N_1 = ? N

Volume of standard FAS solution V_2 = 20 ml

Normality of standard FAS solution N_2 = 0.1 N

According to normality equation:

$$V_1 \text{ x } N_1 = V_2 \text{ x } N_2$$

$$N_1 = \frac{V_2 \text{ x } N_2}{V_1} =$$

Normality $KMnO_4$ (link) solution N_1 = ______________ N

Titration–II

(Unknown oxalic acid) Vs (Link $KMnO_4$)

Burette is washed with water, rinsed with $KMnO_4$ solution and filled with same $KMnO_4$ solution up to the zero mark. Exactly 20 ml of unknown oxalic acid solution is pipetted out into the clean, washed conical flask. To this oxalic acid solution approximately 20ml of 2N sulphuric acid is added. This mixture is heated to 60 – 70^{0}C using Bunsen burner and that hot solution is titrated against $KMnO_4$ Link solution from the burette. $KMnO_4$ is added drop wise till the appearance of permanent pale pink colour. Burette reading are noted, the same procedure is repeated to get concordant values.

Titration –II

(Link $KMnO_4$)Vs (Unknown oxalic acid)

s.no	Volume of Unknown oxalic acid (ml)	Burette readings		Concordant value (Volume of $KMnO_4$) (ml)
		Initial (ml)	Final (ml)	
1	20			
2	20			
3	20			

Calculation :

Volume of Unknown oxalic acid solution V_1 = 20 ml

Normality of Unknown oxalic acid solution N_1 = ? N

Volume of $KMnO_4$ (link) solution V_2 = ml

Normality $KMnO_4$ (link) solution N_2 = N

According to normality equation:

$$V_1 \text{ x } N_1 = V_2 \text{ x } N_2$$

$$N_1 = \frac{V_2 \text{ x } N_2}{V_1}$$

Normality of Unknown oxalic acid solution N_1 = ____Y____ N

Weight calculation:

The amount of oxalic acid dissolved in 1 lit of the solution =(Normality) x (equivalent weight)

The amount of oxalic acid dissolved in 500 ml of the solution $= \frac{Y \times 63 \times 500}{1000}$

$$= \frac{\quad \text{ x } 63 \text{ x } 500}{1000}$$

= g

Report :

The amount of oxalic acid dissolved in 500 ml of given the solution = g

4. Estimation of sodium hydroxide

Aim :

To estimate the amount of sodium hydroxide dissolved in 250 ml of the given unknown solution volumetrically. For this you are given with a standard solution of sodium carbonate solution of normality 0.0948 N and hydrochloric acid solution as link solution.

Principle:

Neutralization of Sodium carbonate by HCl is given below. To indicate the end point, methyl orange is used as an indicator.

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + CO_2 + H_2O$$

Neutralization of Sodium hydroxide by HCl is given below. To indicate the end point, phenolphthalein is used as an indicator.

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

Short procedure:

s.no	Content	Titration-I	Titration-II
1	Burette solution	HCl (link solution)	HCl (link solution)
2	Pipette solution	20 ml of standard Na_2CO_3 solution	20 ml of unknown NaOH solution
4	Temperature	Lab temperature	Lab temperature
5	Indicator	Methyl orange	Phenolphthalein
6	End point	Colour change from straw yellow to pale pink	Disappearance of pink colour
7	Equivalent weight of NaOH = 40		

Procedure :

Titration–I

(Link HCl)Vs (standard Na_2CO_3)

Burette is washed with water, rinsed with HCl solution and filled with same HCl solution up to the zero mark. Exactly 20 ml of standard Na_2CO_3solution is pipetted out into the clean, washed conical flask. To This solution 2 to 3 drops of methyl orange indicator is added and titrated against HCl link solution from the burette. HCl is added drop wise till the colour change from straw yellow to pale pink. Burette reading is noted and the same procedure is repeated to get concordant values.

Titration –I

(Link HCl)Vs (standard Na_2CO_3)

s.no	Volume of standard Na_2CO_3 (ml)	Burette readings		Concordant value (Volume of HCl) (ml)
		Initial (ml)	Final (ml)	
1	20			
2	20			
3	20			

Calculation :

Volume of HCl (link) solution V_1 = ml

Normality HCl (link) solution N_1 = ? N

Volume of standard Na_2CO_3 solution V_2 = 20 ml

Normality of standard Na_2CO_3 solution N_2 = 0.0948 N

According to normality equation:

According to normality equation: $V_1 \times N_1 = V_2 \times N_2$

$$N_1 = \frac{V_2 \times N_2}{V_1}$$

Normality of HCl (link) solution(N_1) = ______X________ N

Titration–II

(Unknown NaOH) Vs (Link HCl)

Burette is washed with water, rinsed with HCl solution and filled with same HCl solution up to the zero mark. Exactly 20 ml of unknown NaOH solution is pipetted out into the clean, washed conical flask. To This solution 2 to 3 drops of phenolphthalein indicator is added and titrated against HCl link solution from the burette. HCl is added drop wise till the pink colour disappears completely. Burette reading is noted and the same procedure is repeated to get concordant values.

Titration –II

(Link HCl)Vs (Unknown NaOH solution)

s.n	Volume of Unknown NaOH (ml)	Burette readings		Concordant value (Volume of HCl) (ml)
		Initial (ml)	Final (ml)	
1	20			
2	20			
3	20			

Calculation :

Volume of Unknown NaOH solution V_1 = 20 ml

Normality of Unknown NaOH solution N_1 = ? N

Volume of HCl (link) solution V_2 = ml

Normality HCl (link) solution N_2 = N

According to normality equation:

$$V_1 \text{ x } N_1 = V_2 \text{ x } N_2$$

$$N_1 = \frac{V_2 \text{ x } N_2}{V_1}$$

Normality of Unknown HCl solution N_1 = ______Y______ N

Weight calculation:

The amount of NaOH dissolved in 1 lit of the solution = (Normality) x (equivalent weight)

The amount of NaOH dissolved in 250 ml of the solution $= \frac{\text{Normality x equivalentweight x 250}}{1000}$

$$= \frac{Y \times 40 \times 250}{1000}$$

$$= \frac{\quad \text{x } 40 \text{ x } 250}{1000} \text{ g}$$

Report :

The amount of NaOH dissolved in 750 ml of the solution = g

5. Estimation of oxalic acid

Aim :

To estimate the amount of oxalic acid dissolved in 1250 ml of the given unknown solution volumetrically. For this you are given with a standard solution of HCl solution of normality 0.1010 N and sodium hydroxide solution as link solution.

Principle:

Neutralization of Sodium hydroxide by HCl is given below. To indicate the end point, phenolphthalein is used as an indicator.

$$\text{NaOH} + \text{HCl} \longrightarrow \text{NaCl} + \text{H}_2\text{O}$$

Neutralization of Sodium hydroxide by oxalic acid is given below. To indicate the end point, phenolphthalein is used as an indicator.

$$2\text{NaOH} + \underset{\text{Oxalic acid}}{(\text{COOH})_2} \longrightarrow \underset{\text{Sodium oxalate}}{(\text{COONa})_2} + 2\text{H}_2\text{O}$$

Short procedure:

s.no	Content	Titration-I	Titration-II
1	Burette solution	HCl (standard solution)	Oxalic acid (unknown solution)
2	Pipette solution	20 ml of NaOH link solution	20 ml of NaOH link solution
4	Temperature	Lab temperature	Lab temperature
5	Indicator	Phenolphthalein	Phenolphthalein
6	End point	Disappearance of pink colour	Disappearance of pink colour
7	Equivalent weight of oxalic acid = 63		

Procedure :

Titration–I

(standard HCl)Vs (link NaOH)

Burette is washed with water, rinsed with HCl solution and filled with same HCl solution up to the zero mark. Exactly 20 ml of NaOH is pipetted out into the clean, washed conical flask. To This solution 2 to 3 drops of phenolphthalein indicator is added and titrated against HCl solution from the burette. HCl is added drop wise till the pink colour disappears completely. Burette reading is noted and the same procedure is repeated to get concordant values.

Titration –I

(standard HCl)Vs (**link** NaOH)

s.no	Volume of NaOH(ml)	Burette readings		Concordant value (Volume of std HCl) (ml)
		Initial (ml)	Final (ml)	
1	20			
2	20			
3	20			

Calculation :

Volume of NaOH(link) solution $V_1 = 20$ ml

Normality NaOH(link) solution $N_1 = ?$ N

Volume of standard HCl solution $V_2 =$ ml

Normality of standard HCl solution $N_2 = 0.1010$ N

According to normality equation:

$$V_1 \text{ x } N_1 = V_2 \text{ x } N_2$$

$$N_1 = \frac{\quad \times 0.1010}{20} =$$

Normality NaOH (link) solution N_1 =_____X_____ N

Titration–II

(Unknown oxalic acid) Vs (Link NaOH)

Burette is washed with water, rinsed with oxalic acid solution and filled with same oxalic acid solution up to the zero mark. Exactly 20 ml of NaOH solution is pipetted out into the clean, washed conical flask. To This solution 2 to 3 drops of phenolphthalein indicator is added and titrated against oxalic acid solution from the burette. oxalic acid is added drop wise till the pink colour disappears completely. Burette reading is noted and the same procedure is repeated to get concordant values.

Titration –II

(Link NaOH)Vs (Unknown oxalic acid solution)

s.no	Volume of NaOH link (ml)	Burette readings		Concordant value (Volume of oxalic acid) (ml)
		Initial (ml)	Final (ml)	
1	20			
2	20			
3	20			

Calculation :

Volume of Unknown oxalic acid solution V_1 = ml

Normality of Unknown oxalic acid solution N_1 = ? N

Volume of NaOH solution V_2 = 20 ml

Normality NaOH solution N_2 = N

According to normality equation:

$$V_1 \text{ x } N_1 = V_2 \text{ x } N_2$$

$$N_1 = \frac{V_2 \text{ x } N_2}{V_1}$$

Normality of Unknown oxalic acid solution N_1 = $\underline{\qquad Y \qquad}$N

Weight calculation:

The amount of oxalic acid dissolved in 1 lit of the solution = (Normality) x (equivalent weight)

The amount of oxalic acid dissolved in 1250 ml of the solution $= \frac{\text{Normality x equivalentweight x 1250}}{1000}$

$$= \frac{Y \times 63 \times 1250}{1000}$$

$$= \frac{\qquad \text{x 63 x 1250}}{1000}$$

$$= \qquad \text{g}$$

Report :

The amount of oxalic acid dissolved in 1250 ml of the solution = g

Glossary - கலைச்சொற்கள்

Acidic oxide	அமிலஆக்சைடு
Activated complex	கிளர்வுற்ற அணைவு
Activation energy	கிளர்வுறு ஆற்றல்
Ambidentate ligand	இருமுனைஈனி
Amorphous solid	படிகவடிவமற்றதிண்மம்
Amphoteric oxide	ஈரியல்புத்தன்மைகொண்டஆக்சைடு
Anionic complex	எதிரயனிஅணைவு
Anisotropy	திசையொப்புபண்புஅற்றவை
Antiferromagnetic	எதிர்பெர்ரோகாந்ததன்மை
Basic oxide	காரஆக்சைடு
Blast furnace	ஊதுஉலை
Bleaching	வெளுப்பான்
BM	போர்மேக்னடான்
Body cantered cubic unit cell	பொருள்மையகனசதுரஅலகுக்கூடு
Brass	பித்தளை
Bronze	வெண்கலம்
Brown ring test	பழுப்புவளையசோதனை
Cast iron	வார்ப்பிரும்பு
Catalysts	வினைவேகமாற்றி
Cationic complex	நேரயனிஅணைவு
Central metal ion	மையஉலோகஅயனி
CFT	படிகபுலக்கொள்கை
Chalcogens	சால்கோஜன்கள்(தாதீனிகள்)
Chelating ligand	கொடுக்கிணைப்புஈனி
Chemiluminescence	வேதி ஒளிர்தல்
Chile saltpeter	சிலிவெடியுப்பு
Chromatography	வண்ணப்பிரிகைமுறை
Close packed arrangement	நெருங்கிபொதிந்தகட்டமைப்பு
Coinage metals	நாணயஉலோகங்கள்
Collision theory	மோதல் கொள்கை
Column chromatography	குழாய்வண்ணப்பரிகைமுறை
Completely filled	முழுவதுமாகநிரம்பிய
Concentration of the ore	தாதுக்களை செறிவூட்டல்

Conductivity	கடத்துத்திறன்
Coordination compounds	அணைவுச்சேர்மங்கள்
Coordination isomerism	அணைவுமாற்றியம்
Coordination number	அணைவுஎண்
Coordination sphere	அணைவுக்கோளம்
Crystal defect	படிகக்குறைபாடு
Crystal field splitting	படிகபுலப்பிரிப்பு
Crystalline solid	படிகவடிவமுடையதிண்மம்
Cupellation	புடமிடுதல்
Decay	சிதைவு
Degenerate orbitals	சமஆற்றல்கொண்டஆர்பிட்டால்கள்
Deliquescent	நீர்உறிஞ்சிநீர்மமாதல்
Density	அடர்த்தி
Dibasic acid	இருகாரத்துவஅமிலம்
Diffraction	விளிம்புவளைவுவிளைவு
Double salts	இரட்டைஉப்புகள்
Ductility	கம்பியாகஇழுபடும்தன்மை
Earth's crust	புவிமேலடுக்கு
Edge	விளிம்பு
Electro metallurgy	மின்வேதிஉலோகவியல்
Electrolytic refining	மின்னாற்தூய்மையாக்கல்
Electroplating	மின்முலாம்பூசுதல்
Enameling	கனிமபூச்சிடுதல்
Excited state	கிளர்வுநிலை
Extraction	பிரித்தெடுத்தல்
Extrinsic semiconductor	புற மாசுக்குறைக்கடத்தி (புறமார்ந்த குறைகடத்தி)
Face	முகப்பு
Face cantered cubic unit cell	முகப்புமையகனசதுரஅலகுக்கூடு
Facial isomer	முகப்பு மாற்றியம்
Ferromagnetic	பெர்ரோகாந்ததன்மை
Flash photolysis	துடிப்பு ஒளிப்பகுப்பாய்வு
Flints	தீக்கல்
Fluorescence	ஒளிர்தல்
Fluorescing surface	ஒளிரும்பரப்புகள்

Froth floatation	நுரைமிதப்புமுறை
Galvanizing	துத்தநாகமுலாம்பூசுதல்
Gangue	கனிமக்கழிவு
Garlic	உள்ளிப்பூண்டு
Geometrical isomerism	வடிவமாற்றியம்
Gravity separation	புவிஈர்ப்புபிரித்தெடுத்தல்
Half filled	பாதிநிரம்பிய
Halogens	ஹேலஜன்கள் (உப்பீனிகள்)
Hardness of water	நீரின்கடினத்தன்மை
Heteroleptic complex	பல்லினஈனிஅணைவு
High spin complex	நிறைசுழற்சிஅணைவு
Hole	துளை
Homoleptic complex	ஓரினஈனிஅணைவு
Hybrid orbitals	இனக்கலப்புஆர்பிட்டால்கள்
Hydration energy	நீரேற்றஆற்றல்
Hydro metallurgy	நீர்ம உலோகவியல்
Hygroscopic	நீர்உறிஞ்சிஇறுத்திவைத்தல்
Incompressibility	அமுக்கஇயலாத்தன்மை
Indian saltpeter	இந்தியவெடியுப்பு
Inert gases	மந்தவாயுக்கள்
Inert pair effect	மந்தஇணைவிளைவு
Inner d orbital complex	உள்dஆர்பிட்டால்அணைவு
Inner transition metals	உள்இடைநிலைத்தனிமங்கள்
Instantaneous rate of reaction	வினைவேகம்
Interfacial angle	முகப்பிடைக்கோணம்
Interstitial defect	இடைச்செறுகல்படிககுறைபாடு
Interstitial void	இடைவெளிவெற்றிடம்
Intrinsic semiconductor	இயல்குறைக்கடத்தி (உள்ளார்ந்தகுறைகடத்தி)
Ionisation enthalpy	அயனியாக்களன்தால்பி
Ionisation isomerism	அயனியாதல்மாற்றியம்
Isotropy	திசையொப்பு பண்பு உடையவை
Kinetic stability	வேகவியல் நிலைப்புத் தன்மை
Lanthanide contraction	லாந்தனைடுகுறுக்கம்
Lattice plane	அணிக்கோவைத்தளம்

Leaching	வேதிக்கழுவுதல்முறை
LFT	ஈனிபுலக்கொள்கை
Ligands	ஈனிகள்
Linkage isomerism	இணைதல்மாற்றியம்
Low spin complex	குறைசுழற்சிஅணைவு
Luminescence	ஒளிர்தல்
Magnetic resonance imaging	காந்தஒத்ததிர்வுபடமாக்கி
Magnetic separation	காந்தப்பிரிப்பு
Malleability	தகடாகநெகிழும்தன்மை
Meridional isomer	நெடுவரை மாற்றியம்
Metal deficiency defect	குறைஉலோகஅயனிக்குறைபாடு
Metal excess defect	அதிஉலோகஅயனிக்குறைபாடு
Metallic lustre	உலோகபளபளப்புத்தன்மை
Metalloids	உலோகபோலிகள்
Metallurgy	உலோகவியல்
Minerals	கனிமங்கள்
Molecularity	வினைமூலக்கூறு எண்
Molten state	உருகியநிலை
Monobasic acid	ஒருகாரத்துவஅமிலம்
MOT	மூலக்கூறுஆர்பிட்டால்கொள்கை
Mustard	கடுகு
Negative catalyst	வினை தளர்த்தி (எதிர்வினைவேக மாற்றி)
Nitrogenous fertilizers	நைட்ரஜன்உரங்கள்
Octahedral	எண்முகி
Opaque	ஒளிபுகா
Optical isomerism	ஒளியியல்மாற்றியம்
Orbital angular momentum	ஆர்பிட்டால்கோணஉந்தம்
Order of the reaction	வினைவகை
Ores	தாதுக்கள்
Outer d orbital complex	வெளிdஆர்பிட்டால்அணைவு
Oxidation number	ஆக்ஸிஜனேற்றஎண்
Oxoanion	ஆக்சோஎதிரயனி
Oxocations	ஆக்சோநேரயனி
Packing fraction	பொதிவுபின்னம்
Phosphorescence	நின்றொளிர்தல்

Photo sensitizer	ஒளிவேதிவினைத் தூண்டி
Photochemical reaction	ஒளி வேதி வினை
Pickling of steel	எஃகுவேதித்தூய்மையாக்கல்
Pig iron	கசடுஇரும்பு
Planar	ஒருதளவடிவம்
Positive catalyst	வினையூக்கி (நேர்வினைவேக மாற்றி)
Preservative	பதப்படுத்தி
Primary valency	முதன்மைஇணைதிறன்
Pulverization	மீநுண்துகளாக்குதல்
Pyro metallurgy	வெப்பவேதிஉலோகவியல்
Quantum efficiency	ஒளிவேதி வினைத்திறன்
Radioactive	கதிரியக்கம்
Rate constant	வினைவேக மாறிலி
Refrigerant	குளிரூட்டி
Rigid	கட்டிறுக்கம்
Roasting	வறுத்தல்
Rocket fuels	ராக்கெட்எரிபொருள்
Seaweeds	கடற்பாசி
Secondary valency	இரண்டாம்நிலைஇணைதிறன்
Self-reduction	சுயஒடுக்கம்
Simple cubic unit cell	எளியகனசதுரஅலகுக்கூடு
Slag	கசடு
Smelting	உருக்கிபிரித்தல்
Solvate isomerism	கரைப்பானேற்றமாற்றியம்
Spectrochemical series	வேதிநிறமாலைதொடர்
Square planar	சதுரதளம்
Stability constant	நிலைப்புத்தன்மைமாறிலி
Stabilizers	நிலைநிறுத்திகள்
Strong field ligands	நிறைபுலஈனி
Structural isomerism	அமைப்புமாற்றியம்
Successive reaction	அடுத்தடுத்து நிகழும் வினைகள்
Super conducting magnets	அதிமின்கடத்துகாந்தங்கள்
Superconductivity	அதிமின்கடத்துத்திறன்
Symmetry	சமச்சீர்த்தன்மை
Synergic effect	ஒருங்கிணைந்த விளைவு

Tetrahedral	நான்முகி
Thermal decomposition	வெப்பச்சிதைவு
Thermodynamic stability	வெப்பஇயக்கவியல்நிலைப்புத்தன்மை
Transition metals	இடைநிலைத்தனிமங்கள்
Transition state	பரிமாற்ற நிலை
Tribasic acid	முக்காரத்துவஅமிலம்
Trigonal bipyramidal	முக்கோணஇருபிரமிடு
Trigonal pyramid	முக்கோணபிரமிடு
Unit cell	அலகுக்கூடு
Unpaired electrons	இணைசேராஎலக்ட்ரான்கள்
Unpleasant	நறுமனமற்ற
Vapour phase refining	வாயுநிலைதூய்மையாக்கல்
VBT	இணைதிறன்பிணைப்புகொள்கை
Void	வெற்றிடம்
Weak field ligand	குறைபுலஈனி
Wool	கம்பளி
Wrought iron	தேனிரும்பு
Zone refining	கரைதிறவேறுபாட்டுபிரித்தெடுத்தல்

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