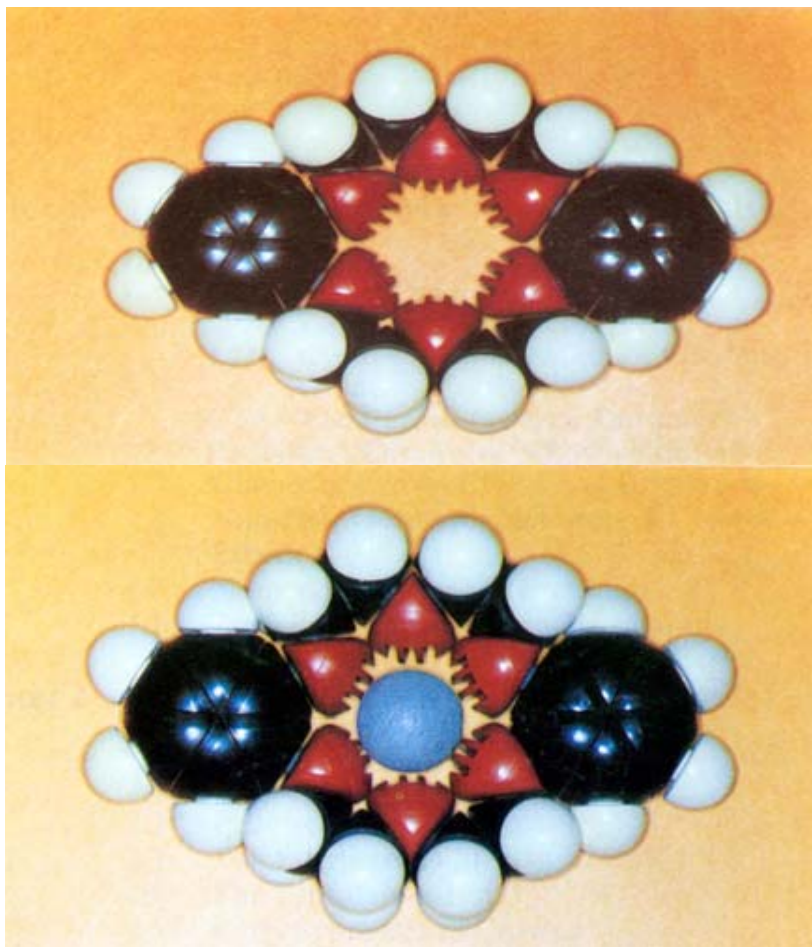


SELECTED TOPICS IN CHEMISTRY



NATIONAL CENTRE FOR CATALYSIS RESEARCH
INDIAN INSTITUTE OF TECHNOLOGY MADRAS
APRIL 2010

Preface

The title and the contents of this presentation may appear to be arbitrary but the topics have been chosen keeping in mind the necessity for stimulating the young minds to the developments in chemistry in this century. This has been amply explained in the first chapter of this presentation. Chemical systems have come very near to the biological systems and the key for understanding the life process certainly needs the understanding of the weak and bonding forces in molecules.

Chemical aggregates follow certain unusual features in terms of geometry, as well as architecture and it is necessary that one understands at an early stage of knowledge accumulation so that the development process can be easily and timely assimilated. Keeping this mind this special summer course for the school going children has been evolved and it is hoped that our efforts will have the necessary impact in the learning community.

As usual this effort has been made possible by the kind cooperation and participation by the Childrens' Club and it is our duty to express our sincere thanks to the secretary of the club Mr. Narayanaswamy whose never diminishing enthusiasm has been the motivation for us to conduct this course year after year.

On behalf of the National Centre for Catalysis Research at the Indian Institute of Technology Madras we would like thank the authorities of the institute for having granted permission to conduct the programme and also for providing the necessary facilities for this programme.

We have attempted to put together the material presented in this course in the form of a compilation with the hope that it will be useful even for those who could not be physically present in the course. However, it will be our endeavour to improve our presentation based on the feed back that we will receive from all those who come across this compilation.

It is our hope that our small effort will have its own effect in fostering chemistry in this country

Chennai
Dated 12th April 2010

B. Viswanathan

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CHAPTER - 1

INTRODUCTION – WHAT IS NEW IN CHEMISTRY FOR THIS CENTURY?

B. Viswanathan

A book entitled **Chemistry for the 21st Century** has been edited by Ehud Keinan and Israel Schechter and has been published by Wiley in March 2001. In this exceptional book, many breakthroughs of modern chemistry are illustrated and explained by leading scientists. Now nearly after ten years, it is necessary for us to look back and see what will be the chemistry in the remaining part of this Century. One can still expect remarkable developments and advancements in the coming years. However, it is necessary to recognize the basic and fundamental concepts of chemistry that has led to the many developments in the last two centuries. Numerous Prize winners of all chemical disciplines have provided the overview of the new ideas and approaches that will shape this dynamic and fast changing science over the forthcoming decades and so will have a decisive influence on our living standards. This glimpse of the comfortable future is naturally based on the findings granted to us by the rapid increase in chemical research during the 20th century. It may be said that a silent "revolution" took place in the 20th century in chemical sciences, the positive results of which are still not fully realized. For example, chemists in research laboratories nowadays are able to develop drugs in increasingly short times to treat diseases once thought incurable. They can design new materials that withstand extreme conditions. They can probably predict the properties of compounds that no one has even seen yet.

In the last century, the domains of Chemistry have seen some remarkable developments. Starting from the remarkable ammonia synthesis in the early part of last century, which saw that at least just sufficient food crops could be cultivated, to the development of oxide based super conductors discovered in 1986 with superconducting transition at 90 K from the transition temperature near to absolute zero in 1911, which threw some hope for the humanity to aspire for an economic greediness, many developments both in fundamental science as well as in industrial practice like the fluid bed operation of catalytic reactions and all other discoveries of the 20th century have

shown how the developments in chemistry can transform the way the society conducts itself with respect to time and derive means for a comfortable life style.

Chemistry has been blamed for causing the environmental degradation as well as for exploiting nature excessively, but it must be remembered that the same branch of science has brought forth the concept of **Green chemistry** with the possible 12 governing principles (Given in Appendix to this chapter) which has dominated the developments in chemistry in the last two or three decades. Chemistry has also brought newer concepts in the domain of energy with less or least pollution in terms of Fuel cells and Batteries. Though these energy sources are in the development stages today, it is hoped that these technologies will dominate and satisfy the energy requirements of humanity in the years to come.

Similarly, the triple sciences, namely Physics/Chemistry/Biology are certain to merge and evolve as one interdisciplinary science with various new domains of understanding of evolution and life as well as provide a disease-less or less number of diseases in the world. This merger of the disciplines of sciences can be expected to bring revolutionary changes in our concept, perception, understanding and knowledge of life systems and of its origin in the world.

From the birth of modern chemistry at the end of the 18th century to the end of the 20th Century, the science of Chemistry has been centered in the molecules which are composed of atoms with covalent and ionic bonds to connect these atomic species in the molecule. The structures, properties and chemical functionalities of the molecules have been usually explained in terms of these bonding characteristics. It has been taken for granted that if one can understand the bonding in each molecule, one can understand the properties and functions of all substances. Chemistry based on such an assumption may be called the Molecular Chemistry.

There were, however, some chemists who suspected such a view might not be able to stand the test of the time. Indeed as early as the 1920s, it was already recognized that there were some materials whose structure or properties and functions could not be explained in terms of simple known bonding in molecules. Around that time, the concept

of hydrogen bonding was successfully introduced to account for the partial association of water, acetic acid and many other molecules. Hydrogen bonding is beyond the scope of the valence theory originally formulated by Kekulé. Although the strength of hydrogen bonding is only 10% of the strength of normal covalent bond, it helps molecules bind weakly to each other. In this sense, hydrogen bonding may be called a kind of a weak chemical bond.

Another concept, **intermolecular force** or **van der Waals force** has been introduced to account for the fact that such nonpolar molecules as H_2 (hydrogen molecules) crystallize at extremely low temperatures. The driving force of ionic bonds, *i.e.*, the Coulomb interaction is proportional to the reciprocal of the square of distance. The van der Waals force is proportional to the reciprocal to the sixth power of the distance, and hence should have a different power.

This concept can be explained by considering the class of compounds called “**Clathrate compounds**”. When an aliphatic hydrocarbon such as octane (C_8H_{18}) was added to a solution of urea ($CO(NH_2)_2$), beautiful crystalline rods were deposited. The crystals were composed of urea and octane, but the ratio was not an integer. By gentle heating, the crystals can be decomposed back into urea and octane. This observation indicated that the two components were not bound by normal covalent or ionic bonds. The structure of the crystals (called urea adducts at that time) as elucidated by X-ray crystallographic analysis showed urea molecules form a chain by hydrogen bonding, and this chain forms a spiral, leaving an empty column in the middle. Octane molecules are trapped in the empty column, and remains in this cavity by weak interaction. . These compounds are now called inclusion compounds or clathrate compounds. Compounds whose role is similar to that of urea are now called hosts, and those whose role is similar to that of octane are called guests. A novel branch of chemistry, namely **host-guest chemistry** has evolved from this. The relevance of this interaction in biomolecules especially in poly peptides has been realized and this will give rise to revolutionary concepts of human evolution itself. Similarly the crown ethers (typical structure of the crown ethers is shown in Fig.1.) originally discovered around 1967 by Charles J Pedersen showed remarkable inclusion of alkali ions within its molecular framework and hence in

the presence of these ions they also showed solubility differences in solvents in addition to other specific physical properties.

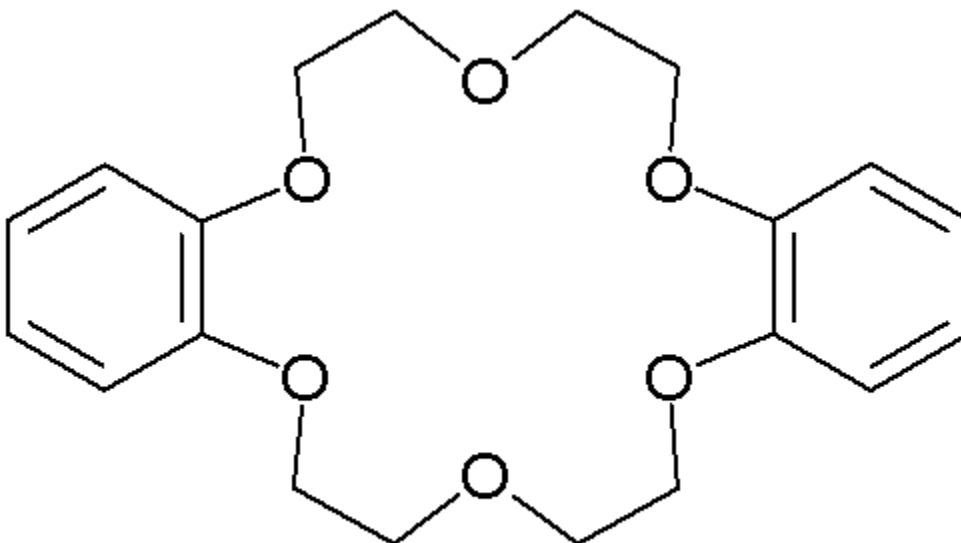


Fig.1. Structure of Dibenzo-18-crown-6 (a typical so called crown like molecule)

The postulate in this discovery was the trapping of the ions in the cavity of the molecules. This has some similarities in the trapping of metallic species in the so called Fullerenes. In fact, the discovery of fullerenes showed how remarkable the carbon atom is in forming new chemical entities even though the remarkable chemistry of carbon compounds was already known in the form of a separate branch of chemistry namely **Organic Chemistry**.

The interaction between crown ethers and alkali metal cations is a weak interaction type, which is different from conventional chemical bonds. It turned out that interactions of this type, which exist not only in crystals but also in solutions, are more general than expected. These trapped alkali metal cations can be brought into living organisms through membranes. Compounds with such a function are called **ionophores**. All these developments have been leading to the merger of organic and inorganic chemistry with life sciences and this has led to the introduction of bio-organic or bio-inorganic chemistry which has led to the understanding of the formation of complexes or membranes and cells. This branch has also enabled a detailed understanding of the

reactions between the enzymes and substrates and also led to the interaction between hormones or drugs and receptors. All these developments have seen remarkable changes in the way one understands life and living beings and their functioning. This amalgamation of organic and inorganic chemistry with biology has taken place since the life species namely, enzymes contain the normal functional groups found in organic chemistry and in many of them the transition metal ions are the so called active centres and hence this evolution of new branches of chemistry appears to be logical and hence both these branches of chemistry deal with all kinds of assemblies formed as a result of weak interactions. These assemblies have been termed by Lehn as supramolecules and the chemistry dealing with these molecules is called **Supramolecular Chemistry**, which has evolved as another new branch of chemistry in the recent decades.

It is normally anticipated that supramolecules should possess less order as compared to the conventional molecules, since the forces involved are weak. However since these weak interactions have some selectivity similar to the enzyme-substrate interactions which are considered as lock and key process, these intermolecular interactions can also result in high order. It is expected that in the coming years the understanding of the supra molecular chemistry will greatly improve which will facilitate the understanding of the behaviour of living organisms. It is necessary to realize that molecular systems like life on earth exist in combination and assembles and hence the chemistry will be predominantly supra molecular in nature. Isolated molecules can probably exist only in cosmic space.

The specific directions that chemistry will take and proceed in the remaining years of the 21st century may be difficult to predict but it is certain that it will go in the direction of keeping the balance with nature. It will be in the direction of understanding of nature as well as preserving environment. This will also lead to newer forms of energy conversion process with restrictions being imposed on global warming as well as on the emission of certain types of chemicals.

The realization that any more degradation of the environment is not acceptable has led to the new branch of chemistry called the **environmental chemistry**. Since chemists are primarily responsible for the observed degradation of the environment, it will be appropriate and fitting if the same chemists find solutions for the preservation of

environment and prevent it from further degradation. It appears that Chemistry has a big role to play in maintaining a **Sustainable Society**.

However there are still a number of challenges facing chemists. The energy sources that are being presently exploited cannot give rise to a sustainable society. It is necessary that chemists will have to come out with alternate energy sources. Though many options exist the chemists have to formulate energy conversion processes either from C₁ carbon based systems or look for alternate energy sources like hydrogen from water.

Development of new synthetic strategies for value added chemicals has always been receiving the attention of chemists. However, it is now imperative that the chemists resort to alternate ways of activation instead of the conventional methods of activation by thermal means and functionality.

Analytical capability (that is for identifying and estimating the chemical species) has reached the ultimate level of identifying and estimation at molecular level. The developed modern microscopic tools have been revealing many of the features for the chemical systems which have not been realized till recently. Systems and chemical species hitherto considered to be inert, have turn to be active species in nano-scale. In spite of the possibility of resolving species at nano-meter dimensions, the basic and fundamental concepts of chemistry are still applicable and can be judiciously employed for the design and building new chemical entities. The concept of self assembly is already exploited for the generation of micro- and meso-porous solids. The building of porous solids follow a template route where in some surfactant template molecules are allowed to aggregate by micelle mechanism on which the inorganic species precipitate or deposit and subsequently the aggregated template is carefully removed. The concept of selectivity has crossed various steps of the ladder and has reached the asymmetry and atom economy. This order follows the chemo-selectivity, region-selectivity, stereo-selectivity and finally atom economy. The concepts of energy conversion and storage have seen many new postulates. The current developments centre around super capacitors, batteries and fuel cells.

Most of the synthetic efforts in chemistry centre around generating or synthesizing molecules of relevance from known small molecules or entities with care for the desired selectivity. These efforts in recent times have turned towards the molecules

that mimic the biological systems for better understanding of life processes. The hope, in this effort, is to be able to rectify or repair the malfunctioning biological molecules which usually cause fatal diseases in living beings.

The chapters in this compilation have been evolved keeping in mind all the conceptual evolutions in chemistry taking place in the recent past. It is our hope that the material contained in this compiled volume will be stimulating to the young innovative minds of this country.

Appendix to Chapter 1

The 12 basic principles of Green Chemistry. (Anastas and Warner have developed these Twelve Principles of Green Chemistry to aid one in assessing how green a chemical, a reaction or a process is.)

1. Prevent waste: Design chemical syntheses to prevent waste, leaving no waste to treat or clean up.
2. Design safer chemicals and products: Design chemical products to be fully effective, yet have little or no toxicity.
3. Design less hazardous chemical syntheses: Design syntheses to use and generate substances with little or no toxicity to humans and the environment.
4. Use renewable feedstock: Use raw materials and feedstock that are renewable rather than depleting. Renewable feedstock is often made from agricultural products or is the wastes of other processes; depleting feedstock is made from fossil fuels (petroleum, natural gas, or coal) or is mined.
5. Use catalysts, not stoichiometric reagents: Minimize waste by using catalytic reactions. Catalysts are used in small amounts and can carry out a single reaction many times. They are preferable to stoichiometric reagents, which are used in excess and work only once.
6. Avoid chemical derivatives: Avoid using blocking or protecting groups or any temporary modifications if possible. Derivatives use additional reagents and generate waste.

7. Maximize atom economy: Design syntheses so that the final product contains the maximum proportion of the starting materials. There should be few, if any, wasted atoms.
8. Use safer solvents and reaction conditions: Avoid using solvents, separation agents, or other auxiliary chemicals. If these chemicals are necessary, use innocuous chemicals. If a solvent is necessary, water is a good medium as well as certain eco-friendly solvents that do not contribute to smog formation or destroy the ozone.
9. Increase energy efficiency: Run chemical reactions at ambient temperature and pressure whenever possible.
10. Design chemicals and products to degrade after use: Design chemical products to break down to innocuous substances after use so that they do not accumulate in the environment.
11. Analyze in real time to prevent pollution: Include in-process real-time monitoring and control during syntheses to minimize or eliminate the formation of byproducts.
12. Minimize the potential for accidents: Design chemicals and their forms (solid, liquid, or gas) to minimize the potential for chemical accidents including explosions, fires, and releases to the environment.

Suggested Reading:

1. [Ehud Keinan](#) (Editor), [Israel Schechter](#) (Editor), Chemistry for the 21st Century, 2001, John Wiley and Sons, Inc.,
2. <http://ce.t.soka.ac.jp/chem/iwanami/intorduct/ch14chemistry21C.pdf>
3. Jiri Janata, Energy and Transportation : Challenges for the Chemical Sciences in the 21st Century, 2003, The National Academies Press.

CHAPTER - 2

PERIODIC PROPERTIES OF ELEMENTS

T. M. Sankaranarayanan

2. 1. INTRODUCTION

With the rapid discovery of elements, scientists gathered more information about the properties of elements. Several attempts were made to classify elements according to their properties. Initially elements were classified as metals and non-metals, but that was not sufficient to explain all the physical characteristics and chemical behaviour of elements. Number of Scientists namely Dobereiner, Newland and Lave contributed a lot to classify the elements.

These classifications formed a basis for Russian chemist Dmitri Mendeleev to propose the periodic law "the physical and chemical properties of the elements are periodic function of their atomic masses". Thus Mendeleev classified the elements on the basis of their atomic masses. In order to overcome the drawbacks of mendeleev periodic table mosely proposed to the long form of periodic table which depend up on the law. in 1869, who intended the table to illustrate recurring ("periodic") trends in the properties of the elements. The layout of the table has been refined and extended over time, as new elements have been discovered, and new theoretical models have been developed to explain chemical behavior. The current standard table contains 118 elements as of March 2010.

2.2. Trends in the Periodic Table

“Atomic Radius” is defined as the half the total distance between the two adjoining atoms. It increases when we go down the group (due to addition of new shells) and decreases along the period on moving from left to right.

2.3. Mendeleev's Periodic Table

In 1869, Mendeleev classified the then known 56 elements on the basis of their physical and chemical properties by giving a law known as the periodic law.

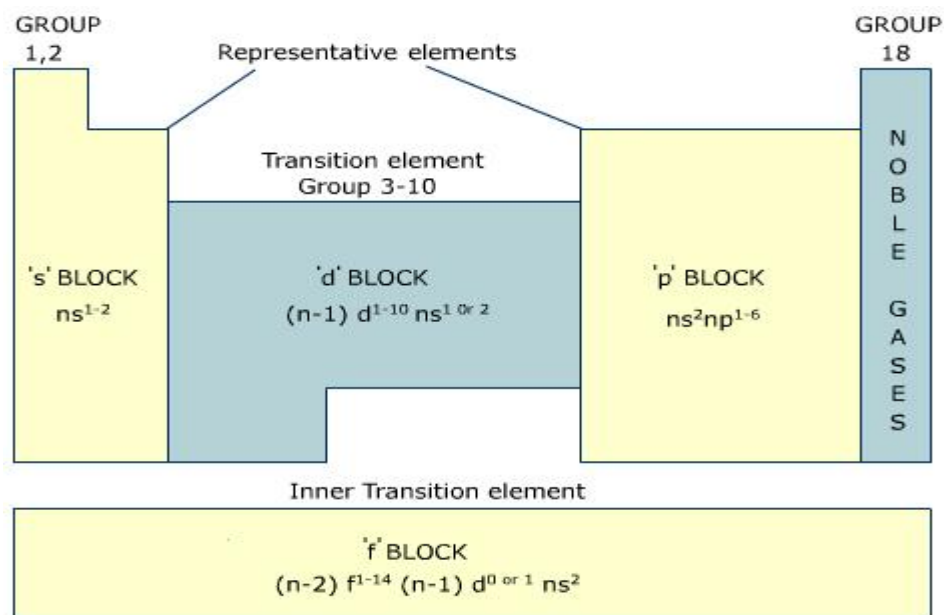


Fig. 2.1. Periodic table

The name periodic law stems from the fact that the properties of the elements orderly recur in a cyclic fashion. His periodic law states that when the elements are arranged in the order of their increasing atomic masses, the elements with similar properties recur at regular intervals. Based on this law all the known elements were arranged in the form of a table known as periodic table. Elements with similar properties recur at regular intervals and fall in certain groups or families. The elements in each group were similar to each other in many properties.

2.4. Long Form of the Periodic Table or Modern Periodic Table

With developments on the structure of atoms, it was discovered that the atomic number (Z) is the important characteristic of the atom and not the atomic mass. This led to the development of the modern periodic law by Moseley in 1942. The modern periodic law states that "the physical and chemical properties of the elements are periodic function of their atomic numbers". Thus, when the elements were arranged in the order of their increasing atomic numbers, the elements of similar properties recur at regular intervals.

2.4.1. Structural Features of the Modern Periodic Table

The periodic table consists of horizontal rows called as 'periods' and vertical columns called as 'groups'.

2.4.1.1. Periods

- i) There are seven periods in the periodic table and each period starts with a different principal quantum number. The first period corresponding to $n = 1$ consists of only two elements hydrogen ($1s^1$) and helium ($1s^2$). This is because the first energy shell has only one orbital (1s), which can accommodate only two electrons.
- ii) In the second period corresponding to $n = 2$, there are four orbitals (one '2s' and three '2p') having a capacity of eight electrons and so contains eight elements. This period starts with lithium ($Z = 3$) with electron entering the '2s' orbital and ends with neon ($Z = 10$) where the second shell is complete ($2s^2 2p^6$)
- iii) In the third period corresponding to $n = 3$, there are nine orbitals (one '3s' three '3p' and five '3d'). As '3d' orbitals are higher in energy, they are filled after the '4s' orbitals. This period involves filling of only four orbitals ('3s' and '3p') containing eight elements. It starts with sodium ($Z = 11$) with electron entering the '3s' orbital and ends with argon ($Z = 18$) where the third shell is partially complete ($3s^2 3p^6$)
- iv) The fourth period corresponding to $n = 4$, consists of filling of one '4s' and three '4p' orbitals. The '4d' and '4f' orbital are higher in energy than the '5s' orbitals and are filled later. The five '3d' orbitals have energies in between '4s' and '4p' orbitals and so are filled accordingly. Totally nine orbitals are filled and therefore, there are eighteen elements in this period starting from potassium with electron entering the '4s' orbital ($Z = 19$) to krypton ($Z = 36$) where the third shell gets completed ($4s^2 3d^{10}4p^6$)
- v) In the fifth period there are 18 elements like the fourth period. It begins with rubidium ($Z = 37$) with the filling of '5s' orbital and ends with xenon ($Z = 54$) with the filling of '5p' orbital
- vi) The sixth period contains 32 elements ($Z=55$ to 86) and the successive electrons enter into '6s', '4f', '5d' and '6p' orbitals in that order. It starts with caesium and ends with radon
- vii) The seventh period, though expected to have 32 elements is incomplete and contains only 19 elements at present.

2.4.1.2. Number of elements in each period

Period	(n)	Orbital filled up	Number of electron/elements in the period
First	(1)	1s	$2 = 2$
Second	(2)	2s 2p	$2 + 6 = 8$
Third	(3)	3s 3p	$2 + 6 = 8$
Fourth	(4)	4s 3d 4p	$2 + 10 + 6 = 18$
Fifth	(5)	5s 4d 5p	$2 + 10 + 6 = 18$
Sixth	(6)	6s 4f 5d 6p	$2 + 14 + 10 + 6 = 32$
Seventh	(7)	7s 5f 6d 7p	$2 + 14 + 10 + 6 = 32$

There is a periodicity occurring at regular intervals of 2, 8, 8, 18, 18 and 32 and so the numbers 2, 8, 18 and 32 are called magic numbers. The first three periods are called short periods while the other three periods are called long periods.

2.4.1.3. Groups

The vertical column in the periodic table is called as group. There are 18 groups in the long form of the periodic table and they are numbered from 1 to 18 in the IUPAC system. In the old system of naming they are numbered as I to VIII with A and B groups. This convention is followed in many places

2.4.1.4. Merits of the long form of the periodic table

- i) This classification is based on the most fundamental property of the elements - the atomic number, so it is more accurate.
- ii) With the atomic number as the basis of this classification, the position of isotopes in one place is justified.

- iii) The systematic grouping of elements into the four blocks of 's', 'p', 'd' and 'f' has made the study of elements simpler.
- iv) The electronic configuration determines the properties of the elements. The position of elements governed by this feature is useful in studying the properties of elements.
- v) The position of the elements, which were misfit on the basis of atomic mass is now justified on the basis of atomic number.
- vi) The lanthanides and actinides have been placed separately due to their properties different from other groups.
- vii) The whole table is easy to remember and reproduce in terms of electronic configuration and properties of the elements.

2.4.1.5. Demerits of the long form of the periodic table

Although the long form of the period table has been able to help in systematic studying the elements to a great extent, it has some minor defects:

- i) Hydrogen resembles both the alkali metals and halogens. But it has been placed with the alkalis.
- ii) The lanthanides and actinides have not been placed in the main body of the table.

2.5. Locating the Position of an Element

Knowing the electronic configuration, one can predict the period, which corresponds to the principal quantum number of the valence shell. The block of the element corresponds to the sub shell, which receives the last electron.

2.6. IUPAC Nomenclature for Elements with $Z > 100$

All elements beyond uranium ($Z=92$) are synthesized in the laboratories and are known as 'trans uranium elements'. The elements, beyond fermium ($Z=100$) are known as 'trans fermium elements'. These elements have atomic numbers 101 onwards.

2.7. Grouping of Elements

In the long form of the periodic table, elements are grouped into four main blocks, purely on the basis of electronic configurations. Elements are grouped in blocks 's', 'p', 'd' and 'f' depending on the nature of orbital(s) into which the last electron of the atom enters.

2.8. Representative or Main Group Elements

These consist of all 's' and 'p' block elements excluding the noble gases (group 18 elements). The chemical properties of the representative elements are determined by the number of valence electrons in their atoms.

2.9. Periodic Properties

When the elements are arranged in the order of increasing atomic numbers there is a recurrence of similar properties after certain regular intervals. This regularity is called the periodicity in properties. The distribution of electrons in the various shells determines their physical and chemical character. It has been observed that the properties of the elements depend more on the arrangements of the electrons in the outermost shell (valence shell) and not on the inner shells. This repetition of similar electronic configuration in the outermost or valence shell after certain regular intervals causes periodicity in the properties of elements.

2.9.1. Periodicity

The recurrence of similar properties of the elements when they are arranged in the order of increasing atomic number, after certain regular intervals, is called periodicity.

2.9.1.1. Cause of periodicity of elements

The modern periodic table is based on the electronic configuration of the elements. The properties of an element are determined largely by the electrons in its outermost or valence shell. Valence electrons interact with other atoms and take part in all chemical reactions, while inner shell electrons have little influence on the properties of elements.

When elements are placed in the order of their increasing atomic number, the elements having the same number of valence shell electron is repeated in such a way, so

as to fall under the same group. Since, the electronic configuration of the valence shell electrons is same they show similar properties.

2.9.2. Atomic radii

The size of the atom is significant in governing its property. If the atom is assumed to be spherical, then the radius of the sphere gives the atomic radius. But it is difficult to exactly determine the radius of the atom because:

- i) The probability of finding the electron is never zero even at large distances from the nucleus and so the atom does not have a well defined boundary.
- ii) It is not possible to isolate an atom and measure its radius.
- iii) The size of the atom changes in going from one set of environment to another and from one bonded state to another.

So, one can arbitrarily define atomic radius as the effective size which is the distance of closest approach of one atom to another atom in a given bonding situation. This approximate radius can be determined by measuring the inter-nuclear distance between the two centres of the neighbouring atoms in a covalent molecule. This is usually done by diffraction and spectroscopic techniques.

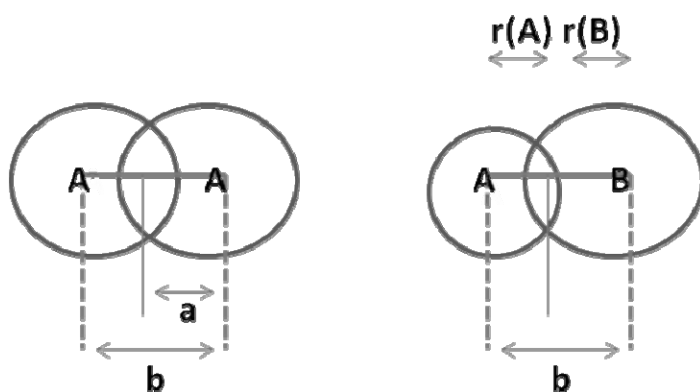


Fig. 2.2. Calculation of atomic radius (a) covalent radius homo nuclear diatomic molecule, $r(A)$, $r(B)$ covalent radius for heteronuclear diatomic molecule (b) bond length

The inter-nuclear distance corresponds to the diameter of the atom and therefore half of this distance gives the atomic radius for a homonuclear molecule like Cl-Cl or Br-Br. Hence, it may be defined as one half of the distance between the centers of the nuclei of

two similar atoms bonded by a single covalent bond. This is also called as covalent radius.

For a hetero-nuclear molecule, the covalent radius is the distance between the center of the nucleus of the atom and the mean position of the shared paired of electrons between the bonded atoms. The covalent radii are smaller than the atomic radii in the uncombined atoms because the overlap region between atomic orbitals of two atoms becomes common in a covalent bond.

The forces of attraction (Van der Waals forces) existing between non-bonded atoms and molecules are weak and the atoms are held at larger inter-nuclear distances. Thus these radii known as Van der Waals radii are always larger than covalent radii.

Van der Waals radius is defined as one half of the inter-nuclear distance between two adjacent atoms belonging to the two nearest neighbouring molecules of the substance in the solid state.

2.9.2.1. Variation of Atomic Radii

2.9.2.2. Variation in a period

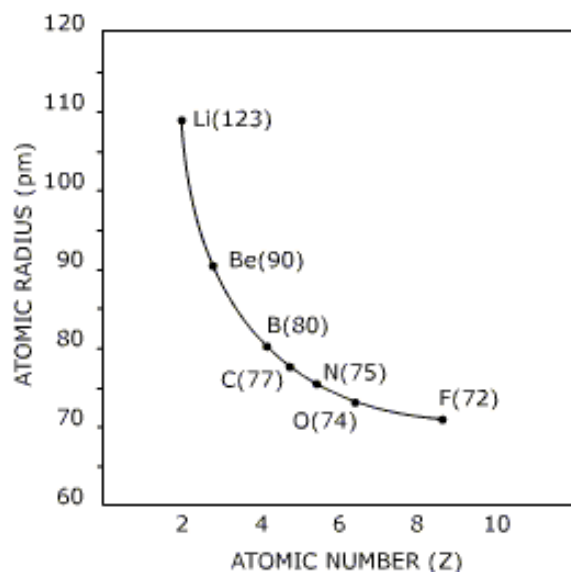


Fig. 2.3. Variation of atomic radius with atomic number in a period

Atomic radii in general, decrease with increase in atomic number, going from left to right in a period. This is explained on the basis of increasing nuclear charge along a period. The nuclear charge increases progressively by one unit while the corresponding addition of one electron takes place in the same principal shell. As the electrons in the same shell do not screen each other from the nucleus, the nuclear charge is not neutralized by the extra valence electron. Consequently the electrons are pulled closer to the nucleus by the increased effective nuclear charge resulting in the decrease in the size of the atom. In this way the atomic size goes on decreasing across the period.

The atomic radius abruptly increases in the case of noble gas element Neon as it does not form covalent bonds. So the value of Neon radius is Van der Waals radius which is considerably higher than the value of other covalent radii.

2.9.2.3. Variation in a group

The atomic radii of elements increases from top to bottom in a group because the nuclear charge increases with increasing atomic number.

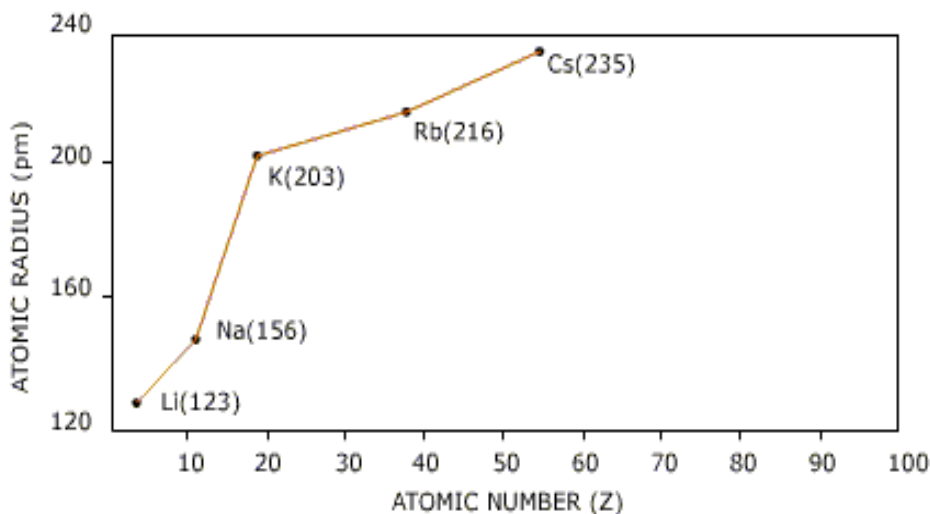


Fig. 2.4. Variation of atomic radius with atomic number in a group

Although, there is an increase in the principal quantum number from one atom to another, the number of electrons in the valence shell remain the same. The effect of increase in the

size of the electron cloud outweighs the effect of increased nuclear charge and so the distance of the valence electron from the nucleus increases down the group. Thus the size of the atom goes on increasing down the group in spite of increasing nuclear charge.

2.9.3. Ionic Radii

These are radii of ions in ionic crystals. Ionic radius may be defined as the effective distance from the center of nucleus of an ion up to which it has an influence on its electron cloud. In ionic compounds the inter nuclear distance may be taken as equal to the sum of the ionic radii of the two ions. The inter nuclear distance in ionic crystals are obtained from X-ray studies.

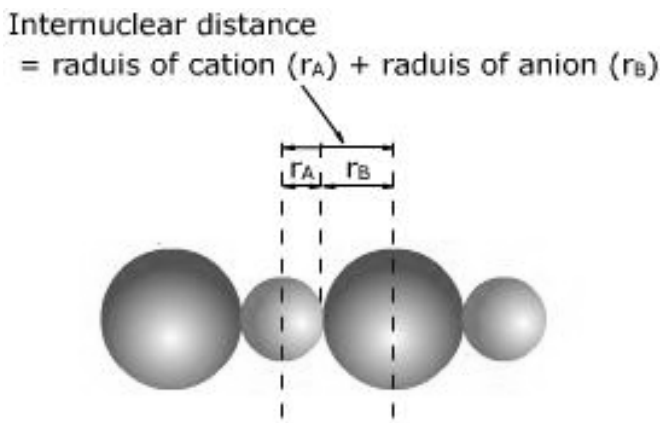
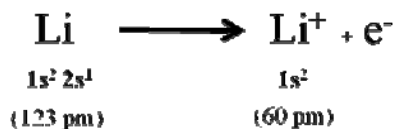


Fig. 2.5. Inter nuclear distance and ionic radii

2.9.3.1. Radius of the cation

A cation is formed by the loss of one or more electrons from the gaseous atom. Thus, the whole of the outer most shell of electrons is removed resulting in the smaller size in the cation.

For example, in lithium atom, there is only one electron in the outermost '2s' shell. As the lithium atom changes to Li^+ ion the outer most '2s' shell disappears completely. This disappearance results in the decrease in size.



With the removal of electrons from an atom the magnitude of the nuclear charge remains the same while the number of electrons decreases. As a result the nuclear charge acts on less number of electrons. The effective nuclear charge per electron increases and the electrons are more strongly attracted and pulled towards the nucleus. This causes a decrease in the size of the ion.

2.9.3.2. Radius of the anion

The negative atom is formed by the gain of one or more electrons in the neutral atom. The number of electrons increases while the magnitude of nuclear charge remains the same. The same nuclear charge acts on larger number of electrons than were present in the neutral atom. The effective nuclear charge per electron is reduced and the electron cloud is held less tightly by the nucleus. This causes an increase in the size of the ion. Thus anions are larger in size than the corresponding atom.

2.9.3.3. Variation of ionic radii in a group:

The ionic radii in a particular group increases in moving from top to bottom because of the increase in the principal quantum number though the number of electrons in the valence shell remains the same.

In isoelectronic series of ions, as the nuclear charge increases the electrons are pulled more and more strongly and the size decreases.

2.9.4. Ionization Energy

The amount of energy required to remove the most loosely bound electron from an isolated gaseous atom is called ionization;



The amount of energy required to remove the most loosely bound electron from an isolated gaseous atom is called ionization energy (IE).



Ionization energy is also called as ionization potential because it is measured as the minimum potential required to remove the most loosely held. $1 \text{ eV per atom} = 96.64 \text{ kJ mol}^{-1} = 23.05 \text{ k cal mol}^{-1}$.

Thus, the ionization energy gives the ease with which the electron can be removed from an atom. The smaller the value of the ionization energy, the easier it is to remove the electron from the atom.

2.9.4.1. Factors Governing Ionization Energy

i) Size of the atom

As the size of the atom increases the outermost electrons are held less tightly by the nucleus (attractive force between the electron and the nucleus is inversely proportional to the distance). As a result it becomes easier to remove the electron and therefore the ionization energy decreases with the increase in atomic size.

ii) Charge on the nucleus

The attractive force between the nucleus and the electron increases with the increase in nuclear charge making it more difficult to remove an electron. The ionization energy thus increases with the increase in the nuclear charge.

iii) Screening effect

In multielectron atoms, the outermost electrons are shielded or screened from the nucleus by the inner electrons. This is known as shielding or screening effect. The outer most electrons do not feel the complete charge of the nucleus and the actual charge felt is called the effective nuclear charge. When the inner electrons are more, the screening effect will be large, the nuclear attraction will be less. Thus when the inner electrons increase the ionization energy will decrease.

iv) Penetration effect

The 's' electrons are more penetrating (maximum probability of finding near the nucleus) towards the nucleus than the p electrons. The order of penetration power in a given shell is $s > p > d > f$.

If the penetration power of the electron is more, it will be closer to the nucleus and will be held more firmly. Thus ionization energy will increase with the increase in the

penetration power of the electrons. For the same sub shell the ionization energy would be more to remove an 's' electron than to remove a 'p' electron which in turn will be more than that for removing a 'd' electron.

v) Electronic arrangement

Certain electronic configuration like half-filled and completely-filled shells have extra stability. It is more difficult to remove electron from these stable configuration and the ionization energy is very high. For example, the noble gases have the most stable configuration and so have high ionization energy; elements like Be and Mg have completely filled orbitals while N and P have exactly half-filled sub shells. Thus, their ionization energies are high. The more stable the electronic configuration, the higher is the ionization energy.

2.9.4.2. Variation along a period

The ionization energy increases with increasing atomic number in a period. This is because:

- i) The nuclear charge increases on moving across a period from left to right.
- ii) The atomic size decreases along a period though the main energy level remains the same.
- iii) Due to the increased nuclear charge and simultaneous decrease in atomic size, the valence electrons are more tightly held by the nucleus. Therefore more energy is needed to remove the electron and hence ionization energy keeps increasing. However some irregularities have been noticed due to the extra stability of the half filled and completely filled configurations.

For example, the nuclear charge on Boron is more than Beryllium, yet there is slight decrease in ionization energy from Be to B. This is because, in boron the last electron goes to '2p' orbital which is at a slightly higher energy than '2s' orbital. Also, the electronic configuration of B is less stable than that of Be (has completely filled orbitals). Hence the ionization energy is less than that of Be. Similarly, nitrogen, which has half filled '2p' orbitals, is more stable than oxygen. Therefore the ionization energy of nitrogen is more than that of oxygen.

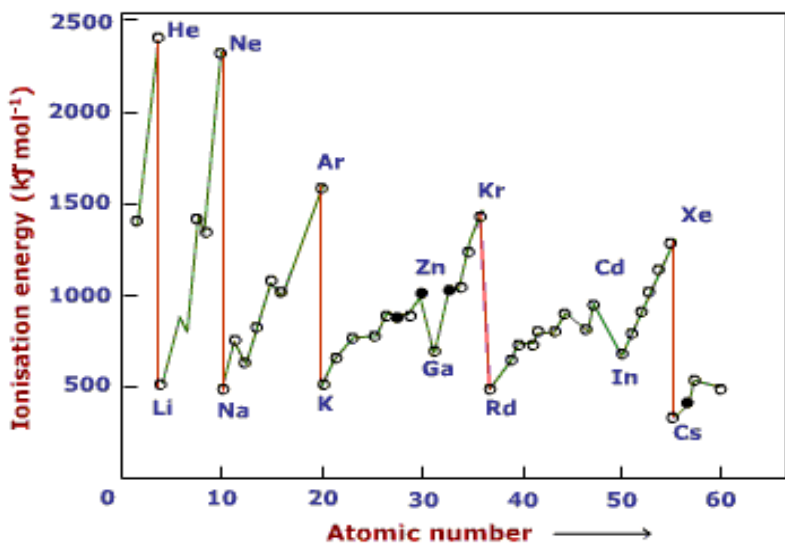


Fig 2.6. Variation of ionization energy with atomic number

2.9.4.3. Variation down a group

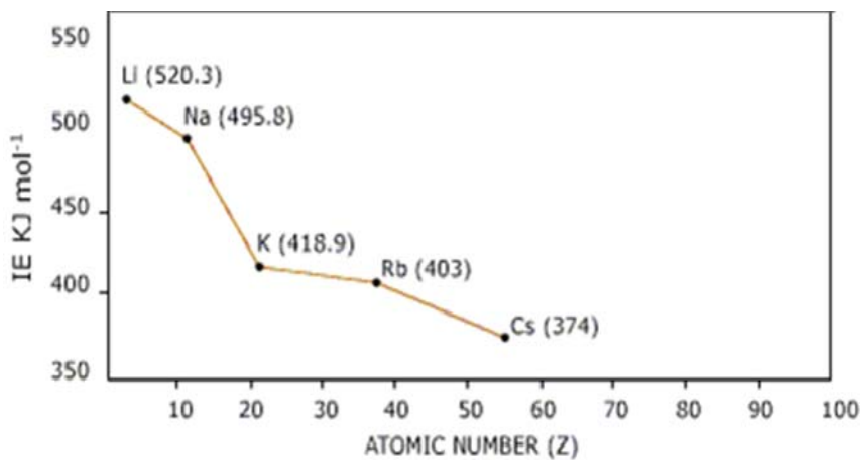


Fig. 2.7. The variation of ionization energy with atomic number

The ionization energy gradually decreases in moving from top to bottom in a group. This is due to the fact that:

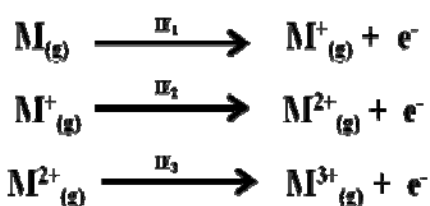
- i) The nuclear charge increases in going from top to bottom in a group.
- ii) An increase in the atomic size due to an additional energy shell (level) 'n'.

iii) Due to the increase in the number of inner electrons there is an increase in the shielding effect on the outer most electron. The effect of increase in atomic size and the shielding effect is much more than the effect of increased nuclear charge.

As a result, the electron becomes less firmly held to the nucleus and so the ionization energy decreases as we move down the group,

2.9.4.4. Successive ionization energies

The energies required to remove subsequent electrons from a gaseous atom is called as successive ionization energies. They are termed as first, second, third ionization energy depending on the removal of the first, second, third electron respectively.



The second ionization energies are higher than the first due to the fact that after the removal of the first electron the atom changes into a monovalent positive ion. In this ion, the number of electrons decreases but the nuclear charge remains same and so the remaining electrons are held more tightly by the nucleus and it becomes difficult to remove the second electron. Hence the value of the second ionization energy (IE_2) is higher than the first (IE_1). In the same way the removal of the second electron will result in the formation of di-positive ion making the attraction between the nucleus and the remaining electrons stronger. This results in higher value of third ionization energy (IE_3).

2.9.5. Electron Affinity

Electron affinity is the amount of energy released when an electron is added to an isolated gaseous atom.



Electron affinity is the ability of an atom to hold an additional electron. If the atom has more tendency to accept an electron then the energy released will be large and consequently the electron affinity will be high. Electron affinities can be positive or

negative. It is taken as positive when an electron is added to an atom. It is expressed as electron volts per atom (eV per atom) or kilo joules per mole.

2.9.5.1. Factors affecting electron affinity

- i) When the nuclear charge is high there is greater attraction for the incoming electron. Therefore electron affinity increases as the nuclear charge increases.
- ii) With the increase in the size of the atom the electron affinity decreases because the distance between the nucleus and the incoming electron increases.
- iii) Electron affinities are low or almost zero in elements having stable electronic configurations (half filled and completely filled valence subshells) because of the small tendency to accept additional electron.

2.9.5.2. Variation along a period

The size of an atom decreases and the nuclear charge increases on moving across a period. This results in greater attraction for the incoming electron. Hence the electron affinity increases in a period from left to right.

2.9.5.3. Variation down a group

As we move down a group the atomic size and nuclear size increases. As the effect of increase in atomic size is more pronounced the additional electron feels less attracted by the large atom. Consequently the electron affinity decreases; However there are some irregularities observed in the above general trend. They are

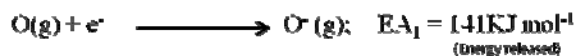
- i) The halogens have highest electron affinity because they have only one electron less than the stable noble gas configuration. They have a strong tendency to accept an additional electron. This makes their electron affinity values high.
- ii) The electron affinity value of noble gases are zero because of the stable electronic configuration of $ns^2 np^6$ which has no tendency to take in additional electron. No energy is released and their electron affinities are zero.
- iii) The electron affinity values for Be, Mg, N and P are almost zero because of the extra stability of completely filled orbitals in Be and Mg and half filled orbitals in N and P.

iv) Electron affinity of fluorine is unexpectedly less than that of chlorine. The low electron affinity value of F is due to the very small size of F atom. This small size results in strong inter electronic repulsions in the relatively compact 2p subshell of fluorine: thus the incoming electron does not feel much attraction. Electron affinity for some third period elements (e.g., P, S, Cl) are greater than corresponding second period elements (e.g., N, O, F) because of the smaller atom size of second period elements, which produces larger electronic repulsions for the additional electron.

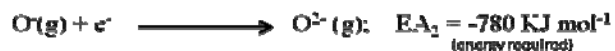
2.9.5.4. Successive electron affinities

The second electron is added to the negatively charged ion and the addition is opposed by coulombic repulsions. The energy has to be supplied to force the second electron into the anion.

First electron affinity:



Second electron affinity:



The second electron affinities in which energy is absorbed have negative values while the first electron affinity have positive values as energy is released.

2.9.6. Electronegativity

The relative tendency of an atom in a molecule to attract a shared pair of electrons towards itself is termed as Electronegativity. The value of electronegativity of an element describes the ability of its atom to compete for electrons with the other atom to which it is bonded. Electronegativity is however not the property of an isolated atom. Electronegativity is measured on a number of scale levels, the most commonly used are of Pauling or Mulliken.

2.9.6.1. Factors Affecting Electronegativity

i) Atomic size

As the size of the atom decreases it has greater tendency to attract the bonding electrons towards itself. Therefore smaller atoms have higher electronegativity values than the larger ones.

ii) Ionisation energy and electron affinity

Higher Ionisation energy and electron affinity lead to higher electronegativity.

iii) Number and nature of atoms

The electronegativity depends on the number and nature of atoms bonded to it.

iv) Type of hybridization

The electronegativity increases with the increase in 's' character in the hybrid orbital. This is because the 's' orbitals being more near to the nucleus have greater tendency to attract the shared pair of electron.

v) Charge on the ion

A cation has high electro negativity while an anion has less electro negativity than its parent atom. A cation with a higher positive charge is more electronegative.

2.9.6.2. Variation along the period

As the nuclear charge increases from going left to right in a period because the electrons enter the same shell, the shielding is less effective. Thus the increased nuclear charge attract the shared pair of electrons more strongly resulting in higher electro negativity from going left to right in a period.

2.9.6.3. Variation down the group

Electronegativity decreases down the group because the atomic size increases. The larger the size of the atom the lesser the tendency to attract the shared pair of electrons.

2.9.7. Electropositive or Metallic Character

The tendency of an element to lose electrons and form positive ions (cations) is called electropositive or metallic character. Elements having low ionization energy are electropositive. For example alkali metals are the most electropositive elements. The tendency of an element to lose electrons and form positive ions (cations) is called

electropositive or metallic character. Elements having low ionization energy are electropositive. For example alkali metals are the most electropositive elements.

2.9.7.1. Variation along the period

The tendency to lose electrons decreases in going from left to right and so the electropositive or metallic character decreases from left to right in a period.

2.9.7.2. Variation down the group

The electropositive or metallic character increases down the group because of the increase in the atomic size, which makes it easier to remove the valence electrons.

2.9.8. Electronegative or Non-metallic Character

The tendency of an element to accept electrons to form an anion is called its non-metallic or electronegative character. Elements that have high electron affinity (or high electronegativity) show greater electronegative or non-metallic character. For example chlorine, oxygen and phosphorous.

2.9.8.1. Variation along the period

Due to the increased nuclear charge across the period, the electronegative or non-metallic character increases in going from left to right in a period.

2.9.8.2. Variation down the group

Due to the increased atomic size the non-metallic or electronegative character decreases as we go down the group.

2.9.9. Chemical Reactivity and Periodicity in the Properties of Compounds

The reactivity of metals decreases from left to right in a period while the reactivity increases down the group. The reactivity of non-metals increases from left to right in a period while the reactivity decreases down the group

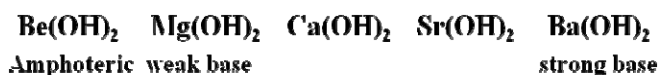
2.9.9.1. Melting and Boiling points of Alkali Metal Halides

The melting and boiling points of alkali metal halides are high due to their ionic nature. For a given alkali metal ion the melting and boiling points decrease in the order $F > Cl > Br > I$. For the same halide ion, the melting point of lithium halide is less than sodium halide and thereafter it decreases as we go down the group. The low melting point of lithium chloride is due to its small size, which makes its compounds covalent.

2.9.9.2. Solubility and Basic character of Hydroxides

The hydroxides of alkali metals are strongly basic in nature due to their low ionization energy. The basic strength increases down the group due to decrease in ionization energy. The M-OH bond is readily cleaved.

The basic character of hydroxides of alkaline Earth metals is less than the corresponding alkali metals of the same period. This is due to their high ionization energy, smaller ionic size and di-positive charge on the ions. The M-OH bond is not readily cleaved. The basic character of these hydroxides increases as we go down the group. For example, $Be(OH)_2$ is amphoteric, $Mg(OH)_2$ is a weak base $Ca(OH)_2$ and $Sr(OH)_2$ are moderately strong bases and $Ba(OH)_2$ is nearly as strong a base as alkali metal hydroxides.



The solubility of these hydroxides increases as we go down the group.

2.9.9.3. Solubilities of carbonates and bicarbonates

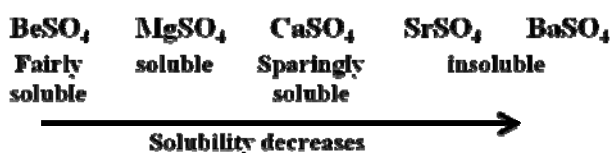
The solubilities of carbonates and bicarbonates of alkali metals increase as we go down the group from lithium to caesium. However, the carbonates of alkaline Earth metals are less soluble and their solubilities decrease on moving down the group. For example, $MgCO_3$ is slightly soluble in water but $BaCO_3$ is almost insoluble.

2.9.9.4. Stability of Carbonates of Alkali and alkaline Earth Metals

All the carbonates of alkali metals are quite stable towards heat except Li_2CO_3 , which decomposes easily on heating. The instability of Li_2CO_3 is due to the small size of lithium ion, which cannot stabilize the bigger carbonate ion. The carbonates of alkaline Earth metals are less stable towards heat and decompose to give CO_2 . Their stability increases as we move down the group.

2.9.9.5. Solubilities of Sulphates of Alkaline Earth Metals

The solubilities of sulphates of alkaline Earth metals decrease as we go down the group.



2.10. Trends in the periodic table

2.10.1. The 's' block elements

's' block elements, (except helium) are those in which the valence-shell is the 'ns' orbital and where the last electron enters into the 's' orbital of the outer element. The general outer electronic configuration of such elements is either ns^1 or ns^2 . The 's' block elements belong to group 1 and 2 of the long form periodic table. They are situated on the left side of the table.

2.10.1.1. Characteristics

The main characteristics of the 's' block elements are;

- i) The general outer electronic configurations of 's' block elements are ns^{1-2} as all inner shells are already full.
- ii) The 's' block elements are either all alkali metals like Li, Na, K, Rb, Cs and Fr, as in group 1 (having ns^1 outer electronic configuration) or alkaline Earth metals like Be, Mg, Ca, Sr, Ba and Ra, as in group 2 (having ns^2 outer electronic configurations).
- iii) The 's' block metals are soft and have a low melting and boiling point.

iv) The metals are very active. They are highly electropositive and lose their valence electrons to form monovalent or divalent cation. For example,



v) Being highly electropositive, these elements lose electrons readily and are strong reducing agents.

vi) The 's' block elements mostly form ionic compounds like NaCl, KCl, CaCl₂ etc.

2.10.2. The 'p' block elements

'p' block elements are those in which the outer electronic configuration is of the type $ns^2 np^1$ to $ns^2 np^6$ and where the last electron enters into any of the outermost 'p' orbitals. These elements belong to groups 13 to 18 of the long form of periodic table and are situated on the right hand side of the table.

2.10.2.1. Characteristics

The main characteristics of the 'p' block elements are;

- i) The general outer electronic configurations of 'p' block elements are $ns^2 np^{1-6}$ as all inner shells are already full.
- ii) The 'p' block elements include metals, non-metals and metalloids. Typical examples are Carbon, Nitrogen, Oxygen, Sulphur, Halogens etc.
- iii) These elements enter into chemical combinations by losing, gaining or sharing the valence electrons. The noble gas elements show no reactivity because their outermost shells are completely filled ($ns^2 np^6$).
- iv) The 'p' block elements mostly form covalent compounds. Halogens however form ionic compounds with 's' block metals.

2.10.3. The 'd' block elements

'd' block elements are those in which the added electron goes into one of the 'd' orbitals. These elements have valence electrons in both their outermost and penultimate shells (second outermost) and have a general outer electronic configuration of $(n - 1) d^{1-10} ns^{1-2}$.

The penultimate shell in these elements is expanded from 8 to 18 by the inclusion of ten 'd' electrons. It is for this reason that these elements are called 'd' block elements. Thus, 'd' block elements are those, which in their elemental or combined forms have partially filled 'd' orbitals. They are also referred to as transition elements.

'd' block elements belong to groups 3 to 12 of the long form of periodic table and are situated in the middle of the table between 's' block and 'p' block elements. All 'd' block elements are classified into four transition series, namely;

3d series in the 4th period having 10 elements.

4d series in the 5th period having 10 elements.

5d series in the 6th period having 10 elements.

6d series in the 7th period having incomplete elements.

2.10.3.1. Characteristics

The main characteristics of the 'p' block elements are;

i) 'd' block elements have valence electrons in both their outermost and penultimate shells. Valence electrons belonging to the outermost shell or both shells may take part in a chemical reaction. Accordingly, more than one oxidation state can be shown by the same element; this is termed as variable oxidation states.

Examples: Fe^{2+} and Fe^{3+} , Cu^+ and Cu^{2+} etc.

ii) 'd' block elements exhibit transitional behaviour intermediate between highly reactive electropositive alkali metals and the covalent compound forming elements. So they are called as transition elements.

(a) These elements are metals having high melting and boiling points.

(b) Most 'd' block elements form coloured salts.

(c) 'd' block elements, their ions and compounds, are generally paramagnetic. There are one or more unpaired electrons present in their atoms or ions.

(e) Most of these transition elements are good catalysts.

2.10.3.2. Properties of 'd' block elements in a period

Because of their characteristic electronic configuration, the properties of transition elements ('d' block elements) in any period do not differ much from each other (unlike nontransition elements from the same period). The electronic configuration of transition elements can be written as: $(n - 1) d^x ns^y$ where, $x = 1$ to 10 and $y = 1, 2$.

This indicates that:

- i) The number of electrons in the outer shell 'ns' is invariably 1 or 2.
- ii) The electronic configuration of transition elements differ from one another only in the number of electrons in the 'd' orbitals of the $(n - 1)^{\text{th}}$ shell.

2.10.4. The 'f' block elements

The 'f' block elements are those, which in their elemental or ionic forms have partially filled 'f' orbitals. The differentiating (last) electron enters 'f' orbitals, which lie inner to the second outermost (penultimate) shell. Thus these elements are also known as inner-transition elements.

There are two series of 'f' block elements, each having 14 elements. Lanthanides (atomic number 58 - 71) are those inner-transition elements in which 4 'f' orbitals are progressively filled. Actinides (atomic number 90 - 103) are those elements in which 5 'f' orbitals are progressively filled.

The 'f' block elements are placed at the bottom of the long form of periodic table in the form of two rows. The general outer electronic configuration of 'f' block elements is, $(n - 2) f^{1-14} (n - 1) d^{0-1} ns^2$.

2.10.4.1. Characteristics

The main characteristics of the 'f' block elements are;

- i) 'f' block elements are metals having high melting and boiling points.
- ii) These elements exhibit variable oxidation states: the most common oxidation state being $3+$
- iii) These elements form coloured salts as their salts absorb light from certain visible wavelengths.

iv) Actinides (5f series) are radioactive elements.

Elements can also be classified according to their chemical behaviour (as apart from electronic configurations and similar properties).

QUESTIONS and ANSWERS

Question 1: The effective nuclear charge experienced by 3p electrons in phosphorus is

- 1) +2 2) +3 3) +5 4) +7

Answer: +5

The effective nuclear charge is given by the equation: $Z_{\text{eff}} = Z - S$ Where, Z represents number of protons in the nucleus and S represents the average number of electrons between the nucleus and the electron.

Question 2: Based on atomic radii, which of the following bonds would be expected to be the shortest?

- 1) H—H 2) H—F 3) F—F 4) Cl—Cl

Answer: H—H

The shortest bonding atomic radius belongs to the H atom, so an H_2 molecule will have the shortest H—X (where X is any atom) bond distance.

Question 3: Which of the following is expected to be the correct order of atomic radii from smallest to largest?

- 1) $\text{H} < \text{C} < \text{F}$ 2) $\text{Mg} < \text{Ar} < \text{Al}$ 3) $\text{S} < \text{Si} < \text{Na}$ 4) $\text{Ne} < \text{B} < \text{H}$

Answer: $\text{S} < \text{Si} < \text{Na}$

Question 4: F^- , Ne, and Na^+ are isoelectronic. Which of the following gives the correct ordering of their ionic size (from smallest to largest)?

- 1) $\text{F}^- < \text{Ne} < \text{Na}^+$ 2) $\text{Ne} < \text{F}^- < \text{Na}^+$ 3) $\text{Na}^+ < \text{Ne} < \text{F}^-$

Answer: $\text{Na}^+ < \text{Ne} < \text{F}^-$

For an isoelectronic series, the most negatively charged species is largest. Or... the species with the higher nuclear charge is the smallest.

Question 5: In which of the following compounds does oxygen have an oxidation number of -1 ?

1) Dioxygen (O_2), 2) Lithium oxide (Li_2O), 3) Sodium peroxide (Na_2O_2), 4) Potassium superoxide (KO_2)

Answer: Sodium peroxide (Na_2O_2)

Question 6: Based on periodic trends, which of the following elements is expected to have the largest (i.e., most negative) electron affinity?

1) K 2) Na 3) Si 4) S

Answer: S

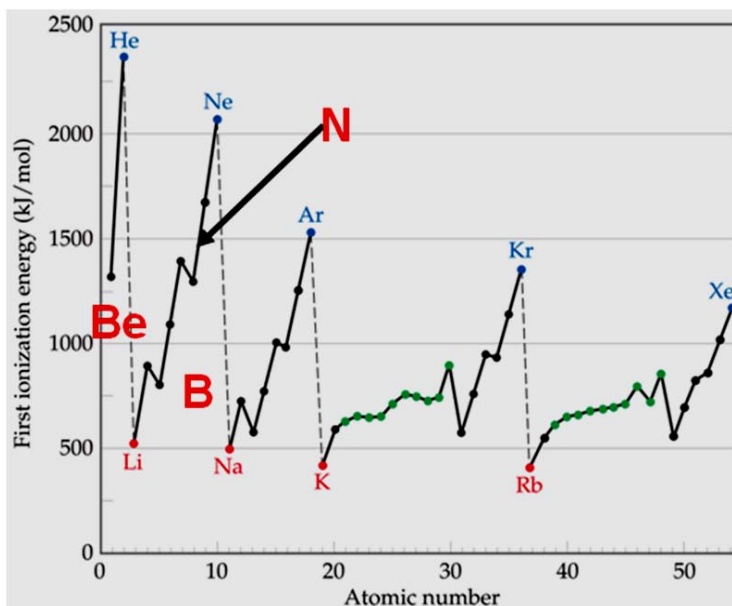
H -73							He > 0
Li -60	Be > 0	B -27	C -122	N > 0	O -141	F -328	Ne > 0
Na -53	Mg > 0	Al -43	Si -134	P -72	S -200	Cl -349	Ar > 0
K -48	Ca -2	Ga -30	Ge -119	As -78	Se -195	Br -325	Kr > 0
Rb -47	Sr -5	In -30	Sn -107	Sb -103	Te -190	I -295	Xe > 0
1A	2A	3A	4A	5A	6A	7A	8A

(which has most negative electron affinity in this list).

Question 7: Based on periodic trends, which of the following elements is expected to have the largest first ionization energy?

- 1) Li 2) Be 3) B 4) N

Answer: N



Question 8: Which of the following metals is expected to react most vigorously with liquid water?

- 1) Lithium 2) Sodium 3) Potassium 4) Beryllium 5) Magnesium

Answer: Potassium

Question 9: The atomic mass of germanium is 72.6 and its density is 5.47g cm⁻³. What is the atomic volume of germanium?

Answer:

$$\text{Atomic volume} = \frac{\text{Gram atomic mass}}{\text{Density}}$$

$$= \frac{72.6 \text{ g}}{5.47 \text{ g cm}^{-3}} = 13.27 \text{ cm}^3$$

Question 10: Out of Na^+ and Na which has the smaller size and why?

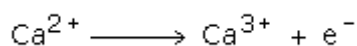
Answer:

Na^+ has a smaller size than Na. Na^+ is formed by the removal of one electron from Na. However both of these possess the same nuclear charge. Therefore electrons in Na^+ are more tightly held than in Na. The removal of one electron from Na also leads to complete removal of the third shell so that in Na^+ , the outermost shell is second. Hence Na^+ has a smaller size than Na.

Question 11: Calcium ($Z = 20$) loses electrons successively to form Ca^+ , Ca^{2+} and Ca^{3+} ions. Which step will have highest ionization energy?

Answer:

The step, which involves the formation of Ca^{3+} from Ca^{2+} would have highest ionization energy.



Question 12: Consider the ground state electronic configurations given below

1) $1s^2 2s^2 2p^6$ 2) $1s^2 2s^2 2p^4$ 3) $1s^2 2s^2 2p^6 3s^2$ 4) $1s^2 2s^2 2p^6 3s^1$ 5) $1s^2 2s^2 2p^5$

Which of the above configuration is associated with the lowest and which is associated with highest ionization energy?

Answer:

Lowest ionization energy = D

Highest ionization energy = A

Question 13:

Why is the ionization energy of nitrogen unexpectedly high

Answer:

The electronic configuration of nitrogen ($1s^2 2s^2 2p^3$) shows that it possesses exactly half-filled 'p' orbitals as its outershell configurations. Since, half-filled orbitals are extraordinarily stable, it is more difficult to remove an electron from this atom. Thus nitrogen has unexpectedly high ionization energy

Question 14:

Arrange the following in the decreasing order of electron affinity: B, C, N, O

Answer:

All these elements belong to the same period. The size of an atom decreases and the nuclear charge increases on moving across a period. This results in greater attraction for the incoming electron. Hence the electron affinity increases in a period from left to right O.

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CHAPTER - 3

NOMENCLATURE AND ISOMERISM OF COORDINATION COMPOUNDS

K. Poliraju

1. Introduction

The structures of coordination compounds are worth noting that transition metal complexes are usually formed from reactions between their salts and Bronsted bases in solution. However, the structures of the compounds formed are usually determined in the solid state using samples crystallized from solution. While it may usually be assumed that the solid state structures are similar to the solution structures, this may not always be so, and some complexes may adopt different structures in solution and the solid state.

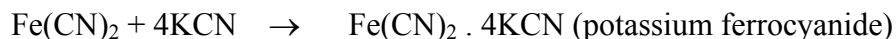
According to a useful, historically-based formalism, coordination compounds are considered to be produced by addition reactions and so they were named on the basis of an additive principle. The name is built up around the central atom name, just as the coordination entity is built up around the central atom.

2. Double salts and Coordination compounds

Addition compounds are formed when stoichiometric amounts of two or more stable compounds join together. For example:



(Tetrammine copper (II) sulfate monohydrate)



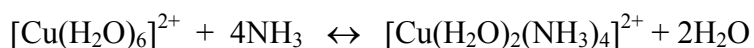
2.1. Addition compounds are of two types

- Those which lose their identity in solution are called double salts
- Those which retain their identity in solution are called complexes.

When crystals of carnallite are dissolved in water, the solution shows the properties of K^+ , Mg^{2+} and Cl^- ions. In similar way, a solution of potassium alum shows the properties of K^+ , Al^{3+} , and SO_4^{2-} ions. The both double salts exist only in the crystalline state. When the other two examples of coordination compounds dissolve they do not form simple ions Cu^{2+} or Fe^{2+} and CN^- but instead their complex ions remain intact. Thus the

cuproammonium ion $[\text{Cu}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{2+}$ and the ferrocyanide ion $[\text{Fe}(\text{CN})_6]^{4-}$ exist as distinct entities both in the solid and solution.

Complex ions are shown by the use of Square brackets. Compounds containing these ions are called coordination compounds. The chemistry of metal ions in solution is essentially the chemistry of their complexes. Transition metal ions, in particular, form many stable complexes. In solution free metal ions are coordinated either to water or to other ligands. Thus Cu^{2+} exists as the pale blue complex ion $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ in aqueous solution (and also hydrated crystalline salts). If aqueous ammonia is added to this solution, the familiar deep blue cuproammonium ion is formed:



Werner's Coordination theory in 1893 was the first attempt to explain the bonding in coordination complexes. Werner was able to explain the nature of bonding in complexes, and he concluded that in complexes the metal shows two different sorts of valency.



Primary valency: These are non-directional. The modern explanation would be as follows. The complex commonly exists as a positive ion. The primary valency is the number of charge on the complex ion. In compound, this charge is matched by the same number of charges from negative ions. Primary valency applies equally well to simple salts and to complexes.

Secondary valency: These are directional. In modern term the number of secondary valency equal the number of ligand atoms coordinated to the metal. This is now called the coordination number. Ligands are commonly negative ions such as Cl^- , or neutral molecules such as NH_3 . Less commonly, ligands may be positive ions such as NO^+ . Each metal has a characteristic number of secondary valencies.

In a series of compounds of cobalt (III) chloride with ammonia, it was found that some of the chloride ions could be precipitated as AgCl on adding excess silver nitrate solution in cold but some remained in solution.

1 mol $\text{CoCl}_3 \cdot 6\text{NH}_3$ (Yellow) gave 3 mol AgCl

1 mol $\text{CoCl}_3 \cdot 5\text{NH}_3$ (Purple) gave 2 mol AgCl

1 mol $\text{CoCl}_3 \cdot 4\text{NH}_3$ (Green) gave 1 mol AgCl

1 mol $\text{CoCl}_3 \cdot 4\text{NH}_3$ (Violet) gave 1 mol AgCl

These observations, together with the results of conductivity measurements in solution can be explained if, (i) six groups in all, either chloride ions or ammonia molecules or both, remain bonded to the cobalt ion during the reaction and (ii) the compounds are formulated as shown in Table 1, where the atoms within the square brackets form a single entity which does not dissociate under the reaction conditions. Werner proposed the term secondary valence for the number of groups bound directly to the metal ion; in each of these examples the secondary valences are six.

Table 3.1 Formulation of Cobalt (III) Chloride - Ammonia Complexes
(reproduced from ref. 3)

Colour	Formula	Solution conductivity corresponds to
Yellow	$[\text{Co}(\text{NH}_3)_6]^{3+} 3\text{Cl}^-$	1:3 electrolyte
Purple	$[\text{CoCl}(\text{NH}_3)_5]^{2+} 2\text{Cl}^-$	1:2 electrolyte
Green	$[\text{CoCl}_2(\text{NH}_3)_4]^+ \text{Cl}^-$	1:1 electrolyte
Violet	$[\text{CoCl}_2(\text{NH}_3)_4]^+ \text{Cl}^-$	1:1 electrolyte

3. Nomenclature of coordination compounds

The International Union of Pure and Applied Chemistry publication nomenclature of inorganic chemistry (1989), Blackwell scientific publishers, contains the rules for the systematic naming of coordination compounds. The basic rules are summarized as follows.

1. The positive ion is named first followed by the negative ion.
2. When writing the name of a complex, the ligands are quoted in alphabetical order, regardless of their charge (followed by metal)

3. When writing the formula of complexes, the complex ion should be enclosed by square brackets. The metal is named first, and then the coordinated groups are listed in the order: negative ligands, neutral ligands, positive ligands (and alphabetically according to the first symbol within each group)

Table 3.2. Names of Some Common Anionic and Neutral Ligands
(reproduced from ref. 5)

Negative Ligands	Names	Neutral Ligands	Names
Br ⁻	Bromo	NH ₃	ammine
F ⁻	Fluoro	H ₂ O	Aqua
O ²⁻	Oxo	NO	Nitrosyl
OH ⁻	Hydroxo	CO	Carbonyl
CN ⁻	Cyano	O ₂	dioxygen
C ₂ O ₄ ²⁻	Oxalate	N ₂	dinitrogen
CO ₃ ²⁻	Carbonato	C ₅ H ₅ N	pyridine
CH ₃ COO ⁻	Acetate	H ₂ NCH ₂ CH ₂ NH ₂	ethylenediamine

Positive ligands: End in --ium, e.g. NH₂-NH₂ Hydrazinium, NO⁺ Nitrosonium.

Negative ligands: End in -o, e.g. halides

Neutral ligands: No special ending, e.g. H₂O

4. Where there are several ligands of the same kind, we normally use the prefixes di, tri, tetra, penta and hexa to show the number of ligands of that type. An exception occurs when the name of the ligand includes a number, e.g. dipyridyl or ethylenediammine. To avoid confusion in the name of the ligand is placed in brackets.
5. The oxidation state of the central metal is shown by Roman numeral in brackets immediately following its name [i.e. no space, e.g. titanium (III)]
6. Complex positive ions and neutral molecules have no special ending but complex negative ions end in -ate.
7. If the complex contains two or more atoms, it is termed polynuclear. The bridging ligands which link the two metal atoms together are indicated by the prefix μ - . If there are two or more bridging groups of the same kind, this is indicated by di- μ , tri- μ etc. Bridging groups are listed alphabetically with the other groups unless the bridges more

than two metal atoms it is shown as μ_3 , μ_4 , μ_5 or μ_6 to indicate how many atoms it is bonded to.

8. Sometimes a ligand may be attached through different atoms. Thus $M-\text{NO}_2$ is called nitro and $M-\text{ONO}$ is called nitrito. Similarly the SCN group may bond $M-\text{NCS}$ isothiocyanato. These may be named systematically thiocyanato-S or thiocyanato-N to indicate which atom is bonded to the metal. This convention may be extended to other cases where the mode of linkage is ambiguous.

A huge variety of ligands appear in coordination complexes and to illustrate this point, some examples of common types of ligand are shown in (**Fig. 3.1, 3.2, 3.3 and 3.4**)

These rules are illustrated by the following examples:

Complex anions

$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	Hexaamminecobalt (III) chloride
$[\text{CoCl}(\text{NH}_3)_5]^{2+}$	Pentaamminechlorocobalt (III) ion
$[\text{CoSO}_4(\text{NH}_3)_4]\text{NO}_3$	Tetraamminesulphatocobalt (III) nitrate
$[\text{Zn}(\text{NCS})_4]^{2+}$	Tetrathiocyanato - N- zinc (II)

Complex cations

$\text{K}_4[\text{Fe}(\text{CN})_6]$	Potassium hexacyanoferrate (II)
$\text{Na}_2[\text{ZnCl}_4]$	Sodium tetrachlorozincate (II)
$\text{K}_2[\text{Cr}(\text{CN})_2\text{O}_2(\text{O}_2)\text{NH}_3]$	Potassium ammine dicyanidoxo peroxo chromate (VI)

Organic groups

$[\text{Fe}(\text{C}_5\text{H}_5)_2]$	Bis (cyclopentadienyl) iron (II)
$[\text{Cr}(\text{C}_6\text{H}_6)_2]$	Bis (benzene)chromium (0)
$[\text{CuCl}_2(\text{CH}_3\text{NH}_2)_2]$	Dichlorobis (methylamine) copper (II)

Bridging groups

$[(\text{NH}_3)_5\text{Co}(\text{NH}_2)\text{Co}(\text{NH}_3)_5](\text{NO}_3)_5$	μ -amidobis[pentaamminecobalt (III)] nitrate
$[(\text{CO})_3\text{Fe}(\text{CO})_3\text{Fe}(\text{CO})_3]$	Tri- μ -carbonyl-bis(tricarbonyliron (0))

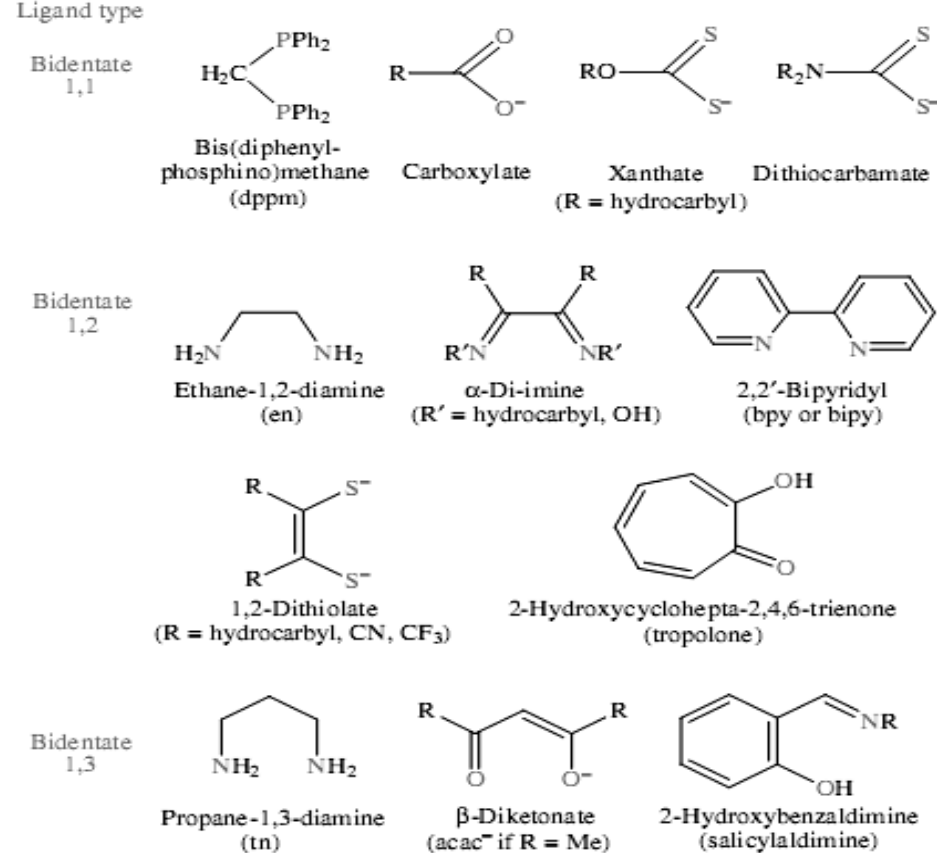
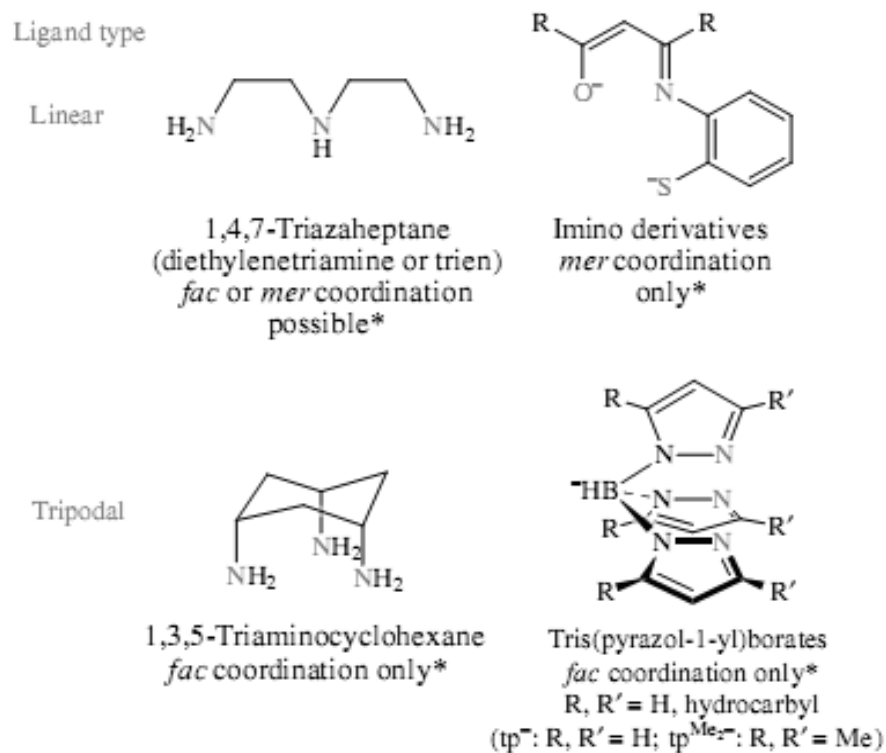


Fig. 3.1. Bidentate ligands (reproduced from ref. 4)



* The terms *fac* and *mer* are defined in Section 4.2.2 on Geometric Isomerism

Fig. 3.2. Tridentate ligands (reproduced from ref. 4)

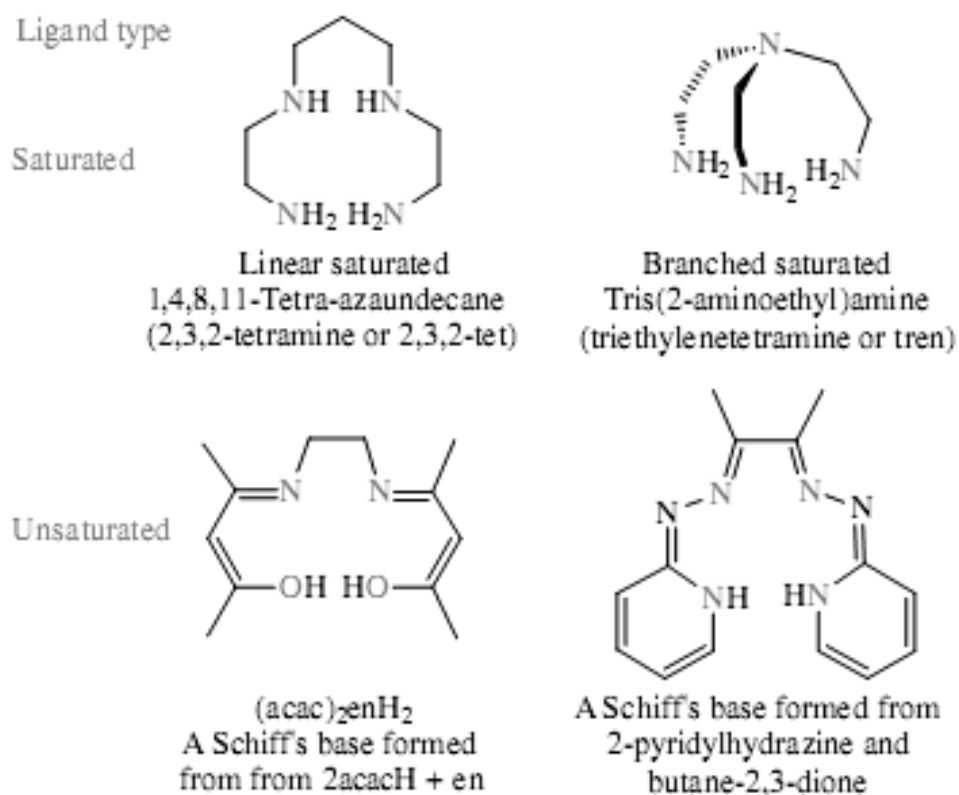


Fig. 3.3. Some quadridentate ligands (reproduced from ref. 4)

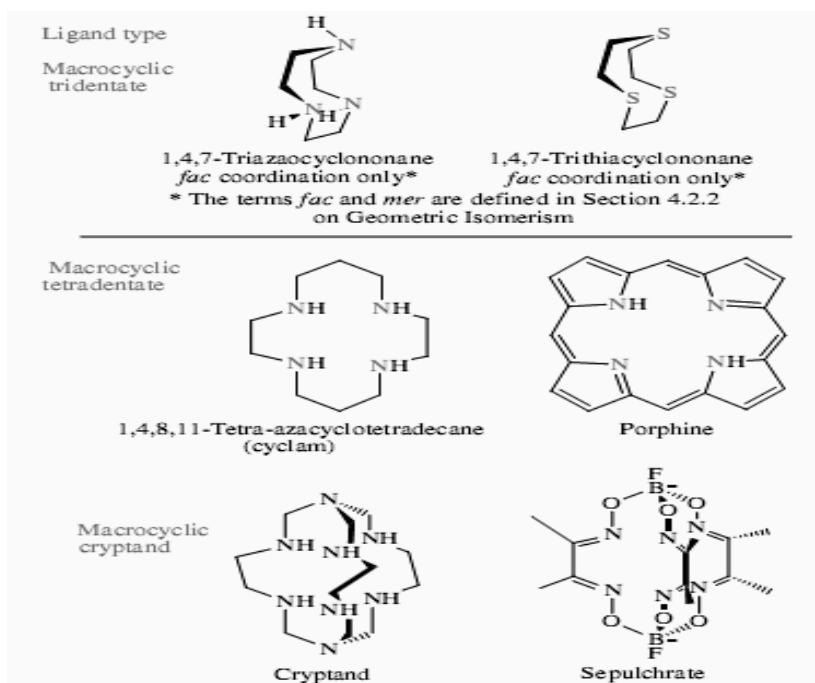
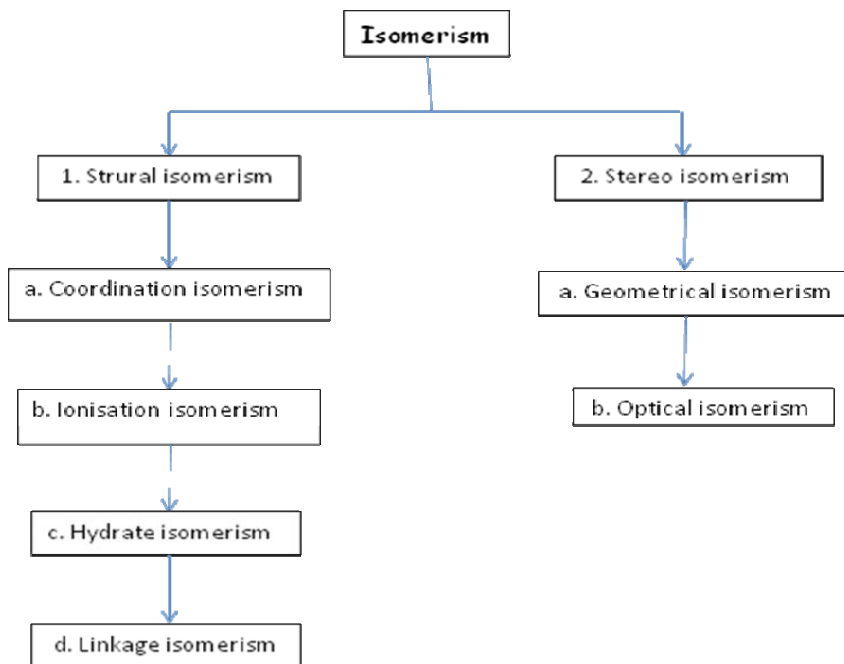


Fig. 3.4. Macro cyclic ligands (reproduced from ref. 4)

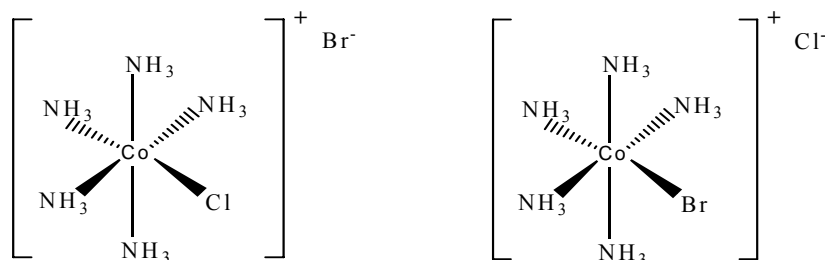
3. Types of Isomerism



3.1. Isomerism in Coordination Compounds

Compound that have the same chemical formula but different structural arrangements are called isomers. Because of the complicated formulae of many coordination compounds, the variety of bond types and the number of shapes possible, many different types of isomerism occur. Wener's classifications into two principal types of isomerism are known among coordination compounds. Each of which can be further subdivided.

a) Coordination isomerism: This type of isomerism arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex. An example is provided by $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$, in which the NH_3 ligands are bound to Co^{3+} and the CN^- ligands to Cr^{3+} . In its coordination isomer $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$, the NH_3 ligands are bound to Cr^{3+} and the CN^- ligands to Co^{3+} and $[\text{Co}(\text{NH}_3)\text{Cl}]\text{Br}$ $[\text{Co}(\text{NH}_3)\text{Br}]\text{Cl}$ shown in **Fig. 3.5**.



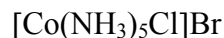
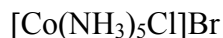
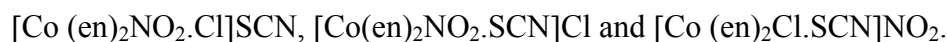
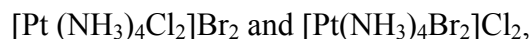
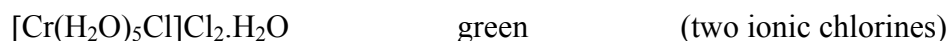


Fig. 3.5. Coordination isomerism in $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Br}$ and $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Cl}$ complexes

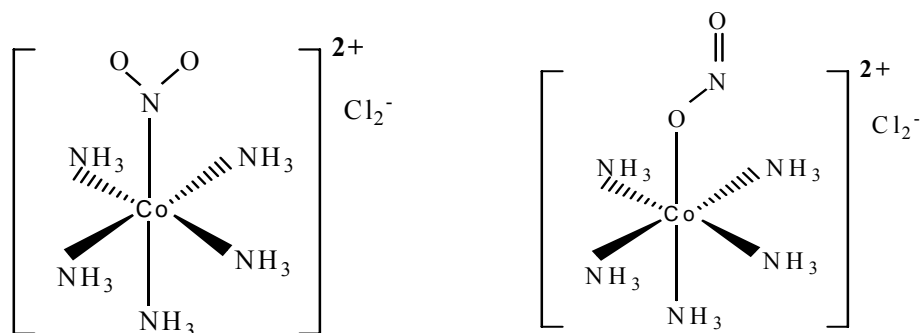
b) Ionization isomerism: This type of isomerism is due to the exchange of groups between the complex ion and the ions outside it. $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ is red-violet. An aqueous solution gives a white precipitate of BaSO_4 with BaCl_2 solution, thus confirming the presence of free SO_4^{2-} ions. In contrast $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ is red. A solution of this complex does not give a positive sulphate test with BaCl_2 . It does give a cream coloured precipitate of AgBr with AgNO_3 , thus confirming the presence of free Br^- ions. Note that the sulphate ion occupies only one coordination position even though it has two negative charges. Some other examples of ionization isomerism are:



c) Hydrate isomerism: Three isomers of $\text{CrCl}_3.6\text{H}_2\text{O}$ are known. From conductivity measurements and quantitative precipitation of ionized chlorine, they have been given the following formula:



d) Linkage isomerism: Linkage isomerism arises in a coordination compound containing ambidentate ligand. A simple example is provided by complexes containing the thiocyanate ligand, NCS^- , which may bind through the nitrogen to give $\text{M}-\text{NCS}$ or through sulphur to give $\text{M}-\text{SCN}$. Jorgensen discovered such behaviour in the complex $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$, which is obtained as the red form, in which the nitrite ligand is bound through oxygen ($-\text{ONO}$), and as the yellow form, in which the nitrite ligand is bound through nitrogen ($-\text{NO}_2$). The complexes are shown in **Fig. 3.6**.



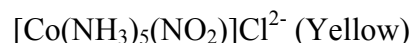


Fig. 3.6. Linkage isomerism in $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}^{2-}$ complex

e) Stereoisomerism: Stereoisomers have the same chemical formula and chemical bonds but they have different spatial arrangement. Structural isomers have different bonds. A detailed account of these isomers are given below

f) Geometric Isomers: The number of geometric isomers expected for common stereochemistries are as follows:

Square planar complexes:

Compound type	Complex	Number of isomers
Ma_2b_2	$[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$	2 (<i>cis</i> - and <i>trans</i> -)
Mabcd	$[\text{PtBrClNH}_3(\text{py})]$	3 (use <i>cis</i> - and <i>trans</i> - relations)

Here a, b, c, and d refer to monodentate ligands.

A number of examples of these types have been isolated and characterized and they show very different chemical and biological properties. Thus for example, *cis*- $\text{PtCl}_2(\text{NH}_3)_2$ is an anti-cancer agent (*cis*-platin) whereas the *trans*- isomer is inactive against cancer (it is toxic), and so not useful in Chemotherapy. *cis*- and *trans*- refer to the position of 2 groups relative to each other. In the *cis*- isomer they are "next to each other" i.e. at 90 degrees in relation to the central metal ion, whereas in the *trans*- isomer they are "opposite each other", i.e. at 180 degrees relative to the central metal ion and the complexes are shown in **Fig. 3.7**.

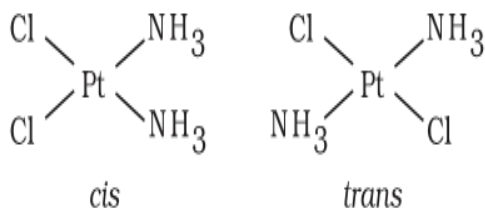


Fig. 3.7. Cis, Trans isomers of $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ complex (reproduced from ref. 3)

Other square planar complex (**Fig. 3.8**) of the type Mabcd (where a, b, c, d are unidentates) shows three isomers-two *cis* and one *trans*. You may attempt to draw these structures. Such isomerism is not possible for a tetrahedral geometry but similar behaviour is possible in octahedral complexes of formula $[\text{Mb}_2\text{a}_4]$ in which the two ligands 'b' may be oriented *cis* or *trans* to each other.

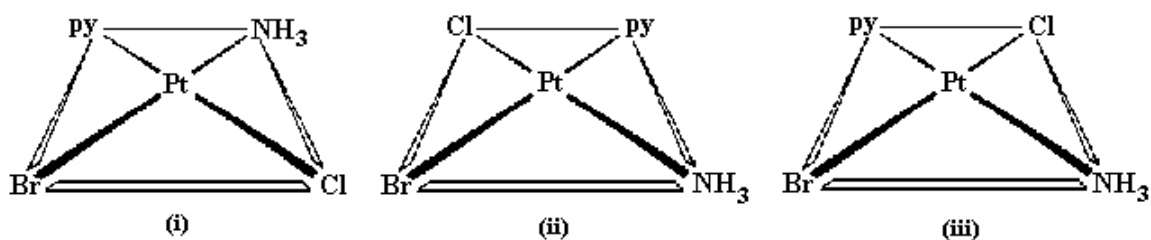


Fig. 3.8. Geometric isomers of a square planar complex $[\text{PtBrClNH}_3(\text{py})]$.

Octahedral complexes:

Compound type	No. of isomers
Ma_4b_2	2 (cis- and trans-)
MAA_2b_2	3 (2 cis- and 1 trans-)
Ma_3b_3	2 (fac- and mer-)

Ma_4b_2 type complexes (**Fig. 3.9**) have two types of cis- and trans- geometrical isomers. In cis- isomer similar ligands are ~ 90 degrees and in trans- isomer ligands are ~ 180 degrees to each other.

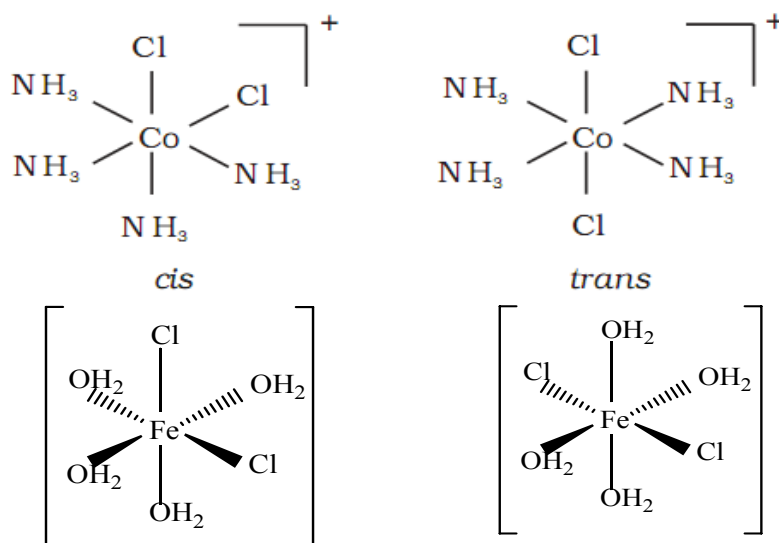
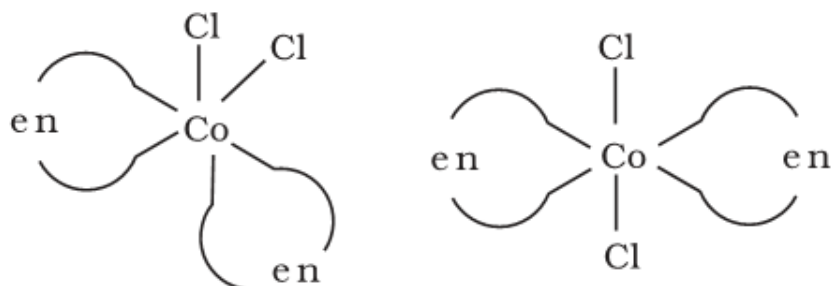


Fig. 3.9. Geometrical isomerism of Ma_4b_2 complexes

Geometrical isomerism also arises when bidentate ligands A-A (e.g., $\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2$ (en)) are present in complexes of formula $[\text{Mb}_2(\text{A}-\text{A})_2]$ and the complex



[CoCl₂(en)₂] is given **Fig. 3.10**.

Fig. 3.10. Geometrical isomers (cis and trans) of [CoCl₂(en)₂]

Another type of geometrical isomerism occurs in octahedral coordination entities of the type [Ma₃b₃] like [Co(NH₃)₃(NO₂)₃]. If three donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face, we have the facial (fac) isomer. When the positions are around the meridian of the octahedron, we get the meridional (mer) isomer shown in **Fig. 3.11**.

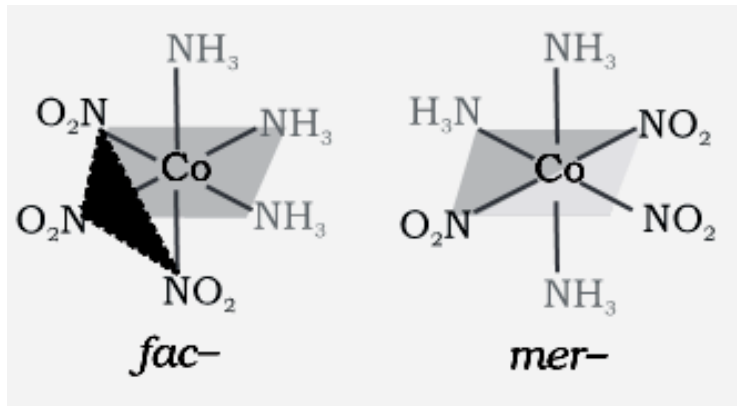


Fig. 3.11. The facial (fac) and meridional (mer) isomers of [Co(NH₃)₃(NO₂)₃]

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

complexes involving didentate ligands and $[\text{Co}(\text{en})_3]^{3+}$ complex optical isomerism shown in **Fig. 3.12**.

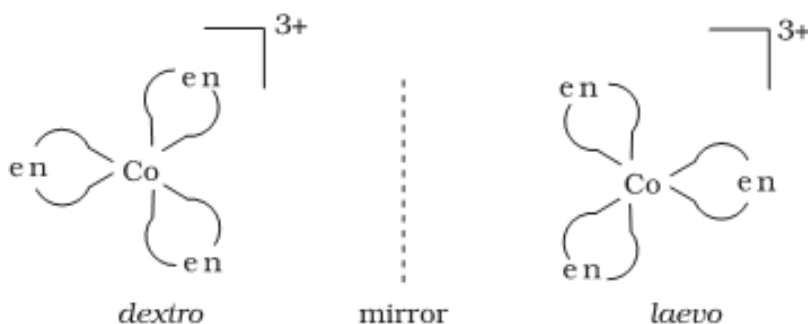


Fig. 3.12. Optical isomers (dextro and laevo) of $[\text{Co}(\text{en})_3]^{3+}$ complex

Hexol is a cobalt compound that was first prepared by Alfred Werner in 1914 and represented the first non-carbon-containing chiral compound. The salt with the molecular formula of $[\text{Co}((\text{OH})_2\text{Co}(\text{NH}_3)_4)_3](\text{SO}_4)_3$ was prepared starting from cobalt(II) sulfate. Optical resolution of this compound was possible by treating the hexol chloride salt with the resolving agent silver D-(+)-bromo camphorsulphonate in dilute acetic acid. The D-hexol salt precipitated out from solution and the filtrate contained the L-hexol species. (D-hexol and L-hexol are enantiomers of each other; see here for D/L notation.) Werner also published a second a chiral hexol (a minor byproduct from the production of Fremy's salt) that he incorrectly identified as a linear trimer shown in **fig.13**.

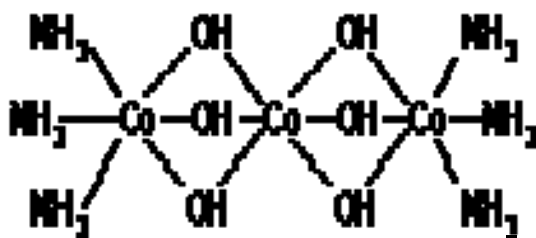


Fig. 3.13. Chiral hexanol

In 2004 the second hexol was reinvestigated and found to be a hexanuclear species **Fig.**

3.14

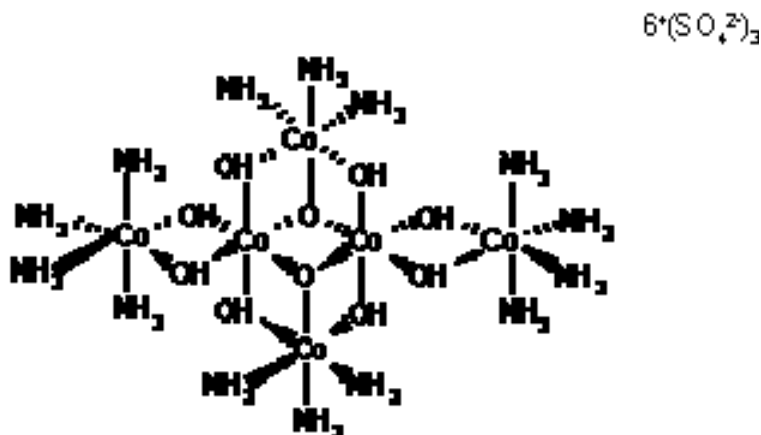


Fig. 3.14. Hexanol (hexanuclear species)

Since the successful resolution of an entirely inorganic ion (containing no C atoms) (hexol) only a handful of truly inorganic complexes have been isolated as their optical isomers e.g. $(\text{NH}_4)_2 \text{Pt}(\text{S}_5)_3 \cdot 2\text{H}_2\text{O}$.

The spatial orientation of ligands is such that the two isomers are non-super imposable mirror images of one another. There are two common occurrences of this type of isomerism.

- (i) cis-isomers of octahedral complexes with 2 bidentate ligands and 2 monodentate ligands in cis- $[\text{CoCl}_2(\text{en})_2]$ complex (cis-bis chelates) **Fig. 3.15**.

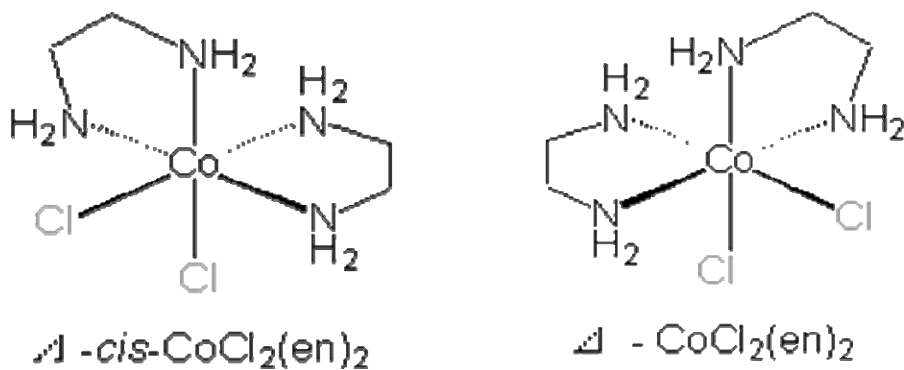


Fig. 3.15. Optical isomers of $[\text{CoCl}_2(\text{en})_2]$ complex

- (ii) Octahedral complexes with 3 bidentate ligands in $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$ complex (tris chelate) Fig. 3.16.

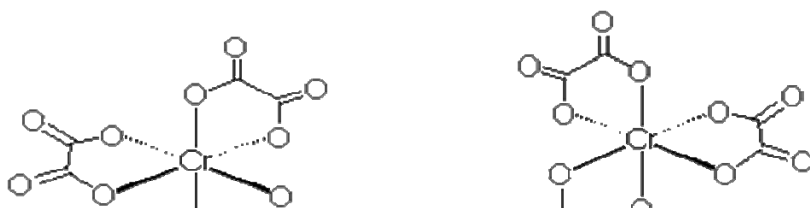


Fig. 3.16. Optical isomers of (tris chelate) $K_3[Cr(C_2O_4)]$ complex

4. CIP rules for optical active complexes

Various methods have been used to denote the absolute configuration of optical isomers such as R or S, Λ or Δ or C and A. The IUPAC rules suggest that for general octahedral complexes C/A scheme is convenient to use and that for bis and tris bidentate complexes the absolute configuration be designated Lambda Λ (left-handed) and Delta Δ (right-handed).

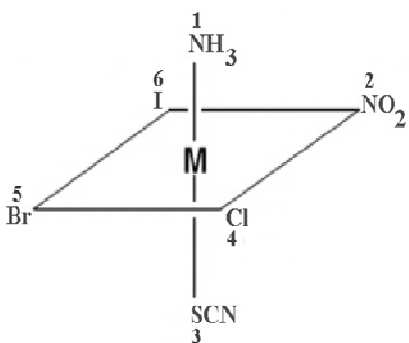


Fig. 3.17. Hypothetical complex $[Co Cl Br I NH_3 NO_2 SCN]^{2-}$
(reproduced from ref. 6)

Priorities are assigned for mononuclear coordination systems based on the standard sequence rules developed for enantiomeric carbon compounds by Cahn, Ingold and Prelog (CIP rules). These rules use the coordinating atom to arrange the ligands into a priority order such that the highest atomic number gives the highest priority number. For example (**Fig. 3.17**) the hypothetical complex $[Co Cl Br I NH_3 NO_2 SCN]^{2-}$ would assign the I- as 6, Br as 5, Cl as 4, SCN as 3, NO₂ as 2 and NH₃ as 1.

The reference axis for an octahedral centre is that axis containing the ligating atom of CIP priority 1 and the trans ligating atom of lowest possible priority (highest numerical value). The atoms in the coordination plane perpendicular to the reference axis are viewed from the ligand having that highest priority (CIP priority 1) and the clockwise and anticlockwise sequences of priority numbers are compared. The structure is assigned the symbol C or A, according to whether the clockwise (C) or anticlockwise (A) sequence is lower at the first point of difference. In the example shown above this would be C.

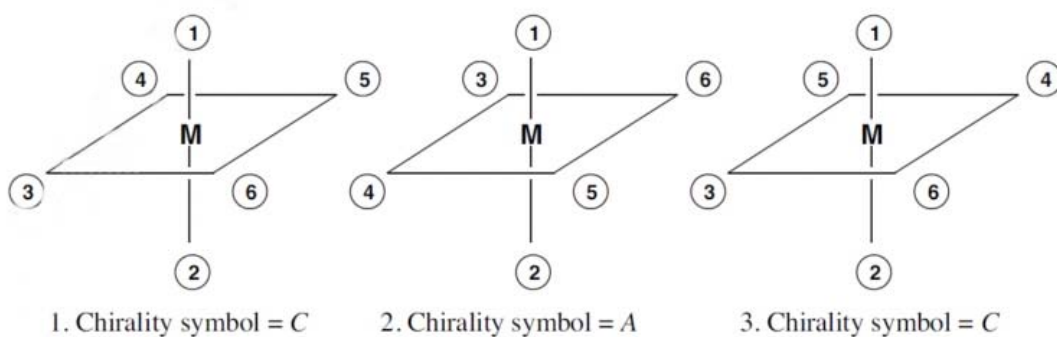


Fig. 3.18. hypothetical complex $[\text{Co Cl Br I NH}_3 \text{NO}_2 \text{SCN}]^{2-}$ different structures

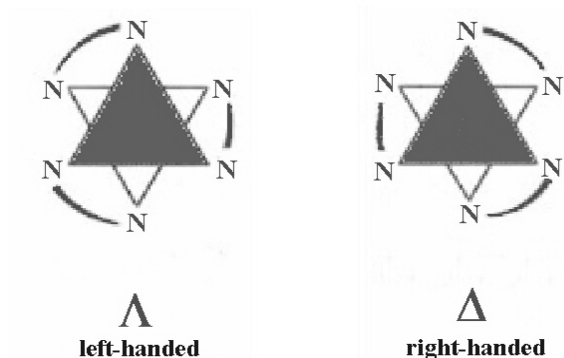


Fig. 3.19. Optical isomers of $[\text{Co}(\text{en})_3]^{3+} - \Lambda$ and $[\text{Co}(\text{en})_3]^{3+} - \Delta$

The two optical isomers of $[\text{Co}(\text{en})_3]^{3+}$ have identical chemical properties and just denoting their absolute configuration does NOT give any information regarding the direction in which they rotate plane-polarised light. This can ONLY be determined from

measurement and then the isomers are further distinguished by using the prefixes laevo ((-) or l) and dextro ((+) or d) depending on whether they rotate left or right. The use of l- and d- is not recommended.

To add to the confusion, when measured at the sodium D line (589nm), the tris(1,2diaminoethane)M(III) complexes (M= Rh(III) and Co(III)) with **IDENTICAL** absolute configuration, rotate plane polarized light in **OPPOSITE** directions. The left-handed (Λ)-[Co(en)₃]³⁺ isomer gives a rotation to the right and therefore corresponds to the (+) isomer. These isomers (Λ or Δ) are shown in **Fig. 3.19**

Many coordination compounds are chiral; for example, the well-known tris(bipyridine)ruthenium (II) complex in which the three bipyridine ligands adopt a chiral propeller-like arrangement.

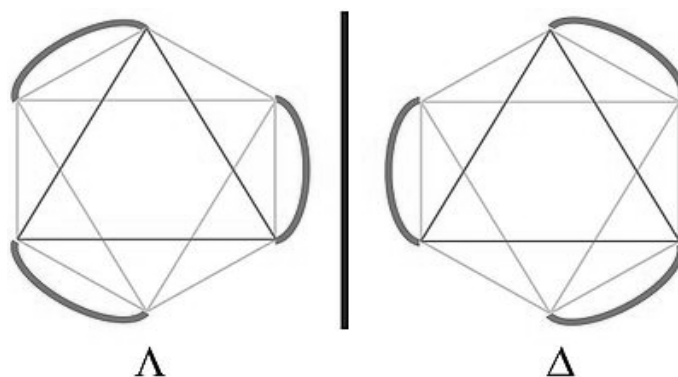
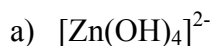


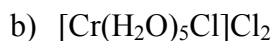
Fig. 3. 20. Optical isomers of [Ru(2,2'-bipyridine)₃]²⁺ complex (reproduced from ref. 7)

In this case, the Ru atom may be regarded as a stereogenic center, with the complex having point chirality. The two enantiomers of complexes such as [Ru(2,2'-bipyridine)₃]²⁺ may be designated as Λ (left-handed twist of the propeller described by the ligands) and Δ (right-handed twist) are shown in **Fig. 3.20**.

5. Some solved problems on Nomenclature and Isomerism of Coordination compounds

1. Write the IUPAC name for the following coordination compounds.

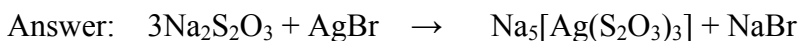




Answer: a) Tetrahydroxozincate (II)

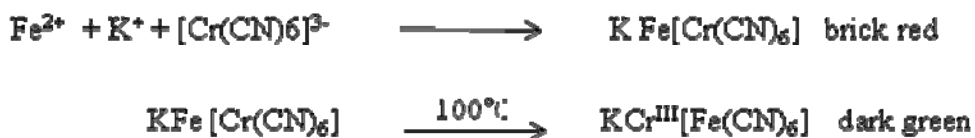
b) Pentaquachlorochromium (III) chloride

2. While developing photography hypo reacts with AgBr to form unknown soluble complex. Find the complex and write down the IUPAC name of it.



[Sodium tris(thiosulphato)argentate (I)]

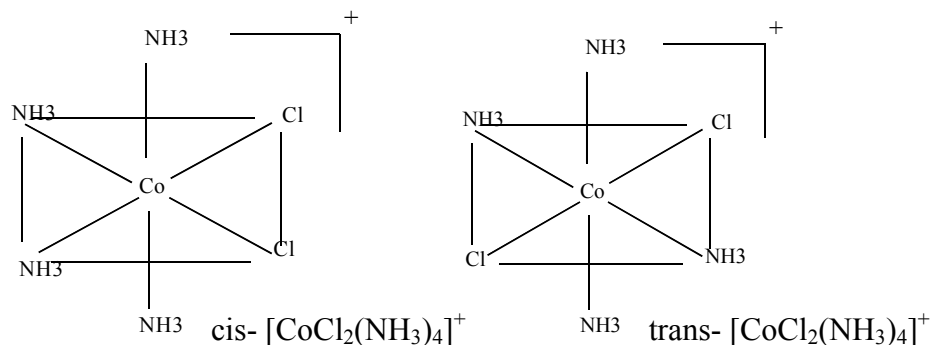
3. Why the following reaction isomeric complexes exhibit colors according to the reaction conditions?



Answer: due to linkage isomerism

4. Draw structure of geometrical isomers of $[\text{CoCl}_2(\text{NH}_3)_4]^+$ complex

Answer:



5. Which out of the following two coordination entities is optically active



Ans: $\text{cis-} [\text{CrCl}_2(\text{OX})_2]^-$

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CHAPTER - 4

NUCLEAR REACTIONS AND CARBON DATING

M. Banu

4.1. Nuclear Chemistry

Nuclear chemistry is the study of the chemical and physical properties of elements as influenced by changes in the structure of the atomic nucleus. Modern nuclear chemistry, sometimes referred to as radiochemistry, has become very interdisciplinary in its applications, ranging from the study of the formation of the elements in the universe to the design of radioactive drugs for diagnostic medicine. In fact, the chemical techniques pioneered by nuclear chemists have become so important that biologists, geologists, and physicists use nuclear chemistry as ordinary tool of their disciplines. While the common perception is that nuclear chemistry involves only the study of radioactive nuclei, advances in modern mass spectrometry instrumentation has made chemical studies using stable, nonradioactive **isotopes** increasingly important.



Fig. 4.1. Lasers focus on a small pellet of fuel in attempt to create a nuclear fusion reaction (the combination of two nuclei to produce another nucleus) for the purpose of producing energy (reproduced from ref. 1)

4.2. Origin of Nuclear Chemistry

Marie Curie was the founder of the field of nuclear chemistry. She was fascinated by Antoine-Henri Becquerel's discovery that uranium minerals can emit rays that are able to expose photographic film, even if the mineral is wrapped in black paper. Using an

electrometer invented by her husband Pierre and his brother Jacques that measured the electrical conductivity of air (a precursor to the Geiger counter), she was able to show that thorium also produced these rays—a process that she called radioactivity. Through tedious chemical separation procedures involving **precipitation** of different chemical fractions, Marie was able to show that a separated fraction that had the chemical properties of bismuth and another fraction that had the chemical properties of barium were much more radioactive per unit mass than the original uranium ore. She had separated and discovered the elements polonium and radium, respectively. Further purification of radium from barium produced approximately 100 milligrams of radium from an initial sample of nearly 2,000 kilograms of uranium ore.

In 1911 Ernest Rutherford asked a student, George de Hevesy, to separate a lead impurity from a decay product of uranium, radium-D. De Hevesy did not succeed in this task (we now know that radium-D is the radioactive isotope ^{210}Pb), but this failure gave rise to the idea of using radioactive isotopes as tracers of chemical processes. With Friedrich Paneth in Vienna in 1913, de Hevesy used ^{210}Pb to measure the solubility of lead salts—the first application of an isotopic tracer technique. De Hevesy went on to pioneer the application of isotopic tracers to study biological processes. He is generally considered to be the founder of a very important area in which nuclear chemists work today, the field of nuclear medicine. De Hevesy also is credited with discovering the technique of neutron activation analysis, in which samples are bombarded by neutrons in a nuclear reactor or from a neutron generator, and the resulting radioactive isotopes are measured, allowing the analysis of the elemental composition of the sample.

In Germany in 1938, Otto Hahn and Fritz Strassmann, skeptical of claims by Enrico Fermi and Irène Joliot-Curie that bombardment of uranium by neutrons produced new so-called transuranic elements (elements beyond uranium), repeated these experiments and chemically isolated a radioactive isotope of barium. Unable to interpret these findings, Hahn asked Lise Meitner, a physicist and former colleague, to propose an explanation for his observations. Meitner and her nephew, Otto Frisch, showed that it was possible for the uranium nucleus to be split into two smaller nuclei by the neutrons, a process that they termed “**fission.**” The discovery of nuclear fission eventually led to the development of nuclear weapons and, after World War II, the advent of nuclear power to

generate electricity. Nuclear chemists were involved in the chemical purification of plutonium obtained from uranium targets that had been irradiated in reactors. They also developed chemical separation techniques to isolate radioactive isotopes for industrial and medical uses from the fission products wastes associated with plutonium production for weapons. Today, many of these same chemical separation techniques are being used by nuclear chemists to clean up radioactive wastes resulting from the fifty-year production of nuclear weapons and to treat wastes derived from the production of nuclear power.

In 1940, at the University of California in Berkeley, Edwin McMillan and Philip Abelson produced the first manmade element, neptunium (Np), by the bombardment of uranium with low energy neutrons from a nuclear accelerator. Shortly thereafter, Glenn Seaborg, Joseph Kennedy, Arthur Wahl, and McMillan made the element plutonium by bombarding uranium targets with deuterons, particles derived from the heavy isotope of hydrogen, deuterium (^2H). Both McMillan and Seaborg recognized that the chemical properties of neptunium and plutonium did not resemble those of rhenium and osmium, as many had predicted, but more closely resembled the chemistry of uranium, a fact that led Seaborg in 1944 to propose that the transuranic elements were part of a new group of elements called the actinide series that should be placed below the lanthanide series on the periodic chart. Seaborg and coworkers went on to discover many more new elements and radioactive isotopes and to study their chemical and physical properties. At the present, nuclear chemists are involved in trying to discover new elements beyond the 112 that are presently confirmed and to study the chemical properties of these new elements, even though they may exist for only a few thousandths of a second.

As early as 1907 Bertram Boltwood had used the discovery of radioactive decay laws by Ernest Rutherford and Frederick Soddy to ascribe an age of over two billion years to a uranium mineral. In 1947 Willard Libby at the University of Chicago used the decay of ^{14}C to measure the age of dead organic matter. The cosmogenic radionuclide, ^{14}C , becomes part of all living matter through photosynthesis and the consumption of plant matter. Once the living organism dies, the ^{14}C decays at a known rate, enabling a date for the carbon-containing relic to be calculated. Today, scientists ranging from astrophysicists to marine biologists use the principles of radiometric dating to study

problems as diverse as determining the age of the universe to defining food chains in the oceans. In addition, newly developed analytical techniques such as accelerator mass spectrometry (AMS) have allowed nuclear chemists to extend the principles of radiometric dating to nonradioactive isotopes in order to study modern and ancient processes that are affected by isotopic fractionation. This isotopic fractionation results from temperature differences in the environment in which the material was formed (at a given temperature, the lighter isotope will be very slightly more reactive than the heavier isotope), or from different chemical reaction sequences.

4.3. Nuclear Structure

An atom consists of an extremely small, positively charged nucleus surrounded by a cloud of negatively charged electrons. Although typically the nucleus is less than one ten-thousandth the size of the atom, the nucleus contains more than 99.9% of the mass of the atom! Nuclei consist of positively charged protons and electrically neutral neutrons held together by the so-called strong or nuclear force. This force is much stronger than the familiar electrostatic force that binds the electrons to the nucleus, but its range is limited to distances on the order of a few $\times 10^{-15}$ meters.

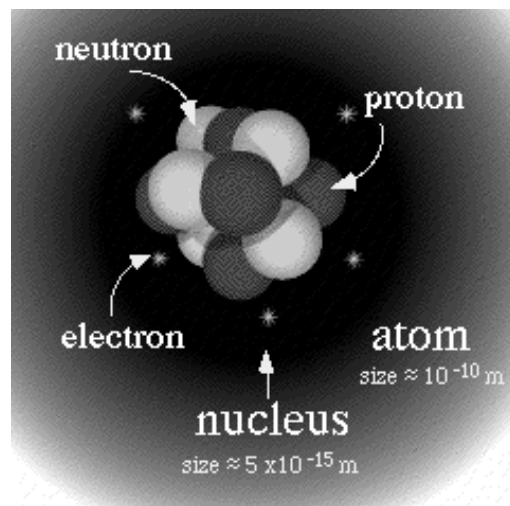


Fig. 4.2. Nuclear Structure

The number of protons in the nucleus, Z , is called the atomic number. This determines what chemical element the atom is. The number of neutrons in the nucleus is denoted by

N . The atomic mass of the nucleus, A , is equal to $Z + N$. A given element can have many different isotopes, which differ from one another by the number of neutrons contained in the nuclei. In a neutral atom, the number of electrons orbiting the nucleus equals the number of protons in the nucleus. Since the electric charges of the proton and the electron are +1 and -1 respectively (in units of the proton charge), the net charge of the atom is zero. At present, there are 112 known elements which range from the lightest, hydrogen, to the recently discovered and yet to-be-named element 112. All of the elements heavier than uranium are man made. Among the elements are approximately 270 stable isotopes, and more than 2000 unstable isotopes.

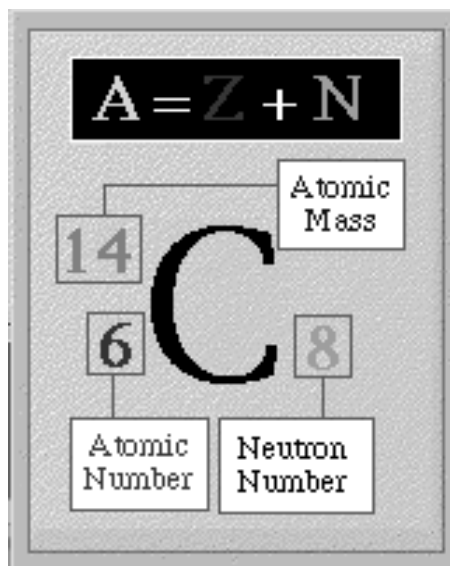


Fig. 4.3. Pictorial representation of C atom (reproduced from ref. 2)

4.4. Radioactivity

In 1896, Henri Becquerel was working with compounds containing the element uranium. To his surprise, he found that photographic plates covered to keep out light became fogged, or partially exposed, when these uranium compounds were anywhere near the plates. This fogging suggested that some kind of ray had passed through the plate coverings. Several materials other than uranium were also found to emit these penetrating rays. Materials that emit this kind of radiation are said to be radioactive and to undergo radioactive decay. In 1899, Ernest Rutherford discovered that uranium compounds produce three different kinds of radiation. He separated the radiations

according to their penetrating abilities and named them *alpha*, *beta*, and *gamma* radiation, after the first three letters of the Greek alphabet. The *alpha* radiation can be stopped by a sheet of paper. Rutherford later showed that an *alpha* particle is the nucleus of a He atom, ${}^4\text{He}$. Beta particles were later identified as high speed electrons. Six millimeters of aluminum are needed to stop most *beta* particles. Several millimeters of lead are needed to stop *gamma* rays, which proved to be high energy *photons*. Alpha particles and *gamma* rays are emitted with a specific energy that depends on the radioactive isotope. Beta particles, however, are emitted with a continuous range of energies from zero up to the maximum allowed for by the particular isotope.

4.4.1 α - decay

The emission of a particle, or ${}^4\text{He}$ nucleus, is a process called α decay. Since a particle contains protons and neutrons, they must come from the nucleus of an atom. The nucleus that results from decay will have a mass and charge different from those of the original nucleus.

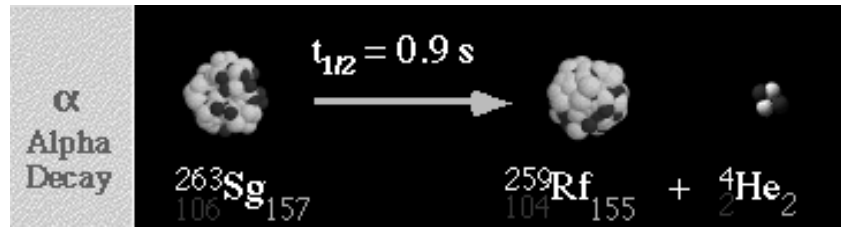


Fig. 4.4. Pictorial representation of α decay (reproduced from ref. 2)

A change in nuclear charge means that the element has been changed into a different element. Only through such radioactive decays or nuclear reactions can transmutation, the age-old dream of the alchemists, actually occur. The mass number, A , of a particle is four, so the mass number, A , of the decaying nucleus is reduced by four. The atomic number, Z , of ${}^4\text{He}$ is two, and therefore the atomic number of the nucleus, the number of

protons, is reduced by two. This can be written as an equation analogous to a chemical reaction. For example, for the decay of an isotope of the element seaborgium, ^{263}Sg :

The atomic number of the nucleus changes from 106 to 104, giving rutherfordium an atomic mass of $263-4=259$. α -decay typically occurs in heavy nuclei where the electrostatic repulsion between the protons in the nucleus is large. Energy is released in the process of α -decay. Careful measurements show that the sum of the masses of the daughter nucleus and the α particle is a bit less than the mass of the parent isotope. Einstein's famous equation, $E = mc^2$, which says that mass is proportional to energy, explains this fact by saying that the mass that is lost in such decay is converted into the kinetic energy carried away by the decay products.

4.4.2 β -decay

Beta particles are negatively charged electrons emitted by the nucleus. Since the mass of an electron is a tiny fraction of an atomic mass unit, the mass of a nucleus that undergoes β decay is changed by only a tiny amount. The mass number is unchanged. The nucleus contains no electrons. Rather, β decay occurs when a neutron is changed into a proton within the nucleus. An unseen neutrino, $\bar{\nu}_e$, accompanies each β decay. The number of protons, and thus the atomic number, is increased by one. For example, the isotope ^{14}C is unstable and emits a β particle, becoming the stable isotope ^{14}N .

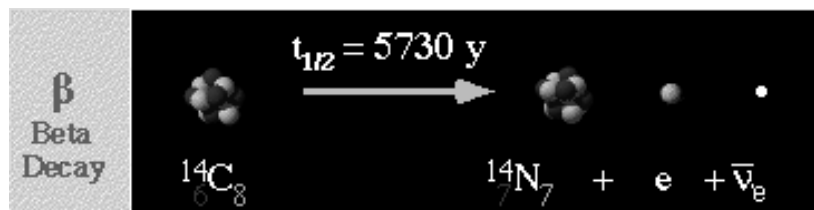


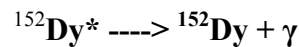
Fig. 4.5. Pictorial representation of β decay (reproduced from ref. 2)

In a stable nucleus, the neutron does not decay. A free neutron, or one bound in a nucleus that has an excess of neutrons, can decay by emitting a β particle. Sharing the energy with the β particle is a neutrino. The neutrino has little or no mass and is uncharged, but, like

the photon, it carries momentum and energy. The source of the energy released in β decay is explained by the fact that the mass of the parent isotope is larger than the sum of the masses of the decay products. Mass is converted into energy just as Einstein predicted.

4.4.3 γ - decay

Gamma rays are a type of electromagnetic radiation that results from a redistribution of electric charge within a nucleus. A γ ray is a high energy photon. The only thing which distinguishes a γ ray from the visible photons emitted by a light bulb is its wavelength; the γ ray's wavelength is much shorter. For complex nuclei there are many different possible ways in which the neutrons and protons can be arranged within the nucleus. Gamma rays can be emitted when a nucleus undergoes a transition from one such configuration to another. For example, this can occur when the shape of the nucleus undergoes a change. Neither the mass number nor the atomic number is changed when a nucleus emits a γ ray in the reaction.



4.5. Penetrating Power

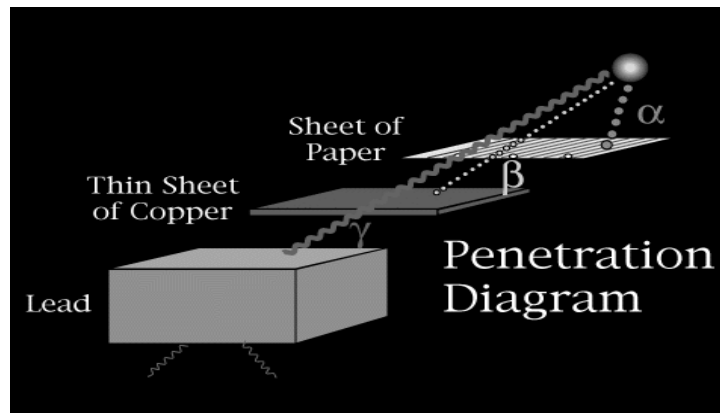


Fig. 4.6. Penetration power (reproduced from ref. 2)

There is a great difference in the penetrating powers for alpha, beta, and gamma rays. Of the three types of radiation, alpha particles are the easiest to stop. A sheet of paper is all that is needed for the absorption of alpha rays. However, it may take a material with a

greater thickness and density to stop beta particles. Gamma rays have the most penetrating powers of all three radiation sources.

4.6. Half-life

The time required for half of the atoms in any given quantity of a radioactive isotope to decay is the half-life of that isotope. Each particular isotope has its own half-life. For example, the half-life of ^{238}U is 4.5 billion years. That is, in 4.5 billion years, half of the ^{238}U on Earth will be decayed into other elements. In another 4.5 billion years, half of the remaining ^{238}U will be decayed. One fourth of the original material will remain on Earth after 9 billion years. The half-life of ^{14}C is 5730 years, thus it is useful for dating archaeological material. Nuclear half-lives range from tiny fractions of a second to many, many times the age of the universe.

4.7. Nuclear Reactions

If nuclei come close enough together, they can interact with one another through the strong nuclear force, and reactions between the nuclei can occur. As in chemical reactions, nuclear reactions can either be exothermic (i.e. release energy) or endothermic (i.e. require energy input). Two major classes of nuclear reactions are of importance: fusion and fission.

4.7.1. Nuclear Fusion

Fusion is a nuclear process in which two light nuclei combine to form a single heavier nucleus. An example of a fusion reaction important in thermonuclear weapons and in future nuclear reactors is the reaction between two different hydrogen isotopes to form an isotope of helium:

This reaction liberates an amount of energy more than a million times greater than one gets from a typical chemical reaction. Such a large amount of energy is released in fusion reactions because when two light nuclei fuse, the sum of the masses of the product nuclei is less than the sum of the masses of the initial fusing nuclei. Once again,

Einstein's equation, $E=mc^2$, explains that the mass that is lost is converted into energy carried away by the fusion products. Even though fusion is an energetically favorable reaction for light nuclei, it does not occur under standard conditions here on Earth because of the large energy investment that is required. Because the reacting nuclei are both positively charged, there is a large electrostatic repulsion between them as they come together. Only when they are squeezed very close to one another do they feel the strong nuclear force, which can overcome the electrostatic repulsion and cause them to fuse.

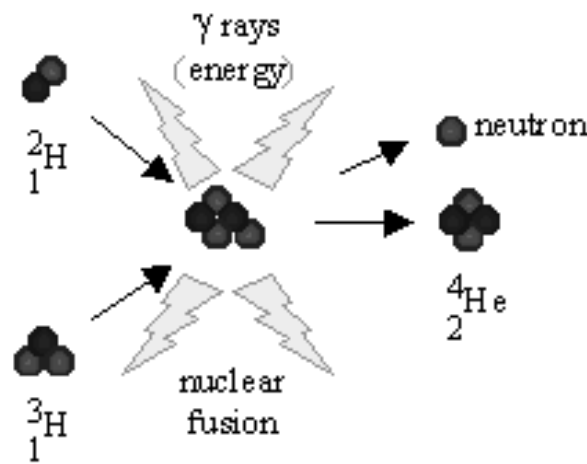


Fig. 4.7. Nuclear fusion of two hydrogen isotopes (reproduced from ref. 2)

Fusion reactions have been going on for billions of years in our universe. In fact, nuclear fusion reactions are responsible for the energy output of most stars, including our own Sun. Scientists on Earth have been able to produce fusion reactions for only about the last sixty years. At first, there were small scale studies in which only a few fusion reactions actually occurred. However, these first experiments later lead to the development of thermonuclear fusion weapons (hydrogen bombs). Fusion is the process that takes place in stars like our Sun. Whenever we feel the warmth of the Sun and see by its light, we are observing the products of fusion. We know that all life on Earth exists because the light generated by the Sun produces food and warms our planet. Therefore, we can say that fusion is the basis for our life.

When a star is formed, it initially consists of hydrogen and helium created in the Big Bang, the process that created our universe. Hydrogen isotopes collide in a star and fuse forming a helium nucleus. Later, the helium nuclei collide and form heavier elements. Fusion is a nuclear reaction in which nuclei combine to form a heavier nucleus. It is the basic reaction which drives the Sun. Lighter elements fuse and form heavier elements. These reactions continue until the nuclei reach iron (around mass sixty), the nucleus with the most binding energy. When a nucleus reaches mass sixty, no more fusion occurs in a star because it is energetically unfavorable to produce higher masses. Once a star has converted a large fraction of its core's mass to iron, it has almost reached the end of its life. The fusion chain cannot continue so its fuel is reduced. Some stars keep shrinking until they become a cooling ember made up of iron. However, if a star is sufficiently massive, a tremendous, violent, brilliant explosion can happen. A star will suddenly expand and produce, in a very short time, more energy than our Sun will produce in a lifetime. When this happens, we say that a star has become a supernova.

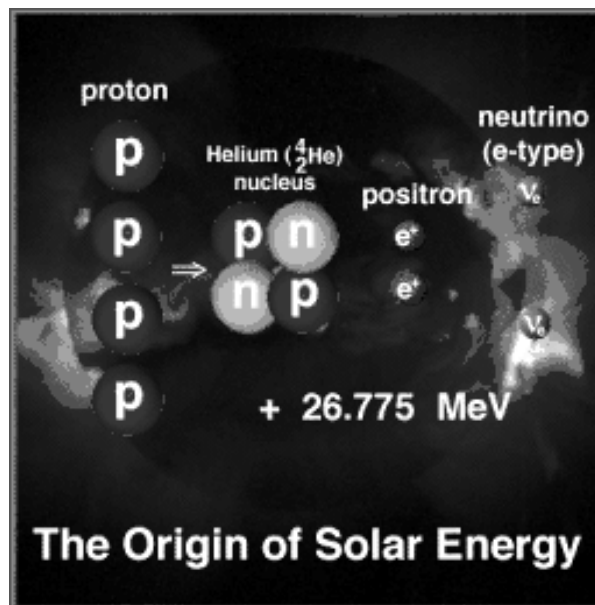


Fig. 4.8. Origin of solar energy (reproduced from ref. 2)

While a star is in the supernova phase, many important reactions occur. The nuclei are accelerated to much higher velocities than can occur in a fusing star. With the added

energy caused by their speed, nuclei can fuse and produce elements higher in mass than iron. The extra energy in the explosion is necessary to overcome the energy barrier of a higher mass element. Elements such as lead, gold, and silver found on Earth were once the debris of a supernova explosion. The element iron that we find all through the Earth and in its center is directly derived from both super novae and dead stars. More peaceful uses of fusion are being researched today with the hope that soon we will be able to control fusion reactions to generate clean, inexpensive power.



Fig. 4.9. Nuclear fusion (reproduced from ref. 2)

4.7.2. Deuterium-Tritium Fusion

The most promising of the hydrogen fusion reactions which make up the deuterium cycle is the fusion of deuterium and tritium. The reaction yields 17.6 MeV of energy but requires a temperature of approximately 40 million Kelvin's to overcome the coulomb barrier and ignite it. The deuterium fuel is abundant, but tritium must be either bred from lithium or gotten in the operation of the deuterium cycle.

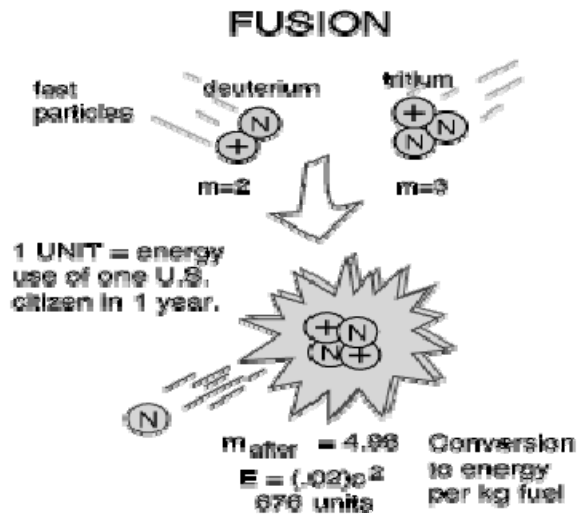
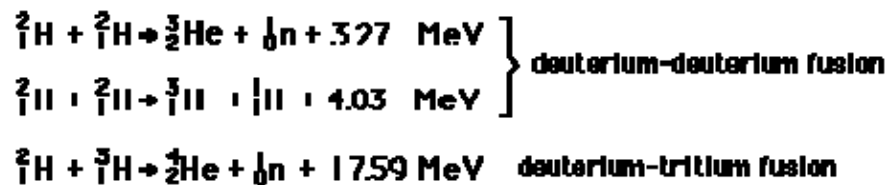


Fig. 4.10. Nuclear fusion (reproduced from ref. 9)

4.7.3. Hydrogen Fusion Reactions

Even though a lot of energy is required to overcome the Coulomb barrier and initiate hydrogen fusion, the energy yields are enough to encourage continued research.

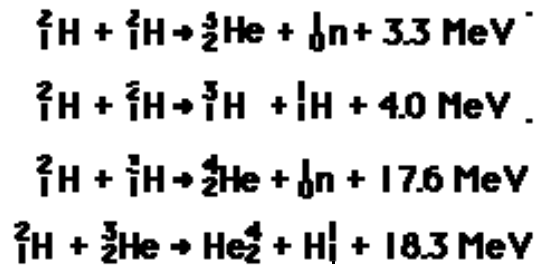
Hydrogen fusion on the earth could make use of the reactions:



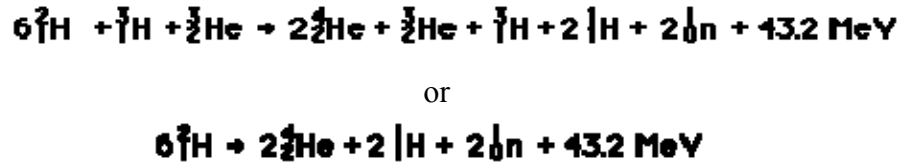
These reactions are more promising than the proton-proton fusion of the stars for potential energy sources. Of these the deuterium-tritium fusion appears to be the most promising and has been the subject of most experiments. In a deuterium-deuterium reactor, another reaction could also occur, creating a deuterium cycle:

4.7.3.1. Deuterium Cycle of ${}^2_1\text{H} + {}^3_2\text{He} \rightarrow {}^4_2\text{He} + {}^1_1\text{H} + 18.3 \text{ MeV}$ Fusion

The four fusion reactions which can occur with deuterium can be considered to form a deuterium cycle.



The above four reactions can be combined as



4.7.4. Fission

Fission is a nuclear process in which a heavy nucleus splits into two smaller nuclei. A example of a fission reaction that was used in the first atomic bomb and is still used in nuclear reactors is

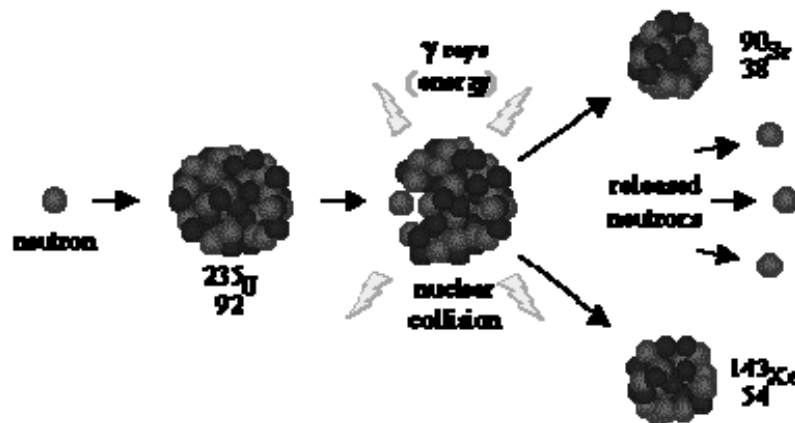


Fig. 4.11. The fission reaction of Uranium-235 (reproduced from ref. 2)

The products shown in the above equation are only one set of many possible product nuclei. Fission reactions can produce any combination of lighter nuclei so long as the number of protons and neutrons in the products sum up to those in the initial fissioning nucleus. As with fusion, a great amount of energy can be released in fission because for

heavy nuclei, the summed masses of the lighter product nuclei are less than the mass of the fissioning nucleus. Fission occurs because of the electrostatic repulsion created by the large number of positively charged protons contained in a heavy nucleus. Two smaller nuclei have less internal electrostatic repulsion than one larger nucleus. So, once the larger nucleus can overcome the strong nuclear force which holds it together, it can fission. Fission can be seen as a "tug-of-war" between the strong attractive nuclear force and the repulsive electrostatic force. In fission reactions, electrostatic repulsion wins.

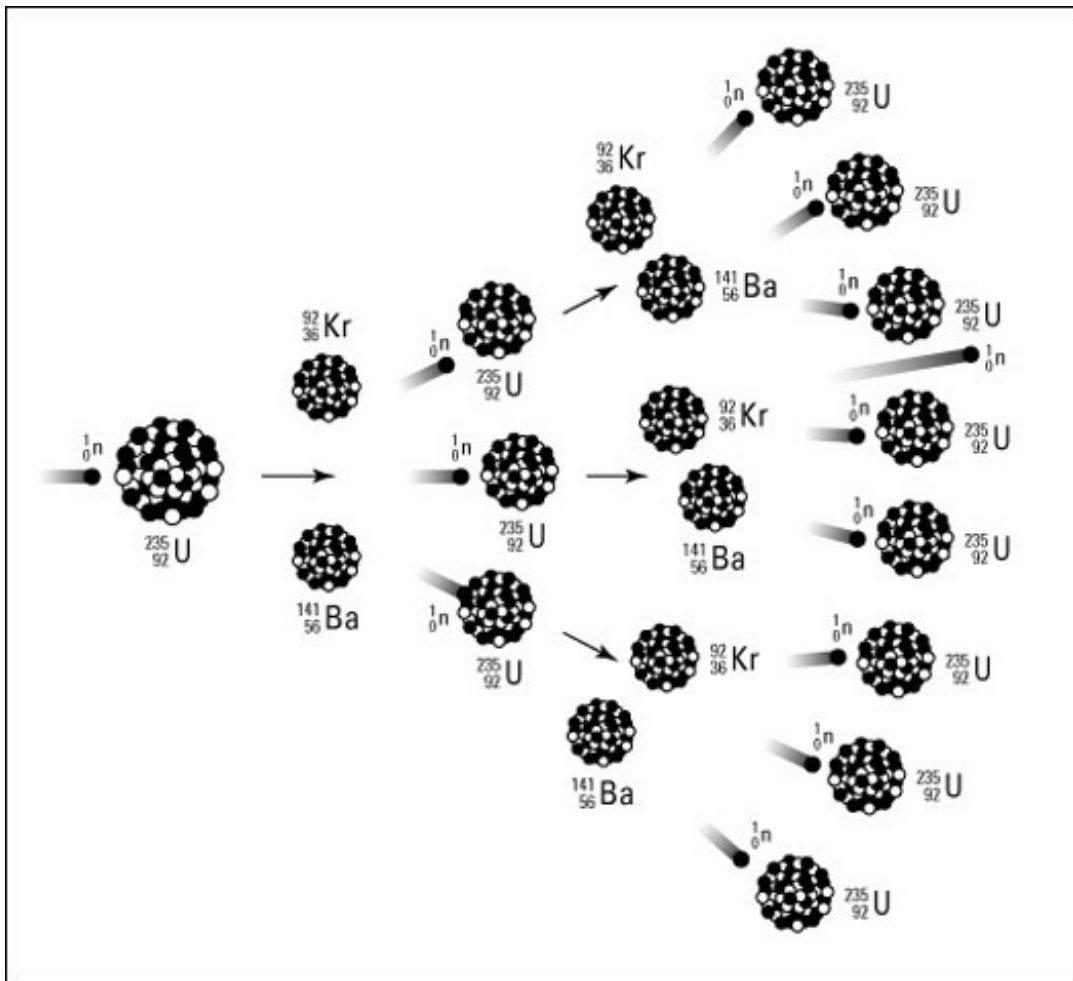


Fig. 4.12. The fission reaction of Uranium-235 (reproduced from ref. 9)

Fission is a process that has been occurring in the universe for billions of years. As mentioned above, we have not only used fission to produce energy for nuclear bombs, but we also use fission peacefully everyday to produce energy in nuclear power plants. Interestingly, although the first man-made nuclear reactor was produced only about fifty years ago, the Earth operated a natural fission reactor in a uranium deposit in West Africa about two billion years ago!

4.8. Nuclear Power generator

Uranium fuel is in the form of uranium oxide, UO_2 , pellets. These pellets are placed end to end in metal tubes. These fuel rods are placed in a water solution of boric acid which is under pressure. This solution is heated well above the boiling temperature of water and is pumped to a steam generator where it boils the water and this steam drives the turbine. Control rods made of cadmium metal are used to moderate the nuclear reaction by absorbing neutrons so that the generation of heat can be controlled.

The safety of nuclear power plants is a major issue in the eye of the public. The most common fear is that of a nuclear explosion. This fear is unfounded as there is not enough uranium-235 in a reactor to achieve the critical mass for a nuclear explosion. However, if the reactor is not cooled adequately, a melt-down can occur which can release enormous quantities of radioactive gases and particles into the environment. The fuel rods can heat up to $3,000^{\circ}C$, which is double the temperature needed to melt steel. The result of the Chernobyl accident in Russia is that huge areas of land will be uninhabitable for hundreds of years. A contributing factor in this accident was the use of cheaper but less efficient carbon control rods in the reactor. The Three Mile Island accident in the United States released only a small amount of radioactive material. Both accidents were the result of human error.

Nuclear power plants have a life expectancy of 30 years because the continual bombardment of plant equipment with neutrons makes the metals brittle. The uranium-235 in the fuel rods, initially at 3%, decreases over a span of three to four years to a point that the fission process cannot be maintained. These spent fuel rods remain radioactive and must be safely stored. The half-life of uranium-235 is 700 million years. The current thought is to encase the spent fuel in ceramic or glass and bury them deep in the earth. The problem with this disposal scheme is that the time element is so long the containers

will more than likely corrode away. If this happens, there is a potential of seepage of nuclear waste into groundwater.

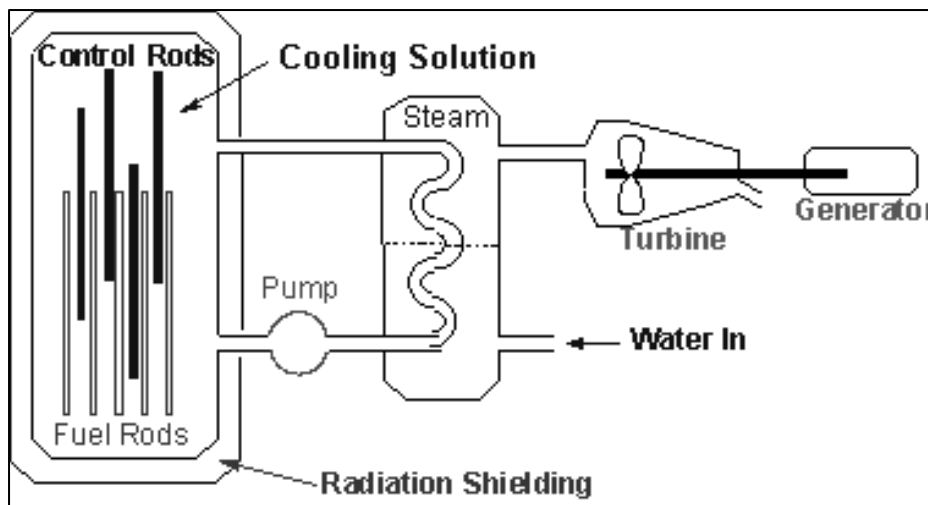


Fig. 4.13. Schematic representation of nuclear power generator (reproduced from ref. 2)

Since there is a limited amount of uranium-235 available, breeder reactors were developed to produce fissionable material. Breeder reactors are nuclear reactors that bombard unfissionable uranium-238 with neutrons to ultimately produce plutonium-239 which is fissionable. These reactors must be cooled with liquid sodium and the reaction is difficult to control. A serious problem with breeder reactors is that plutonium-239 is one of the most toxic substances known and has a half-life of 24,000 years. Another problem is that nuclear weapons are easier to make with plutonium-239 than with uranium-235. This creates a security problem of grave concern.

4.9. Geiger-Muller Counter

A typical G.M. tube consists essentially of a cylindrical cathode in the form of a graphite coating on the inner wall of a glass envelope and an anode in the form of fine tungsten wire which stretches within and along the axis of the tube. Usually it is filled with a mixture of an inert gas (argon or neon) at a partial pressure of about 100 torr and a quenching gas (halogens or organic vapours) at about 10 torr. To allow ionising particles to enter the tube, a window covered with a thin sheet of mica is provided at one end of a tube.

In operation, a sufficiently large potential difference i.e. applied across the anode and cathode of the tube so that a high radial electric field near the central wire is obtained. Under this condition, electrons produced by ionizing collisions between a high-speed particle entering the tube and the inert gas atoms are accelerated towards the anode wire by the strong electric field and acquire within a very short distance a high speed of their own. Because of this speed, they too can ionize other atoms and free more electrons. This multiplication of charges repeats itself in rapid succession producing within a very short interval of time an avalanche of electrons.

The electron avalanche is concentrated near the central wire while the positive ions, being much heavier, drift slowly toward the cathode. For a G.M. tube with a cathode of radius 1cm, the time of flight of the positive ions is roughly about 100 microseconds, which is about 100 times longer than the time necessary to build up the electron avalanche. The consequence of this is that after the initiation of an electron avalanche by an entering particle the slowly moving positive ion sheath around the anode wire increases the effective radius of the anodes. The electric field round the wire therefore drops to a value below that which is capable of supporting ionization by collision. The electron avalanche ceases and a pulse of current due to this avalanche is subsequently produced.

The object of the counter is to produce a single pulse for each particle entering the tube. This can only be achieved if spurious pulses due to secondary electrons released from the cathode surface by the bombardment of ions are completely suppressed so that the tube can recover as quickly as possible to be in a state when it is able to record the next entering particle. A quenching gas (it must be both polyatomic and of low ionization potential) introduced into the tube is to serve this purpose. The idea is to allow the inert gas ions on their way to the cathode to collide with the heavy molecules thereby transfer their charges to the molecules and become neutralized - a process known as quenching. The molecular ions thus produced move slowly to the cathode and on reaching there, capture electrons from the cathode surface to become neutral molecules. Any excess energy that the neutral molecules have will cause them to dissociate into individual atoms rather than be imparted to the cathode to produce fresh electrons that would take part in further ionizing collisions.

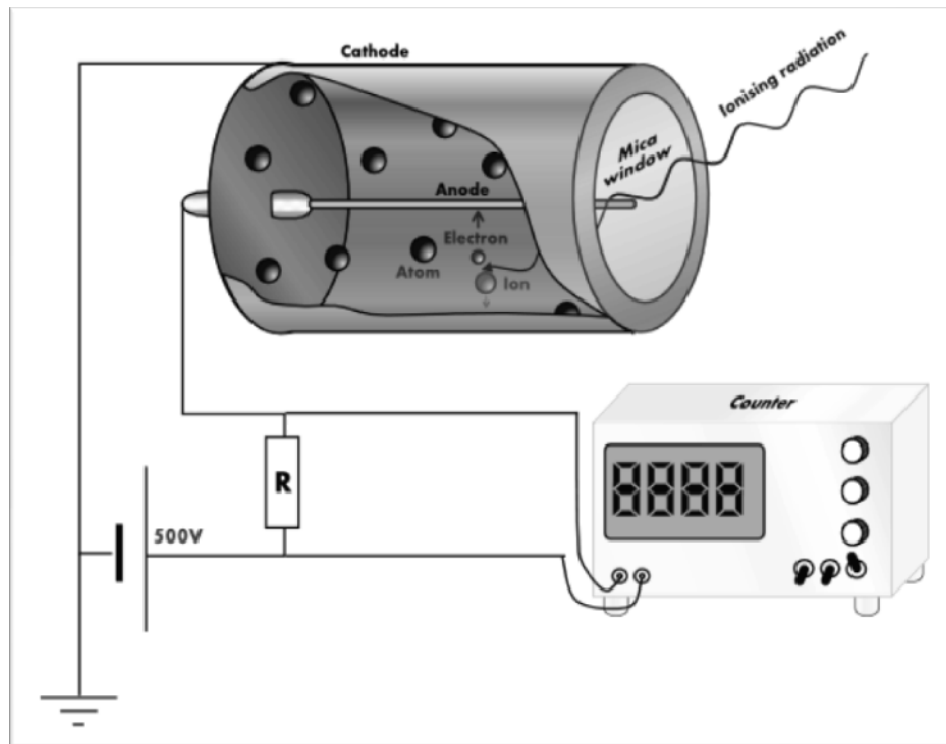


Fig.

4.14. Geiger Muller counter (reproduced from ref. 4)

Typically, the counting rate of a G.M. counter depends on the applied voltage. Below a minimum voltage, the threshold voltage, no counts will be registered. This minimum voltage is a function of the gas pressure and the anode diameter, and may be between 300V and 900V. As the voltage is increased, more and more counts are registered. Over a range of voltages, called the plateau range, the counting rate is relatively insensitive to applied voltage. The change in counting rate over a 100V range of applied voltage may be as little as 5V. Organic quenched tubes usually have a flatter plateau than halogen quenched tubes. For still higher applied voltages the tube may go into continuous discharge. It is particularly important that an organic-quenched tube not be permitted to go into continuous discharge, as the quenching gas may be exhausted in this way. In this experiment a counter, which incorporates all the decade necessary components, described above in one single unit is provided. The G. M. tube connected to the decade counter is of type Mullard MX168. It has a mica window and uses halogens as quenching gas.

4.9.1 Experiment

4.9.1.1. G.M. tube characteristics

Using handling forceps, place the radium source on the lowest shelf of the lead castle directly below the window of the G.M. tube. Switch on the counter and allow it to warm up for a couple of minutes. Increase the applied voltage from 320V in steps of 10V up to 450V. At each setting, note down the number of counts over a period of 2 minutes.

Plot a graph of count rate per minute against the applied voltage. Indicate on your graph the plateau, the Geiger threshold voltage and the operating voltage (i.e. the voltage at the middle of the plateau).

4.9.1.2. Background count

Remove all radioactive sources from the vicinity of the G.M. tube. Set the counter voltage at the operating voltage and take a 5-minute background count. The background count rate per minute should be subtracted from all counts in subsequent experiments in order to obtain the true count rates due to radioactive sources alone.

4.9.1.3. The resolution time of a G.M. Counter

After a pulse is registered, a sheath of positive ions that gradually increases in radius remains about the anode wire. This effectively decreases the potential gradient near the wire and not until this space charge has drifted sufficiently far from the anode will the counter become sensitive again. The total time taken for the tube to recover to its fully sensitive state to give the next pulse, is called the resolution time.

For a tube having a resolution time t , it means that for each single count registered. The tube is inoperative for t sec. Thus if we have n record sounds registered per sec., the lost time in one sec is nt and the effective operating time is $(1 - nt)$ sec. Following from this, if we assume that the corrected count rate is N counts per sec. Then

$$N = \frac{n}{(1 - nt)} \quad (1)$$

The resolution time can be found readily using the "two-source" method. This is carried out experimentally by counting the two sources one at a time and then both together. If

n_1, n_2, n_s are the counts registered per minute for the first source, the second source and the combination of the two sources respectively, we can write:

$$N_1 = \frac{n_1}{(1 - n_1 t)} \quad (2)$$

$$N_2 = \frac{n_2}{(1 - n_2 t)} \quad (3)$$

and
$$N_s = \frac{n_s}{(1 - n_s t)} \quad (4)$$

Since $N_s = N_1 + N_2$

which follows

$$N_s = \frac{n_1}{(1 - n_1 t)} + \frac{n_2}{(1 - n_2 t)} \quad (5)$$

From (4), we have

$$n_s = \frac{N_s}{(1 + N_s t)} \quad (6)$$

Substituting (5) into (6), we obtain after manipulating:

$$n_s = \frac{n_1 + n_2 - 2n_1 n_2 t}{1 - n_1 n_2 t^2} \quad (7)$$

Normally $n_1 n_2 t^2 \ll 1$, we can approximate (7) to

$$n_s = n_1 + n_2 - 2n_1 n_2 t$$

Which yields

$$t = \frac{n_1 + n_2 - n_s}{2n_1 n_2} \quad (8)$$

Using forceps, place a radium source left of center on the bottom shelf of the lead castle.

Then add another radium source symmetrically to the right of center on the same shaft

and finally remove the first source without disturbing the second source. At each of these stages make a two-minute count. Correct all the observed counts for background and calculate the resolution time of the counter.

4.9.1.4. Verification of inverse square law

Remove the G.M. tube from the lead castle and attach it horizontally to a stand provided. Using forceps, place radium source ($5\mu\text{C}$) on another stand and align it until its active face faces the tube window and lies along the axis of the tube. Starting with a separation d between the window and the source equal to 10cm and thereafter increase d successively by 10cm until it reaches 70cm, note down the number of counts per minute at each setting.

Correct the observed counts for background and resolution time using equation (1), and hence plot the corrected count rate against $\frac{1}{d^2}$ to verify the inverse square law.

Repeat the above experiment with ^{60}Co – source in place of the ^{226}Ra – source. On the same graph paper, give a plot of the inverse-square law for the ^{60}Co – source and hence from the gradients of the two linear plots deduce the strength of ^{60}Co – source .

4.9.1.5. Attenuation of γ – ray by matter

The attenuation of a beam of γ – rays passing through matter depends on photoelectric absorption, Compton scattering and pair production. The relative importance of each of these processes, in any given case, is a function of the initial energy of the γ -photons and the atomic weight of the absorbing material. Experimentally it has been found that the attenuation follows closely the exponential law i.e. I is the initial intensity of the γ – rays, then after transversing a layer of matter of thickness ℓ , its intensity I is reduced to

$$I = I_0 e^{-\mu\ell}$$

Where μ is known as the linear absorption coefficient of the matter. The value of ℓ when the initial intensity is reduced to half is called the half value layer (HVL).

Note that in experiments using a G.M. counter, I is proportional to N (the counting rate corrected for background and resolution time), hence

$$N = N_0 e^{-\mu t}$$

Place the ^{60}Co – source at a distance of about 20cm from the window of the G.M. tube. Take a one-minute count to determine the initial count rate. Without disturbing the setup, take a series of one-minute counts as a succession of aluminum sheets is placed vertically in the region between the G.M. tube and the source using the data obtained, plot a suitable graph and hence deduce the μ and HVL for ^{60}Co – source

4.10. Carbon dating

Carbon dating is a variety of radioactive dating which is applicable only to matter which was once living and presumed to be in equilibrium with the atmosphere, taking in carbon dioxide from the air for photosynthesis. Cosmic ray protons blast nuclei in the upper atmosphere, producing neutrons which in turn bombard nitrogen, the major constituent of the atmosphere. This neutron bombardment produces the radioactive isotope carbon-14. The radioactive carbon-14 combines with oxygen to form carbon dioxide and is incorporated into the cycle of living things. The carbon-14 forms at a rate which appears to be constant, so that by measuring the radioactive emissions from once-living matter and comparing its activity with the equilibrium level of living things, a measurement of the time elapsed can be made. Presuming the rate of production of carbon-14 to be constant, the activity of a sample can be directly compared to the equilibrium activity of living matter and the age calculated. Various tests of reliability have confirmed the value of carbon data, and many examples provide an interesting range of application. Carbon-14 decays with a half-life of about 5730 years by the emission of an electron of energy 0.016 MeV. This changes the atomic number of the nucleus to 7, producing a nucleus of nitrogen-14. At equilibrium with the atmosphere, a gram of carbon shows an activity of about 15 decays per minute. The low activity of the carbon-14 limits age determinations to the order of 50,000 years by counting techniques. That can be extended to perhaps 100,000 years by accelerator techniques for counting the carbon-14 concentration.

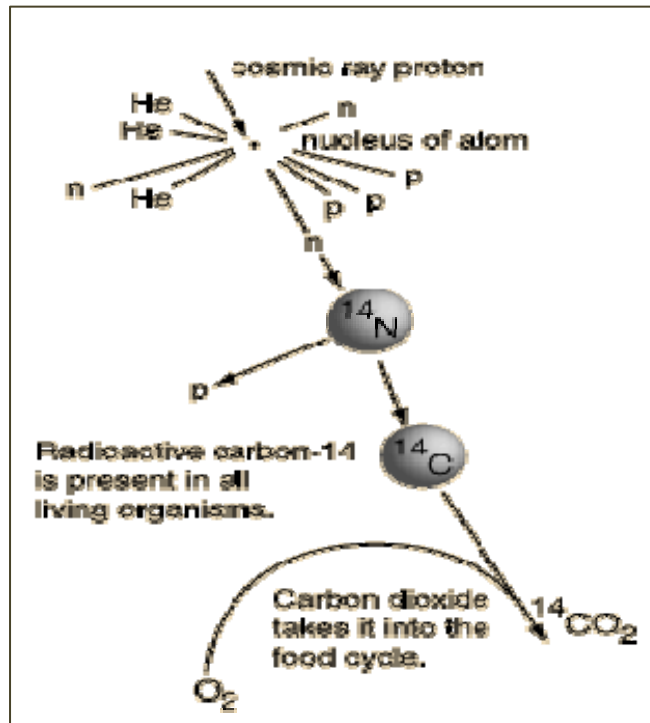


Fig. 4.15. Pictorial representation of Carbon dating (reproduced from ref. 5)

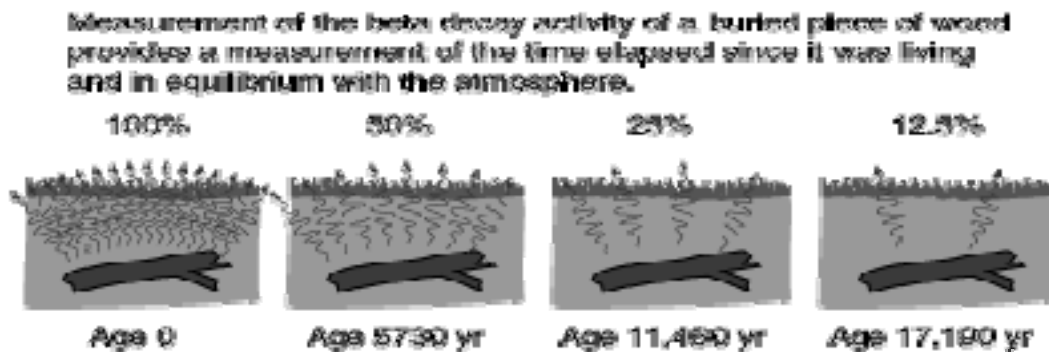


Fig. 4.16. Origin of C-14 (reproduced from ref. 5)

4.10.1. Carbon-14 equilibrium activity

Since living organisms continually exchange carbon with the atmosphere in the form of carbon dioxide, the ratio of C-14 to C-12 approaches that of the atmosphere.

$$\frac{^{14}\text{C}}{^{12}\text{C}} \approx 1.3 \times 10^{-12}$$

From the known half-life of carbon-14 and the number of carbon atoms in a gram of carbon, you can calculate the number of radioactive decays to be about 15 decays per minute per gram of carbon in a living organism. Radioactive carbon is being created by this process at the rate of about two atoms per second for every square centimeter of the earth's surface. The rate of production of carbon-14 in the atmosphere seems to be fairly constant. Carbon dating of ancient bristlecone pine trees of ages around 6000 years have provided general corroboration of carbon dating and have provided some corrections to the data.

4.10.2 Reliability of Carbon Dating

4.10.2.1. Bristlecone pine trees

From the dating of ancient bristlecone pine trees from the western U.S., a correction curve for the carbon dating over the range back to 5000 BC has been developed. Trees dated at 4000 BC show the maximum deviation of between 600 and 700 years too young by carbon dating.

4.10.2.2. Glacier measurements

Prior to carbon dating methods, the age of sediments deposited by the last ice age was surmised to be about 25000 years. "Radiocarbon dates of a layer of peat beneath the glacial sediments provided an age of only 11,400 years." These examples are from The Earth through Time, 2nd Ed. by Harold L. Levin

Krane points out that future carbon dating will not be so reliable because of changes in the carbon isotopic mix. Fossil fuels have no carbon-14 content, and the burning of those fuels over the past 100 years has diluted the carbon-14 content. On the other hand, atmospheric testing of nuclear weapons in the 1950s and 1960s increased the carbon-14 content of the atmosphere. Krane suggests that this might have doubled the concentration compared to the carbon-14 from cosmic ray production.

Accelerator techniques for carbon dating have extended its range back to about 100,000 years, compared to less than half that for direct counting techniques. One can count atoms of different masses with a mass spectrometer, but that is problematic for carbon dating because of the low concentration of carbon-14 and the existence of nitrogen-14 and CH₂ which have essentially the same mass. Cyclotrons and tandem

accelerators have both been used to fashion sensitive new mass spectrometer analyses. The tandem accelerator has been effective in removing the nitrogen-14 and CH_2 , and can be followed by a conventional mass spectrometer to separate the C-12 and C-13. A sensitivity of 10^{-15} in the $^{14}\text{C}/^{12}\text{C}$ ratio has been achieved. These techniques can be applied with a sample as small as a milligram.

4.10.3 How is carbon dating done?

Carbon 14 ($\text{C}14$) is an isotope of carbon with 8 neutrons instead of the more common 6 neutrons.



Fig. 4.17. Picture of bone for Carbon dating (reproduced from ref. 6)

It is unstable, and scientists know that it radioactively decays by electron emission to Nitrogen 14, with a half life of 5730 years. This means that given a statistically large sample of carbon 14, we know that if we sit it in a box, go away, and come back in 5730 years, half of it will still be carbon 14, and the other half will have decayed. Or in other words, if we have a box, and we don't know how old it is but we know it started with 100 carbon 14 atoms, and we open it and find only 50 carbon 14 atoms and some other stuff, we could say, 'Aha! It must be 1 carbon 14 half-life (or 5730 years) old.'

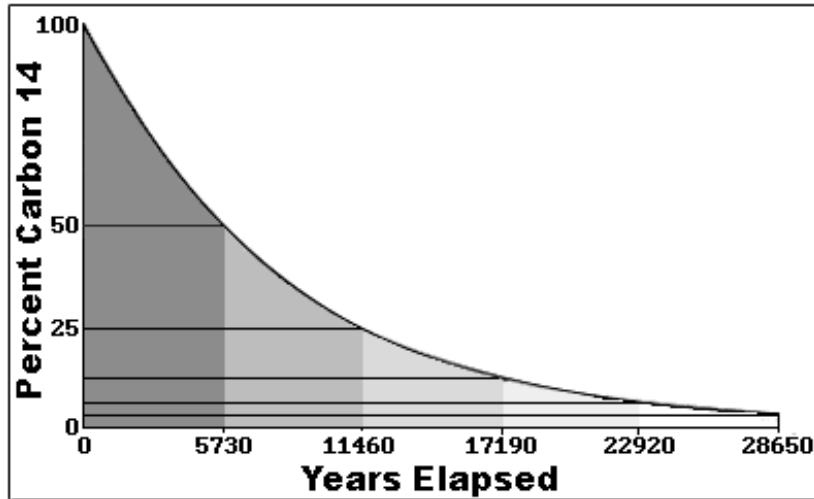


Fig. 4.18. Graphical representation of Carbon dating (reproduced from ref. 6)

This is the basic idea behind carbon dating. So in the real world, looking at a sample like say a bone dug up by an archaeologist, how do we know how much carbon 14 we started with? In the atmosphere, cosmic rays smash into normal carbon 12 atoms (in atmospheric carbon dioxide), and create carbon 14 isotopes. This process is constantly occurring, and has been for a very long time, so there is a fairly constant ratio of carbon 14 atoms to carbon 12 atoms in the atmosphere. Now living plants 'breathe' CO₂ indiscriminately (they don't care about isotopes one way or the other), and so (while they are living) they have the same ratio of carbon 14 in them as the atmosphere. Animals, including humans, consume plants a lot (and animals that consume plants), and thus they also tend to have the same ratio of carbon 14 to carbon 12 atoms. This equilibrium persists in living organisms as long as they continue living, but when they die, they no longer 'breathe' or eat new 14 carbon isotopes. Now it's fairly simple to determine how many total carbon atoms should be in a sample given its weight and chemical makeup. And given the fact that the ratio of carbon 14 to carbon 12 in living organisms is approximately 1: 1.35x10⁻¹², we can figure out how many carbon 14 atoms were in the sample when it ceased to replenish its supply.

In actually measuring these quantities, we take advantage of the fact that the rate of decay (how many radioactive emissions occur per unit time) is dependent on how many atoms there are in a sample (this criteria leads to an exponential decay rate). We

have devices to measure the radioactivity of a sample, and the ratio described above translates into a rate of 15.6 decays/min per gram of carbon in a living sample. And if we play with the exponential decay equations, we can come up with the nice formula $(1/2)^n = (\text{current decay rate}) / (\text{initial decay rate})$, where n is the number of half lives that have passed. Voila, now you can tell how old a sample of organic matter is.

4.11. Applications of Radioactivity and Radioisotopes

Radioisotopes find numerous uses in different areas such as medicine, chemistry, biology, archaeology, agriculture, industry and engineering.

4.11.1 Tracer Techniques

Radioisotopes are frequently used as tracers or tagged atoms in various fields. In tracer technique, a radioactive isotope is added to the reactants and its movement is studied by measuring radioactivity in different parts. Tracer technique is also used for the detection of thyroid disorder and brain tumours

4.11.2 Application in Medicine

Bone imaging is an extremely important use of radioactive properties. Suppose a runner is experiencing severe pain in both shins. The doctor decides to check to see if either tibia has a stress fracture. The runner is given an injection containing ^{99}Tcm . This radioisotope is a gamma ray producer with a half-life of 6 hours.

After a several hour wait, the patient undergoes bone imaging. At this point, any area of the body that is undergoing unusually high bone growth will show up as a stronger image on the screen. Therefore if the runner has a stress fracture, it will show up on the bone imaging scan. This technique is also good for arthritic patients, bone abnormalities and various other diagnostics.

4.11.3 Applications in Agricultures

Radioisotopes can be used to help understand chemical and biological processes in plants. This is true for two reasons:

- i) Radioisotopes are chemically identical with other isotopes of the same element and will be substituted in chemical reactions and
- ii) Radioactive forms of the element can be easily detected with a Geiger counter or other such device.

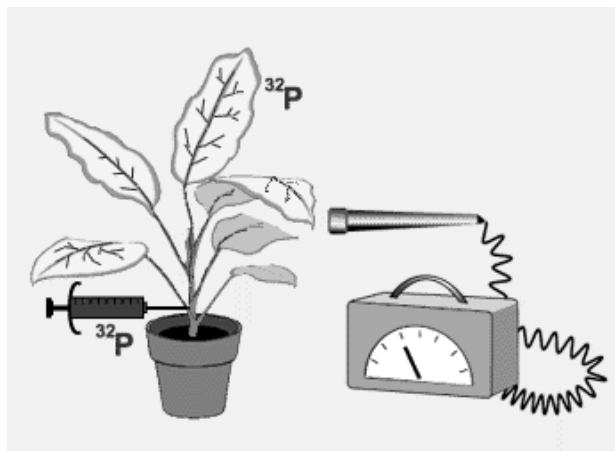


Fig. 4.19. Pictorial representation of radioactive element application in agricultural field (reproduced from ref. 7)

Example:

A solution of phosphate, containing radioactive phosphorus-32, is injected into the root system of a plant. Since phosphorus-32 behaves indentially to that of phosphorus-31, the more common and non-radioactive form of the element, it is used by the plant in the same way. A Geiger counter is then used to detect the movement of the radioactive phosphorus-32 throughout the plant. This information helps scientists understand the detailed mechanism of how plants utilized phosphorus to grow and reproduce.

4.11.4 Application in Food Industry

Food irradiation is a method of treating food in order to make it safer to eat and have a longer shelf life. This process is not very different from other treatments such as pesticide application, canning, freezing and drying. The end result is that the growth of disease-causing microorganisms or those that cause spoilage are slowed or are eliminated altogether. This makes food safer and also keeps it fresh longer.

Food irradiated by exposing it to the gamma rays of a radioisotope -- one that is widely used is cobalt-60. The energy from the gamma ray passing through the food is enough to destroy many disease-causing bacteria as well as those that cause food to spoil, but is not strong enough to change the quality, flavor or texture of the food. It is important to keep in mind that the food never comes in contact with the radioisotope and is never at risk of becoming radioactive.

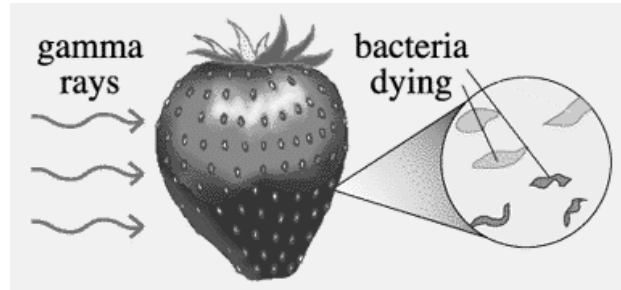


Fig. 4.20. Pictorial representation of radioactive element application in food industry (reproduced from ref. 7)

4.11.5 Smoke Detectors

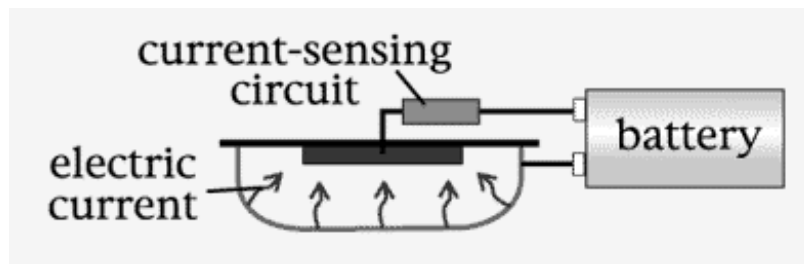


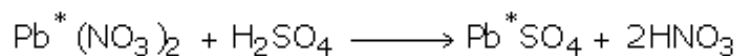
Fig. 4.21. Pictorial representation smoke detector (reproduced from ref. 7)

By utilizing the radioactive properties of this smoke detector, smoke from a fire can be detected at a very early stage. This early warning capability has saved many lives. In fact, studies have shown that 80% of fire injuries and 80% of fire fatalities occur in homes without smoke detectors.

4.11.6. In Chemistry

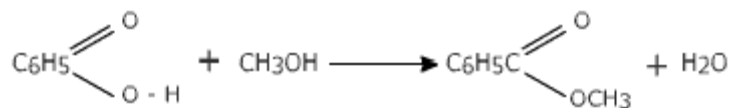
4.11.6.1 Tracer technique is used

a) To find the solubility of sparingly soluble salt like lead sulphate. A lead salt containing known amount of radioactive lead is dissolved in water. Sulphuric acid is added to the aqueous solution to precipitate lead as lead sulphate.



The precipitate is filtered. The radioactivity of filtrate is measured which gives the amount of lead still remaining in solution. This gives a measure of the solubility of PbSO_4 i.e., the amount going into solution.

b) Tracer technique is also used to study the path or mechanism of the reaction



Consider the reaction; the question is how the elimination of water takes place - does the oxygen atom in water come from the alcohol or acid. This is studied by labeling or tagging the oxygen in the alcohol molecule. In other words, the alcohol is prepared with O^{18} . Results show that the ester formed has the radioactive oxygen. This shows that the starred oxygen comes from the alcohol. Thus the -OH group of the acid and the H atom of the alcohol are eliminated in the form of water. Many other mechanistic applications have been reported. ^{14}C has also been used as a radioactive tracer.

$^{32}_{15}\text{P}$ is used for relief in leukaemia and $^{132}_{53}\text{I}$ is used in the treatment of goitre.

4.11.7. Cancer Therapy

γ - rays emitted by the radioisotopes can be used in the treatment of cancer. These radiations tend to destroy cancerous cells and the way can arrest the spreading of the cancerous cells. ^{60}Co is used in the treatment of tumours and cancers.

4.11.8. Neutron Activation Analysis

This technique is of gaining importance in analytical chemistry. In this technique, the sample containing very small amount of the stable isotope of the element to be investigated is bombarded with neutrons. This element is activated into its radioactive isotope. The radioactivity of this radioisotope is measured. Quantitative measurement of radioactivity and the knowledge of other factors such as half-life of radioisotope, efficiency of radiation detector, rate of neutron bombardment etc, help in the calculation of the amount of the element in the sample. This technique is advantageous because:

- (i) Trace amounts of the elements can be determined, even one part of the element per billion parts of the sample.
- (ii) Sample can be tested without destroying it.
- (iii) Sample can be in any state of matter including biological material.

4.11.9. In Industry

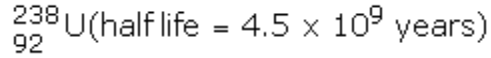
a) Metal casting can be tested for cracks by putting them in baths of radioactive salts. The castings are then inspected for radioactivity to find out any penetration of salts into cracks. Absence of salt penetration indicates absence of cracks.

b) Radioactive isotopes can be used to detect any leakage in underground pipes carrying oils, gas or water. To check the point of leakage a small quantity of compound of radioactive isotope is introduced at the starting place and the detector is moved along the pipe. At the point of crack or leakage, the detector will show high level of radiations.

4.11.10. Age of Minerals and Rocks

The determination of age of minerals and rocks involves determination of either a species formed during a radioactive decay or of the residual activity of an isotope which is undergoing decay.

The former is illustrated by helium dating. Helium present in uranium mineral is almost certainly formed from α - particles. 1 gm of uranium on decay produces approximately 10^{-7} g of helium per year. So if the helium and uranium contents of a mineral are known, the age of the mineral can be estimated. In order to calculate the age of a rock containing



We measure the ratio of the concentration of ${}_{92}^{238}\text{U}$ and its end product ${}_{82}^{206}\text{Pb}$. We assume that the rock did not contain any lead isotope initially.

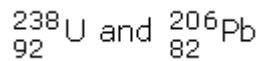
The equation used for the calculation is $N = N_0 e^{-kt}$.

N_0 = Amount of U-238 isotope originally present in a small quantity of the rock or mineral at the time the rock was formed.

N = Amount of U-238 still left undecayed after the lapse of time t which represents the age of the rock.

k = the decay constant of U-238.

We can determine the age of the rock by measuring the ratio of



and using the above equation.

Suppose the ratio of uranium-238 and lead-206 is unity. It implies that half of the uranium originally present has been converted into lead isotope. The age of the rock must therefore be equal to the half-life of uranium-238 i.e., 4.5×10^9 years. Pb/U ratio of most rocks is

1.33×10^{-2} indicating that their age is of the order of 10^8 years.

The age of the earth - The abundance ratio of two isotopes of uranium i.e., ${}^{238}\text{U}$: ${}^{235}\text{U}$ at present is 1:140. The half-life period of ${}^{238}\text{U}$ is 7×10^8 years. Assuming that in the beginning the proportions of two isotopes were equal, the above data determines the age of the earth as 5×10^9 years.

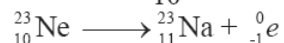
4.12. Problems

1. ${}_{11}^{23}\text{Na}$ is a stable nucleus. Predict which of the following unstable nuclei decay by $\tilde{\beta}$ or β^+ emission.

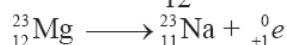
β^+ - decay occurs when the N/P ratio is less than 1. During this decay, a proton is converted to a neutron and a positron(β^+).

The N/P ratios and the decay processes are given below.

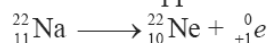
i) $\frac{N}{P}$ ratio for ${}^{23}_{10}\text{Ne} = \frac{13}{10} = 1.3$; Hence it undergoes β^- decay.



ii) $\frac{N}{P}$ ratio for ${}^{23}_{12}\text{Mg} = \frac{11}{12} = 0.92$; Hence it undergoes β^+ decay.

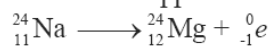


iii) $\frac{N}{P}$ ratio for ${}^{22}_{11}\text{Na} = \frac{11}{11} = 1$; It should be stable. But it undergoes β^+ decay ???



Reason: Always the nuclides with N/P ratio =1 are not stable. The nuclides present in the stability belt are only stable. ${}^{22}_{11}\text{Na}$ is present below the stability belt. Hence undergo positron decay.

iv) $\frac{N}{P}$ ratio for ${}^{24}_{11}\text{Na} = \frac{13}{11} = 1.18$; Hence it undergoes β^- decay.



2. Which isotope is produced by an (n, γ) reaction starting from ${}^{230}\text{Th}$?

In the conversion of ${}^{238}\text{U}_{92} \longrightarrow {}^{206}\text{Pb}_{82}$,

Mass number is decreased by $238-206 = 32$.

Hence the number of alpha particles emitted will be $32/4 = 8$

Hence the decrement in atomic number should be $8 \times 2 = 16$.

But the observed decrement is $92 - 82 = 10$.

Therefore, 6 Beta particles are also released (which increase the Z value by 6).

3. 1.0×10^{-3} g of a sample of Tc-99 is showing 6.3×10^5 disintegrations per second.

Calculate its decay constant.

Ans:- rate of disintegrations = $r = \lambda N_t$

where

λ = decay constant;

$$N_t = \text{number of 'Tc' nuclei} = \frac{N_0 \times \text{wt. of sample}}{M_{\text{Tc}}}$$

where N_0 = avogadro number; M_{Tc} = molecular weight of Technitium

$$N_t = \frac{6.02 \times 10^{23} \times 1.0 \times 10^{-3} \text{ g}}{99 \text{ g}} = 6.08 \times 10^{18} \text{ nuclei}$$

Hence

$$\lambda = \frac{r}{N_t} = \frac{6.3 \times 10^5 \text{ nuclei} \cdot \text{sec}^{-1}}{6.08 \times 10^{18} \text{ nuclei}} = 1.036 \times 10^{-13} \text{ sec}^{-1}$$

4. **The decay constant of radioactive disintegration of a nuclide is $3.010 \times 10^{-3} \text{ s}^{-1}$. What are the half life and average life of that nuclide?**

Ans:- Since radioactive disintegration is a first order process,

$$\text{Half life} = t_{\frac{1}{2}} = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda} = \frac{0.693}{3.010 \times 10^{-3} \text{ s}^{-1}} = 230.3 \text{ s}$$

where λ = decay constant

$$\text{Average life} = \tau = \frac{1}{\lambda} = \frac{t_{\frac{1}{2}}}{0.693} = 1.44 \times t_{\frac{1}{2}} = 1.44 \times 230.3 = 331.6 \text{ s}$$

5. **In how many days will a 12-gram sample of a radioactive isotope decay, leaving a total of 1.5 grams of the original isotope? (The half-life of isotope is 8.07 days)**

$$\text{Ans:- } 2^n = \frac{N_0}{N} = \frac{W_0}{W} \quad \text{where } n = \text{no. of half lives}$$

$$\therefore 2^n = \frac{12}{1.5} = 8 = 2^3$$

Hence the no. of half lives = 3

$$\begin{aligned} \text{Time taken for } W_0 (12\text{g}) &\xrightarrow{\text{to become}} W(1.5\text{g}) \\ &= n \times t_{1/2} = 3 \times 8.07 \text{ days} = 24 \text{ days} \end{aligned}$$

6. **A scrap of paper taken from the Dead Sea Scrolls was found to have a $^{14}\text{C}/^{12}\text{C}$ ratio of 0.795 times that found in plants living today. Estimate the age of the scroll.**

Solution.

The half-life of carbon-14 is known to be 5720 years. Radioactive decay is a first order rate process, which means the reaction proceeds according to the following equation:

$$\log_{10} X_0/X = kt / 2.30$$

Where X_0 is the quantity of radioactive material at time zero, X is the amount remaining after time t , and k is the first order rate constant, which is a characteristic of the isotope undergoing decay. Decay rates are usually expressed in terms of their half-life instead of the first order rate constant, where

$$k = 0.693 / t_{1/2}$$

So for this problem:

$$k = 0.693 / 5720 \text{ years} = 1.21 \times 10^{-4}/\text{year}$$

$$\log X_0 / X = [(1.21 \times 10^{-4}/\text{year}) \times t] / 2.30$$

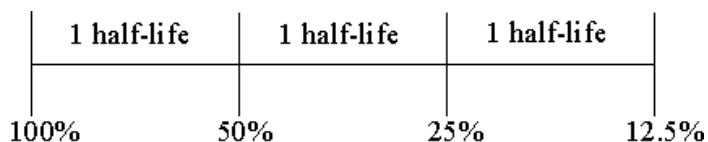
$$X = 0.795 X_0, \text{ so } \log X_0 / X = \log 1.000/0.795 = \log 1.26 = 0.100$$

$$\text{Therefore, } 0.100 = [(1.21 \times 10^{-4}/\text{year}) \times t] / 2.30$$

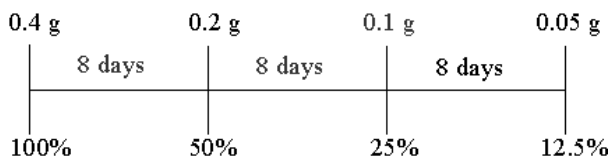
$$t = 1900 \text{ years}$$

7. A hospital needs 0.1 gram of iodine-131 for a thyroid therapy. It takes 16 days to receive the shipment. How many grams of iodine-131 should they order if the half life for iodine-131 is 8 days?

If you started with 0.4 g, in 8 days you would have 0.2 g and in another 8 days you would have 0.1 g. These are easy to solve by using block diagrams.



The block diagram would look like the following for this problem.



8. The half-life of carbon-14 is 5,730 years. How old would an artifact be if it had a carbon-14 percent that was 25%.?

The block diagram would look like the following and the answer would be $2 \times 5,730$ years or 11,460 years.



9. If a watch contains a radioactive substance with a decay rate of 1.40×10^{-2} and after 50 years only 25 mg remain, calculate the amount originally present.

If a watch contains a radioactive substance with a decay rate of 1.40×10^{-2} and after 50 years only 25 mg remain, calculate the amount originally present.

Decay Solution:

$$\ln \frac{25}{N_0} = -(1.4 \times 10^{-2})(50)$$

$$N_0 = 50.3 \text{ mg}$$

10. A rock contains 0.257 mg of lead-206 for every mg of uranium-238. The half-life decay for uranium to turn into lead is 4.5×10^9 yr. How old is the rock?

Half -Life Solution :

assume 1.000 mg of U at present

$$\text{original } {}_{92}^{238}\text{U} = 1.000 + \frac{238}{206}(0.257) = 1.297 \text{ mg}$$

$$k = \frac{.693}{4.5 \times 10^9} = 1.5 \times 10^{-10}$$

$$\ln \frac{1.000}{1.297} = -1.5 \times 10^{-10} t$$

$$t = 1.7 \times 10^9 \text{ yr}$$

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Chapter 5

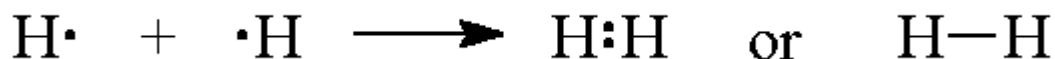
TYPES OF HYBRIDIZATION AND GEOMETRY OF MOLECULES

K.Suthagar

Chemical Bonds

Chemical bonds are the attractive forces that hold atoms together in the form of compounds. They are formed when electrons are shared between two atoms. There are 3 types of bonds (covalent bonds, polar covalent bonds and ionic bonds).

The simplest example of bonding can be demonstrated by the H₂ molecule. We can see from the periodic table that each hydrogen atom has a single electron. If 2 hydrogen atoms come together to form a bond, then each hydrogen atom effectively has a share in both electrons and thus each resembles an inert gas a more stable species. The two electrons that are shared can be represented either by 2 dots or a single dash between the atoms.



Valence bond theory describes a chemical bond as the overlap of atomic orbitals. In the case of the hydrogen molecule, the 1s orbital of one hydrogen atom overlaps with the 1s orbital of the second hydrogen atom to form a molecular orbital called a sigma bond. Attraction increases as the atoms get closer but nuclear-nuclear repulsion becomes important if the atoms approach too close.

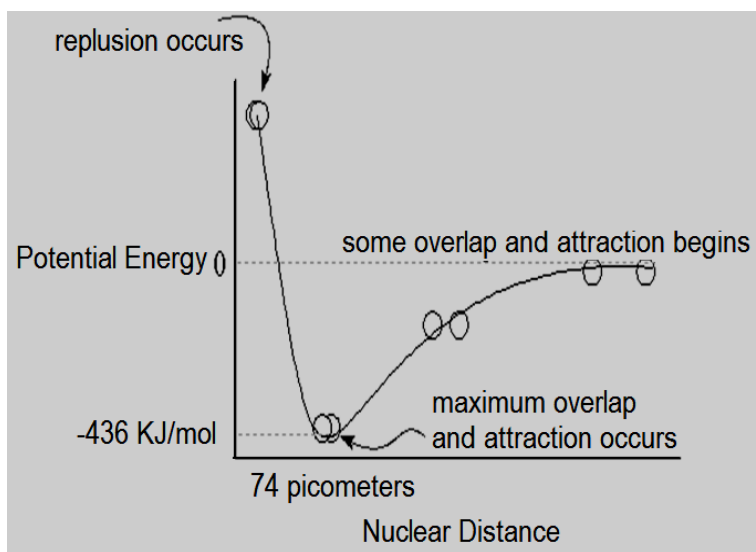


Fig 1: Potential Energy Diagram of H – H Covalent bond

Important concepts in chemical bonding and molecular structure

1. The attractive force which holds together the constituent particles (atoms, ions or molecules) in chemical species is known as chemical bond.
2. Tendency of atoms of various elements to attain stable configuration of eight electrons in their valence shell is the cause of chemical combination.
3. The principle of attaining a maximum of eight electrons in the valence shell or outermost shell of atoms is known as octet rule.

Electronic Theory: Kossel-Lewis approach to chemical Bonding

Atoms achieve stable octet when they are linked by chemical bonds. The atoms do so either by transfer or sharing of valence electrons. Inner shell electrons are not involved in combination process.

Lewis Symbols or electron dot symbols

The symbol of the element represents the whole of the atom except the valence electrons (i.e. nucleus and the electrons in the linear energy shells). The valence electrons are represented by placing dots (•) or crosses (x) around the symbol. Each bond is the result of sharing of an electron pair between the atoms comprising the bond.

- Each combining atom contributes one electron to the shared pair.
- The combining atoms attain the outer filled shells of the noble gas configuration.

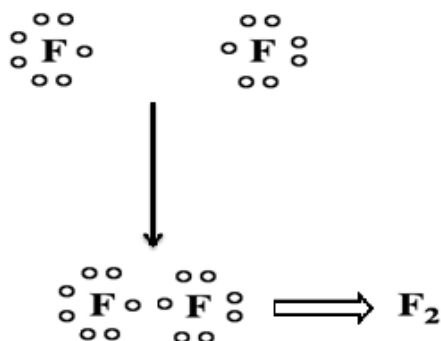


Fig 2 : Electron dot symbol representation of F₂

If the two atoms share a pair of electrons, a single bond is said to be formed and if two pairs of electrons are shared a double bond is said to be formed etc. All the bonds formed from sharing of electrons are called as covalent bonds.

Sharing of electrons

Significance of Lewis Symbols

- The Lewis symbols indicate the number of electrons in the outermost or valence shell which helps to calculate common or group valency.
- The common valency of an element is either equal to number of dots or valence electrons in the Lewis symbol or it is equal to 8 minus the number of dots or valence electrons.
- The bond formed by mutual sharing of electrons between the combining atoms of the same or different elements is called a covalent bond.
- If two atoms share one electron pair, bond is known as single covalent bond and is represented by one dash (–).
- If two atoms share two electron pairs, bond is known as double covalent bond and is represented by two dashes (=).
- If two atoms share three electron pairs, bond is known as triple covalent bond and is represented by three dashes (≡).

- The formal charge of an atom in a polyatomic ion or molecule is defined as the difference between the number of valence electrons in an isolated (or free) atom and the number of electrons assigned to that atom in a Lewis structure.

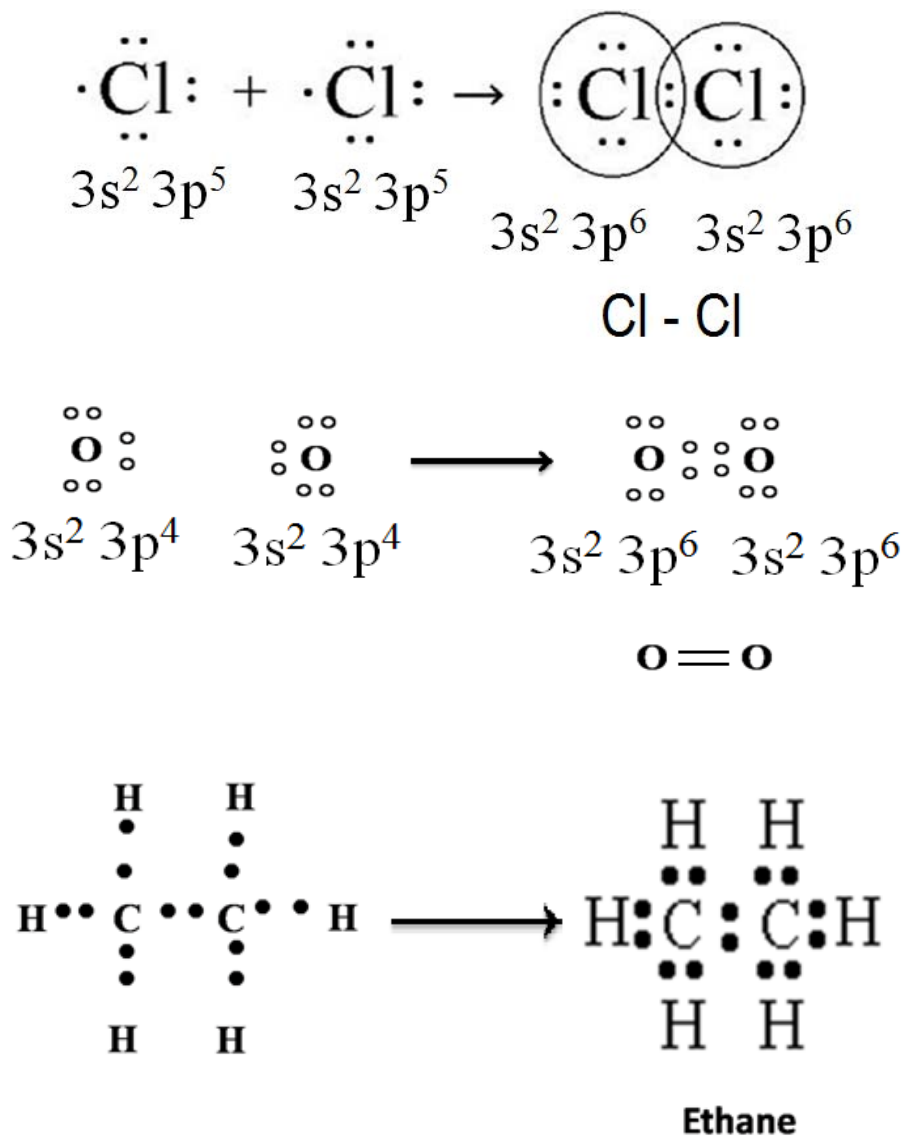


Fig 3 : Lewis dot structures of (a) Cl₂ (b) O₂ and (c) ethane molecules

Formal may be expressed as

$$\text{Formal charge on an atom in free atom} = \left[\begin{array}{c} \text{Number of} \\ \text{valance electrons} \\ \text{in free atom} \end{array} \right] - \left[\begin{array}{c} \text{Number of} \\ \text{non bonding} \\ \text{(lone pair) electrons} \end{array} \right] - \frac{1}{2} \left[\begin{array}{c} \text{Number of} \\ \text{bonding (shared)} \\ \text{electrons} \end{array} \right]$$

Significance of Formal charge

The formal charges help in selection of lowest energy structure from a number of possible Lewis structures for a given molecule or ion. Lowest energy structure is the one which has lowest formal charges on the atoms.

Expanded octet

Compounds in which central atom has more than eight electrons around it, atom is said to possess an expanded octet.

Exceptions to the Octet Rule

Hydrogen molecule: Hydrogen has one electron in its first energy shell ($n = 1$) It needs only one more electron to fill this shell, because the first shell cannot have more than two electrons. This configuration ($1s^2$) is similar to that of noble gas helium and is stable. In this case, therefore, octet is not needed to achieve a stable configuration. Incomplete octet of the central atom: The octet rule cannot explain the formation of certain molecules of lithium, beryllium, boron, aluminum, etc. (LiCl , BeH_2 , BeCl_2 , BH_3 , BF_3) in which the central atom has less than eight electrons in the valence shell.

Expanded octet of the central atom

There are many stable molecules which have more than eight electrons in their valence shells. For example, PF_5 , has ten; SF_6 has twelve and IF_7 has fourteen electrons around the central atoms, P, S, and I respectively.

Odd electron molecules

There are certain molecules which have odd number of electrons, like nitric oxide, NO and Nitrogen dioxide, NO_2 . In these cases, octet rule is not satisfied for all the atoms. It may be noted that the octet rule is based upon the chemical inertness of

noble gases. However, it has been found that some noble gases (especially xenon and krypton) also combine with oxygen and fluorine to form a large number of compounds such as XeF_2 , KrF_2 , XeOF_2 , XeOF_4 , XeF_6 , etc.

This theory does not account for the shape of the molecules. It cannot explain the relative stability of the molecule in terms of the energy.

General Properties of Covalent Compounds

The covalent compounds do not exist as ions but they exist as molecules. The melting and boiling points of covalent compounds are generally low. Covalent compounds are generally insoluble or less soluble in water and other polar solvents. However, these are soluble in non-polar solvents. Since covalent compounds do not give ions in solution, these are poor conductors of electricity in the fused or dissolved state.

Molecular reactions are quite slow because energy is required to break covalent bonds. Since the covalent bond is localized in between the nuclei of atoms, it is directional in nature.

Characteristics of covalent compounds

1. Covalent compounds are formed by the mutual sharing of electrons. There is no transfer of electrons from one atom to another and therefore no charges are created on the atom. No ions are formed. These compounds exist as neutral molecules and not as ions. Although some of the covalent molecules exist as solids, they do not conduct electricity in fused or molten or dissolved state.
2. They possess low melting and boiling points. This is because of the weak intermolecular forces existing between the covalent molecules. Since, no strong coulombic forces are seen; some of covalent molecules are volatile in nature. Mostly covalent compounds possess low melting and boiling points.
3. Covalent bonds are rigid and directional therefore different shapes of covalent molecules are seen.
4. Most of the covalent molecules are non polar and are soluble in nonpolar (low dielectric constant) solvents like benzene, ether etc and insoluble in polar solvents

like water. Carbon tetrachloride (CCl_4) is a covalent nonpolar molecule and is soluble in benzene.

Co-Ordinate Covalent Bond

Covalent type bond in which both the electrons in the shared pair come from one atom is called a coordinate covalent bond. Co-ordinate covalent bond is usually represented by an arrow (\rightarrow) pointing from donor to the acceptor atom.

Co-ordinate Covalent bond is also called as dative bond, donor – acceptor bond, semi- polar bond or co-ionic bond. The electrostatic force of attraction which holds the oppositely charged ions together is known as ionic bond or electrovalent bond.

Ionic compounds will be formed more easily between the elements with comparatively low ionization enthalpy and elements with comparatively high negative value of electron gain enthalpy. A quantitative measure of the stability of an ionic compound is provided by its lattice enthalpy and not simply by achieving octet of electrons around the ionic species in the gaseous state. Lattice enthalpy may also be defined as the energy required to completely separate one mole of a solid ionic compound into gaseous ionic constituents.

Factor affecting lattice enthalpy

- ❖ **Size of the ions:** Smaller the size of the ions, lesser is the inter-nuclear distance and higher will be lattice enthalpy.
- ❖ **Magnitude of charge:** Larger the magnitude of charge on the ions, greater will be the attractive forces between the ions. Consequently, the lattice enthalpy will be high.

General Properties of Ionic Compounds

Ionic compounds usually exist in the form of crystalline solids. They have high melting and boiling points and this ionic compounds are generally soluble in water

and other polar solvents having high dielectric constants. Ionic compounds are good conductors of electricity in the solutions or in their molten states. The chemical reactions of ionic compounds are characteristic of the constituent ions and are known as ionic reactions. In ionic - compounds, each ion is surrounded by oppositely charged ions uniformly distributed all around the ion and therefore, electrical field is non-directional.

Bond length

It is defined as the average distance between the nuclei of two bonded atoms in a molecule. Covalent radius is half of the distance between two similar atoms joined by single covalent bond in same molecule. Vander Waals radius is one half of the distance between two similar adjacent atoms belonging to two nearest neighboring molecules of the same substance in the solid state. It is always larger than covalent radii.

Bond length is the average distance between the centres of the nuclei of two bonded atoms in a molecule. It is expressed in Angstrom units (\AA) or picometers (pm). $1\text{\AA} = 10^{-10}\text{m}$ and $1\text{pm} = 10^{-12}\text{m}$. It is determined with the help of X-rays diffraction and other spectroscopic methods.

Bond length depends upon the following factors

1. Bond multiplicity

Bond length decreases with increase in bond multiplicity. $\text{C}\equiv\text{C}$ bond length is shorter than $\text{C}=\text{C}$ bond which in turn is shorter than $\text{C}-\text{C}$. Similarly, $\text{N}\equiv\text{N} < \text{N}=\text{N} < \text{N}-\text{N}$ and $\text{O}=\text{O} < \text{O}-\text{O}$. The bond lengths of some simple bonds (in pm) are:

Average Single Bond Lengths (Picometers)

	H	C	N	O	F	Si	P	S	Cl	Br	I
H	74	110	98	94	92	145	138	132	127	142	161
C		154	147	143	141	194	187	181	176	191	210
N			140	136	134	187	180	174	169	184	203
O				132	130	183	176	170	165	180	199
F					128	181	174	168	163	178	197
Si						234	227	221	216	231	250
P							220	214	209	224	243
S								208	203	218	237
Cl									200	213	232
Br										228	247
I											266

Average Multiple Bond Lengths (Picometers)

C = C	134	C ≡ C	121
C = N	127	C ≡ N	115
C = O	122	C ≡ O	113
N = O	115	N ≡ O	108

$$1 \text{ pm} = 1 \times 10^{-12} \text{ m}$$

2. Size of the atom

The bond length increases with increase in the size of the atom. From the above values it is clear that the bond lengths for a given family increase with increase in atomic number.

For example, C-C < Si-Si < Ge-Ge.

This is because with the increase in size of the atom, the distance of the electrons from the nucleus increases successively with the addition of a new shell. Therefore the average distance between the bonding nuclei (bond length) increases.

3. Bond angle:

It is defined as the average angle between the orbitals of the central atom containing the bonding electron pairs in the molecule. It is expressed in degree/minute/second. This gives an idea about the distribution of orbitals around the central atom in a molecule. Therefore bond angle determines the shape of a molecule.

For example, the H-O-H bond angle in H₂O is 104.5° and H-N-H bond angle is NH₃ 107°.

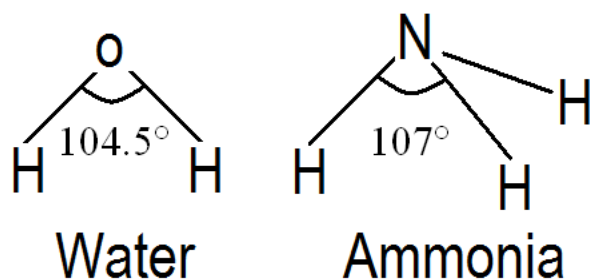


Fig 4 : Bond angle of water and ammonia

4. Energy (Bond Dissociation Energy):

It is defined as the amount of energy required to break one mole of bonds of a particular type between the atoms of a molecule in the gaseous state. It is expressed in terms of kJ mol^{-1} . When a bond is formed between the atoms, energy is released and the bonded atoms have lesser energy than the separated individual atoms. Then, same amount of energy will be needed to form the bond. This energy is called the bond dissociation energy and is a measure of bond strength. Larger the bond dissociation energy, stronger will be the bond in the molecule.

Bond dissociation energy depends upon:

A. Size of the bonded atoms

The smaller the size of the bonded atoms, the stronger is the bond and larger is the value of bond dissociation energy. For example, the bond dissociation energy of H-H bond in hydrogen molecules is 433 kJ mol^{-1} . This is larger than the bond dissociation energy of Cl-Cl in Cl_2 , which is $242.5 \text{ kJ mol}^{-1}$.

B. Bond length

Shorter the bond length, larger is the value of bond energy. For example, bond length (154 pm) is larger than C=C bond length (134 pm). Consequently, the dissociation energy of C-C bond (348 kJ mol^{-1}) is smaller than that of C=C bond (619 kJ mol^{-1}).

C. Bond polarity

When the atoms forming bonds are different, the electron attracting powers of the two atoms in a bond may differ. Then, the shared pair will be displaced towards the atom having more electronegativity. For example, in a molecule of HCl, the electronegativities of Cl and H are 3.0 and 2.1 respectively. Due to the larger electronegativity of chlorine, the bonding pair will be attracted more towards chlorine atom. The chlorine atom will experience more negative charge around it and the other atom will experience less as if it has lost some of its negative charge.

Due to this, the chlorine end of the molecule will acquire slightly negative charge and the hydrogen end will have slightly positive charge. These are represented as $-\delta$ and $+\delta$ (delta meaning small) charges. Such molecules having oppositely charged poles are called polar molecules and the bond is said to be polar covalent bond. The magnitude of electronegativity difference reflects the degree of polarity. Greater the difference in the electronegativities of the atoms forming the bond, greater will be the charge separation and hence greater will be the polarity of the molecule.

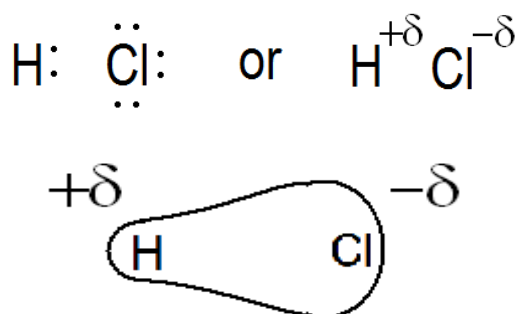


Fig 5 : Distorted electron cloud

Bond order

The bond order is defined as the number of bonds between two atoms in a molecule;

$$\text{B.O.} = \frac{\text{number of bonding electrons} - \text{number of antibonding electrons}}{2}$$

Non-polar covalent bond

When a covalent bond is formed between two similar atoms, the shared pair of electrons is equally attracted by the two atoms and is placed exactly in between identical nuclei. Such a bond is called non-polar covalent bond. Molecules having two oppositely charged poles are called polar molecules and the bond is said to be polar covalent bond. Greater the difference in the electro-negativity of the atoms forming the bond, greater will be the charge separation and hence greater will be the polarity of the molecule.

Dipole moment

It is defined as the product of the magnitude of the charge and the distance of separation between the charges.

Molecules having two equal and opposite charges separated by certain distance are said to possess an electric dipole. In the case of such polar molecules, the centre of negative charge does not coincide with the centre of positive charge. The extent of polarity in such covalent molecules can be described by the term Dipole moment.

$$\text{Dipole moment } (\mu) = \text{charge } (q) \times \text{distance of separation } (d)$$

Dipole moment in diatomic molecules

A diatomic molecule has two atoms bonded to each other by a covalent bond. In such a molecule, the dipole moment of the bond gives the dipole moment of the molecule. Thus, a diatomic molecule is polar if the bond formed between the atoms is polar. Greater the electronegativity difference between the atoms more will be the dipole moment.

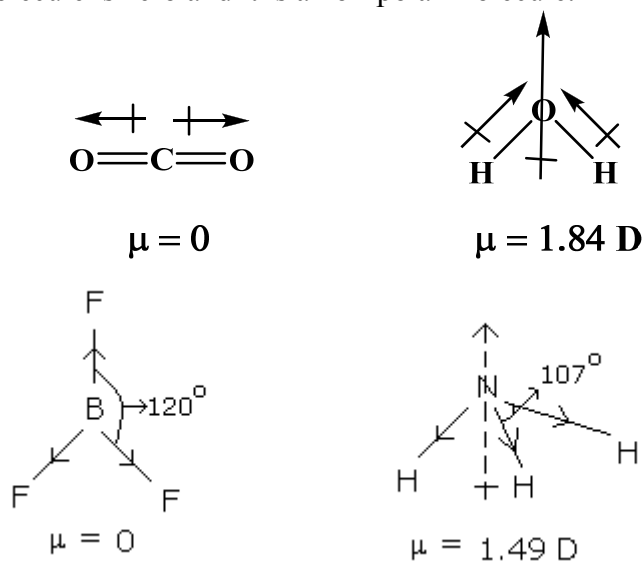
The dipole moment of hydrogen halides decreases with decreasing electronegativity of halogen atom.

Dipole moment in polyatomic molecules

In polyatomic molecules the dipole moment not only depends upon the individual dipole moments of the bonds but also on the spatial arrangement of the various bonds in the

molecule. In such molecules the dipole moment of the molecule is the vector sum of the dipole moments of various bonds.

For example, Carbon dioxide (CO_2) and water (H_2O) are both tri atomic molecules but the dipole moment of carbon dioxide is zero whereas that of water is 1.84 D. This is because CO_2 is a linear molecule in which the two $\text{C}=\text{O}$ ($m=2.3\text{D}$) bonds are oriented in opposite directions at an angle of 180° . Due to the linear geometry the dipole moment of one $\text{C}=\text{O}$ bond cancels that of another. Therefore, the resultant dipole moment of the molecule is zero and it is a non-polar molecule.



Water molecule has a bent structure with the two OH bonds oriented at an angle of 104.5° . The dipole moment of water is 1.84D, which is the resultant of the dipole moments of two O-H bonds. Similarly in tetra-atomic molecules such as BF_3 and NH_3 , the dipole moment of BF_3 molecule is zero while that of NH_3 is 1.49 D. This suggests that BF_3 has symmetrical structure in which the three B-F bonds are oriented at an angle of 120° to one another. Also the three bonds lie in one plane and the dipole moments of these bonds cancel one another giving net dipole moment equal to zero.

NH_3 has a pyramidal structure. The individual dipole moments of three N-H bonds give the resultant dipole moment as 1.49 D. Thus, the presence of polar bonds in a polyatomic molecule does not mean that the molecules are polar.

Importance of dipole moment

Dipole moment plays very important role in understanding the nature of chemical bonds.

- The measurement of dipole moment helps in distinguishing between polar and non-polar molecules. Non-polar molecules have zero dipole moment while polar molecules have some value of dipole moment.

For example:

- ❖ Non-polar molecules: O_2 , Cl_2 , BF_3 , CH_4
 - ❖ Polar Molecules: HF (1.91 D), HCl (1.03 D), H_2S (0.90 D).
-
- Dipole moment measurement gives an idea about the degree of polarity in a diatomic molecule. The greater the dipole moment the greater is the polarity in such a molecule.
 - Dipole moment is used to find the shapes of molecules. This is because the dipole moment not only depends upon the individual dipole moment of the bonds but also on the arrangement of bonds.
 - It is possible to predict the nature of chemical bond formed depending upon the electronegativities of atoms involved in a molecule. The bond will be highly polar if the electronegativities of two atoms is large. However, when the electron is completely transferred from one atom to another, an ionic bond is formed (ionic bond is an extreme case of polar covalent bonds). The greater the difference in electronegativities of the bonded atoms, the higher is the ionic character. When the electronegativity difference between two atoms is 1.7, then the bond is 50% ionic and 50% covalent. If the electronegativity difference is more than 1.7, then the chemical bond is largely ionic (more than 50% ionic character) and if the difference is less than 1.7, the bond formed is mainly covalent.
 - The percentage of ionic character can be calculated from the ratio of the observed dipole moment to the dipole moment for the complete electron transfer (100% ionic character).

Partial Covalent Character in Ionic Bonds

When two oppositely charge ions A^+ and B^- are brought together; the positive ion attracts the outermost electrons of the negative ion. This results in distortion of electron clouds around the anion towards the cation. This distortion of electron cloud of the negative ion by the positive ion is called polarization. Tendency of cation to polarize and polarisability of anion are summarized and given below;

Fajan's rules

- Smaller the size of the cation, greater is its polarizing power.
- Polarisation increases with increase in size of anion. This is because the electron cloud on the bigger anion will be held less firmly by its nucleus and, therefore, would be more easily deformed towards the cation.
- Larger the charge on cation greater is polarizing power and larger the charge on anion greater is its tendency to get polarized.

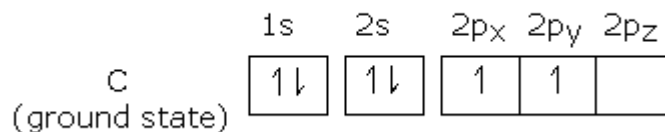
Hybridization

Hybridization is the phenomenon of redistribution of energies of the orbitals of slightly different energies so as to give a new set of orbital's of equivalent energies. The new orbitals are called hybrid or hybridized orbitals. The number of hybridized orbitals formed is equal to the number of atomic orbitals taking part in hybridization. This phenomenon is more predominant in carbon containing compounds and so to understand this concept, a study of the electronic structure of carbon is essential.

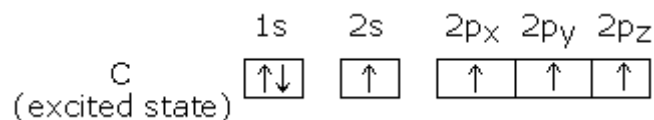
Tetravalency of Carbon

Carbon forms a large number of fascinating varieties of compounds. This is because of its unusual property of catenation in which one carbon unites with the other to form long chains and rings. It is this property, which is responsible for the existence of millions of compounds of carbon. This feature can be explained on the basis of tetravalency of carbon.

The electronic configuration of carbon is $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^0$. In the box notation this is represented as:



As there are two half filled orbitals in the valence shell of carbon, its bonding capacity should be two. However, in actual practice carbon exhibits a bonding capacity of four and forms molecules of the type CH_4 , CCl_4 etc. In order to explain this tetravalency, it is proposed that one of the electrons from the '2s' filled orbital is promoted to the empty '2p' orbital ($2p_z$), which is in a higher energy state. In this way four half filled orbitals are formed in the valence shell which can account for the bonding capacity of four bonds of carbon. This state is known as the excited state in which the electronic configuration of carbon is:



From the above configuration it is clear that all the four bonds of carbon will not be identical. This is because one bond will be formed by the overlap of '2s' orbital which will have more of 's' character. The other three bonds will be formed by the overlap of the '2p' orbitals, which will have more of 'p' character. Therefore all the four bonds will not be equivalent.

But in practice, most of the carbon compounds have all the four bonds equal. This behavior can be explained in terms of Hybridization.

Characteristics of hybridization

- The hybridised orbitals are always equivalent in energy and shape.
- The number of hybridised orbitals formed is equal to the number of orbitals that undergo hybridization.
- Hybridized orbitals form more stable bonds.

- Hybridized orbitals orient themselves in preferred directions in space and so give a fixed geometry or shape to the molecules.

Conditions for hybridization

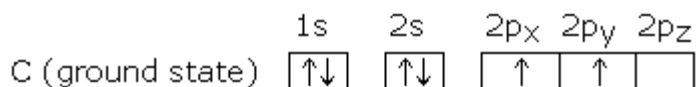
- Only the valence shell orbitals of the atom are hybridised.
- Orbitals undergoing hybridization should have only a small difference in their energies.
- It is not necessary that only half filled orbitals participate in hybridisation. Even filled orbitals of the valence shell can take part in hybridization.
- Rearrangement by way of promotion to different orbitals is not an essential condition for hybridization.

Hybridization in carbon compounds

The most popular hybridization in carbon containing compounds are sp , sp^2 and sp^3

Sp^3 hybridization

In this hybridization one '2s' and three '2p' orbitals present in the valence shell of the excited carbon atom get hybridised to give rise to four new orbitals of equivalent energies. Each sp^3 hybrid orbital is an average of one '2s' orbital and three '2p' orbital having one fourth s character and three fourth p character. The original '2s' orbital is spherically symmetrical (non-directional) while the three '2p' orbitals are dumb bell shape (directional) orienting along the three axes perpendicular to each other. But the newly formed sp^3 hybrid orbitals consist of two lobes one big and the other small. These orbitals tend to lie as far apart in space due to mutual repulsion of the electron clouds in them. They get directed towards the four corners of a regular tetrahedron with the carbon atom in the center. Therefore this hybridisation is also called as tetrahedral hybridisation with an angle of 109.5° between the hybrid orbitals.



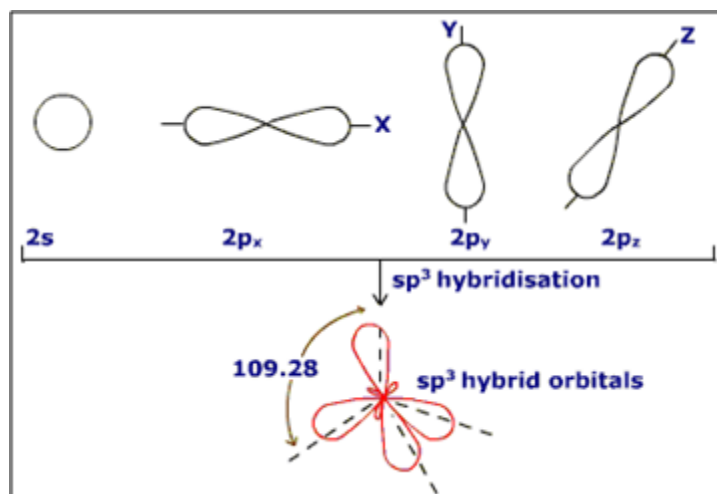
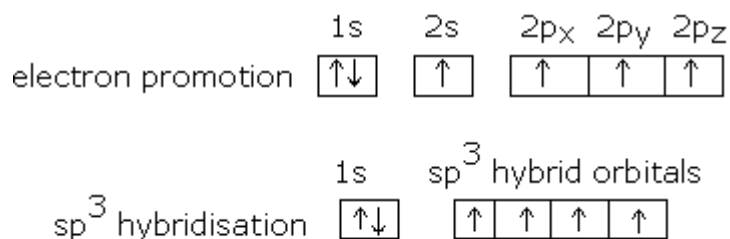


Fig 6 : sp³ hybridization

For Example

Methane - CH₄

In methane, the carbon atom undergoes sp³ hybridisation and forms four sp³ hybridised orbitals. Each of the hybrid sp³ orbitals of carbon overlaps axially with half filled '1s' orbital of hydrogen atom forming four sigma bonds. The four sp³ orbitals are directed towards the corner of a regular tetrahedron making an angle of 109.5°.

In this hybridization one '2s' and three '2p' orbitals present in the valence shell of the excited carbon atom get hybridised to give rise to four new orbitals of equivalent energies. Each sp³ hybrid orbital is an average of one '2s' orbital and three '2p' orbital having one fourth s character and three fourth p character. The original '2s' orbital is

spherically symmetrical (non-directional) while the three '2p' orbitals are dumb bell shape (directional) orienting along the three axes perpendicular to each other.

But the newly formed sp^3 hybrid orbitals consist of two lobes one big and the other small. These orbitals tend to lie as far apart in space due to mutual repulsion of the electron clouds in them. They get directed towards the four corners of a regular tetrahedron with the carbon atom in the center. Therefore this hybridisation is also called as tetrahedral hybridisation with an angle of 109.5° between the hybrid orbitals.

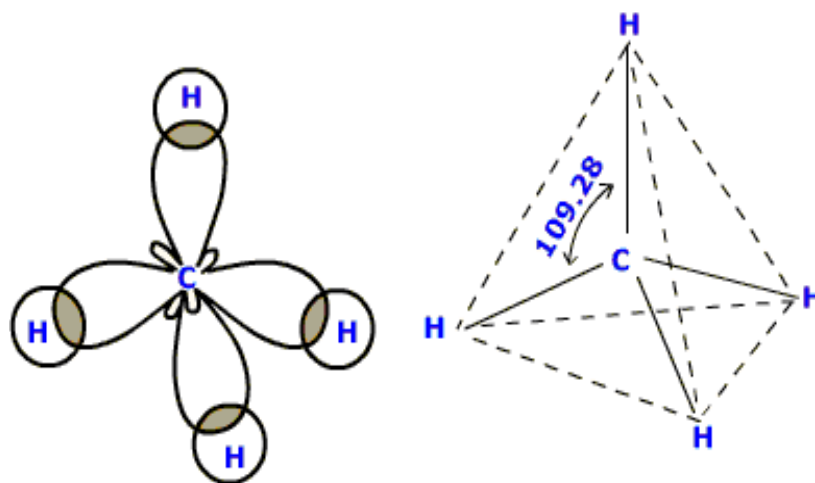
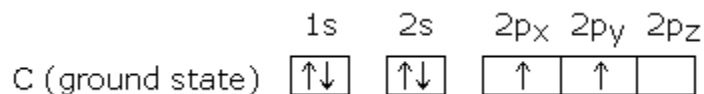


Fig 7 : Orbital picture and structure of methane

sp^2 hybridisation

In this type of hybridisation one '2s' and two 'p' orbitals ($2p_x$ and $2p_y$) get hybridised to form three equivalent orbitals called ' sp^2 ' hybrid orbitals. Each hybrid orbital has one third 's' character and two third 'p' character. The bond angle between the two hybridised orbital is 120° . The unhybridised orbital ($2p_z$) of carbon is oriented in a plane at right angles to the plane containing the three hybridised orbitals.



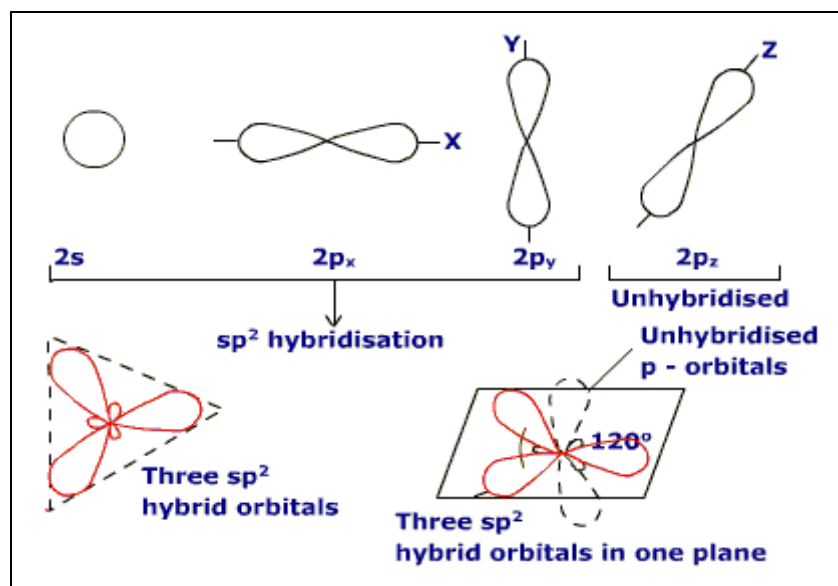
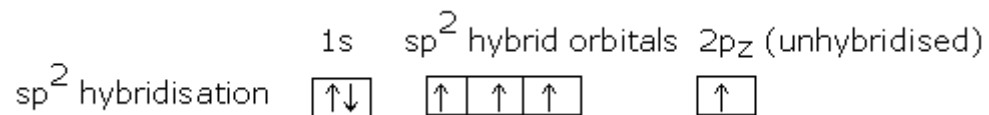
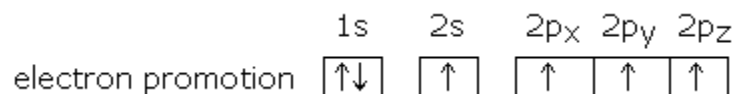


Fig 8 : Representation of sp² hybridisation

Ethene - C₂H₆

In the formation of ethylene, each carbon atom undergoes sp² hybridisation leaving 2p_z orbital unhybridised. One of the sp² hybridised orbital of one carbon atom overlaps axially with sp² hybridised orbital of the other carbon atom to form a stable sigma bond (C-C). The remaining two sp² hybrid orbitals of both carbon overlap axially with the half filled '1s' orbital of hydrogen atoms forming four C-H sigma bonds. The unhybridised orbital (2p_z) of one carbon atom overlaps sidewise with the similar orbital of the other carbon atom to form a weak pi bond. Thus, in ethylene all the six atoms containing the sigma bonds lie in one plane while the pi bond is at a plane perpendicular to the plane of the six atoms.

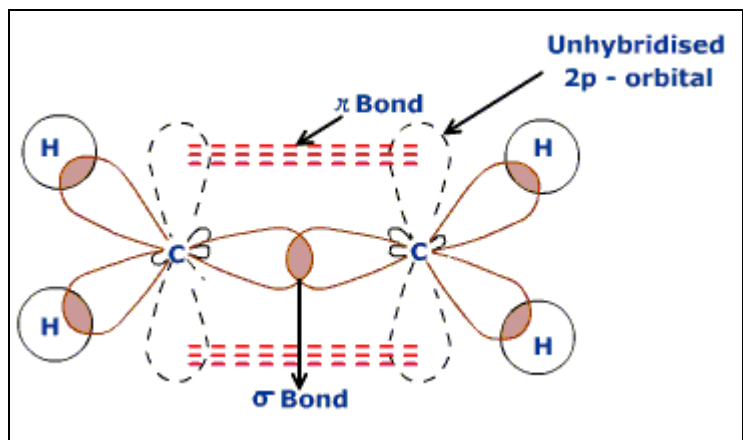
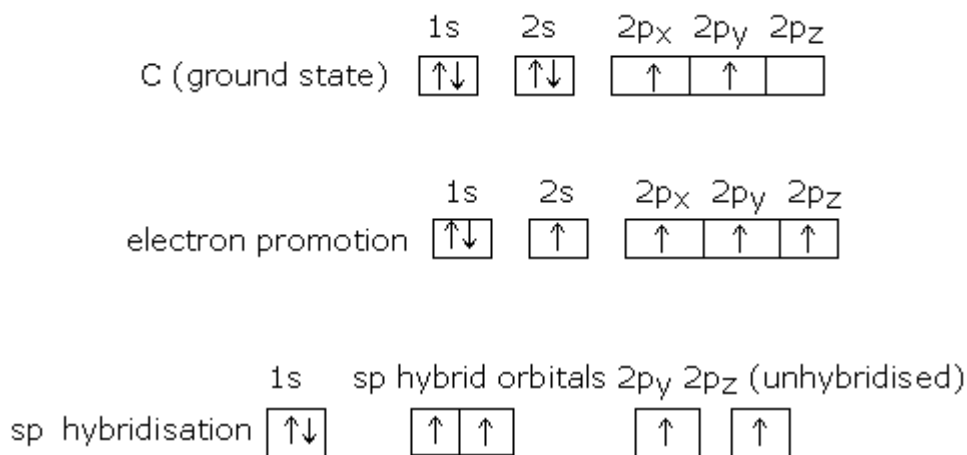


Fig 9 : Orbital picture of ethylene

'sp' hybridization

In this type of hybridisation one '2s' and one '2p_x' orbitals get hybridised to form two equivalent orbitals called 'sp' hybrid orbitals. The remaining 2p_y and 2p_z do not take part in hybridisation. The two unhybridised orbitals are directed along the 'y' and 'z' axes while the two hybridised orbitals are directed towards the 'x' axis. This hybridisation is often known as diagonal hybridisation as the two hybridised orbitals are at 180° due to mutual repulsion of their electron clouds. Each hybrid orbital has equal 's' and 'p' character.



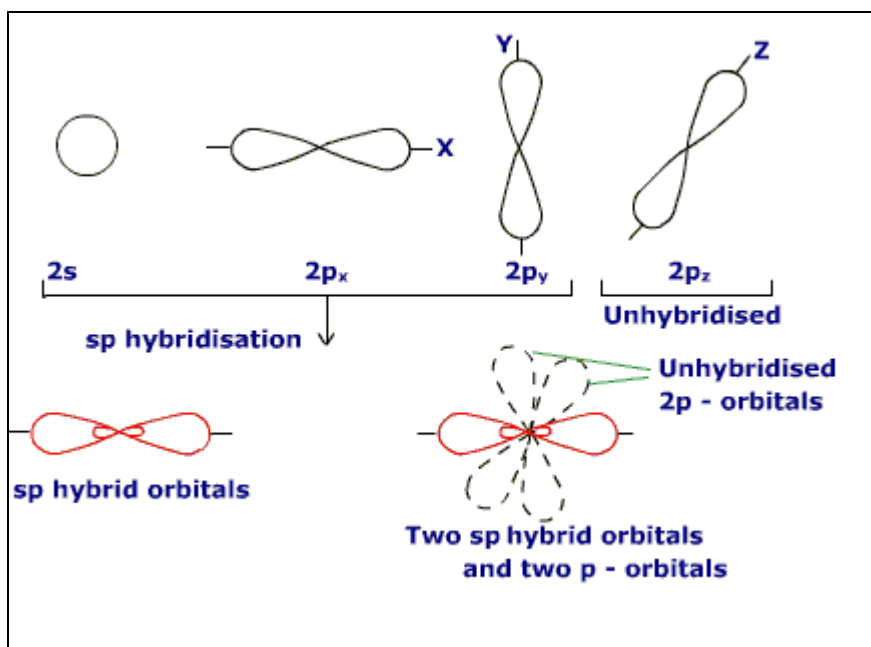


Fig 10 : Representation of sp hybridization

Ethyne

In the formation of ethyne both the carbon atoms undergo 'sp' hybridisation leaving two unhybridised orbitals on each ($2p_y$ and $2p_z$). One 'sp' hybrid orbital of one carbon atom overlaps axially with the 'sp' hybrid orbital of the other carbon atom to form C-C sigma bond. The remaining hybridised orbital of each carbon atom overlap axially with half filled orbital of hydrogen forming sigma bond. Each of the two unhybridised orbitals of one carbon atom overlaps sidewise with the similar orbitals of the other carbon atom to form two pi bonds.

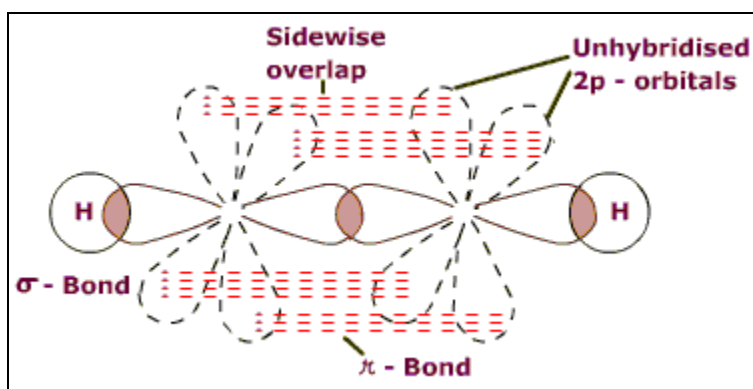
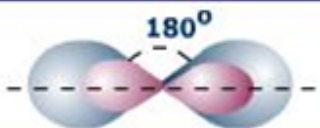
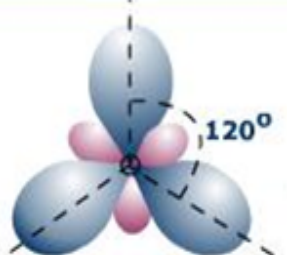
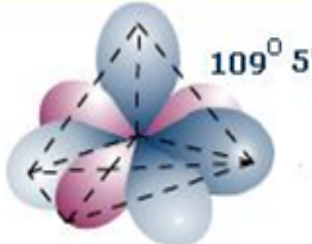


Fig 11 : Orbital picture of ethyne

Hybridization and molecular shapes of some molecules involving sp-orbitals are summarized in the table given below:

Type of Hybridization	Atomic orbitals involved	Orientation of hybrid orbitals	Shape of the molecule	Examples
sp	One s + One p		Linear	BeF ₂ , BeCl ₂ , BeH ₂ , C ₂ H ₂ , HgCl ₂
sp ²	One s + Two p		Tri- angular planar	BF ₃ , C ₂ H ₄ , NO ₃ ⁻ , CO ₃ ²⁻
sp ³	One s + Three p		Tetra- hedral	CH ₄ , CCl ₄ , NH ₄ ⁺

The elements of the third period contain d-orbitals also in addition to s- and p-orbitals. The 3d-orbitals are comparable in energy to the 3s- and 3p-orbitals. These d-orbitals are also involved in the hybridization and they explain the geometries of molecules of elements of third period. This results in covalencies of 5, 6 and 7, which are not known amongst the compounds of second period elements.

VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

Following are the important postulates of VSEPR's theory proposed by Nyholm, Gillespie.

- ❖ The shape of a molecule can be determined from the arrangement and repulsions between the electron pairs present in the valence shell of central atom of that molecule.

- ❖ There are two types of valence shell electron pairs viz., i) Bond pair and ii) Lone pair
- ❖ The electron pairs in the valence shell repel each other and determine the shape of the molecule. The magnitude of the repulsion depends upon the type of electron pair.
- ❖ The bond pair is attracted by nuclei they occupy less space and hence it causes less repulsion. Whereas, the lone pairs are only attracted by one nucleus and hence occupy more space. As a result, the repulsion caused by them is greater.
- ❖ The order of repulsion between different types of electron pairs is as follows :

$$\text{Lone pair - Lone pair} > \text{Lone Pair -Bond pair} > \text{Bond pair- Bond pair}$$
- ❖ When the valence shell of central atom contains only bond pairs, the molecule gets symmetrical structure, whereas the symmetry is distorted when there are lone pairs along with bond pairs.
- ❖ The bond angle decreases due to the presence of lone pairs.
- ❖ The repulsion increases with increase in the number of bonds between two atoms. Triple bond causes more repulsion than double bond which in turn causes more repulsion than single bonds.
- ❖ The repulsion between electron pairs increases with increase in electronegativity of central atom and hence the bond angle increases.
- ❖ Shapes of molecules can be predicted from the number of electron pairs in the valence shell of central atom as follows:

Hybridization involving d orbitals

Due to the availability of d-orbitals, phosphorus and sulphur can exhibit covalency of 5 and 6 respectively whereas the corresponding elements of same group, nitrogen and oxygen of second period cannot extend their octets. The following are some common types of hybridization involving d-orbitals:

- | | |
|----------------------------|----------------------------|
| a) sp^3d hybridization | b) sp^3d^2 hybridization |
| c) sp^3d^3 hybridization | d) dsp^2 hybridization |

sp^3d hybridization

This Hybridization involves the mixing of one s, three p and one d-orbital. These five orbitals hybridize to form five sp^3d -hybrid orbitals. The mixing of five orbitals is

shown in figure 1.23. These hybrid orbitals point towards the corners of a trigonal bipyramidal geometry. In this case, the three orbitals forming a plane are directed towards the corners of an equilateral triangle while the other two are perpendicular to the plane of the triangle lying above and below it.

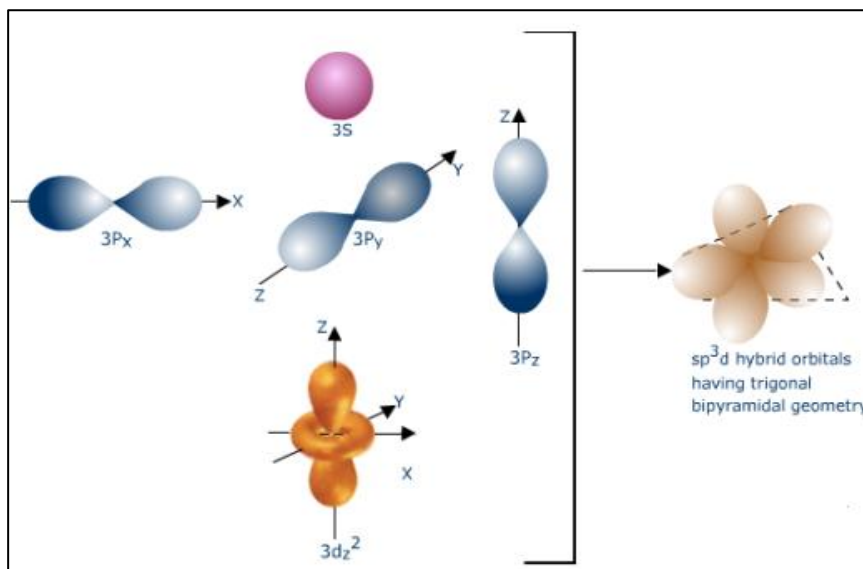


Fig 12 : Formation of five sp^3d hybrid orbitals, which adopt trigonal bipyramidal geometry Phosphorus penta fluoride involves sp^3d -Hybridization

Geometry of PF_5 molecule

The outer electronic configuration of phosphorus, the central atom, is $3s^2 3p^3$ which may be represented as shown below. It has three unpaired electrons in the ground state:

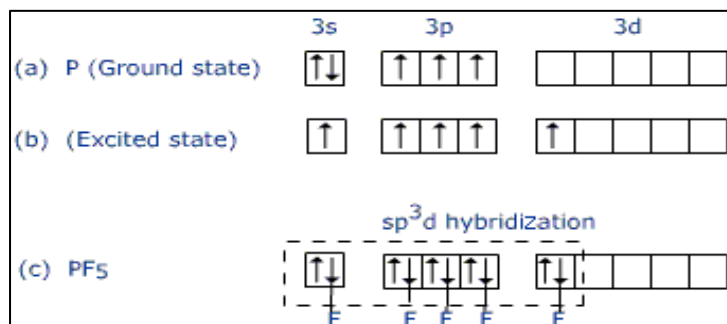


Fig 13 : Formation of PF_5 molecule involving sp^3d Hybridization

To explain the pentavalency of phosphorus in PF_5 , one of the electrons in 3s orbital is promoted to the higher 3d orbital so that it has five unpaired electrons. This is

called the excited state of phosphorus and is represented below. These five orbitals hybridize to form five sp^3d hybrid orbitals, which adopt trigonal bipyramidal arrangement. Each of the sp^3d hybrid orbitals overlaps with 2p orbital of fluorine forming five P-F bonds as shown in fig 14.

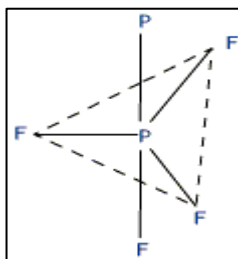


Fig 14 : Structure of PF_5

Thus, PF_5 molecule has trigonal bipyramidal geometry. It may be noted that all the bond angles in trigonal bipyramidal geometry are not equivalent. Three bonds lie in one plane at an angle of 120° to one another as in a triangular planar arrangement. These bonds are termed as equatorial bonds. The remaining two bonds are lies above and below in the equatorial plane both making an angle of 90° with the plane. These bonds are called axial bonds. It may be remembered that this geometry is not symmetrical. The axial bonds have been found to be larger than equatorial bonds. For e.g., in case of PF_5 molecule each P - F axial bond = 219 pm and each P - F equatorial bond = 204 pm. As the axial bonds suffer more repulsion, the axial bond will be slightly elongated when compared to equatorial bond.

sp^3d^2 hybridization

In this case one s, three p and two d-orbitals get hybridized to form six sp^3d^2 hybrid orbitals which adopt octahedral arrangement as given in Fig.15

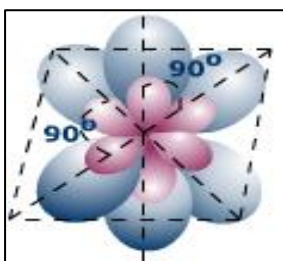


Fig 15 : Six sp^3d^2 hybrid orbitals

Geometry of SF₆ molecule

The geometry of SF₆ molecule can be explained on the basis of sp³d² Hybridization. In SF₆ the central sulphur atom has the ground state configuration, 3s²3p⁴ as shown.

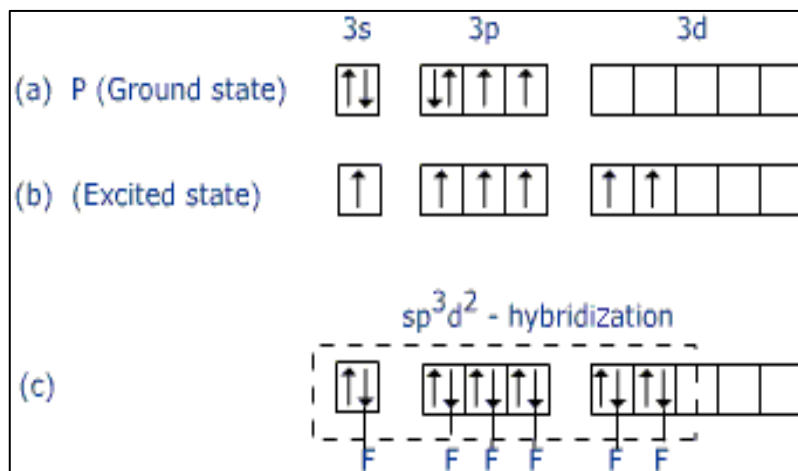


Fig 16 : Formation of SF₆ molecule involving sp³d² Hybridization

To account for the hexavalency in SF₆ one electron each from 3s and 3p orbitals is promoted to 3d orbitals as shown. These six orbitals get hybridised to form six sp³d² hybrid orbitals. Each of these sp³d² hybrid orbitals overlaps with 2p orbital of fluorine to form S-F bond.

Thus, SF₆ molecule has octahedral structure as shown. The dotted electrons represent electrons from F-atoms.

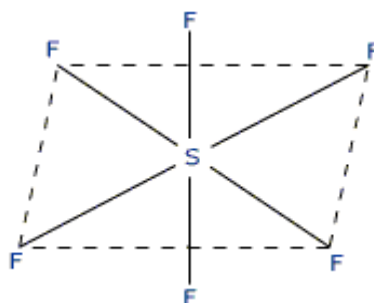


Fig 17 : Octahedral geometry of SF₆ molecule

sp^3d^3 hybridization

This involves the mixing of one s three p and three d-orbitals forming seven sp^3d^3 hybrid orbitals having pentagonal bipyramidal geometry. The geometry of IF_7 molecule can be explained on the basis of sp^3d^3 Hybridization.

Geometry of IF_7 molecule

The outer electronic configuration of iodine atom is $5s^2 5p^5$. To make seven bonds, one s and two p orbitals are promoted to the higher vacant 5d orbitals as shown,

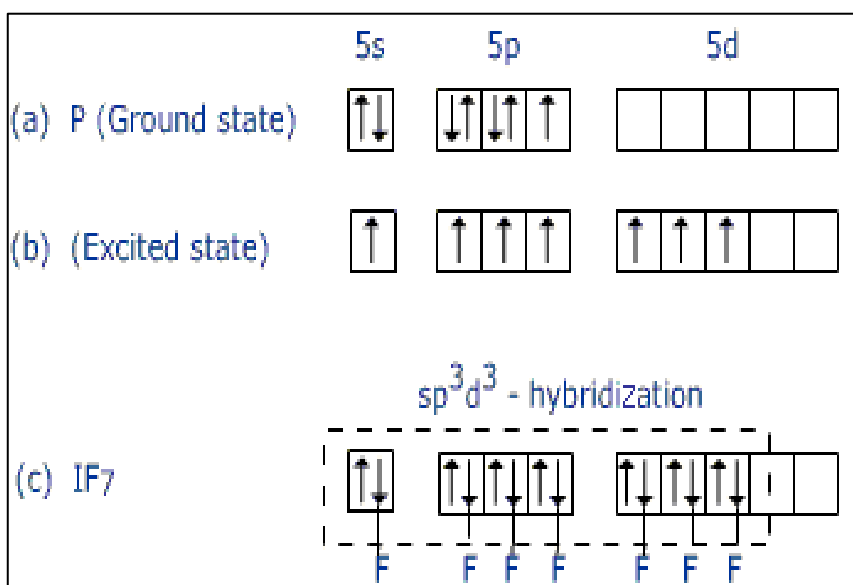


Fig 18 : Formation of IF_7 molecule involving sp^3d^3 -Hybridization

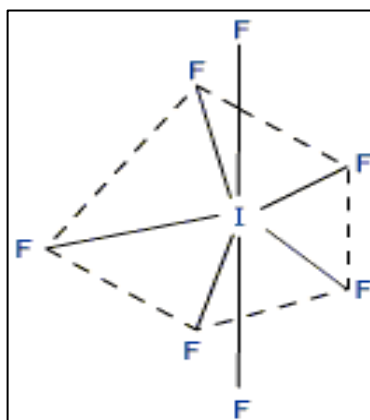


Fig 19 : Pentagonal bipyramidal geometry of IF_7 molecule

These seven orbitals are then hybridized to give seven sp^3d^3 hybrid orbitals. Each of these sp^3d^3 hybrid orbitals overlaps with 2p orbitals of fluorine to form IF_7 molecule having pentagonal bipyramidal geometry. In this geometry, all the bond angles are not equal. Five F atoms are directed towards the vertices of a regular pentagon making an angle of 72° . The other two F-atoms are at right angles (90°) to the plane. Due to different bond angles, the bonds are different in length. The axial bonds are larger than equatorial bonds.

dsp^2 hybridization

In addition to above types of Hybridization, dsp^2 type of hybridization is also known particularly in case of transition metal ions. The orbitals involved in this type of Hybridization are $d_{x^2-y^2}$, s and two p. The four dsp^2 hybrid orbitals adopt square planar geometry.

Geometry of $[Ni(CN)_4]^{2-}$

The complex ion $[Ni(CN)_4]^{2-}$ involves dsp^2 Hybridization as explained below. In this case, the oxidation state of nickel is +2. The outer electronic configuration of Ni^{2+} is $3d^8$ as given in the below figure:

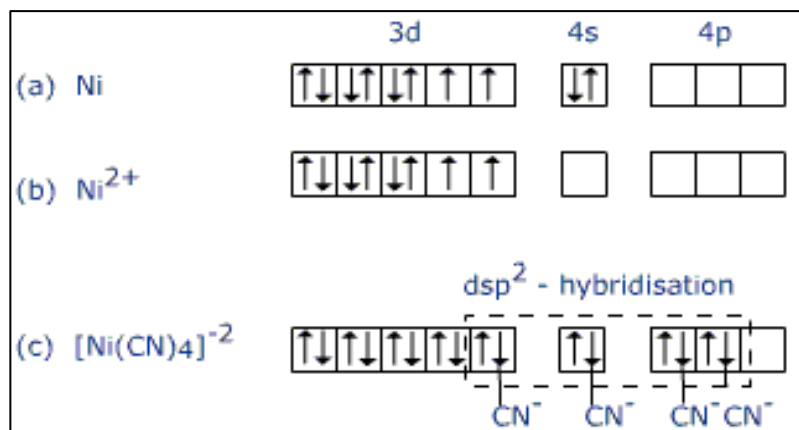


Fig 20 : Formation of $[Ni(CN)_4]^{2-}$ involving dsp^2 Hybridization

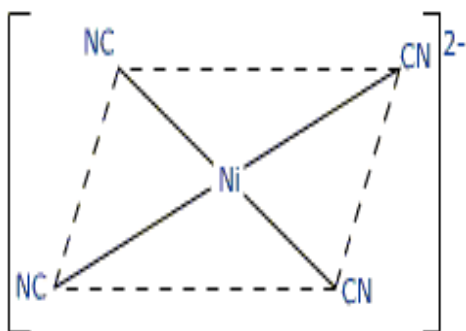




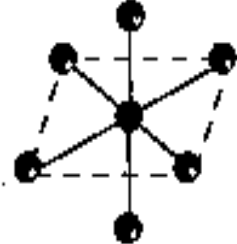
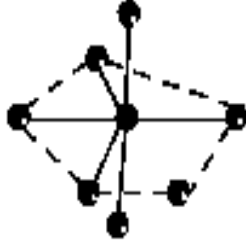
Fig 21 : Structure of $[\text{Ni}(\text{CN})_4]^{2-}$

In the formation of the complex ion, the two unpaired d electrons are paired up making one 3d orbital empty. The four empty orbitals (one 3d, 4s and two 4p) hybridize to form four dsp^2 hybrid orbitals, which point towards square planar arrangement. Each one of the four CN-groups donates lone pair of electrons to vacant hybrid orbitals forming four Ni - CN bonds. Thus, $[\text{Ni}(\text{CN})_4]^{2-}$ has square planar arrangement as shown.

Geometry of molecules containing one or more lone pairs in central atom

Total number of electron pair	Number of bond pairs	Number of lone pairs	Formula	Shape of the molecule	Bond angle	Example
3	2	1	AB_2E	Angular	120°	SO_2
4	3	1	AB_3E	Trigonal pyramidal	$107^\circ 48'$ $120^\circ 30'$	NH_3 NF_3
	2	2	AB_2E_2	Angular (V shaped)	$104^\circ 28'$ 103°	F_2O H_2O
5	4	1	AB_4E	See-saw		$\text{SCl}_4, \text{SF}_4$
	3	2	AB_3E_2	T-shaped	90°	ClF_3
	2	3	AB_2E_3	Linear	180°	XeF_2, I_3
6	5	1	AB_5E	Square pyramidal	90°	BrF_5
	4	2	AB_4E_2	Square pyramidal	90°	XeF_4

Hybridization and molecular shapes of some molecules involving d-orbitals are summarized in the table given below;

Type of hybridization	Atomic orbitals	Shape	Bond angle	Examples
dsp^2 (d is $d_{x^2-y^2}$)	$d+s+2(p)$	 Square planar	90°	$[Ni(CN)_4]^{2-}$ $PtCl_4^{2-}$
sp^3d (d is d_{z^2})	$s+3(p)+d$	 Trigonal bipyramidal	$90^\circ, 120^\circ$	PF_5, PCl_5
sp^3d^2 (d are $d_{x^2-y^2}, d_{z^2}$)	$s+3(p)+2(d)$	 Octahedral	90°	SF_6, CrF_6^{3-}
sp^3d^3 (d are d_{xy}, d_{yz}, d_{zx})		 Pentagonal bipyramidal	90° 72°	IF_7

SUMMARY

- Chemical bonding is defined and Kossel-Lewis approach to understand chemical bonding by using the octet rule is studied.
- Ionic bonding results due to complete electron transfer from electropositive elements to electronegative elements forming cation and anion. Electrostatic force of attraction between ions describes the ionic bonding. Mutual sharing of electrons between the two atoms result covalent bonding. The directional characters, partial ionic character by the pure orbital overlaps are also studied with suitable examples.
- The geometry of simple molecules are predicted using the postulates VSEPR model BeCl_2 : linear; CH_4 : Tetrahedral; BCl_3 : trigonal; PCl_5 trigonal bipyramidal; SF_6 : Octahedral.

References:

1. www.wikipedia.com
2. www.tutorvista.com/content/chemistry/chemistry-iii/chemical-bonding
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QUESTION & ANSWERS

HYBRIDIZATION AND GEOMETRY OF MOLECULES QUESTIONS

1. In which one of the following pairs the species have similar geometry?

1. CO₂ and SO₂
2. NH₃ and BH₃
3. CO₃²⁻ and SO₃²⁻
4. SO₄²⁻ and ClO₄⁻

Explanation:

- a). CO₂ is linear whereas SO₂ is angular with a lone pair
- b). NH₃ is pyramidal with a lone pair whereas BH₃ is trigonal planar
- c). CO₃²⁻ is trigonal planar whereas SO₃²⁻ is pyramidal with a lone pair
- d). Both SO₄²⁻ and ClO₄⁻ are tetrahedral.**

2. The bond angle of Cl₂O is

- a) Smaller than that of F₂O b) Greater than that of H₂O
- c) Smaller than that of H₂O d) Same as that of F₂O

Ans:- Greater than that of H₂O

Explanation: The central atom (oxygen) in Cl₂O, F₂O and H₂O undergoes sp³ hybridization.

But there are two lone pairs on it. In case of H₂O, the bond angle is decreased to 104.5° due to repulsion from lone pair. In case of F₂O, the bond angle is decreased to 103°. (here, the lone pair repulsion is predominant factor). In case of Cl₂O, the bond angle is increased to 117.6° due to repulsion between bulky Cl atoms

3. Using the VSEPR theory, predict the number of lone pairs and draw the structures of

IF₅ and SOF₄

No. of lone pairs = (v-b)/2

Where v = no. of valence electrons in the central atom, b = no. of (σ & π) bonds formed by central atom.

The structure and hybridization are decided by no. of lone pairs and no. of atoms around the

central atom. For e.g. if this number is 5, then the hybridization is sp_3d and the shape is based on trigonal bipyramidal structure.

IF₅ :

$$\text{No. of lone pairs} = (v-b)/2 = (7-5)/2 = 1$$

$$\text{No. of lone pairs} + \text{no. of ligand atoms} = 1 + 5 = 6$$

Hence the hybridization is sp_3d_2 and the shape is based on octahedral structure. As there is

one lone pair, the shape is square pyramidal.

SOF₄:

$$\text{No. of lone pairs} = (v-b)/2 = (6-6)/2 = 0$$

$$\text{No. of lone pairs} + \text{no. of ligand atoms} = 0 + 5 = 5$$

Hence the hybridization is sp_3d and the shape is trigonal bipyramidal. No lone pair and no distortion.

4. Which one of the following statements is correct for XeO₂F₂?

- a) It has a square planar structure.
- b) It has a trigonal bipyramid based structure.
- c) It is isostructural with XeF₄.
- d) It has a tetrahedral structure.

Ans: It has a trigonal bipyramid based structure.

5. Which among the following pairs is square pyramidal in shape?

- a) BrF₅, XeOF₄ b) PCl₅, XeO₂F₂ c) AsF₅, BrF₅ d) IF₇, XeF

Ans: BrF₅, XeOF₄

6. The square pyramidal molecular shape is adopted by

- a) SOF_4 b) XeOF_4 c) ScOCl_4 d) PF_5

Ans: XeOF_4

7. The structure of XeO_2F_2 based on VSEPR theory is best described as

- a) A square planar structure with the fluorines trans to each other.
b) See-saw structure with F-Xe-F bond angle close to 120° .
c) A perfect tetrahedral arrangement of substituents around Xe.
d) See-saw structure with O-Xe-O bond angle close to 120° .

Ans: See-saw structure with O-Xe-O bond angle close to 120° .

8. The B-F bond distance in $\text{H}_3\text{N}\rightarrow\text{BF}_3$ is much _____ than in BF_3

Ans: longer

9. The molecule ClF_3 has _____ non-bonded electron pairs.

Ans: 2

10. The pair of compounds having the same hybridization for the central atom is

- a) XeF_4 and $[\text{SiF}_4]^{2-}$ b) $[\text{NiCl}_4]^{2-}$ and $[\text{PtCl}_4]^{2-}$
c) $\text{Ni}(\text{CO})_4$ and XeO_2F_2 d) $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$

Ans: XeF_4 and $[\text{SiF}_4]^{2-}$

11. Why the C-Cl bond is polar but CCl_4 molecule is non-polar? Explain

Solution: The C-Cl bond is polar because the chlorine atom being more electronegative pulls the shared electron pair towards itself. In CCl_4 , there are four C-Cl bonds. Since these polar bonds are symmetrically arranged, the polarities of individual bonds cancel each other resulting in a zero dipole moment for the molecule. The net result is that CCl_4 molecule is non-polar.

12. Calculate the ionic character of HCl. Its measured dipole moment is 3.436×10^{-30} coulomb meter. The HCl bond length is 2.29×10^{-10} meter.

Solution:

Dipole moment corresponding to 100 % ionic character of HCl

$$= 1.602 \times 10^{-19} \text{ C} \times 2.29 \times 10^{-10} \text{ m}$$

$$= 20.67 \times 10^{-30} \text{ Cm}$$

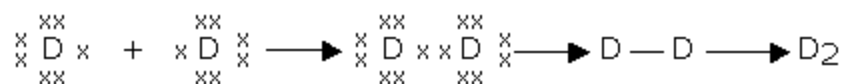
Actual dipole moment of HCl = 3.436×10^{-30} Cm

$$\therefore \text{Percentage ionic character} = \frac{3.436 \times 10^{-30} \text{ Cm}}{20.67 \times 10^{-30} \text{ Cm}} \times 100 = 17 \%$$

13. The electronic configuration of a neutral atom 'D' is given as: $1s^2 2s^2 2p^5$.

What is its Lewis structure (empirical formula)?

Solution: The electronic configuration of atom 'D' has seven electrons in the outermost shell. Each 'D' atom should share a pair of electrons with another 'D' atoms to form a substance containing only 'D' .i.e.,



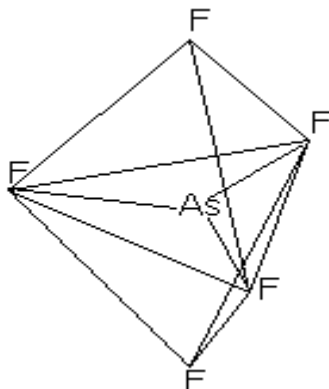
Hence, the formula of the substance is D_2 . It is a covalent compound.

14. Predict the shapes of the following molecules using the valence shell electron pair repulsion (VSEPR) theory. AsF_5 , HgBr_2 ,

Solution: According to the VSEPR theory, the electron pairs present in the valence-shell of the central atom/ion arrange them in the space around it so as to keep them as far as possible from each other, so as to minimize the electrostatic repulsions.

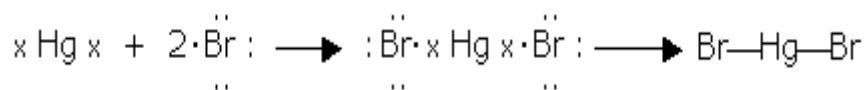
AsF_5

As has five electrons in its outermost orbit. Due to sharing of 5 electrons from 5F-atoms, there are in all 5 electron pairs. These are distributed in space to form a trigonal bipyramid as shown here.



HgBr₂

Hg has only two electrons in its outermost orbit and sharing these electrons with two Br gives 2 pairs of electrons around Hg. This gives a linear structure to HgBr₂ (electron pairs are positioned at 180° to each other).



15. Why does KHF₂ exist but KCl₂ does not?

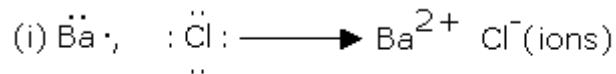
Solution: Due to hydrogen bonding in HF as HF..... HF..... HF,

It can be dissociate as HF₂⁻ ion and therefore forms KHF₂

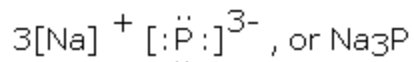
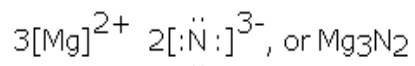
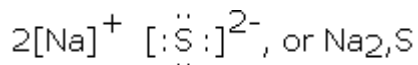
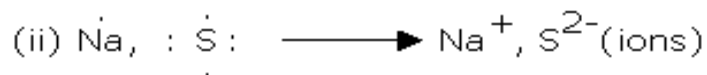
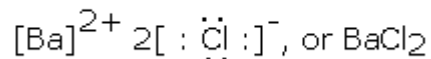
But there is no hydrogen bonding in HCl and so HCl₂ ion cannot be formed. Therefore, KCl₂ does not exist.

16. Give the Lewis structures and empirical formulae for the ionic compound formed between the following pairs of elements : (i) Ba, Cl (ii) Na, S (iii) Mg, N (iv) Na, P.

Solution: From the charges on the ions, the number of positive and negative ions in the compound can be found out. This gives the empirical formula (E.F.)



Lewis formula:



CHAPTER - 6

CHEMICAL EQUILIBRIUM AND UNDERSTANDING OF LE CHATELIAR'S PRINCIPLE

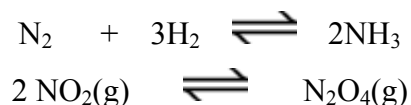
S. Mahendran

6.1. Introduction

If you look up the meaning of “equilibrium” in a dictionary you will find it explained using words like “state of balance. A meter stick suspended at its centre of gravity

remains stationary or static. Thus, this type of equilibrium is often referred to as **static equilibrium**. In other words, the entire system is not moving. Consider now the case of a man running on a treadmill. Overall, there is no change in the position of the man. He is running forward at the same speed as the belt is moving in the opposite direction. The two opposing motions balance each other. This is an example of a type of equilibrium called **dynamic equilibrium**. The word dynamic means “moving”. In all reactions, there are in fact two reactions occurring, one where the reactants produce the products, and the other where the products react to form the reactants. In some reactions, this second reaction is insignificant, but in others there comes a point where the two reactions exactly cancel each other out...thus the reactants and products remain in equal proportions, though both are continually being used up and produced at the same time. Chemical equilibrium is a state of dynamic balance where the rate of the forward reaction is the same as the rate of the backward reaction. Generally, Chemical equilibrium macroscopically static, but is microscopically dynamic.

Examples of reactions at equilibrium



6.2. Chemical Equilibrium and Equilibrium Constant

Consider a general reversible chemical reaction,



According to the law of mass action, assuming that active masses are equivalent to molar concentrations,

$$\text{Rate of forward reaction} = k_f [\text{A}]^a [\text{B}]^b$$

$$\text{Rate of reverse reaction} = k_r [\text{C}]^c [\text{D}]^d$$

in which the proportionality constants k are called *rate constants* and the quantities in square brackets represent concentrations. At equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction, that is,

$$k_f [\text{A}]^a [\text{B}]^b = k_r [\text{C}]^c [\text{D}]^d$$

$$K_{eq} = k_f/k_r = [C]^c [D]^d / [A]^a [B]^b \quad \dots\dots$$

(1)

The constant K_{eq} is called the *equilibrium constant* of the reaction. Eq.1 represents the *law of chemical equilibrium*.

Examples

1. $2 \text{SO}_{2(g)} + \text{O}_{2(g)} \rightleftharpoons 2 \text{SO}_{3(g)}$

$$K_c = [\text{SO}_3]^2 / [\text{SO}_2]^2 [\text{O}_2]$$
2. $4 \text{NH}_{3(g)} + 5 \text{O}_{2(g)} \rightleftharpoons 4 \text{NO}_{(g)} + 6 \text{H}_2\text{O}_{(g)}$

$$K_c = [\text{NO}]^4 [\text{H}_2\text{O}]^6 / [\text{NH}_3]^4 [\text{O}_2]^5$$
3. $\text{Pb}(\text{NO}_3)_{2(s)} \rightleftharpoons \text{PbO}_{(g)} + 2 \text{NO}_{2(g)} + \frac{1}{2} \text{O}_{2(g)}$

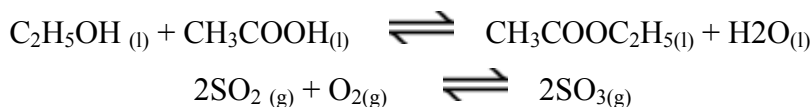
$$K_c = [\text{PbO}] [\text{NO}_2]^2 [\text{O}_2]^{1/2}$$

The equilibrium constant has specific names for several classes of reactions,

1. Gas-phase reactions that use units of partial pressure: K_p
2. Dissociation of water: dissociation constant of water, K_w
3. Dissociation of acids: acid dissociation constant, K_a
4. Reaction of bases with water: base dissociation constant, K_b
5. Solubility of precipitates: solubility product, K_{sp}

6.3. Homogeneous and Heterogeneous Equilibria

1. Equilibrium in which all the reactants and products are on the same phase is called homogeneous equilibrium reaction.

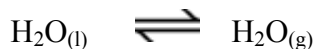


For such reactions the equilibrium constants are written as,

$$\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightleftharpoons 2\text{NH}_{3(g)}$$

$$\text{Equilibrium Constant, } K_c = \frac{[\text{NH}_{3(g)}]^2}{[\text{N}_{2(g)}][\text{H}_{2(g)}]^3}$$

1. Equilibrium in which the reactants and products are present in different phases is called heterogeneous equilibrium reaction.





For heterogeneous reactions, the concentration terms for pure solids and pure liquids are not included in the expression for equilibrium constant. The concentration of pure solids and liquids remain constant, and these terms are merged into equilibrium constant or by convention i.e., [solid] =1, [liquid] =1. For example, the equilibrium constant for the reaction,



So, the equilibrium constant is,

$$K_p = \frac{p_{\text{H}_2(g)}^4}{p_{\text{H}_2\text{O}(g)}^4}$$

Equilibrium constant is used to determine the amount of each component that will present at equilibrium.

6.3.1. Important Considerations

1. The equilibrium constant is normally dimensionless even though its evaluation may produce units.
2. The value of equilibrium constant cannot be interpreted unless it is accompanied by a balanced chemical equation and a specification of the standard state of each reactant and product.
3. A catalyst does not affect either K_c or the position of equilibrium. This is because a catalyst speeds up the forward and back reaction to the same extent. So, it can't affect the position of equilibrium.
4. The equilibrium constant of a reaction is related to thermo chemical property, by the following relation, $\Delta G = -RT \ln K$. where, ΔG =Gibbs free energy change.

6.3.2. Reaction Quotient

The expression for the reaction quotient Q , looks like that used to calculate equilibrium constant but Q can be calculated for any set of conditions, not just for equilibrium.

Q can be used to determine which direction a reaction will shift to reach equilibrium.

- If $K > Q$, a reaction will proceed forward, converting reactants into products.

- If $K < Q$, the reaction will proceed in the reverse direction, converting products into reactants.
- If $Q = K$ then the system is already at equilibrium.

In order to determine Q we need to know:

- The equation of the reaction, including the physical states,
- The quantities of each species (molarities and/or pressures), all measured at the same moment in time.

6.3.3. Quantitative Considerations

When K_c is greater than 1, products exceed reactants (at equilibrium). When K_c is less than 1, reactants exceed products.

When $K \gg 1$, formation of products is favored

When $K \ll 1$, reactants are favored.

Note: (K_c can never be negative...so when it is close to zero).

6.3.4. Relating K_c and K_p

The ideal gas law: $PV = nRT$ rearranges into $P = (n/V)RT$

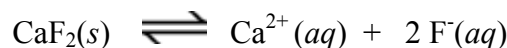
for gases (n/V) will be the molar concentration, $[C]$:

Thus, $P = [C]RT$

and $K_p = K_c (RT)^{\Delta n}$, where, Δn = number of moles of gas in products - number of moles of gas in reactants.

6.4. Solubility and Solubility Product

A saturated solution of a slightly soluble salt is in contact with undissolved salt, which involves equilibrium reaction as shown below;



The equilibrium constant expression for the equilibria is as follows;

$$K_{sp} = [\text{Ca}^{2+}][\text{F}^-]^2$$

This equilibrium constant is called a *solubility-product constant*. In general, the solubility product constant (K_{sp}) is the equilibrium constant for the equilibrium that exists

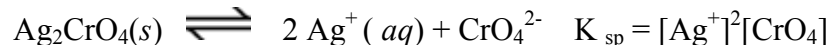
between a solid ionic solute and its ions in a saturated aqueous solution hence it is a phase equilibria.

The rules for writing the solubility-product expression are the same as those for writing any other equilibrium constant expression. The solubility product is equal to the product of the concentrations of the ions involved in the equilibrium, each raised to the power of its coefficient in the equilibrium equation.

Example 1

Analysis of a saturated solution of silver chromate, Ag_2CrO_4 , indicates that the concentration of silver ion is 1.3×10^{-4} M. What is the K_{sp} of Ag_2CrO_4 ?

The equilibrium equation and the solubility product expression are,



From the equation we can see that at equilibrium, the concentration of CrO_4^{2-} is going to be half that of Ag^+ .

$$\begin{aligned} [\text{CrO}_4^{2-}] &= 1/2 [\text{Ag}^+] = 1/2 (1.3 \times 10^{-4} \text{ M}) \\ &= 6.5 \times 10^{-5} \\ K_{\text{sp}} &= [\text{Ag}^+]^2[\text{CrO}_4^{2-}] = (1.3 \times 10^{-4})^2 (6.5 \times 10^{-5}) \\ &= 1.1 \times 10^{-12} \end{aligned}$$

6.5. Effect of Temperature on the Equilibrium Constant or Van't Hoff equation

If $\Delta G = -RT \ln K$ is substituted into Gibbs-Helmholtz equation; we obtain

$$\frac{d \ln K}{dT} = \frac{\Delta H^\ominus}{RT^2}$$

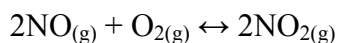
This equation is called the van't Hoff equation. Thus, for an endothermic reaction the equilibrium constant increases as the temperature is increased, and for an exothermic reaction the equilibrium constant decrease as the temperature is increased.

6.6. Le Chatelier's Principle

If a system at equilibrium is disturbed by a change in temperature, pressure, or the concentration of one of the components, the system will shift its equilibrium position so as to counteract the effect of the disturbance.

6.6.1. Example involving change of concentration

In the equation;



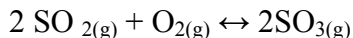
If you add more $\text{NO}_{(g)}$ the equilibrium shifts to the right producing more $\text{NO}_{2(g)}$

If you add more $\text{O}_{2(g)}$ the equilibrium shifts to the right producing more $\text{NO}_{2(g)}$

If you add more $\text{NO}_{2(g)}$ the equilibrium shifts to the left producing more $\text{NO}_{(g)}$ and $\text{O}_{2(g)}$.

6.6.2. Example involving pressure change

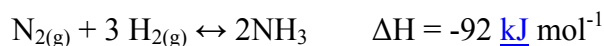
In the equation;



An increase in pressure will cause the reaction to shift in the direction that reduces pressure, that is the side with the fewer number of gas molecules. Therefore an increase in pressure will cause a shift to the right, producing more products. (A decrease in volume is one way of increasing pressure).

6.6.3. Example involving temperature change

In the equation

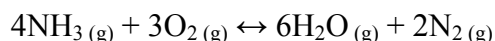


An increase in temperature will cause a shift to the left because the reverse reaction uses the excess heat. An increase in forward reaction would produce even more heat since the forward reaction is exothermic. Therefore the shift caused by a change in temperature

depends upon whether the reaction is exothermic or endothermic. In this reaction finely divided iron is used to speed the reaction (finely divided to maximize the surface area).

Example 2

The following reaction is at equilibrium;



How will the equilibrium shift if

a. The volume is increased

Since the volume is being increased, the pressure is dropping. In response, the equilibrium will shift right to attempt to make more moles of gas and increase the pressure.

b. Four moles of Helium gas is added

The equilibrium will not change. To change a gaseous equilibrium, the partial pressures of at least one gas need to be changed. Since He is un-reactive with all of the gases present, the total pressure will change but the partial pressures will not.

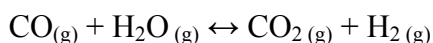
c. A lit match is placed inside the container

The match is a combustion reaction and requires O_2 to proceed. Thus, the oxygen in the system will be used and the equilibrium will shift left in order to compensate for the loss.

6.7. Questions

Problem 1

This equation is at equilibrium:



- A. If a 10.00L vessel has 2.50 mol CO_2 and H_2O , and 5.00 mol CO and H_2 gas at 588°K , which way will the reaction proceed? ($K_c = 31.4$ at 588°K)
- B. What are the concentrations of all species at equilibrium?

Problem 2

0.100 L of 0.003 M $\text{Pb}(\text{NO}_3)_2$ is added to 0.400 L of 0.005 M Na_2SO_4 . Will PbSO_4 precipitate? $K_{\text{sp}}=1.6 \times 10^{-8}$, K_{sp} for $\text{SrSO}_4=7.6 \times 10^{-7}$. K_{sp} for $\text{SrF}_2=7.9 \times 10^{-10}$.

- a) What is the molar solubility of SrSO₄ in pure water?
- b) What is the molar solubility of SrF₂ in pure water?
- c) Sr(NO₃)₂(aq) is added to 1.0 L of solution containing 0.020 mol F⁻ and 0.10 mol SO₄²⁻ with constant volume. 1: which salt precipitates first? 2: What is [Sr²⁺] in solution when precipitate forms?

Problem 3

- The K_{sp} for lead (II) chloride is 1.7x10⁻⁵. If you place 3.00g of this solid in water, how much solid will be left after the system reaches equilibrium? (Hint: Find the molarity of the disassociated lead ion. It is equal to how much the molarity of the PbCl₂ decreases by since they are in a 1:1 ratio)
- How much of the above solid will be left if the solid is instead placed in a 0.01M HCl solution?

Problem 4

Table 6.1. Some examples based on the application of Le Chatelier's principle.

System	Change	Result
CO ₂ + H ₂ → H ₂ O(g) + CO	a drying agent is added to absorb H ₂ O	
H ₂ (g) + I ₂ (g) → 2HI(g)	Some nitrogen gas is added	
NaCl(s) + H ₂ SO ₄ (l) → Na ₂ SO ₄ (s) + HCl(g)	reaction is carried out in an open container	
H ₂ O(l) → H ₂ O(g)	water evaporates from an open container	
HCN(aq) → H ⁺ (aq) + CN ⁻ (aq)	the solution is diluted	
AgCl(s) → Ag ⁺ (aq) + Cl ⁻ (aq)	some NaCl is added to the solution	
N ₂ + 3 H ₂ → 2 NH ₃	a catalyst is added to speed up this reaction	
N ₂ + O ₂ → 2 NO	An increase in pressure of the reaction	
2 CrO ₄ ²⁻ (aq.yellow) + 3H ₃ O ⁺ (aq.) ↔ Cr ₂ O ₇ ²⁻ (aq.orange) + 3H ₂ O(l)	NaOH is added to equilibrium mixture	
The binding of oxygen with	During muscle exercise lactic acid is	

<p>hemoglobin to produce oxyhemoglobin is partially regulated by the concentrations of H^+ and CO_2 in the blood.</p> $HbO_2 + H^+ + CO_2 \rightleftharpoons CO_2HbH^+ + O_2$	<p>produced source of H^+ and CO_2</p>	
<p>Tooth decay is the result of dissolving of tooth enamel, $Ca_5(PO_4)_3OH$ (s). In the mouth the following equilibrium is established.</p> $Ca_5(PO_4)_3OH (s) \rightleftharpoons 5 Ca^{2+} (aq) + 3PO_4^{3-} (aq) + OH^- (aq)$	<p>When sugar ferments, acid or H^+ is formed on the teeth</p>	

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CHAPTER - 7

COLLOIDS AND THEIR APPLICATIONS IN EVERY DAY LIFE

7.1. Introduction

Colloidal systems are the ones in which one of three states (solid, liquid and gas) is finely dispersed in another. These are nothing but much talked nano particles. It was named first in the early 19th century by the Father of Physical Chemistry, Thomas Graham (1805-1869), to distinguish those materials in aqueous solution that would not pass through a parchment membrane from those that would. Colloids received little attention until the end of the century, when van't Hoff, Oswald and Nernst founded modern physical chemistry and they, and others, became fascinated by colloid phenomena. There also had been famous observations by Tyndall and others in the meantime. In 1920's and 1930's, the importance of colloids to industrial processes and biochemistry changed everything making it a hot field.

Colloidal dimensions can be considered to be from about 10 nm up to 1000 nm, or 1 μm, but mere size is not the important thing about colloids. A colloidal system consists of an *internal phase (dispersion phase)*, which is the material of colloidal dimensions, and an *external phase (dispersion medium)*, which is the material in which the colloid is dispersed similar to the terms *solute* and *solvent* used for simple solutions. For example, when salt or sugar is added to water it forms true solution but when sand or glass is added to water, they get settled down. Such solutions are called suspensions. Colloid solutions are the ones with particle size in between size of true solutions and suspensions. Differences between these are tabulated in table 1. As the particles of a colloid system become smaller and smaller, we go over imperceptibly from a two-phase colloid to a single-phase solution, and there is no definite boundary i.e true solution. The important property of colloids is that they have very large surface area (interfacial area) and all their properties are those of their surfaces.

Total interfacial area (NA_p) per 1cm³ of colloid is given by,

$$NA_p = N4\pi R^2 = 4\pi R^2 \Phi / (4/3\pi R^3) = 3\Phi/R$$

Where R = radius, Φ = volume fraction

Number of particles per 1cm³ of colloid

$$N = \Phi/V_p = \Phi / (4/3\pi R^3)$$

The large area emphasizes surface effects relative to volume effects, giving colloids different properties than those of bulk matter. For example, if a cubic centimeter of water were divided into 10 nm cubes as above, the coalescence of the cubes would release enough surface energy to heat the water by about 10 °C more than its boiling point. In any colloidal system, there must be at least one structural dimension of colloidal size in order for the large surface area to exist in a limited volume, however. This broadened definition of colloid is not only reasonable, it is useful. Colloids are generally known as sols

Colloid particles show electrical, optical, mechanical and kinetic properties due to their size and surface properties. Because of these properties colloidal systems have many applications in various industries like food industry (diary products, chocolate etc.), pharmaceutical and cosmetic industry (gels and emulsions), Photographic industry (films, carbon paper, ink etc.), Electrical and electronic industry (liquid crystals, isolating materials etc), paint industry and agrochemical industry.

Table 7.1. Characteristics of Suspension, Colloid and Solution

S. No.	Properties	Suspension	Colloid	Solution
1.	Particle size	>100nm	1-100nm	<1nm
2.	Separation 1)ordinary filtration 2) ultra filtration	possible possible	not possible possible	not possible not possible
3.	Settling	Settles under gravity	Settles on Centrifugation	Does not settle
4.	Appearance	opaque	Generally clear	clear
5.	Diffusion	Not possible	Diffuses slowly	Diffuses rapidly
6.	Brownian motion	shows	shows	Not observable
7.	Tyndall effect	shows	shows	Not observable

7.2. Classification of Colloids

Colloids can be mainly classified, based on dispersion medium and dispersion phase (or) based on affinity of dispersion phase towards dispersion medium (or) type of particles in dispersed phase.

7.2.1. Classification based on the state of the dispersed phase and the dispersion medium

Basing on different dispersed phases and dispersion medium, Colloids can be classified in to eight systems as shown in Table 7.2.

Table 7.2. Types of colloids

Dispersion Medium	Dispersed phase	Type of colloid	Example
Gas	Liquid	Aerosol	Fog, clouds
Gas	Solid	Aerosol	Smoke
Liquid	Gas	Foam	Whipped cream, soda water
Liquid	Liquid	Emulsion	Milk, hair cream
Liquid	Solid	Sol	Paints, cell fluids
Solid	Gas	Foam	Pumice, plastic foams
Solid	Liquid	Gel	Jelly, cheese
Solid	Solid	Solid Sol	Ruby glass

7.2.2. Classification of colloids based on type of particles of the dispersed phase

a) Multimolecular colloids: In this type of colloids the colloidal particles are aggregates of atoms or small molecules with molecular size less than one nanometer (1 nm). They have usually lyophobic character.

Ex. gold and sulphur sols

b) Macromolecular colloids: Macromolecular colloidal particles are formed when on dissolution in a suitable solvent, the macromolecules have sizes which are in the colloidal range. These colloids are quite stable and resemble true solutions in many respects.

Ex: proteins, cellulose, starch and polymers such as polyethylene, nylon and polystyrene form these type of sols.

c) Associated colloids (Micelles): These are the substances (surfactants) which on dissolved in a medium behave as normal electrolytes at low concentration but behave, as

colloidal particles at higher concentration due to the formation of aggregated particles. The aggregates particles thus formed are called micelles. Normal micelle will be having head group outside and hydrophobic group forming a core but where as reverse micelle will be having hydrophobic group outside and hydrophobic group in the core. which type of micelle it forms depends on the nature of solvent (hydrophilic or hydrophobic).The formation of micelles takes place only above a particular temperature called Kraft Temperature (T_k) and above particular concentration called the Critical micelle concentration (CMC). Micelles have both a lyophilic and lyophobic parts. Micelles may consist of more than 100 molecules. Ex: soaps and synthetic detergents form associated colloids in water

7.2.3. Classification based on the nature of interaction between the dispersed phase and the dispersion medium

Table 7.3. Distinguition between lyophilic and lyophobic colloids

Property	Lyophilic sols (suspensoid)	Lyophobic sols (Emulsoid)
Surface tension	Lower than that of the medium	Same as that of the medium
Viscosity	Much higher than that of the medium	Same as that of the medium
Reversibility	Reversible	Irreversible
Stability	More stable	Less stable
Visibility	Particles can't be detected even under ultramicroscope	Particles can be detected under ultramicroscope.
Migration	Particles may migrate in either direction or do not migrate in an electric field because do not carry any charge.	Particles migrate either towards cathode or anode in an electric field because they carry charge.
Action of electrolyte	Addition of smaller quantity of electrolyte has little effect	Coagulation takes place
Hydration	Extensive hydration takes place	No hydration
Examples	Gum, gelatin, starch, proteins, rubber etc.	Metals like Ag and Au, hydroxides like $Al(OH)_3$, $Fe(OH)_3$ metal sulphides like AS_2S_3 etc.

Basing on affinity of dispersed phase for dispersion medium, colloids can be classified in to lyophilic colloids (solvent loving) and lyophobic colloids (solvent hating).Differences between them is tabulated in Table 7.3.

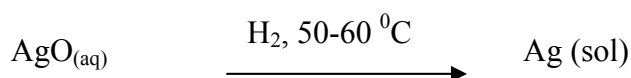
7.3. Preparation of colloids

Lyophilic sols which are stable can be obtained when warmed with a suitable solvent whereas lyophobic sols which are unstable and irreversible have to be obtained by special methods. Two methods that are mainly used are:

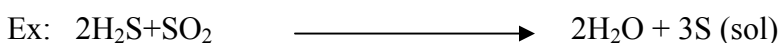
7.3.1. Condensation or aggregation method: In this method the particles in true solutions are allowed to grow in size to particles of colloidal dimensions. Chemical reactions or by physical changes under controlled conditions of temperature and concentration can be used to achieve these.

7.3.1.1. Chemical methods

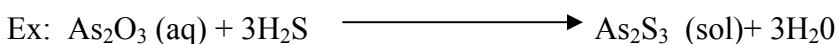
i) By Reduction: Metal sols are generally prepared by this method. The method involves reduction of soluble metal salts by reducing agents such as hydrogen, hydrazine (N₂H₄), formaldehyde (HCHO) etc.,



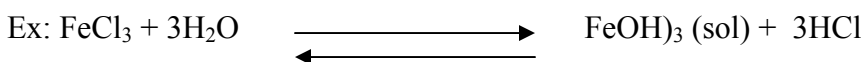
ii) By Oxidation: Sulphur sols are easily obtained by the oxidation of aqueous hydrogen sulphide solution by sulphur dioxide, nitric acid or bromine water.



iii) By double decomposition: By mixing two salt solutions, their constituents are being exchanged and one of the products gets precipitated and is stabilized by excess of cations or anions present.



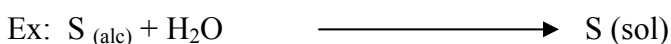
By hydrolysis: This method is used to obtain sols of oxides or hydroxides of weakly electropositive metals like iron, aluminum, chromium etc by hydrolyzing their chlorides or nitrates. Excess ions will catalyze the sols.



7.3.1.2. Physical methods

i) By excessive cooling: A colloidal solution of ice in an organic solvent like ether or chloroform can be prepared by freezing a solution of water in the solvent. The molecules of water which can no longer be held in solution separately combine to form particles of colloidal size.

ii) By exchange of solvent: Colloidal solution of certain substances such as sulphur, phosphorus, which are soluble in alcohol but insoluble in water can be prepared by pouring their alcoholic solution in excess of water.



iii) By change of physical state: Sols of substances like mercury and sulphur are prepared by passing their vapour's through cold water containing a suitable stabilizer such as ammonium salt or citrate.

iv) Dispersion method: In this method bigger particles are reduced in size of colloidal dimensions which remain in the dispersion medium. Various methods used in dispersion are:

(a) Mechanical disintegration: In this method, the substance is first ground to coarse particles, which is mixed with the dispersion medium in order to get a suspension. The suspension along with a protective agent is then grinded in colloidal mill. Colloidal mill consists of two metallic discs nearly touching each other and rotating in opposite directions at a very high speed about 7000 revolution per minute. The space between the discs of the mill is so adjusted that coarse suspension is subjected to great shearing force giving rise to particles of colloidal size. Colloidal solutions of black ink, paints, varnishes, dyes etc. and food products like concentrated milk, food additives etc. are also obtained by this method.

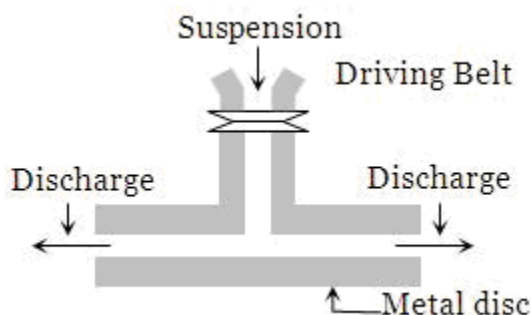
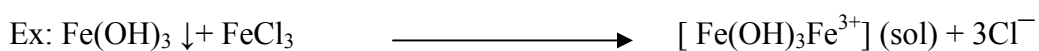


Fig. 7.1. Pictorial view of colloidal mill

(b) Peptization: The process of dispersing a precipitate in to a colloidal solution by adding small quantity of electrolyte is called peptization. The electrolyte is used for this purpose is called peptizing agent or stabilizing agent. The ions of electrolyte get adsorbed on to precipitate making them charged.



(c) Bredig's arc method:

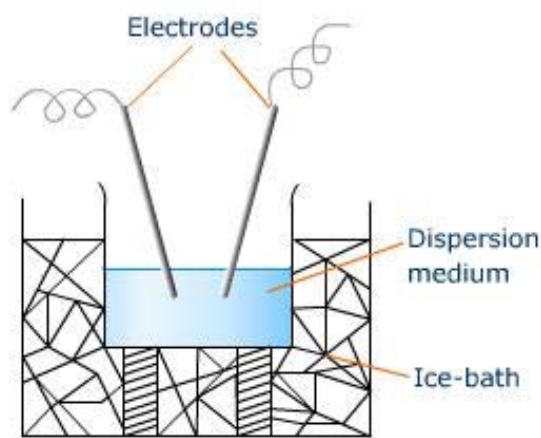


Fig. 7.2. Bredig's arc method

This method is used to prepare sols of platinum, silver, copper or gold. The metal whose sol is to be prepared is made as two electrodes which immersed in dispersion medium such as water etc. The dispersion medium is kept cooled by ice. An electric arc is struck between the electrodes. The generated heat evaporates the metal and the vapours are condensed in water. Traces of KOH are required to stabilize the colloidal solution.

7.3.1.3. General methods used in the preparation of colloids:

The following methods are usually used to prepare other colloidal systems:

- a) Aerosol is formed by passing gas jet to a liquid spray. This process helps in separating the liquid into droplets with electrostatic repulsions, done by applying a charge to the liquid.
- b) Emulsions are usually prepared by vigorously shaking the two constituents together, often with the addition of an emulsifying agent, in order to stabilize the product formed. The function of emulsifying agent is to reduce the interfacial tension between two liquids forming emulsion. Emulsions can be classified into two types, namely, (i) oil in water emulsions and (ii) water in oil emulsions. Which emulsion is formed is decided by excess one, as one in excess forms the outer layer and other forms the inner layer. The phase in which emulsifier is more soluble forms the outer layer. Emulsions show similar characteristics to that of lyophobic colloids.
- c) Gels are often formed by cooling lyophilic sols that contain large linear molecules and have a much greater viscosity than the solvent. Gels are broadly divided into two types, i.e., elastic and rigid gels. An elastic gel, For ex: gum, on partial loss of water becomes an elastic solid and on addition of water it retains back its former state but where as rigid gels, For ex., Silica which loses its elasticity on dehydration can't come back to original on water addition.
- d) Foams are formed when gas and liquid are mixed together in a container and shaken along with a foaming agent. Foaming agent, for ex: surfactants, macromolecules or finely divided solids, decrease the surface tension and it forms a protective layer on bubble avoiding its coalescence with another bubble.

7.4. Purification of colloidal solutions

Colloidal solutions prepared by the above methods contain some soluble impurities and excess of electrolytes; these have to be removed to obtain pure sols. Generally, Dialysis, ultra filtration and ultra centrifugation are used to achieve this purpose.

7.4.1. Dialysis

We know that colloidal particles cannot be passed through parchment paper. This property is used in dialysis. The colloidal solution kept in parchment bag is dipped in beaker containing water, so that impurities may pass into aqueous medium leaving the colloidal particles inside the bag. The aqueous solution is renewed on timely basis to avoid rediffusion of impurities back into parchment bag. Pure colloidal solution is left inside the parchment paper. In some sols, particles of dispersed phase are too small to be retained by cellophane. Therefore, dialysis is carried out at high temperature which allows growth in particle size. This is known as hot dialysis. To make this process faster process of electrolysis in which two electrodes are dipped in the solvent and electric field is applied. On passing an electric current, ionic impurities migrate out of colloidal solutions. The entire process is called electro-dialysis. The same process is used for purification of blood in case of kidney failure.

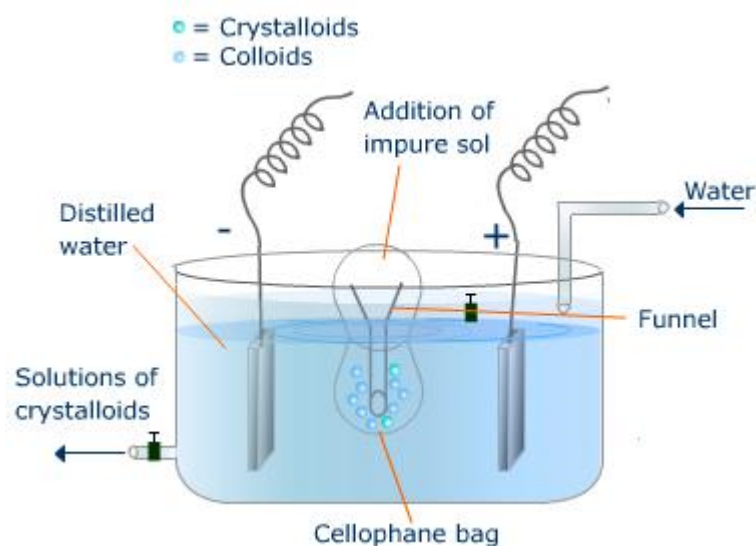


Fig. 7.3. Electro-dialysis

7.4.2. Ultra filtration

In this method, colloidal sols are filtered through graded filters called ultra-filtrers. These ultra-filters are normal filter paper treated with solution of gelatin or colloidon and

subsequently hardening them by soaking in formaldehyde in order to decrease the pore size of filter paper such that it will restrict the passage of colloidal particles.

7.4.3. Ultra-centrifugation

This method is used to separate colloidal particles from the impurities by centrifuging the colloidal sol. Centrifugation is carried out in a centrifuging machine where the tube containing the colloidal sol is rotated at very high speeds. The colloidal particles settle down at the bottom of the tube and the impurities remain in the solution called centrifugate. The settled colloidal particles are then mixed with an appropriate dispersing medium to regenerate the sol.

It is important to note that above methods to purify colloidal solution do not produce 100% solution. Absolute purity is not required as well as traces of small amount of electrolytes (impurities) are necessary for stability of colloidal solution.

7.5. Properties of Colloids

7.5.1. Optical properties

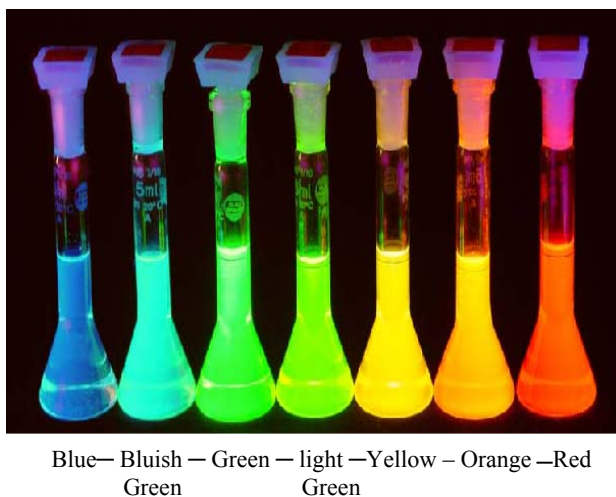


Fig. 7.4. Size dependent change of colour in Au sol

Colloidal solutions are colored color of the sol depends on the size and shape of the colloidal particles. In Figure 4, how Au sol colour is changed with vary in Au particle size is shown as particle size is increased, Au sol colour changes from red to blue. All colloids exhibit Opalescence, it is a type of dichroism seen in highly dispersed systems.

The material appears yellowish-red in transmitted light and blue in the scattered light perpendicular to the transmitted light. The best example to explain this is sky as when we look at cloudless sky against dark background of space it looks bluish but when seen against source of light it appears reddish. This also varies with size of particles and degree of dispersion.

Opalescence in colloids is due to scattering of light by particles. This effect was studied by Tyndall and is generally known as Tyndall effect. If a beam of light is passed through a colloidal solution in a dark room, solution becomes luminescent when viewed through a microscope at right angle to the path of incident light. Tyndall observed that scattered beam to be polarized and intensity of the same to be dependent on position of observer, nature of system and wavelength of light used.

7.5.2. Colligative properties of colloidal solutions

Colloidal solutions exhibit colligative properties, i.e., lowering of vapour pressure, elevation in boiling point, depression in freezing point and osmotic pressure in the same way as the true solutions of electrolytes and non-electrolytes do. However, the magnitudes of these properties for colloidal solutions are much smaller than those obtained for true solutions. This is because colloidal particles exist as aggregates. For a given mass of the substance, the number of colloidal particles present in the colloidal solution of the substance will be much less than the number of particles present in its true solutions. Since a colligative property depends upon the number of particles, a colloidal solution will exhibit much lower value of a colligative property as compared to that exhibited by a true solution having the same mass of the same substance. As colloidal solutions have low values of colligative properties, it is quite difficult to measure them accurately. However, they exhibit measurable osmotic pressures. The osmotic pressures of colloidal solutions can be measured with a reasonable degree of accuracy. This property is used for the determination of the average molecular masses of the colloids.

7.5.3. Kinetic property

Particles suspended in a liquid undergoes continuous chaotic and random motions. This motion of the particles is called Brownian motion, named after the botanist, Robert

Brown. This motion is due to constant molecular impacts on dispersed particles on all directions by medium. This Brownian motion is found to increase by increase in particle size or by increase in viscosity of medium.

The study of optical and kinetic properties of colloids was made easy with the invention of ultra microscope by Zsigmondy in 1903. The pictorial view of this is shown in figure 5. A strong beam of light is passed through colloidal solution which is viewed in a microscope placed at right angle to the source of light. The colloidal particles appear as bright spots against a dark background. The radius of the particles can be calculated by using the equation;

$$r = (3bv / 4\pi nd)^{1/3}$$

where, b = number of grams of substance per dm^3

n = number of particles observed in view

v = volume dm^3

d = density of dry substance

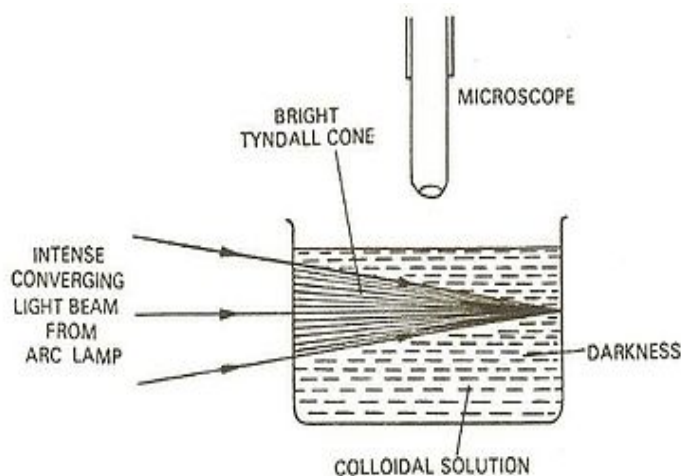


Fig. 7.5. Schematic drawing of ultra microscope

7.5.4. Electrical properties

Lyophobic sols carry charge, because of which they get repelled on approaching another particle avoiding their coagulation. All particles will be having opposite and equal charge to dispersion medium making whole system neutral. Metallic hydroxides and metal such

as bismuth, lead, iron etc. are positively charged where as metallic sulphides and metals such as gold, silver, platinum etc. are negatively charged.

The origin of charge on colloidal particles is due to the following reasons:

(a) Sols are generally associated with minute amounts of electrolytes and their presence is responsible for sols stability. The charge on the colloidal particles is due to preferential adsorption of either positive or negative ions on their surface.

Ex: (i) positive charge on ferric hydroxide sol prepared by hydrolysis of ferric chloride is due to adsorption of Fe^{3+} ions on surface.

(ii) An ionic colloid adsorbs ions common to its own lattice structure. For e.g., AgCl particles can adsorb Cl^- ions if excess of KCl solutions is used for its preparation where as the same colloid can adsorb Ag^+ ion if AgNO_3 solution is used. Hence in the first case, AgCl colloid will be negatively charged while in the second case it will be positively charged.

(b) Colloids can get charged by dissociation of molecular electrolytes adsorbed on the surface of particles. This happens in the case where H_2S molecules get adsorbed on sulphides during precipitation. H_2S undergoes dissociation and the hydrogen ions are lost. The particles become negatively charged due to (S^{2-}) which are left on the colloidal particles.

(c) Colloids can acquire charge by dissociation of surface molecules. For e.g., soaps expel alkali ions to acquire a negative charge. Proteins have both acidic and basic groups in its structure. In acidic solution, it acquires positive charge due to protonation of basic groups and in basic solution it acquires negative charge due to ionization of basic groups. The pH at which net charge on the molecule is zero is called isoelectric point and molecule at this point is called zwitter ion as it has both positive and negative charge with net charge equal to zero. The stability of zwitter ions is less.

Development of a net charge at the particle surface affects the distribution of ions in the surrounding interfacial region, resulting in an increased concentration of counter ions (ions of opposite charge to that of the particle) close to the surface. Thus an electrical double layer exists round each particle. An electrical double layer exists around each

particle. The liquid layer surrounding the particle exists as two parts; an inner region (Stern layer) where the ions (oppositely charged to net charge) are strongly bound and an outer (diffuse) region where they are less firmly associated. The influence of net charge decreases with distance and so the number of oppositely charged ions, equaling the number of ions of both charges prevailing electro neutrality.

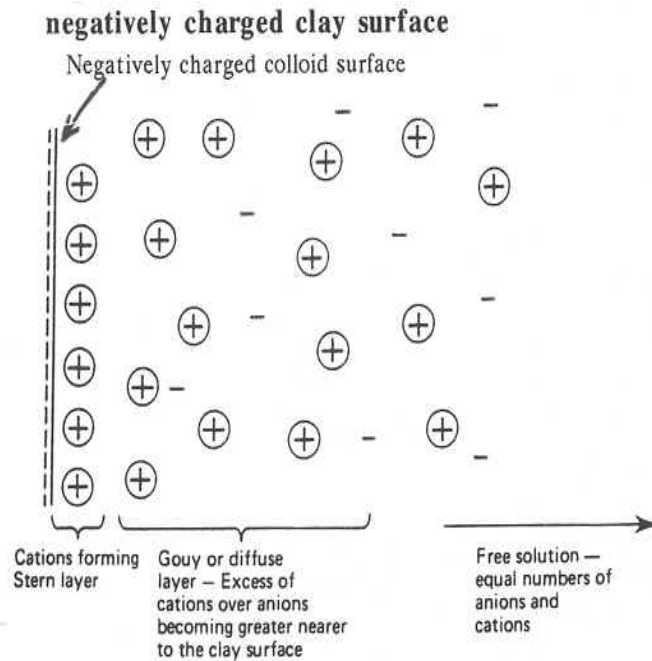


Fig. 7.6. Electrical double layer

The diffuse layer between stern layer and electrically neutral part of system is known as Guoy-Chapman layer. The difference in potential between the surface of shear plane and electro neutral region of solution is called Zeta potential (ζ), which is given by Helmholtz- Smoluchowski equation.

$$\zeta = 4\pi\eta u/\epsilon_r$$

where η = viscosity of dispersion medium

ϵ_r = relative permittivity of dispersion medium

u = mobility of colloidal particle

The addition of oppositely charged ions to colloidal sol decreases the repulsion between two particles and they come together to form a bigger particle. The phenomenon of changing colloidal state to a suspension is known as coagulation or flocculation. Coagulation can be achieved by large amounts of electrolytes as colloidal particles adsorb oppositely charged species reducing their repulsion. Hardy and Schulz formulated some rules on coagulation;

- (i) Coagulation is brought about by ions having opposite charge to that of the sol.
- (ii) The efficiency of an ion to cause coagulation depends upon the square of its valency. Thus efficacy of cations $\text{Al}^{3+} > \text{Mg}^{2+} > \text{Na}^+$ and $\text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{Cl}^-$.
- (iii) The minimum concentration of an electrolyte required to cause coagulation of a sol is called its flocculation value. Generally lyophobic sols are coagulated by electrolytes at 0.0001 – 0.1 M concentration and are reversible. On the other hand lyophilic sols require high amounts of electrolytes (usually 1M) for coagulation. Their coagulation is due to removal of solvation water as electrolytes binds them. Thus efficacy of cations $\text{Al}^{3+} > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Ba}^{2+} > \text{Na}^+ > \text{K}^+$ and efficacy of anions $\text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^- > \text{ClO}_3^- > \text{I}^-$ for coagulation of lyophilic sols and this is known as lyotropic series or Hofmeister series.

The other methods to coagulate sol are by mutual mixing of oppositely charged sols, persistent dialysis and by mechanical means.

In the case of lyophilic sols, water of solvation (cage of water surrounding) prevents particles from coagulation. When lyophilic sol is added to a lyophobic sol, later found to be more resistant to precipitating action of electrolyte as lyophilic sol captures lyophobic sol inside them. Therefore, gelatin, gum etc are known as protective colloids. Zsigmondy quantified stabilizing action of protective colloids by gold number, which is defined as largest number of milligrams of a protective colloid when added to 10 ml of standard gold sol, just fails to prevent the colour change from red to blue upon addition of 1 ml of 10% sodium chloride solution. The protective action of lyophilic sol is influenced by sol dispersity, molecular mass of lyophilic sol and pH of solution at which experiment is carried out.

The phenomenon of movement of colloidal particles under an applied electric field is called electrophoresis. The positively charged particles accumulate near the

negative electrode and vice versa. By the movement of particles in electric field we can determine their charge. The rate at which colloidal particles migrate in a electric field is given by electrophoresis mobility, distance traveled by a particle in one second under a potential gradient of one volt per centimeter. This effect is studied by an apparatus consisting of a U-tube with two Pt-electrodes in each limb. When electrophoresis of a sol is carried out with out stirring, the bottom layer gradually becomes more concentrated while the top layer which contains pure and concentrated colloidal solution may be decanted. This is called electro decanation and is used for the purification as well as for concentrating the sol. The reverse of electrophoresis is called Sedimentation potential or Dorn effect. The sedimentation potential is setup when a particle is forced to move in a resting liquid. This phenomenon was discovered by Dorn and is also called Dorn effect.

Electro-osmosis is a phenomenon in which dispersion medium is allowed to move under the influence of an electrical field, whereas colloidal particles are not allowed to move.

7.6. Applications of colloids

7.6.1. Purification of water by alum (coagulation)

Water contains colloidal impurities .These impurities can be weeded out by using electrolyte like Alum. Alum is positively charged Al^{3+} ion which attracts negatively charged colloidal impurities. These neutralized particles settle down and pure water is decanted off. Thus Alum is used to remove dirt and impurities present in the colloidal solution.

7.6.2. In rubber and tanning industry (coagulation and mutual coagulation)

Several industrial processes such as rubber plating, chrome tanning, dyeing, lubrication etc are of colloidal nature

i) In rubber plating, the negatively charged particles of rubber (latex) are made to deposit on the wires or handle of various tools by means of electrophoresis. The article on which rubber is to be deposited is made anode.

ii) In tanning the positively charged colloidal particles of hides and leather are coagulated by impregnating, them in negatively charged tanning materials (present in the barks of trees). Among the tanning agent chromium salts are most commonly used for the coagulation of the hide material and the process is called chrome tanning.

7.6.3. Artificial rains

It is possible to cause artificial rain by throwing the electrified sand or silver iodide from an aeroplane and thus coagulating the mist hanging in air. Cloud consists of charged particles of water dispersed in air. These particles are neutralized by spraying oppositely charged particles over a cloud. These neutralized particles of water combine to form large water drops. Thus, artificial rain is caused by the aggregation of minute particles of water to form large particles.

7.6.4. Smoke precipitation (Coagulation)

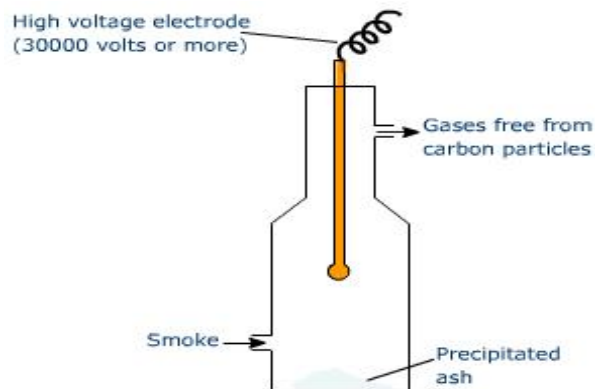


Fig. 7.7. Schematic diagram of Cottrell smoke precipitator

Smoke particles are the electrically charged colloidal particle suspended in air. To remove these particles from air, Cottrell precipitator is used. Cottrell precipitator uses principle of electrophoreses (movement of colloidal particles under influence of electric field) to weed out smoke particles. Air containing smoke and dust particles are allowed to pass through metal electrodes present inside Cottrell precipitator. These charged particles

moves towards oppositely charged electrodes and get deposited there from which they are scrapped mechanically.

7.6.5. Formation of deltas (coagulation)

River water consists of negatively charged clay particles of colloidal dimension. When the river falls into the sea, the clay particles are coagulated by the positive Na^+ , K^+ , Mg^{2+} ions etc. present in sea water and new lands called deltas are formed.

7.6.6. Clot formation

Blood consists of negatively charged colloidal particles (albuminoid substance). The colloidal nature of blood explains why bleeding stops by applying a ferric chloride solution to the wound. Actually ferric chloride solution causes coagulation of blood to form a clot which stops further bleeding.

7.6.7. Colloidal medicine

Argyrol and protargyrol are colloidal solution of silver and are used as eye lotions .Colloidal sulphur is used as disinfectant and colloidal gold, calcium and iron are used as tonics. A wide variety of medicines are emulsions. For ex: Cod Liver Oil.

7.6.8. Coating of photographic plates

These are thin glass plates coated with gelatin containing a fine suspension of silver bromide. The particles of silver bromide are colloidal in nature.

7.6.9. Sewage disposal

Dirt and mud particles are electrically charged. By applying electric field in sewage tank, dirt particles reach the oppositely charged electrode, get neutralized and are coagulated. These coagulated particles are suspended in solution and are easily removed.

7.6.10. Metallurgy

In metallurgical operations the metal ores are concentrated by froth-flotation process which involves the treatment of the pulverized ore in emulsion of pine oil.

7.7. Conclusion

Colloids present in every part of our daily life. It was classified by 3 different ways. Various preparation procedures of colloids were discussed. The properties of colloids which make them special are explained here along with some of their applications in daily life. Over all a brief overview of the topic was presented here.

Problems:

1) L-arginine isoelectric point is 11.5, at what pH range it can be used to coagulate noble metal nano particles? (Answer: below 11.5)

2) What is emulsifying agent in milk? (Answer: protein casein)

3) The silver iodide sol is (Answer: c)
a) positively charged b) negatively charged c) neutral d) positive or negative

4) When a solution of NaCl is added to $\text{Fe}(\text{OH})_3$ sol (Answer: d)
a) $[\text{Fe}(\text{OH})_3\text{Fe}^{3+}]$ is formed b) $[\text{Fe}(\text{OH})_3\text{Na}^+]$ is formed
c) $[\text{Fe}(\text{OH})_3\text{Cl}^-]$ is formed d) $\text{Fe}(\text{OH})_3$ is coagulated

5) one day, your biology teacher asked you to visualize hibiscus tip using a microscope. Out of your curiosity you calculated volume fraction of pollen grains to be 0.4 and suppose if numbers of pollen grains are 1.2×10^6 what is the radius of pollen grain and what is its interfacial area?

(Answer: $R = 20 \text{ nm}$ and total interfacial area = 60 m^2)

6) Aluminum sulphate is more effective in coagulating turbid water than sodium sulphate. Why?

7) On holi, you want to make a red colour solution, for that you mixed 50 gm of colour in to one litre of water. The density of the colour is 1.5. After mixing, if you are able to count 500 colored particles, what will be the radius of particle?

8) While preparing starch gel, a metal salt is added. Why?

9) What are the methods used to measure critical micelle concentration of a surfactant?

10) what type of a colloid is thermocol?

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1. A. S. Negi and S. C. Anand, A Textbook of Physical Chemistry, New Age International (p) limited, 1998, 744 – 759.
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CHAPTER - 8

FARADAY'S LAWS AND APPLICATIONS OF KOHLRAUSCH'S LAW

P. Ramana Murthy

8.1. Chemistry and electricity and Introduction

The connection between chemistry and electricity is a very old one, going back to Alessandro Volta's discovery, in 1793, that electricity could be produced by placing two dissimilar metals on opposite sides of a moistened paper. In 1800, Nicholson and Carlisle, using Volta's primitive battery as a source, showed that an electric current could decompose water into oxygen and hydrogen. This was surely one of the most significant experiments in the history of chemistry, for it implied that the atoms of hydrogen and oxygen were associated with positive and negative electric charges, which must be the source of the bonding forces between them. By 1812, the Swedish chemist Berzelius could propose that all atoms are electrified, hydrogen and the metals being positive, the nonmetals negative. In electrolysis, the applied voltage was thought to overpower the attraction between these opposite charges, pulling the electrified atoms apart in the form of ions (named by Berzelius from the Greek for "travelers"). It would be almost exactly a hundred years later before the shared electron pair theory of Gilbert Newton Lewis could offer a significant improvement over this view of chemical bonding. Meanwhile the use of electricity as a means of bringing about chemical change continued to play a central role in the development of chemistry. Humphry Davy prepared the first elemental sodium by electrolysis of a sodium hydroxide melt. It was left to Davy's former assistant, Michael Faraday, to show that there is a direct relation between the amount of electric charge passed through the solution and the quantity of electrolysis products. James Clerk Maxwell immediately saw this as evidence for the "molecule of electricity", but the world would not be receptive to the concept of the electron until the end of the century.

8.2. Classification of Conductors

All forms of matter appear to be able to conduct the electric current to some extent, but the conducting powers of different substances vary over a wide range; thus silver, one of

the best conductors, is 10^{24} times more effective than paraffin wax, which is one of the poorest conductors. It is not easy to distinguish sharply between good and bad conductors, but a rough division is possible; the systems studied in electrochemistry are generally good conductors. These may be divided into three main categories; they are: (I) gaseous, (II) metallic and (III) electrolytic.

8.2.1. Gases conduct electricity with difficulty and only under the influence of high potentials or if exposed to the action of certain radiations. Metals are the best conductors, in general, and the passage of current is not accompanied by any movement of matter; it appears, therefore, that the electricity is carried exclusively by the electrons, the atomic nuclei remaining stationary. This is in accordance with modern views which regard a metal as consisting of a relatively rigid lattice of ions together with a system of mobile electrons. Metallic conduction or electronic conduction as it is often called, is not restricted to pure metals, for it is a property possessed by most alloys, carbon and certain solid salts and oxides.

8.2.2. Metallic or electronic conductors

Conductors which transfer electric current by transfer of electrons, without transfer of any matter, are known as metallic or electronic conductors. Metals such as copper, silver, aluminum, etc., non-metals like carbon (graphite - an allotropic form of carbon) and various alloys belong to this class. These materials contain electrons which are relatively free to move. The passage of current through these materials has no observable effect other than a rise in their temperature.

8.2.3. Electrolytic conductors

Conductors like aqueous solutions of acids, bases and salts in which the flow of electric current is accompanied by chemical decomposition are known as electrolytic conductors. The substances whose aqueous solutions allow the passage of electric current and are chemically decomposed, are termed electrolytes. The substances whose aqueous solutions do not conduct electric current are called non-electrolytes. Solutions of cane sugar, glycerine, alcohol, etc., are examples of non-electrolytes.

In order to account for the phenomenon observed during the passage of an electric current through solutions, Faraday (1833) assumed that the flow of electricity was associated with the movement of particles of matter carrying either positive or negative charges. These charged particles were called ions; the ions carrying positive charges and moving in the direction of the current, i.e., towards the cathode, were referred to as cations, and those carrying a negative charge and moving in the opposite direction, i.e., towards the anode, were called anions (see Fig. 8.1). The function of the applied E.M.F. is to direct the ions towards the appropriate electrodes where their charges are neutralized and they are set free as atoms or molecules. It may be noted that since hydrogen and metals are discharged at the cathode, the metallic part of a salt or base and the hydrogen of an acid form cations and carry positive charges. The acidic portion of a salt and the hydroxyl ion of a base consequently carry negative charges and constitute the anions.

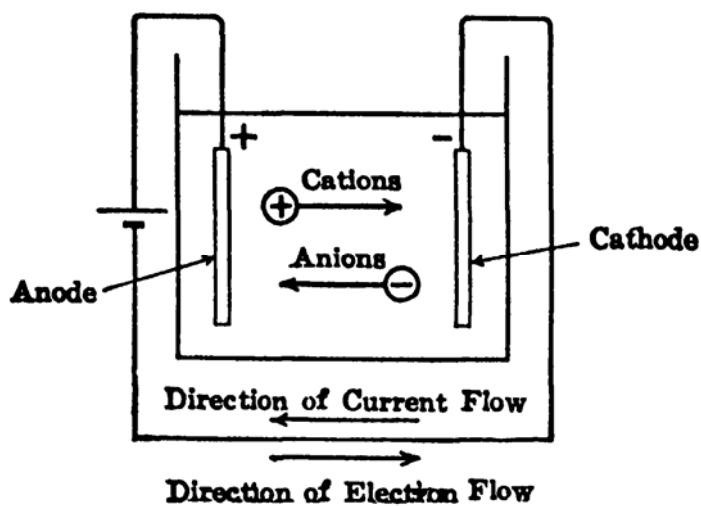


Fig. 8.1. Illustration of electro chemical terms

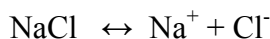
8.3. Electrolysis: Preferential discharge theory

If an electrolytic solution consists of more than two ions and the electrolysis is done, it is observed that all the ions are not discharged at the electrodes simultaneously but certain ions are liberated at the electrodes in preference to others. This is explained by preferential discharge theory. It states that if more than one type of ions are attracted towards a particular electrode, then the one discharged is the ion which requires least

energy. The potential at which the ion is discharge or deposition potential. The values of discharge potential are different for different ions. For example, the discharge potential of H^+ ions is lower than Na^+ ions when platinum or most of the other metals are used as cathodes. Similarly, discharge potential of Cl^- ions is lower than that of OH^- ions. This can be explained by some examples given below.

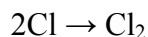
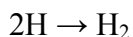
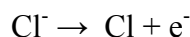
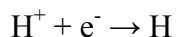
8.3.1. Electrolysis of sodium chloride solution

The solution of sodium chloride besides Na^+ and Cl^- ions possesses H^+ and OH^- due to ionization of water. However, the number is small as water is a weak electrolyte. When potential difference is established across the two electrodes, Na^+ and H^+ ions move towards cathode and Cl^- and OH^- ions move towards anode. At cathode H^+ ions are discharged in preference to Na^+ ions as the discharge potential of H^+ ions is lower than Na^+ ions. Similarly at anode, Cl^- ions are discharged in preference to OH^- ions.



At cathode

At Anode



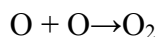
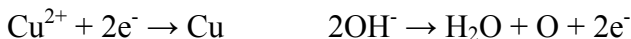
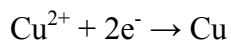
Thus, Na^+ and OH^- ions remain in solution and the solution when evaporated yields crystals of sodium hydroxide

8.3.2. Electrolysis of copper sulphate solution using platinum electrodes



At cathode

At Anode



Copper is discharged at cathode as Cu^{2+} ions have lower discharge potential than H^+ ions. OH^- ions are discharged at anode as these have lower discharge potential than ions. Thus, copper is deposited at cathode and oxygen gas is evolved at anode.

Table 8.1. Some more examples of electrolysis

Electrolyte	Electrode	Cathodic reaction	Anodic reaction
Aqueous acidified CuCl ₂	Pt	$\text{Cu}^{2+} + 2\text{e}^{-} \rightarrow \text{Cu}$	$2\text{Cl}^{-} \rightarrow \text{Cl}_2 + 2\text{e}^{-}$
Molten PbBr ₂	Pt	$\text{Pb}^{2+} + 2\text{e}^{-} \rightarrow \text{Pb}$	$2\text{Br}^{-} \rightarrow \text{Br}_2 + 2\text{e}^{-}$
Sodium chloride solution	Hg	$2\text{Na}^{+} + 2\text{e}^{-} \rightarrow 2\text{Na}$	$2\text{Cl}^{-} \rightarrow \text{Cl}_2 + 2\text{e}^{-}$
Silver nitrate solution	Pt	$\text{Ag}^{+} + \text{e}^{-} \rightarrow \text{Ag}$	$2\text{OH}^{-} \rightarrow 1/2 \text{O}_2 + \text{H}_2\text{O} + 2\text{e}^{-}$
Sodium nitrate solution	Pt	$2\text{H}^{+} + 2\text{e}^{-} \rightarrow \text{H}_2$	$2\text{OH}^{-} \rightarrow 1/2 \text{O}_2 + \text{H}_2\text{O} + 2\text{e}^{-}$

The decreasing order of discharge potential or the increasing order of deposition of some of the ions is given below:

For cations: K^{+} , Na^{+} , Ca^{2+} , Mg^{2+} , Al^{3+} , Zn^{2+} , H^{+} , Cu^{2+} , Hg^{2+} , Ag^{+}

For anions: SO_4^{2-} , NO_3^{-} , OH^{-} , Cl^{-} , Br^{-} , I^{-}

8.4. Faraday's laws of electrolysis

The laws, which govern the deposition of substances (In the form of ions) on electrodes during the process of electrolysis, is called Faraday's laws of electrolysis. These laws given by Michael Faraday in 1833.

8.4.1. Faraday's first law

It states that, the mass of any substance deposited or liberated at any electrode is directly proportional to the quantity of electricity passed. i.e., $W \propto Q$

W = Mass of ions liberated in gm,

Q = Quantity of electricity passed in Coulombs

= Current in Amperes (i) \times Time in second (t)

$$W \propto i \times t \text{ or } W = Z \times i \times t$$

In case current efficiency (η) is given, then

$$W = Z \times i \times t \times \eta/100$$

Where, Z = constant, known as electrochemical equivalent (ECE) of the ion deposited.

When a current of 1 Ampere is passed for 1 second (i.e., $Q = 1$), then, $W = Z$

Thus, electrochemical equivalent (ECE) may be defined as “the mass of the ion deposited by passing a current of one Ampere for one second (i.e., by passing Coulomb of electricity)”. Its unit is gram per coulomb.

Coulomb is the unit of electrical charge.

$$96500 \text{ Coulombs electrons} = 1 \text{ mole electrons.}$$

$$1 \text{ Coulomb} = 6.023 \times 10^{23} / 96500 = 6.85 \times 10^{18} \text{ electrons,}$$

$$\text{or } 1 \text{ electronic charge } 1.6 \times 10^{-19} \text{ Coulomb.}$$

8.4.2. Faraday's second law

It states that, when the same quantity of electricity is passed through different electrolytes, the masses of different ions liberated at the electrodes are directly proportional to their chemical equivalents (Equivalent weights).

$$W_1/W_2 = E_1/E_2 \text{ or } Z_1it / Z_2it \text{ or } Z_1/Z_2 = E_1/E_2 \quad (W = Zit)$$

Thus the electrochemical equivalent (Z) of an element is directly proportional to its equivalent weight (E), i.e., $E \propto Z$ or $E = FZ$ or $E = 96500 \times Z$

$$\text{Where, } F = \text{Faraday constant} = 96500 \text{ C mol}^{-1}$$

So, 1 Faraday = 1F = Electrical charge carried out by one mole of electrons.

$$1F = \text{Charge on an electron} \times \text{Avogadro's number.}$$

$$1F = e^- \times N = (1.602 \times 10^{-19} \text{c}) \times (6.023 \times 10^{23} \text{ mol}^{-1})$$

$$\text{Number of Faraday} = \text{number of electrons passed} / 6.023 \times 10^{23}$$

8.4.3. Faraday's law for gaseous electrolytic product for the gases, we use $V = It$
 $V_e/96500$

Where, V = Volume of gas evolved at S.T.P. at an electrode

V_e = Equivalent volume = Volume of gas evolved at an electrode at S.T.P. by 1 Faraday charge

8.5. Quantitative aspects of electrolysis

We know that, one Faraday (1F) of electricity is equal to the charge carried by one mole (6.023×10^{23}) of electrons. So, in any reaction, if one mole of electrons are involved, then that reaction would consume or produce 1F of electricity. Since 1F is equal to 96,500 Coulombs, hence 96,500 Coulombs of electricity would cause a reaction involving one mole of electrons.

If in any reaction, n moles of electrons are involved, then the total electricity (Q) involved in the reaction is given by, $Q = nF = n \times 96500 \text{ C}$

Thus, the amount of electricity involved in any reaction is related to,

- (i) The number of moles of electrons involved in the reaction,
- (ii) The amount of any substance involved in the reaction.

Therefore, 1 Faraday or 96,500 C or 1 mole of electrons will reduce,

(a) 1 mole of monovalent cation, (b) 1/2 mole of divalent cation, (c) 1/3 mole of trivalent cation, (d) 1/n mole of n valent cations.

8.5.1. D. I. Ohm's law

Metallic as well as electrolytic conductors obey Ohm's law which states the strength of current (i) flowing through a conductor is directly proportional difference (V) applied across the conductor and is inversely proportional to the resistance (R) of the conductor

$$I = V/R$$

R - Resistance in $V/A = \Omega$ (Ohm)

V - Voltage or potential difference in Volts, V

I - Current in Amperes, A

If a material has a resistance of 1Ω , it means that when applying a potential difference of 1 V , the current in the material is 1 A .

8.5.2. Conductance

Electricity is a study that is frequently explained in terms of opposites. The term that is the opposite of resistance is Conductance. Conductance is the ability of a material to pass electrons. The factors that affect the magnitude of resistance are exactly the same for conductance, but they affect conductance in the opposite manner. Therefore, conductance is directly proportional to area, and inversely proportional to the length of the material. The unit of conductance is the mho or Ω^{-1}

$$C = 1 / R \quad \dots (i)$$

8.5.2.1. Specific conductance or conductivity

The resistance of any conductor varies directly as its length (l) and inversely as its cross sectional area (a), i.e.,

$$R \propto l/a \text{ or } R \propto \rho l/a \quad \dots (ii)$$

Where ρ is called the specific resistance.

If $l = 1 \text{ cm}$ and $a = 1 \text{ cm}^2$, then

$$R = \rho \quad \dots (iii)$$

The specific resistance is, thus, defined as the resistance of one centimeter cube of a conductor.

The reciprocal of specific resistance is termed the specific conductance or it is the conductance of one centimeter cube of a conductor.

$$K = 1/\rho, \quad K = \text{kappa} - \text{the specific conductance} \quad \dots (iv)$$

Specific conductance is also called conductivity.

From Eq. (ii), we have $\rho = a/l \cdot R$ or $1/\rho = 1/a \cdot 1/R$

$$K = 1/a \times C \quad (1/z = \text{cell constant})$$

or Specific conductance = Conductance \times cell constant

The unit of specific conductance is $\text{ohm}^{-1} \text{ cm}^{-1}$.

In the case of electrolytic solutions, the specific conductance is defined as the conductance of a solution of definite dilution enclosed in a cell having two electrodes of unit area separated by one centimeter apart as shown in Fig.2.

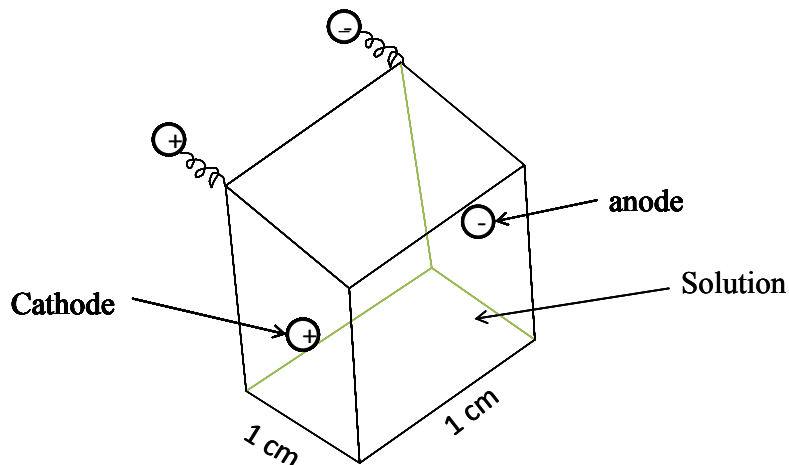


Fig. 8.2. Representation of specific conductance

8.5.2.2. Equivalent conductance

One of the factors on which the conductance of an electrolytic solution depends is the concentration of the solution. In order to obtain comparable results for different electrolytes, it is necessary to take equivalent conductances. Equivalent conductance is defined as the conductance of all the ions produced by one gram equivalent of an electrolyte in a given solution. It is denoted by Λ .

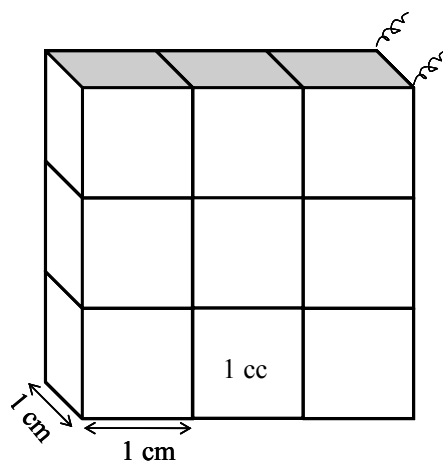


Fig. 8.3. Representation of equivalent conductance

To understand the meaning of equivalent conductance, imagine a rectangular trough with two opposite sides made of metallic conductor (acting as electrodes) exactly 1 cm apart. If 1 cm^3 (1 mL) solution containing 1 gram equivalent of an electrolyte is placed in this container is measured. According to definitions,

$$\begin{aligned} \text{Conductance} &= \text{Specific conductance (K)} \\ &= \text{Equivalent conductance } (\Lambda) \end{aligned}$$

If the solution is diluted to say 9 cm^3 (9 mL), the conductance of the solution will be the same but specific conductance becomes $1/9^{\text{th}}$ as it contains nine cubes. The conductance is also equal to the equivalent because the solution still has 1 g equivalent of the electrolyte. This is shown in Fig. 8.3. Thus,

$$\text{Equivalent conductance } (\Lambda) = 9 \times k$$

In general, $\Lambda = k \times V$ (v)

where V is the volume in mL containing 1 g equivalent of the electrolyte.

In case, if the concentration of the solution is c g equivalent per litre, then the volume containing 1 g equivalent of the electrolyte will be $1000/c$.

So equivalent conductance

$$\Lambda = k \times 1000/c \quad \dots (vi)$$

$$\Lambda = k \times 1000/N$$

Where N = normality

The unit of equivalent conductance is $\text{ohm}^{-1} \text{cm}^2 \text{equi}^{-1}$.

8.5.2.3. Molar conductance

The molar conductance is defined as the conductance of all the ions produced by ionization of 1 g mole of an electrolyte when present in V mL of solution. It is denoted by.

$$\text{Molar conductance } \Lambda_m = k \times V \quad \dots (vii)$$

Where V is the volume in mL containing 1 g mole of the electrolyte. If c is the concentration of the solution in g mole per litre, then

$$\Lambda_m = k \times 1000/c$$

Its units are $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$.

Equivalent conductance = (Molar conductance)/ n

Where $n = (\text{Molecular mass}) / (\text{Equivalent mass})$

8.5.2.4. Effect of dilution on equivalent conductance

The value of equivalent conductance increases with dilution. This is due to the fact that degree of ionization increases with dilution thereby increasing the total number of ions in solution. Solution which contains large number of ions compared to another solution of the same concentration at the same temperature has more conductances and is said to be stronger electrolyte. The one which has relatively small number of ions is called a weak electrolyte. The number of ions from an electrolyte depends on the degree of dissociation. The curve (Fig.4.) shows the variation of the equivalent conductance of some electrolytes with dilution. It shows that electrolytes behave in two ways on dilution.

(i) Electrolytes like KCl have high value of conductance even at low concentration and there is no rapid increase in their equivalent conductance on dilution. Such electrolytes

are termed strong electrolytes. In the case of strong electrolytes, there is a tendency for equivalent conductance to approach a limiting value when the concentration approaches zero. When the whole of the electrolyte has ionized, further addition of the water does not bring any change in the value of equivalent conductance. This stage is called infinite dilution. The equivalent conductance has a limiting value at infinite dilution and is represented by Λ_{∞} .

(ii) Electrolytes like acetic acid have a low value at high concentration and there is a rapid increase in the value of equivalent conductance with dilution. Such electrolytes are termed weak electrolytes. There is no indication that a limiting value of equivalent conductance can be attained even when the concentration approaches zero. Thus, graphically, Λ_{∞} of weak electrolytes cannot be obtained.

It is thus concluded that equivalent conductance of electrolytes whether strong or weak increases with dilution and reaches to a maximum or limiting value which is termed Λ_{∞} (equivalent conductance at infinite dilution.). Λ_{∞} in the case of strong electrolytes cannot be obtained by extrapolation of the graph of equivalent conductance to zero concentration but in the case of weak electrolytes it cannot be obtained accurately. An indirect method for obtaining Λ_{∞} for weak electrolyte has been given by Kohlrausch.

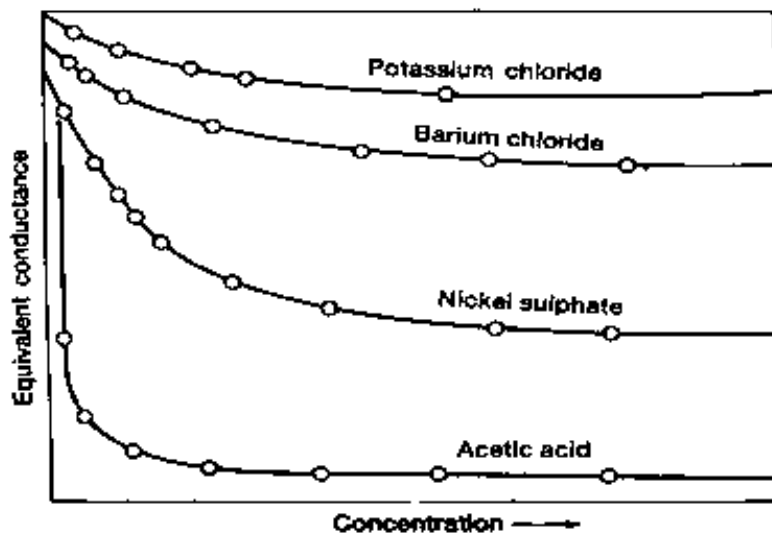


Fig . 8.4. Conductance's of electrolytes of different type

8.6. Kohlrausch law

Kohlrausch law states that, "At time infinite dilution, the molar conductivity of an electrolyte can be expressed as the sum of the contributions from its individual ions" i.e.

$\Lambda_m^\infty = v_+ \lambda_+^\infty + v_- \lambda_-^\infty$. Where, v_+ and v_- are the number of cations and anions per formula unit of electrolyte respectively and, λ_+^∞ and λ_-^∞ are the molar conductivities of the cation and anion at infinite dilution respectively. The use of above equation in expressing the molar conductivity of an electrolyte is illustrated as, the molar conductivity of HCl at infinite dilution can be expressed as,

$$\Lambda_{\text{HCl}}^\infty = V_{\text{H}^+} \lambda_{\text{H}^+}^\infty + V_{\text{Cl}^-} \lambda_{\text{Cl}^-}^\infty; \text{ For HCl, } V_{\text{H}^+} = 1 \text{ and } V_{\text{Cl}^-} = 1.$$

$$\Lambda_{\text{HCl}}^\infty = (1 \times \lambda_{\text{H}^+}^\infty) + (1 \times \lambda_{\text{Cl}^-}^\infty)$$

$$\Lambda_{\text{HCl}}^\infty = \lambda_{\text{H}^+}^\infty + \lambda_{\text{Cl}^-}^\infty$$

8.6.1. Applications of Kohlrausch's law

Some typical applications of the Kohlrausch's law are described below.

8.6.1.1. Determination of Λ_m^∞ for weak electrolytes

The molar conductivity of a weak electrolyte at infinite dilution (Λ_m^∞) cannot be determined by extrapolation method. However, Λ_m^∞ values for weak electrolytes can be determined by using the Kohlrausch's equation.

$$\Lambda_{\text{CH}_3\text{COOH}}^\infty = \Lambda_{\text{CH}_3\text{COONa}}^\infty + \Lambda_{\text{CHI}}^\infty - \Lambda_{\text{NaCl}}^\infty$$

8.6.1.2. Determination of the degree of ionization of a weak electrolyte

The Kohlrausch's law can be used for determining the degree of ionization of a weak electrolyte at any concentration. If λ_m^c is the molar conductivity of a weak electrolyte at any concentration C and, λ_m^∞ is the molar conductivity of a electrolyte at infinite dilution.

Then, the degree of ionization is given by, $a_c = \Lambda_m^c = \Lambda_m^\infty = \Lambda_m^c / (v_+ \lambda_+^\infty + v_- \lambda_-^\infty)$

Thus, knowing the value of Λ_m^c , and Λ_m^∞ (From the Kohlrausch's equation), the degree of ionization at any concentration (a_c) can be determined.

8.6.1.3. Determination of the ionization constant of a weak electrolyte

Weak electrolytes in aqueous solutions ionize to a very small extent. The extent of ionization is described in terms of the degree of ionization (a). In solution, the ions are in dynamic equilibrium with the unionized molecules. Such an equilibrium can be described by a constant called ionization constant. For example, for a weak electrolyte AB, the

ionization equilibrium is, $AB \leftrightarrow A^+ + B^-$; If C is the initial concentration of the electrolyte AB in solution, then the equilibrium concentrations of various species in the solution are,

$$[AB] = C(1 - a), [A^+] = Ca \text{ and } [B^-] = Ca$$

Then, the ionisation constant of AB is given by

$$K = \frac{[A^+][B^-]}{[AB]} = \frac{Ca \cdot Ca}{C(1 - a)} = \frac{Ca^2}{(1 - a)}$$

We know, that at any concentration C, the degree of ionisation (a) is given by

$$a = \frac{\Lambda_m^c}{\Lambda_m^\infty}$$

Then, $(K) = \frac{C(\Lambda_m^c / \Lambda_m^\infty)^2}{[1 - (\Lambda_m^c / \Lambda_m^\infty)]} = \frac{C(\Lambda_m^c)^2}{\Lambda_m^\infty - \Lambda_m^c}$; Thus, knowing Λ_m^∞ and Λ_m^c at any concentration, the ionisation constant (K) of the electrolyte can be determined.

8.6.1.4. Determination of the solubility of a sparingly soluble salt

The solubility of a sparingly soluble salt in a solvent is quite low. Even a saturated solution of such a salt is so dilute that it can be assumed to be at infinite dilution. Then, the molar conductivity of a sparingly soluble salt at infinite dilution (Λ_m^∞) can be obtained from the relationship,

$$\Lambda_m^\infty = v_+ \lambda_+^\infty + v_- \lambda_-^\infty \quad \dots\dots (i)$$

The conductivity of the saturated solution of the sparingly soluble salt is measured. From this, the conductivity of the salt (K_{salt}) can be obtained by using the relationship, $K_{\text{salt}} = K_{\text{sol}} - K_{\text{water}}$, where, K_{water} is the conductivity of the water used in the preparation of the saturated solution of the salt.

$$\Lambda_{\text{salt}}^\infty = 1000 k_{\text{salt}} / C_m \quad \dots\dots (ii)$$

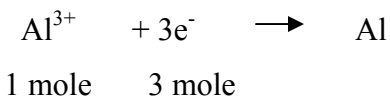
From equation (i) and (ii) ;

$C_m = 1000 k_{\text{salt}} / (v_+ \lambda_+^\infty + v_- \lambda_-^\infty)$, C_m is the molar concentration of the sparingly soluble salt in its saturated solution. Thus, C_m is equal to the solubility of the sparingly soluble salt in the mole per litre units. The solubility of the salt in gram per litre units can be obtained by multiplying C_m with the molar mass of the salt.

8.7. Problems

Example 1. How much charge is required to reduce (a) 1 mole of Al^{3+} to Al and (b) 1 mole of Mn^{7+} to Mn^{2+} ?

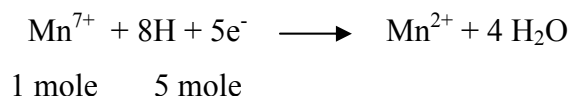
Solution: (a) The reduction reaction is



Thus, 3 mole of electrons are needed to reduce 1 mole of Al^{3+} .

$$\begin{aligned} Q &= 3 \times F \\ &= 3 \times 96500 = 289500 \text{ coulomb} \end{aligned}$$

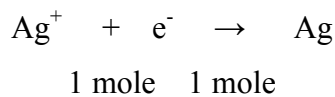
(b) The reduction is



$$\begin{aligned} Q &= 5 \times F \\ &= 5 \times 96500 = 48500 \text{ coulomb} \end{aligned}$$

Example 2. Exactly 0.4 faraday electric charge is passed through three electrolytic cells in series, first containing AgNO_3 , second CuSO_4 and third FeCl_3 solution. How many gram of metal will be deposited assuming only cathodic reaction in each cell?

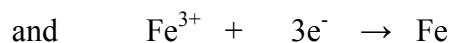
Solution: The cathodic reactions in the cells are respectively.



$$108 \text{ g} \quad 1 \text{ F}$$



$$63.5 \text{ g} \quad 2 \text{ F}$$



$$56 \text{ g} \quad 3 \text{ F}$$

$$\text{Hence, Ag deposited} = 108 \times 0.4 = 43.2 \text{ g}$$

$$\text{Cu deposited} = 63.5/2 \times 0.4 = 12.7 \text{ g}$$

$$\text{Fe deposited} = 56/3 \times 0.4 = 7.47 \text{ g.}$$

Example 3. Calculate the quantity of electricity obtained from 2 moles of electrons

Solution.

$$Q = n \times F$$

$$Q = ?$$

$$n = 2 \text{ mol}$$

$$F = 96,500 \text{ C mol}^{-1}$$

$$Q = 2 \times 96,500 = 193,000 \text{ C}$$

Example 4. Calculate the moles of electrons obtained from 250 C of electricity

Solution.

$$n(e) = ? \text{ mol}$$

$$Q = 250 \text{ C}$$

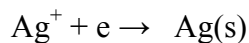
$$F = 96,500 \text{ C mol}^{-1}$$

$$n(e) = 250 / 96,500 = 2.59 \times 10^{-3} \text{ mol}$$

Example 5. Calculate the time required to deposit 56g of silver from a silver nitrate solution using a current of 4.5A.

Solution.

I. Calculate the moles of electrons required for the reaction:



moles of Ag(s) deposited, $n(\text{Ag}) = \text{moles of electrons required, } n(e)$

moles of Ag = $n(\text{Ag}) = \text{mass} / \text{MM}$

mass Ag deposited = 56g

MM = 107.9 g mol⁻¹ (from Periodic Table)

$n(\text{Ag}) = 56 / 107.9 = 0.519 \text{ mol} = n(e)$

II. Calculate the quantity of electricity required: $Q = n(e) \times F$

$$Q = ? \text{ C}$$

$$n(e) = 0.519 \text{ mol}$$

$$F = 96,500 \text{ C mol}^{-1}$$

$$Q = 0.519 \times 96,500 = 50,083.5 \text{ C}$$

III. Calculate the time required: $t = Q / I$

$$Q = 50,083.5 \text{ C}$$

$$I = 4.5 \text{ A}$$

$$t = 50,083.5 / 4.5 = 11,129.67 \text{ seconds}$$

$$t = 11,129.67 / 60 = 185.5 \text{ minutes}$$

$$t = 185.5 / 60 = 3.1 \text{ hours}$$

Example 6. What mass of copper could be deposited from a copper (II) sulphate solution using a current of 0.50 A over 10 seconds?

Solution.

I. Calculate the quantity of electricity: $Q = I \times t$

$$I = 0.50 \text{ A}$$

$$t = 10 \text{ seconds}$$

$$Q = 0.50 \times 10 = 5.0 \text{ C}$$

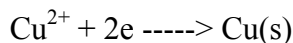
II. Calculate the moles of electrons: $n(e) = Q / F$

$$Q = 5.0 \text{ C}$$

$$F = 96,500 \text{ C mol}^{-1}$$

$$n(e) = 5.0 / 96,500 = 5.18 \times 10^{-5} \text{ mol}$$

III. Calculate mass of copper $\text{mass} = n \times \text{MM}$



1 mole of copper is deposited from 2 moles electrons

$$n(\text{Cu}) = \frac{1}{2}n(e) = \frac{1}{2} \times 5.18 \times 10^{-5}$$

$$= 2.59 \times 10^{-5} \text{ mol}$$

$$\text{MM} = 63.55 \text{ g mol}^{-1}$$

$$\text{mass (Cu)} = (2.59 \times 10^{-5}) \times 63.55 = 1.65 \times 10^{-3} \text{ g} = 1.65 \text{ mg}$$

Example 7. 1.0 N solution of a salt surrounding two platinum electrodes 2.1 cm apart and 4.2 sq.cm in area was found to offer a resistance of 50 ohm. Calculate the equivalent conductivity of the solution.

Solution: Given, $l = 2.1 \text{ cm}$, $a = 4.2 \text{ sq cm}$, $R = 50 \text{ ohm}$

Specific conductance, $k = l/a.1/R$

$$\text{or } k = 2.1/4.2 \times 1/50 = 0.01 \text{ ohm}^{-1} \text{ cm}^{-1}$$

Equivalent conductivity = $k \times V$

V = the volume containing 1 g equivalent = 1000 mL

$$\begin{aligned}\text{So Equivalent conductivity} &= 0.01 \times 1000 \\ &= 10 \text{ ohm}^{-1} \text{ cm}^{-2} \text{ equiv}^{-1}\end{aligned}$$

Example 8. The specific conductivity of 0.02 M KCl solution at 25 °C is 2.768×10^{-3} $\text{ohm}^{-1} \text{ cm}^{-1}$. The resistance of this solution at 25 °C when measured with a particular cell was 250.2 ohms. The resistance of 0.01 M CuSO_4 solution at 25°C measured with the same cell was 8331 ohms. Calculate the molar conductivity of the copper sulphate solution.

Solution. Cell constant = (Sp.cond.of KCl) / (Conductance of KCl)

$$\begin{aligned}&= (2.768 \times 10^{-3}) / (1 / 250.2) \\ &= 2.768 \times 10^{-3} \times 250.2\end{aligned}$$

For 0.01 M CuSO_4 solution

$$\begin{aligned}\text{Sp. conductivity} &= \text{Cell constant} \times \text{conductance} \\ &= 2.768 \times 10^{-3} \times 250.2 \times 1/8331\end{aligned}$$

$$\begin{aligned}\text{Molar conductance} &= \text{Sp. cond.} \times 1000/c \\ &= (2.768 \times 10^{-3} \times 25.2) / 8331 \times 1000 / (1/100) \\ &= 0.837\end{aligned}$$

Example 9. Λ_m^0 for NaCl, HCl, and NaAc are 126.4, 425.9 and 91.0 $\text{S cm}^2 \text{ mol}^{-1}$ respectively. Calculate Λ^0 for HAc.

Solution.

$$\begin{aligned}\Lambda_{\text{HAc}}^0 &= \lambda_{\text{H}^+}^0 + \lambda_{\text{Cl}^-}^0 + \lambda_{\text{Ac}^-}^0 + \lambda_{\text{Na}^+}^0 - \lambda_{\text{Cl}^-}^0 - \lambda_{\text{Na}^+}^0 \\ &= \Lambda_m^0(\text{HCl}) + \Lambda_m^0(\text{NaAc}) - \Lambda_m^0(\text{NaCl}) \\ &= 425.9 + 91 - 126.4 \\ \Lambda_{\text{HAc}}^0 &= 390.5 \text{ S cm}^2 \text{ mol}^{-1}\end{aligned}$$

Example 10. Ionic conductance of M^{+2} , X^- are 80 and 40 $\text{mho cm}^2 \text{ mole}^{-1}$ respectively, k of saturated solution of $\text{MX}_2 = 1.6 \times 10^{-5} \text{ mho cm}^{-1}$, its solubility in moles/liter

Example 11. Equilent conductance at infinite dilution of KCl is 130 and transport no. of Cl^- is 0.6 determine ionic velocities of K^+ , Cl^- ions.

Example 12. Specific conductance of 500 ml solution containing 2.08 gm of BaCl_2 is $1 \times 10^{-3} \text{ mho cm}^{-1}$. Calculate its equivalent conductance and molar conductance.

Example 13. Resistance of centi normal H_2SO_4 solution in a cell having a distance of 2 cm between the two electrodes and area of cross section of 4 sq,cm is 100 mho , calculate specific , equivalent and molar conductance of H_2SO_4 .

References

1. Samul Glasstone, An introduction of Electro Chemistry, Affiliated East - West press Pvt. Ltd., 1942, p. 1-80.
2. B. R. Puri, L. R. Sharma, M. S. Pathania, Principles of Physical Chemistry, Shoban Lal Nagin Chand and Co., 1998, p. 876- 907.
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CHAPTER – 9

GENERAL METHODS INVOLVED IN THE EXTRACTION OF METALS

S. Smitha

9.1. Introduction

The process of extracting a metal from its ore and refining it, is called metallurgical process or simply as metallurgy.

9.2. Earth as a Source of Elements

Most elements are formed due to fusion of simple nuclei to give heavier nuclei i.e., nucleosynthesis or nuclear fusion reactions taking place in the stars. Atoms of these elements began to fall together about six billion years ago to form a system, presently called the solar system. A part of these elements formed in space and such a condensed phase of matter, formed the Earth

The Earth was a huge molten mass in the initial stages of formation. As this mass cooled, partial solidification and separation of different materials took place. The more easily crystallizable and light materials formed the upper layer called the crust and the molten mass formed the core (central part) of the earth. During cooling, the gases dissolved in the molten mass and escaped out, to form the atmosphere around Earth.

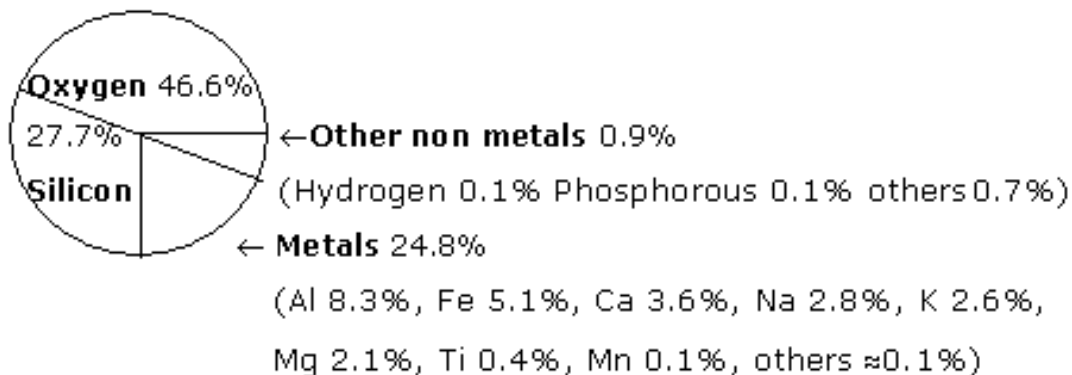


Fig. 9.1. Distribution of various elements in the earth's crust

Water is one of the most abundant compounds on Earth; hence sea water is a vast source of a large number of elements. The Earth's atmosphere contains mainly nitrogen (78%), oxygen (21%), and other gases e.g., CO₂, He, Ne (≈ 1% volume).

9.3. Structure of the earth

During the formation of the Earth, cooling of gaseous mixtures took place and molten earth condensed to form different earth zones or layers. Each layer that formed on top of the other had a definite chemical composition and thus a distinct distribution of elements within it. The innermost layer or core was metallic and molten, the intermediate core was sulphide and a silicate layer formed on top, which was exposed to the Earth's atmosphere layer, creating the Earth's solid crust. This structure formation was suggested by Goldschmidt.

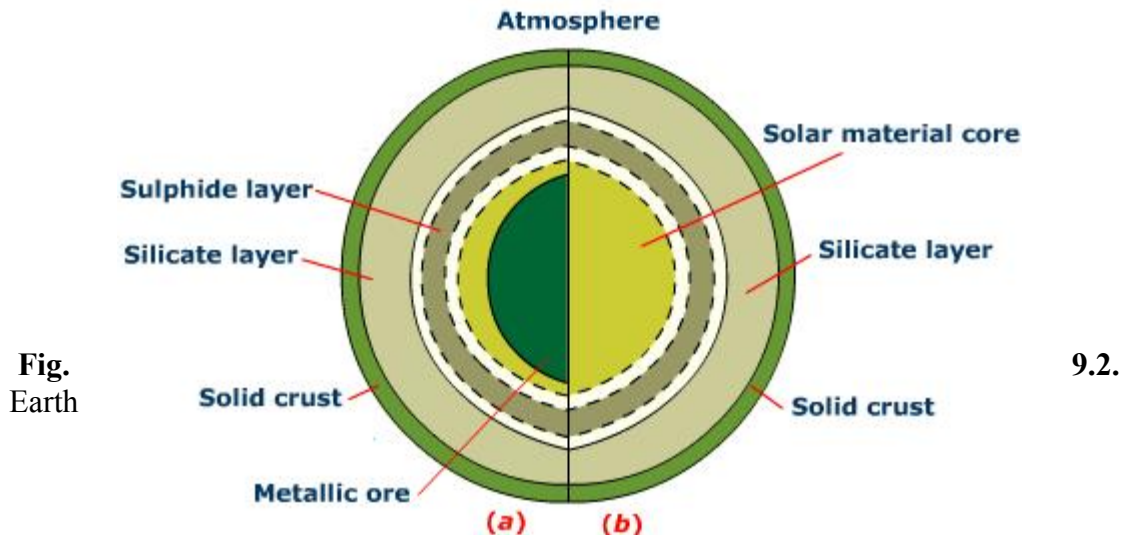


Fig.
Earth

9.2.

structure according to (a) Goldschmidt (b) Kuhn and Rittman

Kuhn and Rittman presented another view. They forwarded the view that the core of the Earth was constituted of solar material containing 30% hydrogen, followed by molten silicates, covered with magma layer and the crust.

Table 9.1. Elements present in various layers of earth

Layer	Elements present
Metallic core (Siderophil)	Mn, Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Re, Os, Ir, Pt, Au
Sulphide layer (Chalcophil)	P, S, Zn, Ga, Ge, As, Se, Cd, In, Sn, Sb, Te, Hg, Tl, Pb, Bi
Silicate layer (Lithophil)	Chlorides, sulphate and carbonates of Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba. Silicates and oxides of Be, Al, Si, Y, La, Ac, Ti, Zr, Hf, Th, V, Cr, Mo, W, U
Atmosphere (Atmophil)	F, Cl, Br, I, B, C, Si, N, O and rare gases

9.3.1. Layers of Earth

9.3.1.1. Siderophil

All those elements, which have a tendency to associate with iron are concentrated in the core of the earth.

9.3.1.2. Chalcophil

All these elements which tend to exist under the Earth as sulphide. These chalcophile form the middle layer of the earth.

9.3.1.3. Lithophil

All those elements which tend to form silicates, oxides, carbonates, sulphates, etc., (tendency to bind through or to the oxide ion). These lithophile form the crust (upper layer) of the earth.

9.3.1.4. Atmophil

All elements, which tend to exist as gases in and above the surface of the earth The atmosphere extends up to about 100 km above the earth surface.

9.3.1.5. Occurrence of Metals

Metals occur in nature in the free as well as in the combined states. The most unreactive metals i.e. which are not affected by air and water, like silver, gold and platinum are generally found in the free state. Most metals however, are found in the combined form as minerals.

9.4. Minerals and Ores

Natural materials found inside the earth containing metals in their combined states (as a single compound or as a mixture of compounds) mixed with non metallic impurities of Earth and rock (called gangue), are termed minerals. These metals do not occur in the native form and need to be extracted for use. All minerals are not suitable for the extraction of metals. Minerals from which the metal can be extracted easily and economically are called ores. Thus, all ores are minerals, but not all minerals are ores.

In the combined state, metals are found in various forms. For example as oxides, sulphides, carbonates, halides, sulphates, phosphates and silicates. Most common forms in which different metals occur in nature are described below.

9.4.1. Native Form

Ag, Au, Pt, Cu, Hg

9.4.2. Combined Form

- i) As Oxides: Cu, Zn, Al, Re
- ii) As Sulphides: Cu, Zn, Ag, Pb, Hg, As, etc
- iii) As Halides; Ag, Na, K, Mg (as chlorides) Al, Ha, Ca, (as fluorides)
- iv) As Carbonates: Cu, Zn, Pb, Ca, Na, Mg
- v) As Sulphates; Ba, Ca, Pb etc
- vi) As Phosphates: P
- vii) As Nitrates: Na, K

9.4.3. What are "ores"?

An ore is any naturally-occurring source of a metal that one can use economically extract the metal.

- i) Aluminium, for example, is the most common metal in the Earth's crust, occurring in all sorts of minerals. However, it isn't economically worthwhile to extract it from most of these minerals. Instead, the usual ore of aluminium is bauxite - which contains from 50 - 70% of aluminium oxide.
- ii) Copper is rarer than aluminium, but fortunately can be found in high-grade ores (ones containing a high percentage of copper) in particular places. Because copper is a valuable metal, it is also worth extracting it from low-grade ores as well.

Ores are commonly oxides - for example Bauxite Al_2O_3 , Haematite Fe_2O_3 , rutile TiO_2
or sulphides - for example: Pyrite FeS_2 , Chalcopyrite CuFeS_2

9.5. Steps involved in a metallurgical process

The extraction of the metal from its ore involves the following steps:

9.5.1. Mining of ore

Most ores are generally occur deep inside the Earth. Some may occur only a few meters under the earth's surface. Mining is the process of taking out the ores from the mines. When an ore occurs near the surface of the Earth, it can be directly dug out. Such mining is termed as open-pit mining. When an ore is taken out from greater depths, then the mining is termed deep-mining.

9.5.2. Crushing of the ore

Extracted ore often occurs in big lumps. It is essential to break it into smaller pieces. The lumps are crushed to smaller pieces by hammering in a hammer mill or by help of a jaw-crusher.

9.5.3. Grinding and pulverization of the crushed ore

The crushed ore is then finally pulverized to fine powder in a stamp mill or a pulveriser.

9.5.4. Concentration of the ore (ore dressing)

The removal of the undesired foreign impurities i.e., gangue, from the ore is called concentration (or beneficiation) of the ore. Either of the following methods is used for concentration the ores.

9.5.4.1. Hand picking

If the impurities present are quite distinct from the ore, and are of large size, these may be removed by hand picking. This method is slow and is generally adopted in the initial stages of concentration.

9.5.4.2. Gravity or levigation method

When the ore particles are heavier than the gangue particles, the ore is fed into a running stream of water and impurities are washed away. This separation is by way of gravity or levigation method and is commonly used for oxide ores such as hematite and native ore of Au, Ag, etc. In order to concentrate the ore in bulk, a slanting vibrating wooden table with wooden strips called riffles is introduced in the process. Such tables are termed Wilfley tables. The ore is continuously washed with a fine washed with a fine spray of water and the rocking motion sieves the heavier portions, while allowing the impurities to filter away.

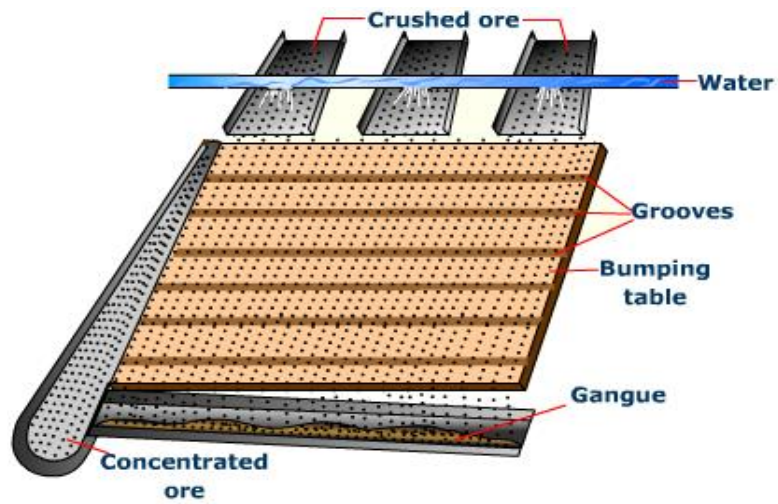


Fig. 9.3. Wilfley table for washing of the ore

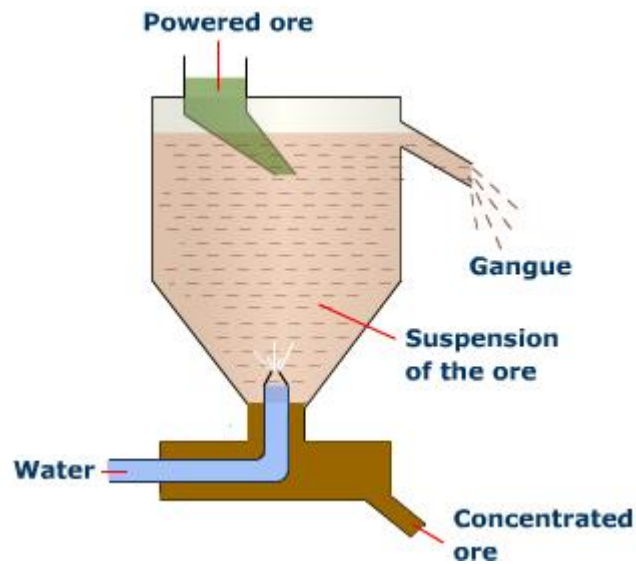


Fig. 9.4. Hydraulic Classifier

Sometimes in the gravity method, a hydraulic classifier based on the gravity method is used. Ore is agitated by a powerful current of water pushing, upwards through the bottom of a conical reservoir. The heavier ore particles settle down and are continuously

removed from another opening near the bottom, while the lighter particles are washed away by water.

9.5.4.3. Magnetic separation

Magnetic separation is done especially in the case of haemetite ore, whereby the powdered ore is dropped on to leather or brass conveyer belt, which moves over two rollers, one of these rollers, is magnetic. When the ore passes over the magnetic roller, it sticks to the belt due to the force of attraction and falls nearer due to the force of attraction of the magnetized roller. The gangue falls over readily, further away. The ore and the magnetic impurity are collected as two separate heaps.

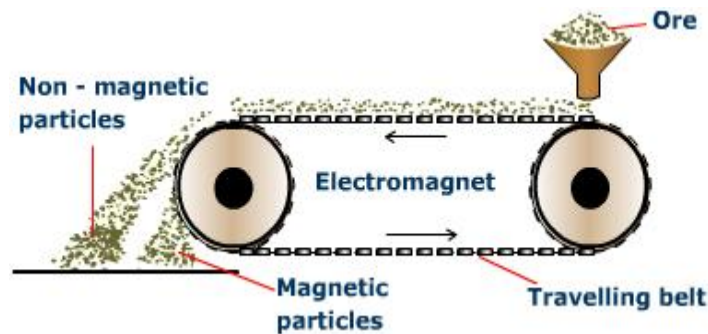


Fig. 9.5. Magnetic separation

9.5.5. Froth floatation process

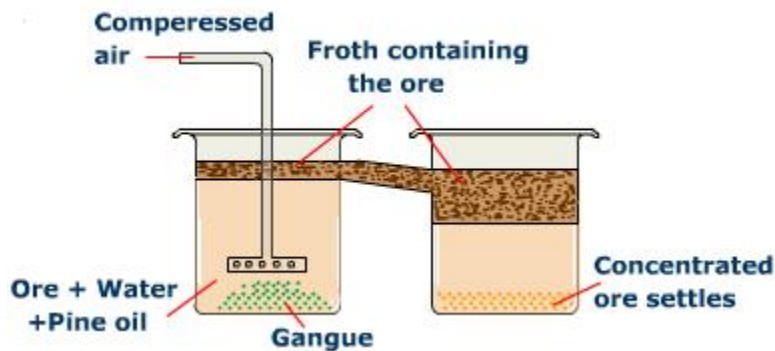


Fig. 9.6. Froth floatation process

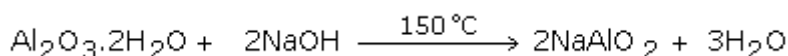
This process is used for concentrating sulphide ores, as such ores are preferentially wetted by oil while the gangue particles are wetted by water. Powdered ore is mixed with water and a little pine oil and the mixture is vigorously stirred by passing compressed air.

The froth, which is produced rises to the surface and carries the ore particles along with it. The gangue is left behind.

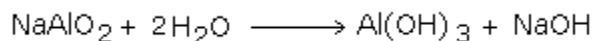
9.5.6. Leaching process

In this method, the ore is treated chemically with a suitable reagent that preferentially dissolves the active component of the ore. The concentrated ore from is then recovered from the solution by a suitable chemical method.

A typical example of ore concentration by leaching process is the purification of bauxite using NaOH solution as a leachant. The bauxite is digested with concentrated solution of caustic soda at 150 °C in an autoclave. The aluminium oxide dissolves in NaOH leaving behind the insoluble impurities, which are removed by filtration.



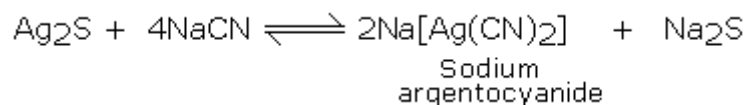
The solution of NaAlO₂ (sodium meta-aluminate) is then treated with freshly prepared Al(OH)₃ when the entire aluminium in the solution gets precipitated as Al(OH)₃



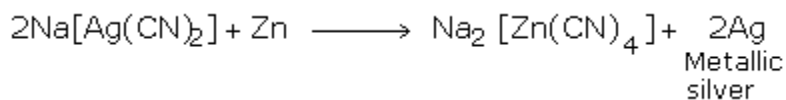
The precipitate of Al(OH)₃ is removed, washed and dried to get Al₂O₃

9.5.6.1. Leaching of silver ore

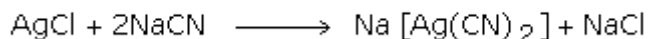
Leaching process is also employed in the recovery of some precious metals. Silver is extracted from its ores (argentite, Ag₂S; horn silver, AgCl) by cyanide process. The finely powdered concentrated ore is treated with a dilute aqueous solution of NaCN (sodium cyanide) and a current of air is passed through the solution. Silver present in the ore gets dissolved due to the formation of soluble sodium argento-cyanide complex Na [Ag(CN)₂] viz.,



Na₂S so formed gets oxidized (by air) to Na₂SO₃, Na₂SO₄ and thus allow the reaction to go in the forward direction. The solution of Na[Ag(CN)₂] is then treated with zinc scrap to recover silver.



With horn silver AgCl, the reaction with NaCN can be written as



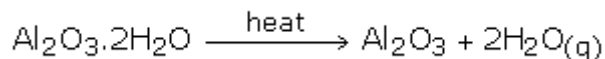
9.5.6.2. Leaching of gold ore

Gold-containing ore gets dissolved in KCN solution in the presence of air to give a solution containing $\text{K}[\text{Au}(\text{CN})_2]$. Gold can then be recovered from this solution by either precipitation or electrolytic method. Electrostatic concentration and liquation are other methods of concentrating of ores. The usage of these methods depends on the nature of the ores and the type of impurities present.

9.6. Calcination

The concentrated ore is converted into oxide by calcinations i.e., heating it strongly in the absence of air or roasting (heating it strongly in presence of air). It removes moisture from the ore. Calcination is done on the earth of a reverberatory furnace. This helps in removing volatile impurities like CO_2 , SO_2 , Organic matter, and moisture from the ore. For example,

i) It removes moisture from bauxite



ii) It removes CO_2 from carbonate ores e.g.

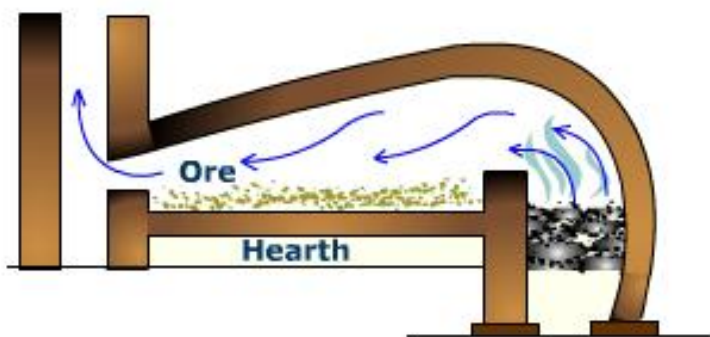
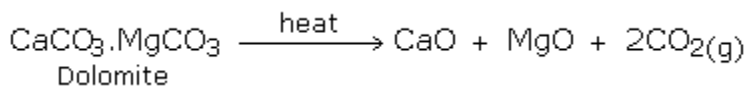
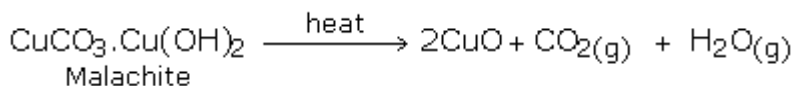
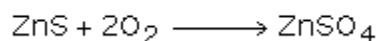
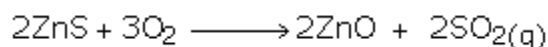
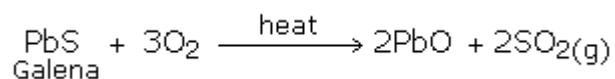


Fig. 9.7. A reverberatory furnace

9.7. Roasting

In this process the ore (usually sulphide) is heated strongly, in the presence of excess of air but below its melting temperature. The result is that it removes the sulphide ore is converted partly into its oxide or sulphate i.e moisture, CO₂, SO₂ and organic matter.



Similarly, roasting is done in a reverberatory furnace or in a blast furnace.

9.8. Extraction of metals

Once the ore is calcined or roasted, the process of reduction obtains the metal. The extraction of metal from the calcined or roasted ore consists of two steps viz.,

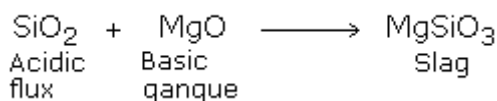
- i) Removal of the Earthly impurities.
- ii) Reduction of the ore to the metal.

The Earthly impurities are removed by adding suitable substance called flux which when heated, combines with the earthly impurities to form easily fusible mass known as slag, is called flux.

There are two types of fluxes;

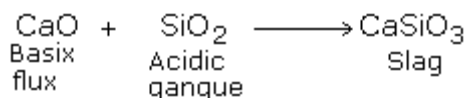
9.8.1. Acidic flux

Acidic flux like silica (SiO_2) is used to remove basic earthy impurities (gangue) such as lime (CaO) or MgO .



9.8.2. Basic flux

Basic fluxes like lime (CaO), magnesium oxide (MgO) are used to remove acidic gangue such as SiO_2 .



9.8.3. Slag

When a flux combines with the earthy impurities, an easily fusible mass is obtained which is called slag. The slag is lighter and insoluble in the molten metal. So it can be easily removed from the surface of the molten metal. Molten mixture of calcium and magnesium silicates forms slag.

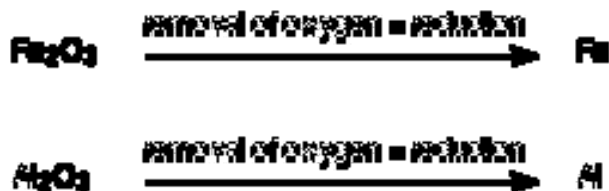
After removing the earthy impurities, the metals are obtained from the calcined or roasted ore by the process of reduction. This can be either chemical reduction or electrolytic reduction processes. The choice of the method depends upon various factors.

9.9. Chemical reduction methods

Reducing the metal compound to the metal

Why is this reduction?

The ore is being reduced because oxygen is being removed.



For sulphides its not of much use.

It is much more helpful to use the definition of reduction in terms of addition of electrons. To a reasonable approximation, one can think of these ores as containing positive metal ions. To convert them to the metal, we need to add electrons - reduction.



In chemical reduction process, the choice of reducing agent depends upon the chemical reactivity of the metal.

9.9.1. Choosing a method of reduction

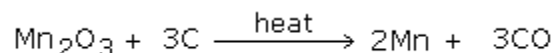
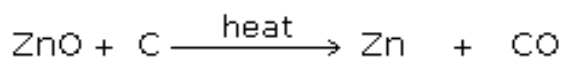
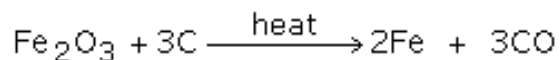
There are various economic factors one need to think about in choosing a method of reduction for a particular ore:

- i) the cost of the reducing agent;
- ii) energy costs;
- ii) the desired purity of the metal.

There may be various environmental considerations as well - some of which will have economic costs.

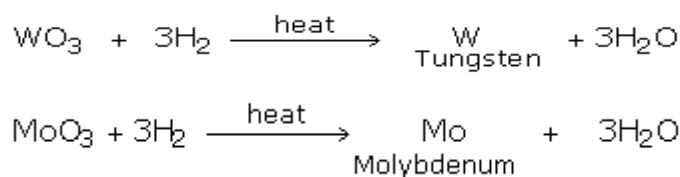
9.9.2. Smelting (Carbon reduction method)

This method is used for the extraction of lead, zinc, iron, copper, manganese and tin. In this method, the roasted oxide ore is mixed with carbon (charcoal, coal or coke) and a flux, and is heated to a very high temperature in a suitable furnace. Carbon reduces the oxide to metal.



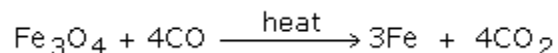
9.9.3. Hydrogen reduction method

Hydrogen can reduce certain oxides to metals e.g.,



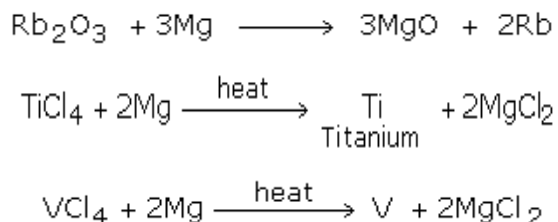
9.9.4. Carbon monoxide reduction method

In certain cases CO gas produced in the furnace itself can be used as a reducing agent. For example,



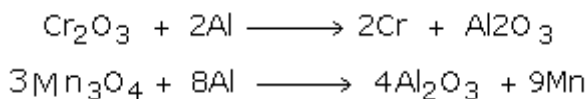
9.9.5. Magnesium reduction method

Oxides of certain metals are reduced by Mg e.g.,



9.9.6. Aluminium reduction method (Alumino Thermic Process)

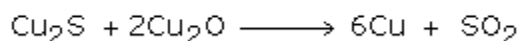
Certain metal oxides cannot be reduced by carbon. Such metallic oxides can be reduced by aluminium powder. This process has been widely used to reduce TiO_2 , Cr_2O_3 and Mn_3O_4 to get the corresponding metal.



9.9.7. Self-reduction method

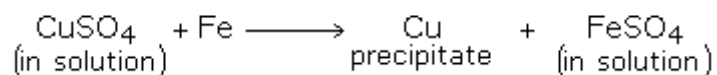
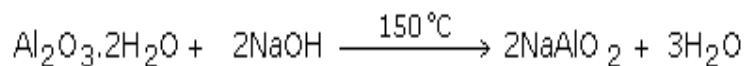
When the sulphide ores of less electropositive metals like Hg, Cu, Pb, Sb etc., are heated in air, a part of the ore gets oxidized to oxide or sulphate, which then reacts with the remaining sulphide ore to give the metal and SO_2 . This process is also known as self-reduction method.





9.9.8. Reduction by more electropositive metals (precipitation or hydrometallurgy)

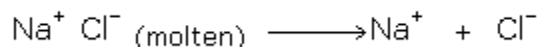
This method is employed when leaching method had been used to concentrate the ore. The metals are obtained by reducing their ions in the solution as precipitates by a more electropositive metal. This method is also called as the hydrometallurgy method of reduction. For example, when a heap of copper glance (Cu_2S) is exposed to air and water, it gets converted to copper sulphate. Copper is recovered from copper sulphate solution by adding some iron scrap to its solution.



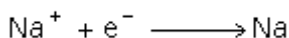
Ag and Au are also recovered from the solutions of their complex cyanide salts by zinc scrap.

9.9.9. Electrolytic reduction

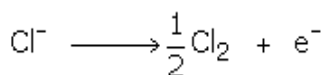
Certain metals can be obtained by affecting the reduction of the corresponding cations electrolytically. For example, sodium metal is obtained by electrolyzing molten sodium chloride



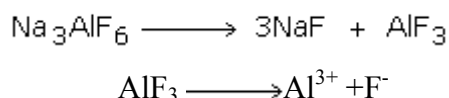
At cathode;



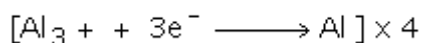
At anode



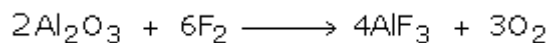
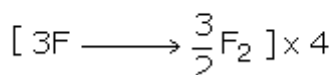
The oxides of alkali metals, alkaline earth metals like Al, Zn etc., are very stable, hence would need very high temperature for carbon reduction. But at high temperatures these metals react with carbon to form carbides. Thus, these metals cannot be obtained by carbon-reduction process. The oxides of these metals however can be reduced electrolytically. For example, the reduction of Al_2O_3 to aluminium by electrolysis method. In actual practice, a solution of Al_2O_3 in cryolite (Na_3AlF_6) is electrolyzed as follows;



At cathode



At anode



9.10. Refining of the metal

Purification of the metal is the last step in metallurgy. Refining is based on the difference between the properties of metals and their impurities.

9.10.1. Liquation

This method is used for refining metals having a low melting point.

e.g. tin, lead, bismuth

Process

- i) The metal to be refined is placed over the sloping hearth of a furnace
- ii) The temperature of the furnace is maintained slightly above the melting point of the metal

iii) Pure metal melt and flow down

iv) Impurities, having higher melting point are left behind.

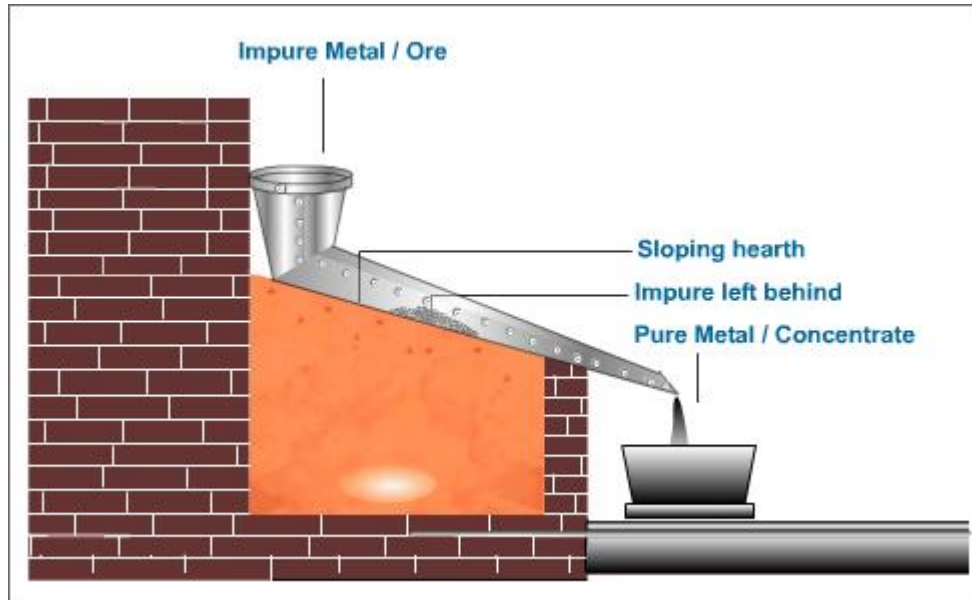


Fig. 9.8. Liquation

9.10.2. Distillation

This method is used for volatile metals having boiling points lower than their impurities.

E.g. zinc, mercury

Process

i) The metal to be refined is heated above its boiling point

ii) Impurities do not vapourise

iii) Pure metal vapourises and is condensed

iv) Impurities are left behind

9.10.3. Electrolysis

In 1834, Michael Faraday studied the passage of electricity through liquids. He called it electrolysis, as it was accompanied by the chemical decomposition of the electrolyte. The

term 'lysis' in Greek means "setting free". The metallic conductors through which the current enters and leaves the electrolyte are called electrodes. The electrode at high potential is called anode and the other at lower potential is called cathode. The passage of current through electrolytes was considered to take place through moving charged particles, which were called 'ions' by Faraday. The term 'ion' in Greek means a 'wanderer'. The ion with negative charge is called 'anion' and the one with positive charge is called 'cation'.

9.10.4. Faraday's Laws of Electrolysis

9.10.4.1. Faraday's first law:

First law states that the mass of a substance deposited or liberated on an electrode during electrolysis is proportional to the total quantity of electric charge passed through the electrolyte.

9.10.4.2. Faraday's second law:

Second law states that if same quantity of charge is passed through several electrolytes, the mass of substance deposited or liberated at electrodes is proportional to their chemical equivalent (equivalent weight).

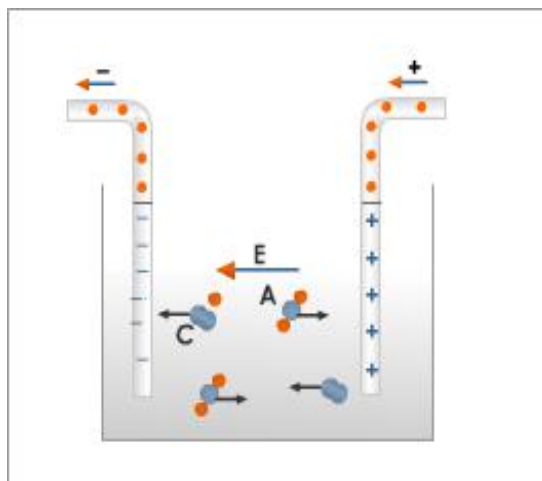


Fig. 9.9. The process of electrolysis

The above statements are the conclusions made by Faraday after conducting a number of experiments on 'electrolysis'. The process of electrolysis is carried out in an apparatus called voltameter.

If the electrolyte is a solution of copper sulphate (CuSO_4) and the electrodes are copper plates, it is called a copper voltameter. On the other hand if the electrolyte is a solution of silver nitrate AgNO_3 and electrodes are silver plates it is called a silver voltameter. When appropriate direct potential difference is applied across the electrodes, the electrolyte starts conducting current.

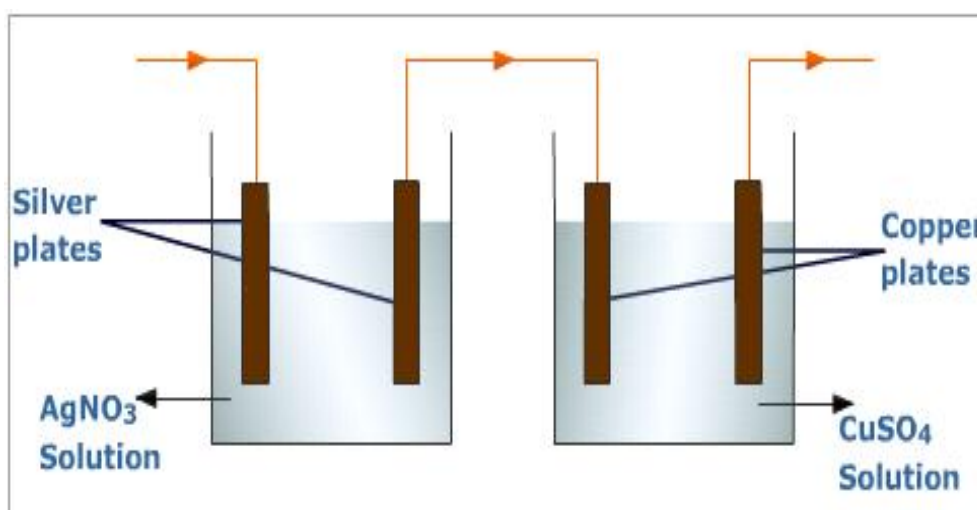


Fig. 9.10. Chemical equivalent

Faraday's second law is illustrated in the figure where silver and copper voltameters are connected in series. For a given time, the same charge will pass through each voltameter. It will be seen that the masses of silver (Ag) and copper (Cu) deposited on the respective cathodes are in the ratio of 108:32. These values of 108 and 32 are called the chemical equivalents of silver and copper respectively.

This method is used for refining copper, silver, tin, nickel

Process

- i) A block of impure metal is made the anode of an electrolytic cell containing an aqueous solution of the metal salt

- ii) A thin sheet of pure metal is made the cathode of the electrolytic cell
- iii) When electric current of a suitable voltage is passed, metal ions from the electrolyte get deposited on the cathode as pure metal $M^{+n} + ne^{-} \rightarrow M$
- iv) Metal ions from the anode enter the electrolyte $M \rightarrow M^{+n} + ne^{-}$
- v) Impurities present in the anode settle down as anode mud under the anode
- vi) Anode finally disintegrates while the cathode gains in weight due to the collection of pure metal.

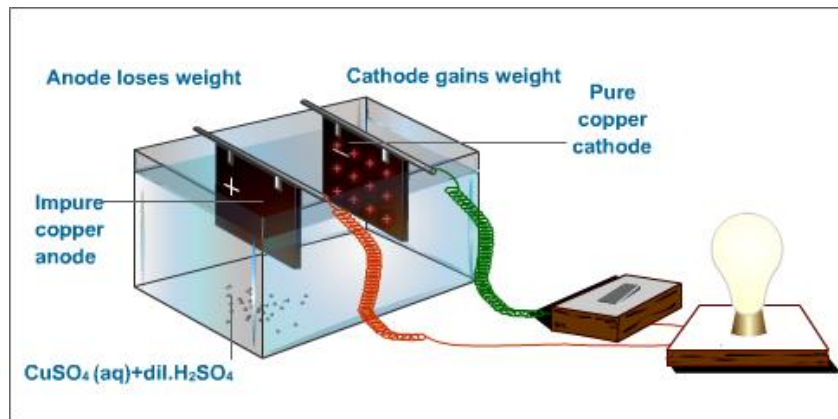
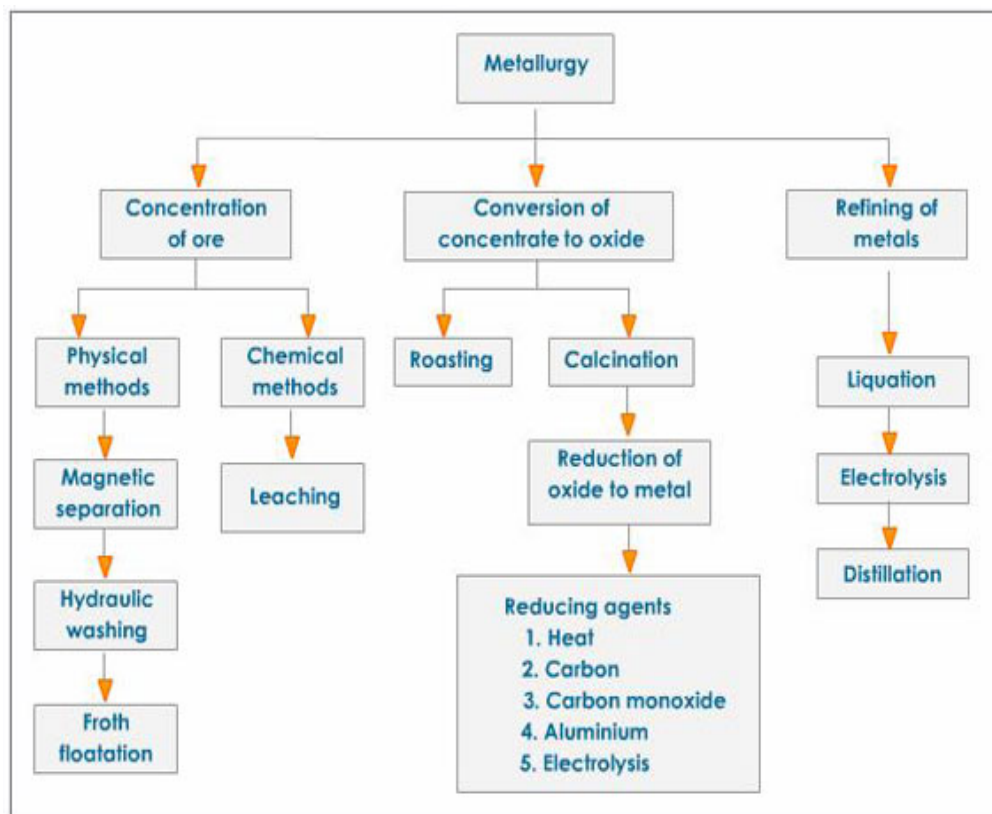


Fig. 9.11. Refining of the metal

**9.11.
Sum
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9.12. Multiple choice questions

Question 1

Of these, the most ductile metal is _____.

1. Al
2. Au
3. Cu
4. Ag

Answer: 2

Question 2

Of these, the least dense metal is _____.

1. Hg
2. Au
3. Cu
4. Na

Answer: 4

Question 3

Of these, the most reactive metal is _____.

1. Fe

2. Zn

3. Al

4. K

Answer: 4

Question 4

Which of the following is displaced by 'Cu'?

1. Fe²⁺

2. Ag⁺

3. Zn²⁺

4. Al³⁺

Answer: 2

Question 5

Which of the following metals does not displace H₂ gas from dilute HCl or dilute H₂SO₄?

1. Mg

2. Cu

3. Zn

4. Al

Answer: 2

Question 6

The metal reacting readily with cold water is _____.

1. Au

2. Ag

3. Na

4. Mg

Answer: 3

Question 7

Of these, which metal will lose electrons most readily and form cations?

1. K
2. Zn
3. Cu
4. Au

Answer: 1

Question 8

Of these, which ion will get reduced most readily?

1. K^+
2. Zn^{2+}
3. Cu^{2+}
4. Ag^+

Answer: 4

Question 9

Of these, the metal which occurs in a free state is _____.

1. Na
2. Mg
3. Zn
4. Pt

Answer: 4

Question 10

Which of the following metals is extracted only by electrolysis?

1. Zn
2. Al
3. Fe

4. Cu

Answer: 2

QUESTIONS & ANSWERS

Question 1

Compare the properties of a typical metal and a non metal on the basis of following.

Fill in column A,B.

<i>Properties</i>	<i>A Metal</i>	<i>B Non- metal</i>
Electronic configuration	?	?
Nature of oxides	?	?
Oxidizing or reducing action	?	?
Conduction of heat and electricity	?	?

Answer

<i>Properties</i>	<i>A Metal</i>	<i>B Non- metal</i>
Electronic configuration	Have 1, 2, 3 valence electrons	Have 4, 5, 6, 7 valence electrons
Nature of oxides	Form metallic oxides i.e., basic or amphoteric oxides	Formic acidic oxides or neutral oxides
Oxidizing or reducing action	Metals are donors of electrons $M - e \rightarrow M^+$ Therefore they act as reducing agents	Non-metals generally accept electrons $X + e \rightarrow X^-$ and act as oxidizing agents
Conduction of heat and electricity	Good conductors of heat and electricity	Non-conductors of heat and electricity

Question 2

Name the following:

1. A molten metal that catches fire in chlorine gas and gives off white fumes
2. A metal that forms two types of oxides and rusts in moisture; write their formulae also
3. A metal used in hot water systems
4. A metal used in long distance cable wires
5. A metal added to gold to harden it

Answer:

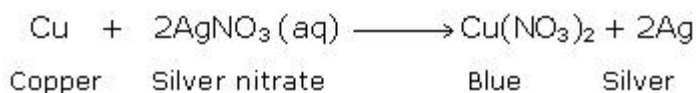
1. The molten metal that catches fire in chlorine gas and gives off white fumes is Sodium.
2. The metal that forms two types of oxides and rusts in moisture is iron. The formulas of its oxides are: FeO; Fe₂O₃
3. The metal used in hot water systems is copper, because it is a good conductor of heat and electricity.
4. The metal used in long distance cables wires is aluminium, because it is a light metal and a very good conductor of electricity
5. The metal added to gold to harden it is copper.

Question 3

A copper plate was dipped in AgNO₃ solution. After certain time silver from the solution was deposited on the copper plate. State the reason why it happened. Give the chemical equation of the reaction involved.

Answer:

Copper is more reactive than silver, therefore it displaces silver from silver nitrate.



Question 4

Name two metals which can displace hydrogen from dilute HCl.

Answer:

Zinc and Iron

Question 5

An element X on reacting with oxygen forms an oxide X₂O. This oxide dissolves in water and turns blue litmus red, . State whether element X is metal or a non metal.

Answer

Since the oxide turns blue litmus red, therefore X is a non-metal because it is an acidic oxide

Question 6

Metals replace hydrogen from acid, whereas non-metal do not . Why?

Answer:

Non-metal cannot supply electrons to convert H^+ to $H_2(g)$ whereas metals can give electrons to convert



Question 7

Name the metal which occurs below copper in the reactivity series. Also name the metal that lies just above hydrogen in the reactivity series

Answer:

Mercury occurs below copper in the reactivity series. Copper is the metal just above hydrogen in the reactivity series.

Question 8

Why are the two non-metals, carbon and hydrogen are important chemical reference points with regard to the method of metal extraction and reactivity towards acids.

Answer:

The six metals K, Na, Li, Ca, Mg, and Al which lie above carbon in the activity series cannot be extracted by carbon reduction. They are usually extracted by electrolysis. Metals below hydrogen i.e, Cu, Ag, Au and Pt are transition metals that will not displace hydrogen from acids

Question 9

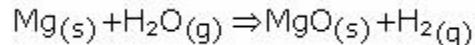
a. What is the behaviour of Mg when it is heated and steam is passed over it?

Represent the equation

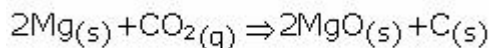
b. Can Carbon dioxide react with Mg?

Answer:

a. When steam is passed over heated Mg a reaction takes place where a white powder Magnesium Oxide is formed along with hydrogen. Magnesium will burn with a bright white flame in steam, if previously ignited in air.



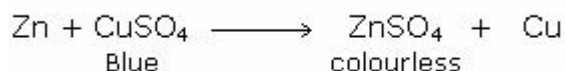
b. Ironically, Magnesium will even burn in carbon dioxide forming black specks of Carbon!



Question 10

A zinc rod was kept in a glass container having CuSO_4 solution. On examining, it was found that the blue colour of the solution had faded. After few days when the zinc rod was taken out of the solution, a number of small holes were noticed in it. State the reason and give chemical reaction involved.

Answer:



Question 11

Carbonates and sulphide ores are usually converted into oxide ores, why?

Answer:

It is easier to reduce oxide as compared to carbonate and sulphide

Question 12

In metallurgy what do the terms gangue, flux, slag stand for? Give examples.

Answer:

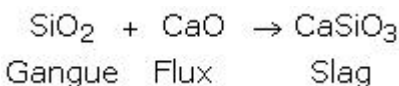
The term gangue is used for all the earthly impurities associated with the ore of the metal. These need to be removed before the extraction step.

Example: In iron ore, sand SiO_2 is the main gangue.

The term Flux refers to the compound added during extraction, which reacts with a non fusible (high melting point) gangue and forms a fusible product called slag. This can then be removed by simple physical method.

Example: In the blast furnace for extraction of iron, the flux added is limestone CaCO_3 . This decomposes to give CaO (basic oxide) which reacts with sand (gangue- an acidic oxide) and forms a fusible slag CaSiO_3 .

The term **slag** refers to the easily fusible product formed between gangue and flux.

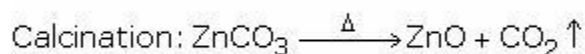
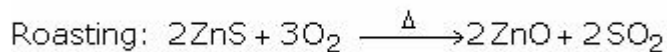


Question 13

How does roasting differ from calcinations? Give equations.

Answer

<i>Sl. No</i>	<i>Roasting</i>	<i>Calcinations</i>
1.	Roasting is heating ore in the presence of air to oxidize it	Calcinations is heating of the ore, in the absence of air to decompose it or drive volatile matter
2.	Roasting occurs at higher temperatures, higher than the melting point of the ore	Calcinations occurs at temperatures lower than the melting point of the ore



In both cases the ore becomes porous for easy reduction.

Question 14

Why are aluminium containers used to transport nitric acid ?

Answers:

Aluminium containers used to transport nitric acid because concentrated HNO_3 renders aluminum passive by forming a thin strong protective oxide layer. This protective layer prevents further reaction with the acid.

Question 15

Why is Al obtained only by electrolytic reduction of Alumina (pure)?

Answer:

Aluminium metal has a strong affinity for oxygen and the oxide of Al is Al_2O_3 , which is a very stable oxide. Hence ordinary chemically reducing agents are not sufficient to reduce Al_2O_3 to Al. Electrolytic reduction is a more powerful reduction method.

Question 16

Name the following:

- 1) A metal used in structural engineering**
- 2) A metal used as fuse wire**
- 3) A brittle metal, which is used to galvanize iron**
- 4) A metal whose chloride and sulphate salts are both insoluble**
- 5) A metallic chloride that is soluble in hot water but insoluble in cold water.**

Answer:

- 1) Iron is used in structural engineering
- 2) Lead, has a low melting point it is therefore used as fuse wire
- 3) Zinc is the brittle metal used to galvanize iron
- 4) Lead metal has its chloride precipitate (PbCl_2) and sulphate precipitate (PbSO_4) as insoluble
- 5) Lead chloride is insoluble in cold water but dissolves in hot water.

Question 17

Arrange the following metals in the decreasing order of chemical reactivity; placing the most active first. Cu, Mg, Fe, Na, Ca, Zn.

Answer:

The decreasing order of chemical reactivity is (most active)

$\text{Na} > \text{Ca} > \text{Mg} > \text{Zn} > \text{Fe} > \text{Cu}$ (least active).

Question 18

Give two metallurgical facts that justify placing magnesium above iron in the activity series.

Answer:

- 1) Magnesium metal is extracted by electrolytic reduction only, whereas iron can be extracted by chemical reduction using coke. Therefore Mg should be above iron.
- 2) Magnesium can displace iron from ferrous sulphate solution, but iron cannot displace magnesium from magnesium sulphate solution. Therefore magnesium should be above iron

Question 19

Name two metals that occur in a free state nature. What is the method of refining them?

Answer:

Gold and Platinum are two metals that occur in a free in state in nature. They only need to be cleaned by physical methods.

Question 20

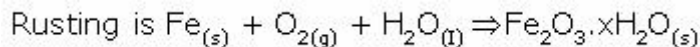
1) Explain the chemical change that causes corrosion in iron.

2) If an iron nail is left in a filled bottle of boiled water how long will it take to corrode?

Answer:

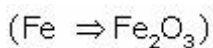
Iron exposed to oxygen and water undergoes an oxidation reaction on the surface of a metal. Iron corrodes more quickly than most other transition metals to form a reddish brown powder of iron oxide. The oxide formed does not firmly adhere to the surface of the metal causing it to flake off easily; this in turn causes further oxidation and rusting causing the surface of the iron metal to get pitted and deteriorate in structural strength.

Rust formation on iron is represented in the following equation (the equation is not meant to be balanced and the amount of water 'x' is variable, from dry to soggy).

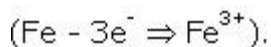


i.e., rust is hydrated iron (III) oxide

Rusting is oxidation because it involves iron gaining oxygen



or iron atoms losing electrons



b) Iron can corrode or rust in three to four days the presence of a moist atmosphere.

However, a full bottle of boiled water contains no oxygen content. So, the oxidization on the surface of the nail will not occur and the iron nail will not rust.

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CHAPTER - 10

SPONTANEOUS AND NON SPONTANEOUS REACTIONS

P. Indra Neel

10.1. An introduction to the concept of Spontaneity

The concept of the spontaneity or the feasibility of a process (or reaction) is the subject of Thermodynamics, especially, comes under the purview of the second law of

thermodynamics. Two important parameters or functions that dictate the spontaneity or feasibility of a process are the entropy and the Gibbs free energy.

A brief introduction to the language and terminology of Thermodynamics is inevitable for the learners to comprehend rightly and clearly the concept of spontaneity and the governing principles for the reactions to be spontaneous.

The word “Thermodynamics” can be defined in various ways. One of the simplest ways being flow of heat. Thermodynamics deals with the energy changes associated with all types of physicochemical processes (reactions). The basis of thermodynamics is human experience rather than formal proof. Thermodynamics is based more on generalization. The two important generalizations that form the basis of thermodynamics are the first and the second laws of thermodynamics. So far nothing contrary to these generalizations has been known. The two laws respectively deal with two fundamental macroscopic properties of matter, namely, the energy and the entropy which are responsible for the behavior of matter.

The two laws of thermodynamics in terms of energy and entropy can be summarized as follows as expressed by Clausius:

The energy of the universe is conserved (The first law of thermodynamics)

The entropy of the universe increases (The second law of thermodynamics)

Thermodynamics can be regarded as one of the foundation stones of Physical Chemistry. The learning of Thermodynamics is analogous to the construction of a building where in care and caution to be exercised to have a strong and sound foundation so as to retain the structural integrity. Thermodynamics is of great significance and forms the foundation of physical chemistry itself due to the fact that most of the generalizations like the van't Hoff law of dilute solutions, Raoult's law of lowering of vapour pressure, distribution law, the law of chemical equilibrium, the phase rule and the law of thermochemistry could be deduced from the laws of thermodynamics. In spite of this many advantages this branch of fundamental science has got its own limitations. The main short coming of the classical thermodynamics being the laws of thermodynamics are not at all concerned (applicable) with the atomic or molecular structure of the matter but rather connected (applicable) with the bulk of the matter itself. To study the thermodynamic behavior at molecular level one need to study statistical thermodynamics.

Thermodynamic laws are to be applied only to study the behavior of the assemblages of large number of molecules but not to individual molecules.

No transformation or change occurring in the world is outside the purview or domain of thermodynamics. Thermodynamics deals with the energy changes occurring in chemical or mechanical systems. Thermodynamics allows to predict whether a reaction or process is spontaneous (with a decrease in the energy of the system) or not under given set of conditions of temperature, pressure and concentration. In addition, the maximum extent to which a process can proceed before the attainment of equilibrium could be determined by the study of the thermodynamics of a process. Thus the knowledge of feasibility or spontaneity of a process can be achieved from the study of thermodynamics. Thermodynamics does not indicate the speed or rate of the reaction. It is more the subject of Chemical Kinetics which gives knowledge of the slowness or fastness of a process which has nothing to do with the concept of spontaneity or feasibility of the process. For instance, by means of thermodynamics, it can be shown that hydrogen and oxygen gases should combine to form liquid water at ordinary temperatures and pressures. But from thermodynamics it is not possible to state whether the reaction will be fast or slow. In practice, in the absence of a catalyst, the combination of H_2 and O_2 gases to form liquid water is so slow that liquid water is undetectable for many years. Thus thermodynamics deals quantitatively with equilibrium conditions (conditions which do not change with time). Thermodynamics does not take into account the rate of approach to the equilibrium state.

10.2. Fundamentals of Thermodynamics

In thermodynamics terms such as system, surrounding, state, property, process and path have specific significance and definite meaning whose understanding is necessary for the better understanding of the subject.

10.2.1. System

A thermodynamic system is a region in space, or a fixed collection of matter enclosed by a real or imaginary boundary. The boundary can be rigid or flexible. The system can be fixed or moving in space. Thus the portion of the universe which is chosen for

thermodynamic consideration is called a system. A system usually consists of definite amount (amounts) of a specific substance (or substances).

10.2.2. Types of systems

Thermodynamic systems can be broadly classified as follows:

(a) Open system, (b) Closed system and (c) Isolated system

(a) **Open system:** In an open system transfer of both energy and matter can take place to its surroundings. In general, an open system is commonly and frequently referred to as a control volume. The boundary of such control volume is called the control surface. Flow of energy and mass can occur across the control surface in an open system. Even though an open system can alter its space, the concept of control volume is limited to a volume of fixed space and fixed orientation relative to an unaccelerated observer. The concept of control volume is more applicable to rigid container which retain their size and shape through out the process.

Ex.,

1. In the case of inflation of a tire as air is admitted into the tire, both the shape and volume of the tire changes and in such a case the system should be called as an open system rather than control volume.

(b) **Closed system:** In a closed system only energy transfer (heat or work) can occur across the boundary but no transfer of material substance or mass takes place across the system boundary.

(c) **Isolated system:** In an isolated system neither mass nor energy crosses the system boundary. In practical real life we encounter with very few or limited isolated systems. The isolated system will not have any interaction with its surroundings.

Thermodynamic systems can be either homogeneous or heterogeneous.

Homogeneous system: Such a system is completely uniform through out.

Example: (i) A gas or a mixture of gases

(ii) A pure liquid or solid

(iii) A liquid or solid solution

Heterogeneous system: When a system is not uniform through out it is said to be heterogeneous. A heterogeneous system may consists of two or more phases which are separated from one another by definite boundaries.

Example: (i) A system with a liquid and its vapour

(ii) Two immiscible (or partially miscible) liquids

(iii) Two or more solids which are not a homogeneous solid solution

10.2.3. Surrounding

Every thing external to the system is regarded as the surrounding to the system. Thermodynamic systems do interact with their surroundings. One of such interactions can be the transfer or exchange of some commodity (heat or work or mass) across the system boundary. It is important to note that, in practice, only those portions of the matter in the surroundings that are or can be affected by changes occurring with in the system are need to be considered.

10.2.4. State of a system

The thermodynamic state of a system can be defined completely by four observable properties, namely, the composition, pressure, volume and temperature.

10.2.4.1. Thermodynamic equilibrium

A system is said to be in a state of thermodynamic equilibrium when the observable properties of the system, namely, the composition, pressure, volume and temperature, do not undergo any change with time.

Thermodynamic equilibrium implies the existence of all the three equilibria, namely, the thermal equilibrium (temperature is same through out), chemical equilibrium (compositoin is same through out) and mechanical equilibrium (no macroscopic movements with in the system with respect to the surroundings) simultaneously.

10.2.5. Properties of a system

Any measurable characteristic or feature of a system is termed as property. Properties of a system such as temperature (T), pressure (P), volume (V) and mass (m) some examples of measurable characteristics which can be termed as the properties that define a system. Some properties can be defined in terms of other properties.

Example:

(i) Density can be defined as the mass per unit volume ($\rho = m/V$)

(ii) Specific volume can be defined as the volume per unit mass ($v = V/m = 1/\rho$)

The physical properties of a system can be broadly classified into two types:

(a) Extensive properties and (b) Intensive properties

10.2.5.1. Extensive properties: The properties that depend on the quantity of the matter specified in the system are called extensive properties. The total value of an extensive property is equal to the sum of the values for the separate parts into which the system may be divided for convenience.

Example: (i) Mass, (ii) Volume and (iii) Energy of a system

10.2.5.2. Intensive properties: The properties that are characteristic of the substance present and are independent of its amount are called intensive properties.

Example: (i) Temperature, T, (ii) Pressure, P, (iii) Refractive index, (iv) Viscosity, (iv) Density, (v) Surface tension

Pressure and temperature are intensive properties because they are independent of the quantity of matter in the system. P and T are frequently used as variables to describe the thermodynamic state of the system.

Note: Extensive property may become intensity property by specifying unit amount of the substance concerned. For example, mass and volume are extensive properties but the mass per unit volume, i.e., the density is an intensive property. Like wise, specific volume, the volume per unit mass is an intensive property of the substance or system. In an analogous way even though heat capacity is an extensity property, specific heat is an intensive property

10.3. The Ideal Gas Equation

An ideal gas is the one which satisfies the equation

$$PV = RT \dots\dots\dots(1)$$

for 1 mole at all temperatures and pressures. P and T are the pressure and the absolute temperature respectively, V is the molar volume and R is the molar gas constant. At a given temperature and pressure, the volume of any gas (ideal or not) will be proportional to its mass or to the number of moles contained in the system. Since equation (1) is applicable to 1 mole of an ideal gas, it equally holds good for 'n' moles also.

Therefore , $PV = nRT \dots\dots\dots (2)$ where V is the total volume occupied by the gas and R is the molar gas constant.

10.3.1. Molar gas constant, R

The gas constant R is frequently used in thermodynamics making its determination inevitable. One mole of an ideal gas occupies 22.414 liters at 1 atm. pressure and a temperature of 273.16 K.

Substituting, $P = 1 \text{ atm.}$, $V = 22.414 \text{ liters mole}^{-1}$ and $T = 273.16 \text{ K}$, equation (2) becomes

$$(1 \text{ atm}) (22.414 \text{ liters}) = (1 \text{ mole}) R (273.16 \text{ K})$$

$$R = (1 \text{ atm}) (22.414 \text{ liters}) / (1 \text{ mole}) (273.16 \text{ K}) = 0.082054 \text{ liter atm. deg}^{-1} \text{ mole}^{-1} \dots\dots(3)$$

R must be expressed in the units of energy per degree since PV has the dimensions of energy.

In (3), energy in liter atm. is equivalent to 1.0133×10^9 ergs

$$R = 0.082054 \times 1.0123 \times 10^9 = 8.3144 \times 10^7 \text{ ergs deg}^{-1} \text{ mole}^{-1} = 8.3144 \text{ J deg}^{-1} \text{ mole}^{-1}$$

$$(1 \text{ J} = 10^7 \text{ ergs})$$

$$\text{Thus } R = 8.3144 \text{ J deg}^{-1} \text{ mole}^{-1}$$

Also, 1 liter-atm is equivalent to 24.218 cal

$$R = 0.082054 \text{ liter atm. deg}^{-1} \text{ mole}^{-1} = 0.082054 \times 24.184 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

$$R = 1.9872 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

10.4. Concept of Heat, Q

Heat is a form of energy. Heat flows from higher temperature to lower temperature unless some work is done on the system. By convention, Q is positive when heat is absorbed by the system from the surroundings. Q is negative if the heat is transferred from the system to the surroundings. Heat gained or lost depends upon the path followed by the system.

The laws of thermodynamics deal with the inter conversion of energy.

Let us examine the concept of heat and temperature. In general, a substance which is hot is said to have a higher temperature than the one which is cold.

Example: If a hot body, for instance, a piece of metal is placed in contact with a similar body which is at a colder condition, then after a short while our senses show that both the bodies are at the same temperature. That is the two bodies have attained a state of thermal equilibrium. A form of energy has transferred from the hotter body to the colder body until the two bodies are at equal temperatures. The energy that is transferred is

called 'heat'. Thus 'heat' may be defined as that which passes from one body to another body solely as a result of difference in temperature.

Heat is energy in transit. It is the form in which energy is transferred from one body to another, either by direct contact or by means of radiation or as the result of a difference in temperature.

10.5. Concept of Work, W

In thermodynamics work is defined as the force multiplied by the distance. If the force F brings about a displacement of ds in a body then the work done is given by, $DW = F ds$. The work done is equal to the products of a generalized force referred to as intensity factor and a generalized displacement referred to as capacity factor. In the case of mechanical work, as shown above, the intensity factor is the force and the capacity factor is the displacement. In addition to mechanical work there are other forms of work which are possible like the electrical work which is a product of the electro motive force (intensity factor or generalized force) and the quantity of electricity (capacity factor or generalized displacement).

Electrical work, $DW = EMF \times \text{current or } \epsilon dq$

Expansion work, $DW = p dv$

Gravitational work, $DW = mg dh$

Surface work, $DW = \gamma dA$

Mechanical work, $DW = F ds$ (1)

where F is the force, p is the pressure exerted on the system by the surroundings, m is the mass, g is the acceleration due to gravity, γ is the surface tension, ϵ is the potential difference, V is the volume of the gas, h is the height, A is the surface area and q is the charge.

The notation DW stands for the small amount of work and also indicate the inexactness of the function. The work done depends on the path of the reaction. The work done, W is regarded and indicated by positive sign if the system does the work on the surroundings. The workdone, W is negative if the work is done on the system by the surroundings. Total work done by the system is obtained by integrating the quantities is

eq. (1). For instance, the total work done in the process of expansion is given by, $W = \int p \, dV$.

Evaluation of the work done by the system and on the system:

Examples

1. One mole of an ideal gas at 3 atm and 300 K is expanded isothermally to double its initial volume against an external pressure of 1.5 atm. Calculate the work done in the process of expansion.

$$\text{Work done, } W = p_{\text{ex}} \Delta V = p_{\text{ex}} (V_2 - V_1) \dots \dots \dots (1)$$

From the ideal gas equation, $PV = nRT$

$$V_1 = nRT/P_1 = (1 \text{ mol}) (0.082 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}) (300 \text{ K}) / (3 \text{ atm}) = 8.2 \text{ dm}^3$$

For an isothermal process, $P_1V_1 = P_2V_2$

$$V_2 = P_1V_1/P_2 = (3 \text{ atm}) (8.2 \text{ dm}^3) / (1.5 \text{ atm}) = 16.4 \text{ dm}^3$$

Substituting the values of p_{ex} , V_1 and V_2 in (1)

$$W = (1.5 \text{ atm}) (16.4 - 8.2) \text{ dm}^3 = 12.3 \text{ atm dm}^3$$

For expressing W in kJ, multiply with $(1.10132 \times 10^2 \text{ J atm}^{-1} \text{ dm}^{-3})$

$$W = 12.3 \text{ atm dm}^3 \times 1.10132 \times 10^2 \text{ J atm}^{-1} \text{ dm}^{-3} = 1.246 \times 10^3 \text{ J}$$

The work done is positive because the work is done by the system on the surroundings.

2. What is the work done on the system if a gas is compressed against a constant pressure of 5 atm and the gas is compressed from 5 dm³ to 1 dm³ at 300 K. Express W in terms of kJ.

Work done in compressing the gas is given by the following equation:

$$W = p \Delta V = p (V_2 - V_1) = (5 \text{ atm}) (1 - 5) \text{ dm}^3 = - 20 \text{ atm dm}^3$$

For expressing, W in kJ, multiply with $(1.10132 \times 10^2 \text{ J atm}^{-1} \text{ dm}^{-3})$

$$W = - 20 \text{ atm dm}^3 \times 1.10132 \times 10^2 \text{ J atm}^{-1} \text{ dm}^{-3} = - 2.2026 \text{ kJ}$$

10.6. Concept of Energy

Energy can be defined as the capacity to do work and bring about a change. Energy is the property which can be produced from or converted into work.

Examples

1. The energy output of an automobile engine provides the necessary capacity to move the vehicle from one place to another.
2. The energy output of a power plant provides the capacity to bring about various changes to operate lights, television, computer, motors and various other machines.

Unlike heat (Q) and work (W), the energy of a system (internal energy) is an exact quantity. It does not depend on the path but on the initial or final state of the system. It is a function of the state and is called as state function.

In general, any system will have number of degrees of freedom or motions. The internal energy of a system is the sum of the contributions due to all these modes. Even though, the energy of a system can be grossly and broadly divided into two categories, namely, the kinetic and the potential energies, it can be also assumed as the sum of the translational, rotational, vibrational, electronic, nuclear, positional and gravitational energies. It is difficult to find out the absolute value of energy of a system and in general in thermodynamics only the energy difference between the final and initial states of the system is considered.

i.e., $\Delta E = E_{\text{final}} - E_{\text{initial}}$

10.7. The First Law of Thermodynamics

The first law of thermodynamics deals with the law of conservation of energy. According to this law, energy can be neither created nor destroyed even though it can be converted from one form to the other. The first law can be stated in several other ways. It has been accepted that the perpetual motion of the first kind is impossible. This means that the production of energy of a particular type without the disappearance of an equivalent of energy of another form is impossible. So far no machine could be designed that would produce mechanical work continuously without drawing upon energy from an outside source. This is one of the aspects of the generalization commonly known as the first law of thermodynamics.

The first law of thermodynamics can be expressed mathematically as follows:

$\Delta E = Q - W$, where Q is the total heat absorbed and W is the work done by the system and ΔE is the change in the energy that has occurred.

The law implies that if the system loses energy W because of the work done and gains energy Q by the transfer of heat, the net gain of energy is $Q-W$. Thus according to the first law of thermodynamics, the quantity $(Q-W)$ must be identical with the increase in the the energy content, ΔE of the system. So the increase in the energy content of the system is equal to the difference between the heat absorbed by the system and the total work done by the system.

In differential form, $dE = DQ - DW \dots\dots (1)$

Equation (1) can also be expressed as follows depending on the process under study.

If no work is done by the system, then $DW = 0$ (constant volume process)

Then the first law can be expressed as : $dE = dQ \dots\dots (2)$

If no heat is absorbed or given out by the system, then $DQ = 0$ and equation (1) becomes $dE = - DW \dots\dots (3)$

Equation (3) represents an adiabatic process where neither heat is absorbed nor given out.

10.7.1. Process at constant volume

When the system performs the work of expansion alone, the work done by the system is given by the following equation:

$$W = p_{\text{ex}} \Delta V \dots\dots (1)$$

For a process that is carried out at constant volume, i.e., for an isochoric process, since the volume change between the final state and the initial state is nil, $\Delta V = 0 \dots\dots (2)$

Substituting (2) in (1) gives, $W = 0 \dots\dots (3)$

From the first law of thermodynamics we have, $\Delta E = Q - W \dots\dots (4)$

Substituting (3) in (5), we get, $\Delta E_v = Q_v$ (at constant volume)(5)

This means that the heat lost or gained by the system at constant volume is a direct measure of the change in the energy of the system. Examples of such processes are the reactions those are carried out in bomb calorimeter (isochoric process).

Examples for constant volume process

1. One mole of gas absorbs 400 J heat at constant volume and its temperature is raised from 20 °C to 25 °C. Calculate the values of W , Q and ΔE .

According to the first law of thermodynamics , $\Delta E = Q - W \dots\dots (1)$

Heat absorbed by one mole of gas (system), $Q = 400 \text{ J}$

Since the process is carried out at constant volume, $\Delta V = 0$

Work done = $p \, dv = 0$

Substituting the values of Q and W in (1) gives, $\Delta E = 400 \text{ J}$

2. Reaction between H_2 and O_2 in a bomb calorimeter.

Hydrogen and oxygen are enclosed in a bomb calorimeter immersed in a thermal bath at 27°C . The mixture is ignited electrically. After the reaction is complete, the temperature of the mixture in the bomb calorimeter is 35°C . Calculate the values of W, Q and ΔE for the process (a) Just after the completion of the reaction and (b) when the temperature of the bomb calorimeter and its contents are brought down to the thermal bath after losing 10 kJ of heat.

(a) Just after the completion of the reaction of formation of water from H_2 and O_2 in a bomb calorimeter by the ignition of an electrical spark at 27°C the change in the internal energy of the system is given by the first law of thermodynamics as follows:

$$\Delta E = Q - W \dots (1)$$

Since the process is a constant volume, isochoric process carried out in a bomb calorimeter, the work done by the system is zero.

$$W = 0 \dots (2) \text{ (Isochoric process)}$$

Immediately after the completion of the reaction, even though there is a raise in the temperature of the system from 27 to 35°C , no heat has left the calorimeter.

$$\text{So, } Q = 0 \dots (3)$$

Substituting (2) and (3) in (1) yields, $\Delta E = 0$

(b) When the temperature of the bomb calorimeter and its contents are brought down to the thermal bath, the heat lost by the system is 10 kJ.

$$\text{i.e., } Q = -10 \text{ kJ} \dots (4)$$

Since the process is still isochoric, $W = 0 \dots (5)$

Substituting the values of (4) and (5) in (1), we have $\Delta E = -10 \text{ kJ}$.

Thus the energy of the system decreases.

10.7.2. The concept of enthalpy, H

Enthalpy is defined as, $H = E + PV \dots (1)$

Change in enthalpy is given by, $\Delta H = \Delta E + \Delta (PV)$ (2)

In differential form, $dH = dE + d(PV)$ (3)

$$dH = dE + PdV + VdP \dots\dots\dots(4)$$

10.7.2.1. The process at constant pressure – Isobaric process

The change in enthalpy is given by the following equation (1)

$$dH = dE + PdV + VdP \dots\dots\dots(1)$$

If the process is carried out at constant pressure, i.e., under isobaric conditions,

$$dP = \Delta P = 0 \dots\dots\dots (2)$$

Substituting (2) in (1), $dH = dE + PdV$ (3)

According to the first law of thermodynamics, $dE = DQ - DW$(4)

Also we know that, the work done, $DW = PdV$...(5) (if only the work of expansion is involved)

Substituting (5) in (4), we have $dE = DQ - PdV$ (6)

Substituting (6) in (3), we have, $dH = DQ - PdV + PdV = DQ$

Thus $dH = dQ_p$

Thus the heat change under isobaric conditions is a direct measure of the enthalpy change of the system. The examples for such processes are the reactions carried out in laboratories in calorimeter, in reaction vessels and so on. Analogous to Q_v , Q_p is also a state function.

10.7.3. Relationship between Enthalpy and Energy:

For ideal gases, the relationship between the changes in enthalpy and energy are given by the following equation:

$$\Delta H = \Delta E + \Delta (PV) \dots\dots\dots (1)$$

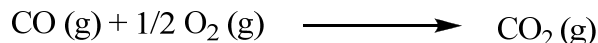
But according to the ideal gas equation, $\Delta (PV) = \Delta nRT$ at constant T, (2)

where Δn is the change in the number of moles of products and the reactants in a reaction.

Substituting (2) in (1), we have $\Delta H = \Delta E + \Delta nRT$(3)

Exercise

1. The change in enthalpy for the following reaction at 298 K is 282.85 kJmole⁻¹. Calculate the change in the internal energy of the reaction.



Given that, $\Delta H = 282.85 \text{ kJmol}^{-1}$; and $\Delta E = ?$

The relationship between the change in enthalpy and the change in internal energy of a system is given by the following equation:

$$\Delta H = \Delta E + \Delta nRT$$

Therefore, $\Delta E = \Delta H - \Delta nRT$ (1)

$\Delta n = (\text{no. of moles of products}) - (\text{no. of moles of reactants})$

$$= (1 \text{ mol of CO}_2) - (1 \text{ mol of CO} + 1 \text{ mol of O}_2) = (1 - 3/2) = - 0.5 \text{ moles}$$

$T = 298 \text{ K}$; $R = 8.314 \text{ Jmol}^{-1}\text{K}^{-1}$

Substituting the values of ΔH , Δn , R and T in (1) gives

$$\Delta E = (282.85 \text{ kJmol}^{-1}) - [(-0.5 \text{ mol}) \times (8.314 \text{ Jmol}^{-1}\text{K}^{-1}) (298\text{K})]$$

$$\Delta E = 283.85 \text{ kJmol}$$

10.8. The Second Law of Thermodynamics

The second law of thermodynamics can be stated in various forms as below:

- (i) Heat can not be completely converted into work without leaving changes either in the system or in the surroundings.
- (ii) Heat cannot be pass from a colder to a warmer body.
- (iii) Entropy increases in irreversible processess

The first law of thermodynamics provides no information related to the spontaneity or feasibility or probability of a process even though it indicates that in any process there is an exact equivalence between the various forms of energy involved.

The main interest for the chemists in the second law of thermodynamics is that is provides a way to predict if a particular reaction can occur under specified conditions. Thus the second law of thermodynamics provides an answer to the question whether a particular process is or is not possible.

Examples:

1. The first law of thermodynamics does not indicate whether water can spontaneously run uphill or not. What all the first law of thermodynamics states is that if water does run

uphill there will be a fall of temperature and the decrease of energy content will be equivalent to the work done against the gravity (unless heat is supplied from outside).

2. In an analogous manner, the first law of thermodynamics do not predict whether a bar of metal or uniform temperature can spontaneously become warmer at one end and cooler at the other. What all the first law can state is that if the process specified above were to occur, the heat energy gained by one end would be exactly equal to that lost by the other.

It is only the second law of thermodynamics that provides the condition or the criterion for the possibility or the probability or the spontaneity of various processes.

10.9. Spontaneous Processes

Those processes which take place without external intervention of any kind are known as the spontaneous processes. It is important to understand the conditions which determine whether a particular process is spontaneous or not.

Example:

1. Expansion of a gas into an evacuated space.
2. Expansion of gas from any region of higher pressure into one of lower pressure takes place spontaneously until the pressure distribution is uniform through out.
3. Diffusion of one gas into another until the mixing is complete and the composition of the system is homogeneous through out the system.
4. Diffusion of a solute from a concentrated solution into pure solvent, or into a dilute solution, will take place with out external intervention.
5. The conduction of heat along a bar of metal which is hot at one end and cold at the other end.
6. The transfer of heat from a hotter body to a colder body by radiation is spontaneous.

All the spontaneous processes represent a tendency to approach a state of thermodynamic equilibrium.

7. Flow of liquids from a higher to a lower level is a spontaneous process; the flow continues until the two levels are equal and a mechanical equilibrium is attained. The reverse process is not observed to occur.

8. When a solute such as ammonium chloride is added to water, it dissolves with the absorption of heat. The dissolution is endothermic and spontaneous while the reverse

process where in the solid ammonium chloride separates from the solution with the evolution of heat leaving pure water is not observed.

9. A piece of zinc when placed in contact with a solution of copper sulphate dissolves spontaneously, precipitating copper. The reaction can be reversed only by passing electric current between a copper rod and a zinc rod immersed in aqueous zinc sulphate solution.

10.9.1. Characteristic features of Spontaneous Processes

1. Spontaneous processes never revert themselves with out the intervention of an external agency. A system in equilibrium under a given set of conditions will not undergo detectable change unless the conditions are altered. Thus the spontaneous processes are not thermodynamically reversible.

2. Spontaneous processes have a natural tendency to move towards a state of equilibrium.

3. All natural processes proceed spontaneously (i.e., without external aid) and are irreversible in character.

10.10. Concept of Entropy

The term entropy means transformation or change. The concept of entropy was introduced by Clausius to account for the tendency of the system to change and also to indicate the direction in which the change can take place. The entropy always increases when a change is produced naturally. As spontaneous processes occur on their own and pass from more ordered state to a more disordered state, *the entropy function is a measure of the randomness of the system.*

10.10.1. General conditions for Spontaneity based on Entropy

Entropy serves as a criterion for spontaneity and equilibrium as this is the only state function that distinguishes between reversible and irreversible processes. The change in entropy of a system plus its surroundings (i.e., the change of total entropy, $\Delta S_{\text{total or universe}}$) provides a criterion for whether a process is spontaneous or non spontaneous or in equilibrium.

$$\Delta S_{\text{universe}} > 0 \text{ (spontaneous)}$$

$$\Delta S_{\text{universe}} = 0 \text{ (equilibrium)}$$

$$\Delta S_{\text{universe}} < 0 \text{ (non spontaneous)}$$

Even though the sign of $\Delta S_{\text{universe}}$ is a completely general criterion for assessing the spontaneity or non spontaneity of a process, its use requires the calculation of the entropy change of the surroundings as well as the entropy change of the system. So it is very desirable to have a state property that would tell us about the spontaneity of a process with out reference to the surroundings.

10.11. Concept of Gibbs Free Energy and the Criterion for Spontaneity

For processes taking place at constant temperature and pressure, Gibbs Free Energy is defined as, $G = H - TS$ (1)

The change in the Gibbs Free Energy (ΔG) alone provides a criterion for the spontaneity of a process at constant pressure and temperature

$$\text{Change in free energy of a system is given by, } \Delta G_{\text{sys}} = \Delta H_{\text{sys}} - \Delta(T_{\text{sys}}S_{\text{sys}}) \dots\dots (2)$$

If the temperature of the system stays constant and equal to the temperature of the surroundings, then T_{sys} can be taken outside the parenthesis and abbreviated at T.

$$\text{Then } \Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}} \dots\dots\dots (3)$$

According to the second law of thermodynamics, at constant pressure and temperature, the change in entropy of the surroundings is given by

$$\Delta S_{\text{surr}} = - \Delta H_{\text{sys}}/T \dots\dots\dots(4)$$

In equation (4), the minus sign is important. If the process were to be exothermic then, ΔH_{sys} is negative and equation (4) becomes positive. i.e., the entropy change of the surrounding is positive.

The total entropy change in a spontaneous process is then

$$\Delta S_{\text{univer}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} - (\Delta H_{\text{sys}}/T) > 0 \dots\dots\dots (5)$$

If we multiply both sides of the in equality by the absolute temperature, which is always positive it becomes that

$$T \Delta S_{\text{sys}} - \Delta H_{\text{sys}} > 0 \dots\dots\dots (6)$$

$$\text{Therefore, } \Delta H_{\text{sys}} - T \Delta S_{\text{sys}} < 0 \dots\dots\dots (7)$$

Comparing (7) and (2), $\Delta H_{\text{sys}} - T \Delta S_{\text{sys}} = \Delta G_{\text{sys}} < 0$

Thus the change in the free energy of the system alone determines the spontaneity of a process. Thus we can conclude that, at constant temperature and pressure,

$\Delta G_{\text{sys}} < 0$ (spontaneous process)

$\Delta G_{\text{sys}} = 0$ (equilibrium process)

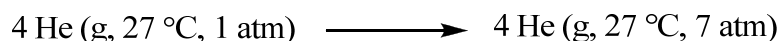
$\Delta G_{\text{sys}} > 0$ (non-spontaneous process)

If $\Delta G_{\text{sys}} > 0$ for a particular process, then $\Delta G_{\text{sys}} < 0$ for the reverse process and the reverse process therefore occurs spontaneously at constant temperature and pressure.

Since the change in G (ΔG) is a measure of the 'useful' work, G is called the free energy.

Problems

1. Calculate the value of free energy change for the following process and comment on the spontaneity.



The change in free energy value is given by the following equation:

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

Since the temperature is constant through out the process of compression, $\Delta H = 0$

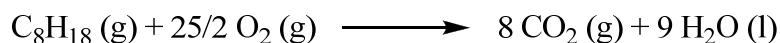
$$p_1 = 1 \text{ atm.}, p_2 = 7 \text{ atm}; T = 27^\circ\text{C} = 27 + 273 = 300 \text{ K}$$

$$\begin{aligned} \Delta S &= nR \ln p_1/p_2 = (4 \text{ mol}) \times (8.314 \text{ Jmol}^{-1}\text{K}^{-1}) \ln 1/7 \\ &= 4 \times 8.314 \times -1.946 = -64.716 \text{ JK}^{-1} \end{aligned}$$

$$\Delta G = - (300 \text{ K}) (-64.716 \text{ JK}^{-1}) = +19,414.8 = +19.415 \text{ kJ}$$

Since the sign of ΔG is positive the reaction is not spontaneous.

2. Calculate the value of free energy change for the following reaction and comment whether the reaction is spontaneous or not.



Given $\Delta H^0 = -5.93 \times 10^3 \text{ kJ}$. The standard entropies of C_8H_{18} , O_2 , CO_2 and H_2O are 463.67 EU, 205.03 EU, 213.64 EU and 69.94 EU respectively. The reaction is carried out in a bomb calorimeter. The reactants were at 1 atm. and 25°C to start with and the reaction is complete.

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

$$\Delta H = -5.93 \times 10^3 \text{ kJ}$$

$$T = 25^\circ\text{C} = 25 + 273 = 298 \text{ K}$$

In the above reaction of the combustion of octane, ΔS (change in entropy of the reaction) can not be calculated as simply the difference in the entropies of the products and the reactants because there is a change in the number of moles in the formation of products from the reactants.

No. of moles of reactants = 13.5 moles

No. of moles of products = 8 moles

Final pressure, $p_{\text{fin}} = p_{\text{ini}} \times n_f / n_i = (1 \text{ atm}) (8 \text{ mol} / 13.5 \text{ mol}) = 0.593 \text{ atm}$

The standard entropy of CO_2 is 213.64 EU

The entropy of CO_2 at 0.593 atm is given by,

$$S = S_0 + R \ln p_1/p_2 = 213.64 + (8.314 \text{ JK}^{-1}\text{mol}^{-1}) (1 \text{ atm} / 0.593 \text{ atm}) = 217.99 \text{ EU}$$

$\Delta S = (\text{entropy of products}) - (\text{entropy of reactants})$

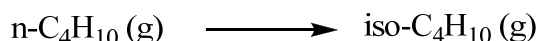
$$= [(8 \text{ mol}) (217.99 \text{ EU}) + (9 \text{ mol}) (69.94 \text{ EU})] - [(1 \text{ mol}) (463.67 \text{ EU}) + (12.5 \text{ mol}) (205.03 \text{ EU})] = - 653.165 \text{ EU}$$

Substituting the values in (1) gives

$$\Delta G = - 5930 \text{ kJ} - (298 \text{ K}) (- 653.165 \text{ EU}) = - 5930 \text{ kJ} + 194.64 \text{ kJ} = - 5735.36 \text{ kJ}$$

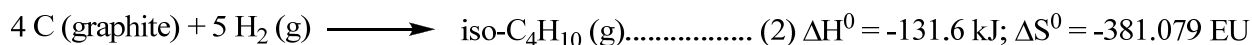
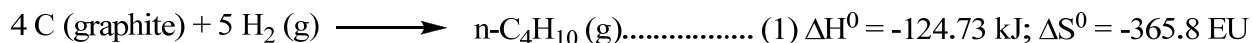
Since the sign of the change in the free energy value is negative, the process of combustion of octane is spontaneous.

3. Evaluate if the following transformation of n-butane to iso-butane



is spontaneous from the following data:

For the reactions



The free energy change for the formation of n-C₄H₁₀ (g) is calculated from the formula:

$$\Delta G^0_{\text{n-butane}} = \Delta H^0 - T \Delta S^0$$

$$\begin{aligned} \Delta G^0_{\text{n-butane}} &= - 124.73 \text{ kJ} - (298 \text{ K}) (- 365.8 \text{ JK}^{-1}) = - 124.73 \text{ kJ} - (298 \times - 0.3658 \times 10^3 \text{ J}) \\ &= - 124.73 \text{ kJ} + (298 \times 0.3658) \text{ kJ} = - 15.722 \text{ kJ} \end{aligned}$$

The free energy change for the formation of iso-C₄H₁₀ (g) is calculated from the formula:

$$\Delta G^0_{\text{iso-butane}} = \Delta H^0 - T \Delta S^0$$

$$\Delta G_{\text{iso-butane}}^0 = -131.6 \text{ kJ} - (298 \text{ K}) (-31.079 \text{ EU}) = -131.6 \text{ kJ} - (298 \text{ K}) (-381.079 \text{ JK}^{-1})$$

$$= -131.6 \text{ kJ} + (298 \times 381.079 \times 10^{-3} \text{ kJ}) = -18.04 \text{ kJ}$$

The free energy change for the final reaction involving the transformation of n-butane to iso-butane is given by:

$$\Delta G^0 = \Delta G_{\text{iso-butane}}^0 - \Delta G_{\text{n-butane}}^0 = -18.04 - (-15.722) = -18.04 + 15.722 = -2.32 \text{ kJ}$$

As the sign of change in free energy value is negative the transformation of isobutene from n-butane is spontaneous.

4. (a) Calculate the change in the free energy involved in an isothermal reversible expansion process if a pressure of one mol of ideal gas drops from 100 atm to 20 atm at a temperature of 25 °C.

(b) Calculate the ΔG if the expansion is carried out against a constant pressure of 2 atm.

(a) The change in free energy for the process of isothermal reversible expansion is given by the formula

$\Delta G = nRT \ln p_2/p_1$ where, p_1 and p_2 are the initial and final pressures and n is the no. of moles of the ideal gas involved.

$$n = 1 \text{ mol}; p_1 = 100 \text{ atm.}, p_2 = 20 \text{ atm.}$$

Substituting the values in (1)

$$\Delta G = (1 \text{ mol}) (8.314 \text{ Jmol}^{-1}\text{K}^{-1}) (298 \text{ K}) \ln 20 \text{ atm}/100 \text{ atm} = -3.988 \text{ kJ}$$

(b) The parameter, free energy (G) is a function of the state (state function) which does not depend on the path. So even if the process of isothermal reversible expansion is carried against a constant pressure of 2 atm., the value of ΔG remains the same as the calculated in (a). This is because the initial and final states are defined.

5. Consider the following reaction:



$$\Delta H_f^0 (\text{CO, g}) = -110.52 \text{ kJmol}^{-1}; \quad \Delta H_f^0 (\text{H}_2\text{O, g}) = -241.83 \text{ kJmol}^{-1};$$

$$\Delta H_f^0 (\text{CO}_2, \text{g}) = -393.54 \text{ kJmol}^{-1};$$

$$S^0 (\text{CO}) = 197.91 \text{ EU}; S^0 (\text{H}_2\text{O}) = 188.72 \text{ EU}$$

$$S^0 (\text{CO}_2) = 213.64 \text{ EU}; S^0 (\text{H}_2) = 130.59 \text{ EU}$$

From the above data indicate whether the reaction (1) is spontaneous or not at 298 K. Calculate the temperature at which the reaction will go in the reverse direction.

Reaction (1) will be spontaneous or feasible if the free energy change involved in the reaction is negative. The net free energy change can be calculated using the equation:

$$\Delta G^0 = \Delta H^0 - T \Delta S^0$$

$$\Delta H^0 = \sum_i^{\text{products}} n_i \Delta H_f^0 - \sum_j^{\text{reactants}} n_j \Delta H_f^0$$

$$= -393.54 - [(-110.52) + (-241.83)] = -41.19 \text{ kJ}$$

$$\Delta S^0 = S^0_{\text{products}} - S^0_{\text{reactants}}$$

$$= 213.64 + 130.59 - 197.91 - 188.72 = -42.4 \text{ J mol}^{-1} \text{ deg}^{-1}$$

$$\Delta G^0 = -41.19 \text{ kJ} - (298 \text{ K})(-42.4 \times 10^{-3} \text{ kJ deg}^{-1}) = -41.19 + 12.64 = -28.55 \text{ kJ}$$

The free energy change of the reaction is -28.55 kJ . So the reaction will be spontaneous.

The reaction will proceed in the opposite direction as soon the free energy change of the reaction turns positive or starts changing the sign.

The minimum temperature at which ΔG^0 becomes zero can be calculated as follows:

It is assumed that ΔH^0 and ΔS^0 do not change appreciably in this temperature range.

$$\text{Thus, } 0 = \Delta H^0 - T_{\text{min}} \times \Delta S^0$$

$T_{\text{min}} = \Delta H^0 / \Delta S^0 = -41.19 \text{ kJ} / -42.4 \text{ JK}^{-1} = 971.5 \text{ K}$, i.e., at a temperature greater than 971.5 K, the reaction will go in the opposite direction.

6. In the cell, Pt/H₂ (1 atm)/H⁺ (1 mol)//Zn²⁺ (1 mol)/Zn, the cell reaction is
 $\text{Zn}^{2+}(\text{aq}) + \text{H}_2(\text{g}) \longrightarrow \text{Zn} + 2 \text{H}^+(\text{aq})$

and e.m.f. is -0.763 V at 25°C . Calculate the free energy change of the reaction and comment on the spontaneity of the reaction.

The electrical work and the change in the free energy are related as follows:

$$\Delta G^0 = -nFE_0 \dots\dots\dots (1)$$

where ΔG^0 is the standard free energy change,

n is the number of electrons transferred

F is the faraday constant ($9.65 \times 10^4 \text{ C mol}^{-1} = 9.65 \times 10^4 \text{ J mol}^{-1} \text{ V}^{-1}$) and

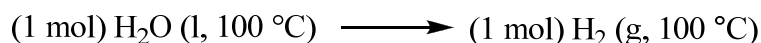
E_0 is the standard cell potential.

Substituting the values in equation (1)

$$\Delta G^0 = - (2) (9.65 \times 10^4 \text{ Jmol}^{-1}\text{V}^{-1}) (- 0.763) = 14.73 \times 10^4 \text{ J} = 147.3 \text{ kJ}$$

Since the sign of ΔG^0 is positive the reaction is not spontaneous.

7. Consider the following phase transition:



What will be the free energy change for the above process at 100 °C?

$T = 100 \text{ }^\circ\text{C}$ is the boiling temperature of water, T_b

The above process is a phase change from liquid state to vapour state at constant temperature. So the change in entropy is given by the following equation,

$$\Delta S = \Delta H_{\text{vaporization}}/T_{\text{boiling}}$$

The change in free energy is given by the following equation:

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

$$\Delta G = \Delta H_{\text{vaporization}} - T_b \times \Delta H_{\text{vaporization}}/T_b = 0$$

Thus, $\Delta G = 0$

This is in general true for any phase transition process as the phase change is an equilibrium process at the phase transition temperature and pressure. As the ΔG value is zero the phase transition is an equilibrium processes.

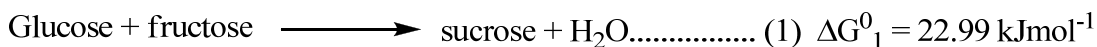
8. Coupled Reactions

Quite often we encounter certain reactions which are non spontaneous with a positive value of change in free energy ($\Delta G > 0$). But if the same reactions were to be coupled with other reactions which are spontaneous, the original reactions become spontaneous or feasible. Such a transformation of non-spontaneity to spontaneity is possible only if the total free energy change (i.e., the sum of the free energies of the second reaction and the original reaction) is negative.

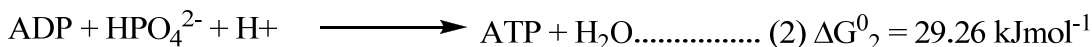
Thus the presence of reactions where the ΔG value is very negative, the non-spontaneous reactions become spontaneous.

Example

1. The following reaction of the formation of sucrose from glucose and fructose is non-spontaneous.



Show that reaction (1) becomes spontaneous when coupled with the reaction (2) given below,



where ADP and ATP are adenosine di phosphate and adenosine triphosphate.

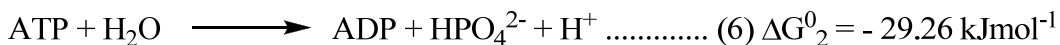
The mechanism for the formation of sucrose from glucose and fructose in the presence of ATP is as follows:



Addition of (3) and (4) yield (5)



Now consider the reverse reaction of (2)



Addition of reaction (1) and (6) yield (7)



Note that reaction (5) and (7) are the same.

The change in free energy for the coupled reaction (7) is given given by

$$\Delta G^0 = \Delta G^0_1 + (- \Delta G^0_2) = 22.99 \text{ kJmol}^{-1} + (- 29.26 \text{ kJmol}^{-1}) = (22.99 - 29.26) \text{ kJmol}^{-1}$$

$$\Delta G^0 = - 6.27 \text{ kJmol}^{-1}$$

As the free energy change accompanied with the coupled reaction is negative, the reaction is spontaneous. Thus coupling reaction (1) and the reverse of reaction (2) makes the complete reaction spontaneous (feasible).

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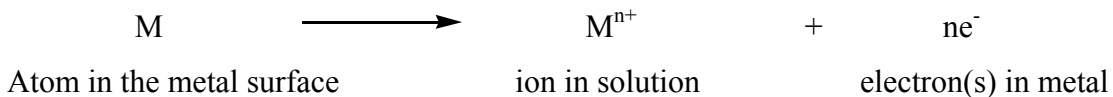
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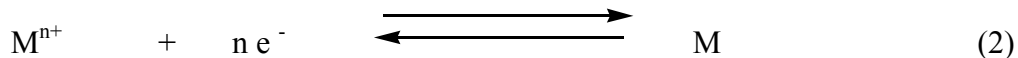
CHAPTER - 11
CORROSION AND ITS PREVENTION ELECTROCHEMICAL
INTERPRETATION

11.1. Introduction

The surfaces of all metals (except gold) in air are covered with oxide films. When such a metal is immersed in an aqueous solution, the oxide film tends to dissolve. If the solution is acidic, the oxide film may dissolve completely leaving a bare metal surface, which is said to be in the active state. In near-neutral solutions, the solubility of the oxide will be lower than in acid solution and the extent of dissolution will tend to be smaller. The underlying metal may then become exposed initially only at localized points where owing to some discontinuity in the metal, e.g. the presence of an inclusion or a grain boundary, the oxide film may be thinner or more prone to dissolution than elsewhere. If the near neutral solutions contains inhibiting anions, this dissolution of the oxide film may be suppressed and the oxide film stabilized to form a passivating oxide film which can effectively prevent the corrosion of the metal, which is then in the passive state. When the oxide-free surface of a metal becomes exposed to the solution, positively charged metal ions tend to pass from the metal into the solution, leaving electrons behind on the metal, i.e.,



The accumulation of negative charge on the metal due to the residual electrons leads to an increase in the potential difference between the metal and the solution. This potential difference is called the electrode potential or, simply, the potential of the metal, which thus becomes more negative. This change in the potential retards the dissolution of metal ions supports the deposition of dissolved metal ions from the solution on to the metal surface. The dissolution and deposition of metal ions reaches a stable potential. Thus the rate of dissolution becomes equal to the rate of deposition. This potential is termed the reversible potential E_r and its value depends on the concentration of dissolved metal ions and the standard reversible potential E_0 for unit activity of dissolved metal ions, aM^{n+} , i.e.,



$$E_{r, Mn+/M} = E_{Mn+/M}^0 + \frac{RT}{nF} \ln a_{M^{n+}} \quad (3)$$

Where,

R is the gas constant,

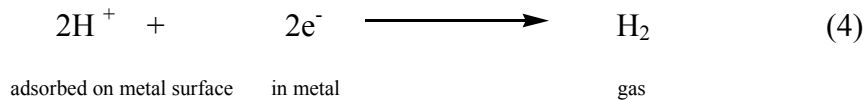
T the absolute temperature,

F the Faraday and

n the number of electrons transferred per ion.

Once the potential reaches the reversible potential, no further net dissolution of metal occurs. The net amount of metal which dissolves during this process is generally very small.

The potential of a metal in a solution does not usually reach the reversible potential but remains more positive because electrons can be removed from the metal by alternative reactions. In acid solutions, electrons can react with hydrogen ions, adsorbed on the metal surface from the solution, to produce hydrogen gas.

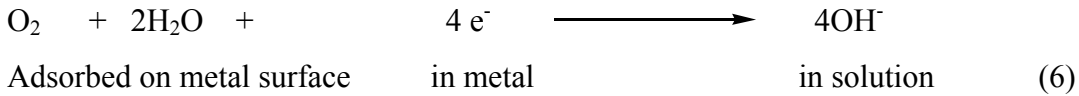


The occurrence of reaction (4) permits the continued passage of an equivalent quantity of metal ions into solution, leading to corrosion of the metal. Reaction (4) is also reversible and has a reversible potential given by

$$E_{r, H^+/H_2} = E_{H^+/H_2}^0 - \frac{RT}{nF} \ln \frac{p_{H_2}^{1/2}}{a_{H^+}}$$

where p_{H_2} is the partial pressure (fugacity) of hydrogen gas. If the partial pressure of hydrogen is allowed to build up, then the reversible potential of reaction (4) could be attained. No further net reaction of hydrogen ions would occur and so the net dissolution of metal ions would effectively cease. Normally hydrogen escapes from the system, so that the potential remains more negative than the reversible potential and corrosion continues.

In neutral solutions, the concentration of hydrogen ions is too low to allow reaction (4) to proceed at a significant rate, but electrons in the metal can react with oxygen molecules, adsorbed on the metal surface from air dissolved in the solution, to produce hydroxyl ions



Again, the potential of the metal remains more negative than the reversible potential for

$$E_{r, \text{O}_2 / \text{OH}^-} = E_{\text{O}_2 / \text{OH}^-}^0 - \frac{RT}{4F} \ln \frac{P_{\text{OH}^-}^4}{P_{\text{O}_2}}$$

Thus corrosion can proceed by the coupling of reactions (1) and (6).

In electrochemical terminology, an electrode at which an oxidation reaction occurs is called an anode. The process of oxidation involves a loss of electrons by the reacting species, as shown in equation (1). Thus an area of a corroding metal where metal dissolution occurs is an anode and metal dissolution is the anodic reaction of corrosion. An electrode at which a reduction reaction occurs is called a cathode. Reduction involves gain in electrons, as shown in equation (4) and (6). These reactions are called cathodic reactions of corrosion and the area of the corroding metal where these reactions occur is called cathode.

11.1. Why do metals corrode?

Any spontaneous reaction in the universe is associated with a lowering in the free energy of the system. All metals except the noble metals have free energies greater than their compounds. So they tend to become their compounds through the process of corrosion. Except noble metal, all metals are unstable to varying degrees in a terrestrial atmosphere. The most widely used metals, namely, Iron, aluminium, copper, nickel, silver and alloys of these metals all decay and lose good mechanical properties.

11.2. What is corrosion ?

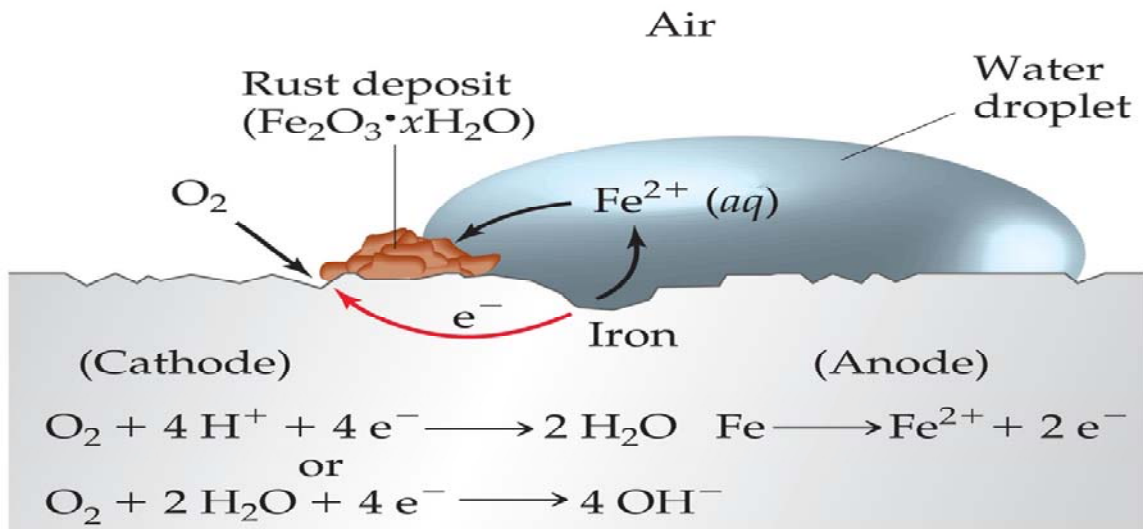


Fig. 11.1. Corrosion of Fe

Corrosion is the deterioration of materials by chemical interaction with their environment. The term corrosion is sometimes also applied to the degradation of plastics, concrete and wood, but generally refers to metals. The most widely used metal is iron (usually as steel) and the following discussion is mainly related to its corrosion.

E.g.

- 1) Rusting conversion of iron in to its oxide (Fe_2O_3 - Heamatite)
- 2) Tarnishing silver is converted in its sulfide (Ag_2S –Silver glance)
- 3) Conversion of copper in to its green colored carbonate (malachite)

11.3. Electrochemistry of corrosion

For corrosion to take place, the formation of a corrosion cell is essentially comprised of the following four components.

- a) Anode
- b) Cathode
- c) Electrolyte
- d) Metallic path.

11.3.1. Anode

An anode is an electrode through which electric current flows in to a polarized electrical device. The misconception is that anode polarity is always positive (+). This is often incorrectly inferred from the correct fact that in all electrochemical device negatively charged anions moves towards the anode (or oppositely charged cations move away from it). Anode polarity depends on the device type and sometimes even in which mode it operates. In Fig 3 Zn rod act as anode.

11.3.2 Cathode

One of the two electrodes in an electrolytic cell represented as a positive terminal of a cell. Reduction takes place at the cathode and electrons are consumed.

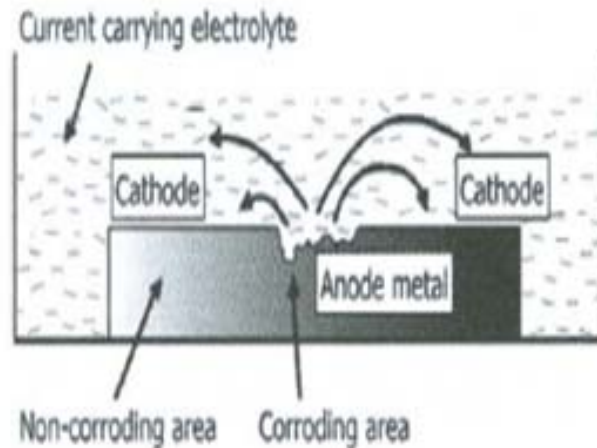


Fig. 11.2. Corrosion cell in action

11.3.3 Electrolyte

It is the electrically conducting solution (e.g. salt solution) that must be present for corrosion to occur. Note that pure water is a bad conductor of electricity. Positive electricity passes from anode to cathode through the electrolyte as cations, e.g. Zn^{++} ions dissolve from a zinc anode and thus carry positive current away from it, through the aqueous electrolyte.

11.3.4 Metallic path

The two electrodes are connected externally by a metallic conductor. In the metallic conductor, 'conventional' current flows from (+) to (—) which is really electrons flowing from (—) to (+). Metals provide a path for the flow of conventional current which is actually passage of electrons in the opposite direction.

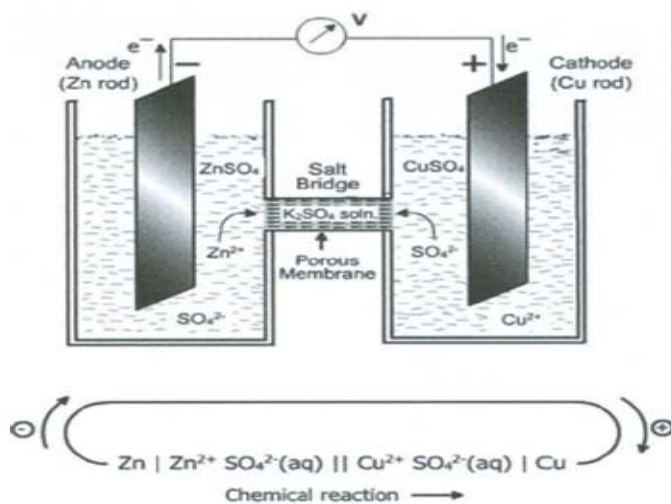


Fig. 11.3. Simple galvanic cell

11.3.5. Current flow

Conventional current flows from anode (—) to cathode (+) as Zn⁺⁺ ions through the solution. The current is carried by these positive charged ions. The circuit is completed by passage of electrons from the anode (—) to the cathode (+) through the external metallic wire circuit (outer current).

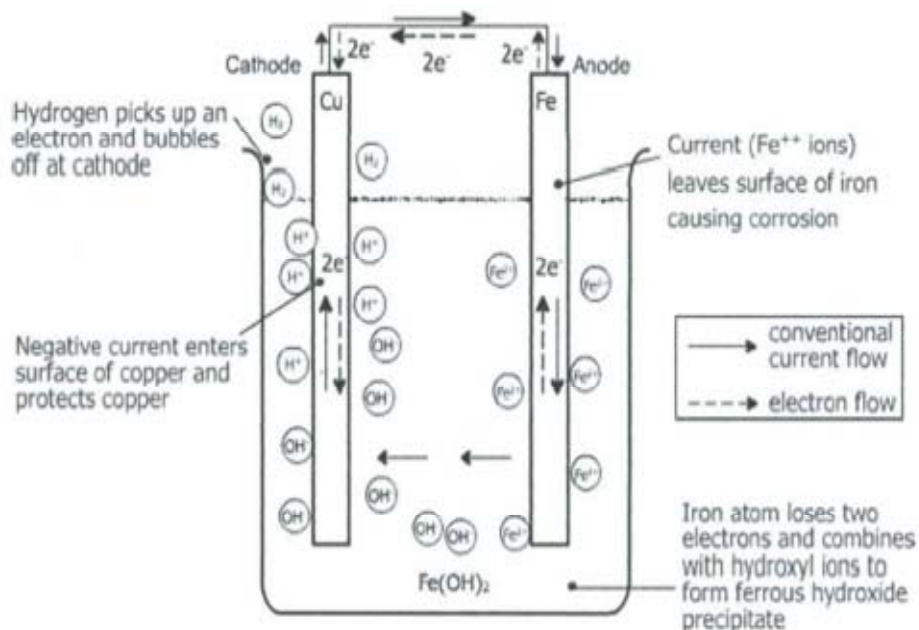
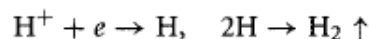


Fig. 11.4. Electrolytic path representing current and electron flow

11.3.6 Electron flow



Although the anode (e.g. Fe or Zn) is the most negative of the two metals in the cell, this reaction does not occur there because its surface is emanating Fe⁺⁺ ions which repel H⁺ ions from discharging there. The circuit is completed by negative ions (—) which migrate from the cathode (+), through the electrolyte, towards the anode (—). They form Fe(OH)₂ when they enter the cloud of Fe⁺⁺ ions coming from the anode.

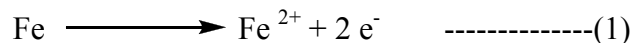
11.3.7 Corrosion of iron

Common structural metals are obtained from their ores or naturally-occurring compounds by the expenditure of large amounts of energy. These metals can therefore be regarded as being in a meta stable state and will tend to lose their energy by reverting to compounds more or less similar to their original states. Since most metallic compounds, and especially corrosion products, have little mechanical strength a severely corroded piece of metal is quite useless for its original purpose. Virtually all corrosion reactions are electrochemical in nature, at anodic sites on the surface the iron goes into solution as

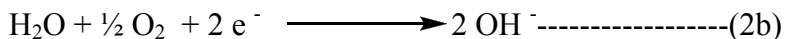
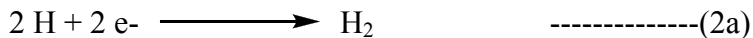
ferrous ions, this constituting the anodic reaction. As iron atoms undergo oxidation to ions they release electrons whose negative charge would quickly build up in the metal and prevent further anodic reaction, or corrosion.

Thus this dissolution will only continue if the electrons released can pass to a site on the metal surface where a cathodic reaction is possible. At a cathodic site the electrons react with some reducible component of the electrolyte and are themselves removed from the metal. The rates of the anodic and cathodic reactions must be equivalent according to Faraday's Laws, being determined by the total flow of electrons from anodes to cathodes which is called the "corrosion current", I_{cor} . Since the corrosion current must also flow through the electrolyte by ionic conduction the conductivity of the electrolyte will influence the way in which corrosion cells operate. The corroding piece of metal is described as a "mixed electrode" since simultaneous anodic and cathodic reactions are proceeding on its surface. The mixed electrode is a complete electrochemical cell on one metal surface. The most common and important electrochemical reactions in the corrosion of iron are thus

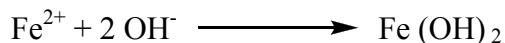
Anodic reaction (corrosion)



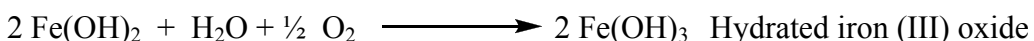
Cathodic reactions



Reaction 2a is most common in acids and in the pH range 6.5 – 8.5 the most important reaction is oxygen reduction 2b. In this latter case corrosion is usually accompanied by the formation of solid corrosion debris from the reaction between the anodic and cathodic products.

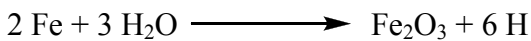


Pure iron (II) hydroxide is white but the material initially produced by corrosion is normally a greenish color due to partial oxidation in air.



Further hydration and oxidation reactions can occur and the reddish rust that eventually forms is a complex mixture whose exact constitution will depend on other trace elements

which are present. Because the rust is precipitated as a result of secondary reactions it is porous and absorbent and tends to act as a sort of harmful poultice which encourages further corrosion. For other metals different types of anodic and cathodic reactions may occur. If solid corrosion products are produced directly on the surface as the result of anodic oxidation, these may provide a highly protective surface film which retards further corrosion, the surface is then said to be “passive”. An example of such a process would be the production of an oxide film on iron in water, a reaction which is encouraged by oxidizing conditions at elevated temperatures.



11.4. Mechanism of corrosion

The mechanism of rusting is found to be electrochemical in nature: Anode and cathode are involved: electrons flow from anode to cathode, oxidation of iron to Fe (II) occurs at the anode, and several reduction reactions occur at the cathode. See Figure 11.5.

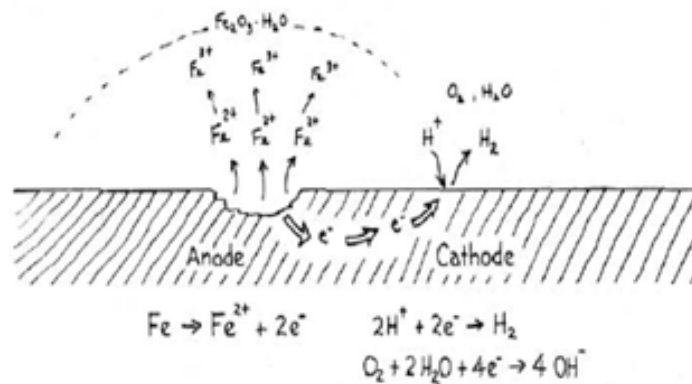


Fig. 11.5. The mechanism of Iron corrosion

At anode areas of iron, the iron is electrochemically oxidized to Fe(II). In an oxygen environment, the Fe(II) is quickly oxidized to Fe(III) which is subsequently changed to Fe(OH)₃ and finally to a hydrated ferric oxide. The degree of hydration of the oxide influences the color of iron rust which may vary from black to yellow to red-brown. The intermediate Fe(III) ion is, incidentally, a promoter of corrosion and the iron oxides are soft, non-adherent deposits that encourage further corrosion of the metal by

occluding moisture and electrolyte, all of which are essential to the electrochemical cell that operates in the corrosion of iron.

11.5. Types of corrosion

Corrosion may be classified in different ways

- i) Wet / aqueous Corrosion
- ii) Temperature Corrosion

11.5.1. Wet/ Aqueous corrosion

Wet / aqueous corrosion is the major form of corrosion. Based on the appearance of the corroded metal, wet corrosion may be classified as

- i) Uniform or General
- ii) Galvanic or Two-metal
- iii) Crevice
- iv) Pitting
- v) Intergranular
- vi) Velocity-assisted
- vii) Environment-assisted cracking

11.5.1.1 Uniform corrosion

Corrosion over the entire exposed surface at a uniform rate. e.g. Atmospheric corrosion. Maximum metal loss by this form. Not dangerous, rate can be measured in the laboratory.

11.5.1.2 Galvanic corrosion

Galvanic corrosion is the term applied to the accelerated corrosion of metal caused by dissimilar metals being in contact in a corrosive medium. Dissimilar metal corrosion is usually a result of faulty design or improper maintenance practices which result in dissimilar metals coming in contact with each other. This is usually seen as a buildup of corrosion at the joint between the metals. For example, when aluminum pieces are attached with steel bolts and moisture or contamination are present, galvanic corrosion occurs around the fastener. When two dissimilar metals are

joined together and exposed, the more active of the two metals corrode faster and the nobler metal is protected. This excess corrosion is due to the galvanic current generated at the junction.

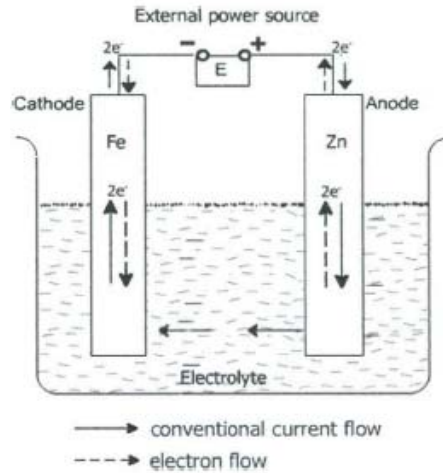


Fig. 11.6. Al sheets covering underground Cu cables

11.5.1.3 Crevice corrosion

Intensive localized corrosion within crevices & shielded areas on metal surfaces Small volumes of stagnant corrosive caused by holes, gaskets, surface deposits, lap joints

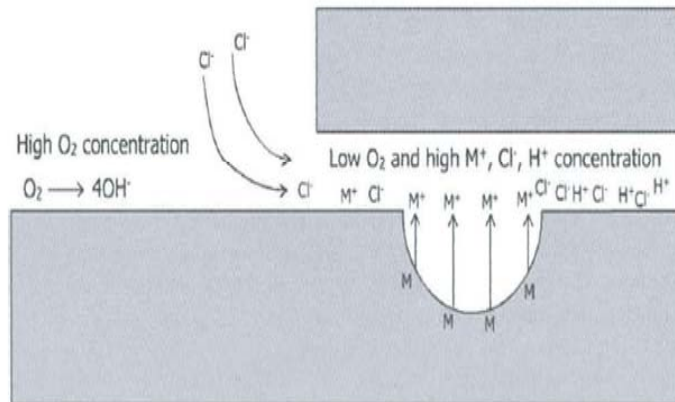


Fig. 11.7. Crevices corrosion

11.5.1.4 Pitting

The most common effect of corrosion on aluminum alloys is pitting. It is caused primarily by variations in the grain structure between adjacent areas on the metal surfaces that are in contact with a corrosive environment. Pitting is first noticeable as a white or gray powdery deposit, similar to dust, that blotches the surface. When the superficial deposit is cleaned away, tiny pits or holes can be seen in the surface. These pits may appear either as relatively shallow indentations or as deeper cavities of small diameters. Pitting may occur in any metal, but it is particularly characteristic of aluminum and aluminum alloys. A form of extremely localized attack causing holes in the metal. Most destructive form Autocatalytic nature.

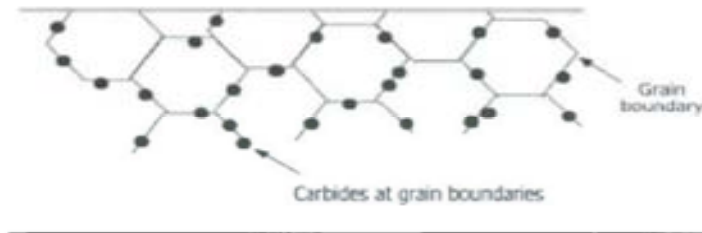


Fig. 11.8. Pitting corrosion

11.5.1.4.1. Prevention of pitting corrosion

- i) Use materials with appropriate alloying elements designed to minimize pitting susceptibility, e.g. molybdenum in stainless steel.
- ii) Provide a uniform surface through proper cleaning, heat treating and surface finishing.
- iii) Reduce the concentration of aggressive species in the test medium, such as chlorides, sulfates, etc.
- iv) Use inhibitors to minimize the effect of pitting, wherever possible.
- v) Make the surface of the specimen smooth and shiny and do not allow any impurities to deposit on the surface.

11.5.1.5. Intergranular corrosion

Intergranular corrosion is an attack on the grain boundaries of some alloys under specific conditions. During heat treatment, these alloys are heated to a

temperature that dissolves the alloying elements. As the metal cools, these elements combine to form other compounds. If the cooling rate is slow, they form predominantly at the grain boundaries. These compounds differ electrochemically from the metal adjacent to the grain boundaries. These altered compounds can be either anodic or cathodic to the adjoining areas, depending on their composition. The presence of an electrolyte will result in an attack on the anodic area. This attack will generally be quite rapid and can exist without visible evidence.

11.5.1.5.1. Method of Prevention

The following are the methods of prevention of austenitic nickel chromium stainless steels from inter granular corrosion:

- (a) Purchase and use stainless steel in the annealed condition in which there is no harmful precipitate. This only applies when the steel is not to be exposed to the sensitizing temperature.
- (b) Select low carbon grade steel with a maximum of 0.03% C, such as 304 L. This would prevent the formation of harmful chromium carbide during fabrication.

11.5.1.6. Velocity assisted corrosion

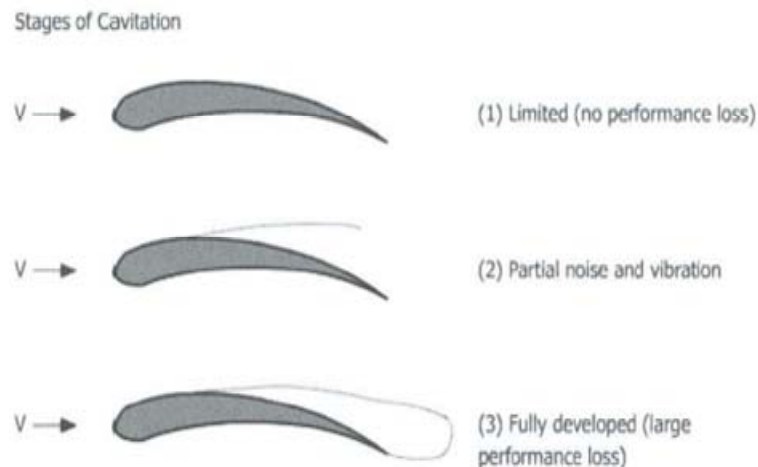


Fig. 11.9. Stages of cavitation

Fast moving corrosives cause

- a) Erosion-Corrosion,
- b) Impingement attack , and
- c) Cavitation damage in metals

11.5.1.6.1. Cavitation damage

Cavitation is a special case of Erosion-corrosion. In high velocity systems, local pressure reductions create water vapor bubbles which get attached to the metal surface and burst at increased pressure, causing metal damage.

11.5.1.7. Environment assisted cracking

When a metal is subjected to a tensile stress and a corrosive medium, it may experience Environment Assisted Cracking. Four types:

- i) Stress Corrosion Cracking
- ii) Hydrogen Embrittlement
- iii) Liquid Metal Embrittlement

11.5.1.7.1. Stress corrosion cracking

Stress, is caused by the simultaneous effects of tensile stress and corrosion. Stress may be internal or applied. Internal stresses are produced by non uniform deformation during cold working conditions, by unequal cooling from high temperatures during heat treatment, and by internal-structural rearrangement involving volume changes. Stresses set up when a piece is deformed. Examples of internal stresses include those induced by press-and shrink fits and those in rivets and bolts. Concealed stress is a more dangerous condition than design stress. Concealed stress corrosion is difficult to recognize before it has overcome the design safety factor. The magnitude of the stress varies from point-to-point within the metal. Stresses in the neighborhood of the yield strength are generally necessary to promote stress corrosion cracking, but failures may occur at lower stresses.

Static tensile stress and specific environments produce cracking

Examples:

- 1) Stainless steels in hot chloride
- 2) Ti alloys in nitrogen tetroxide
- 3) Brass in ammonia

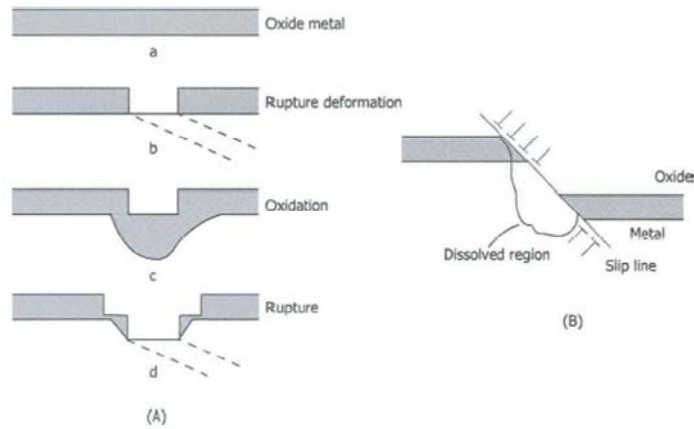


Fig . 11.10. Stress corrosion cracking

11.5.1.7.2. Hydrogen embrittlement

High strength materials stressed in presence of hydrogen crack at reduced stress levels.

A) Film rupture model (B) slip step dissolution model.

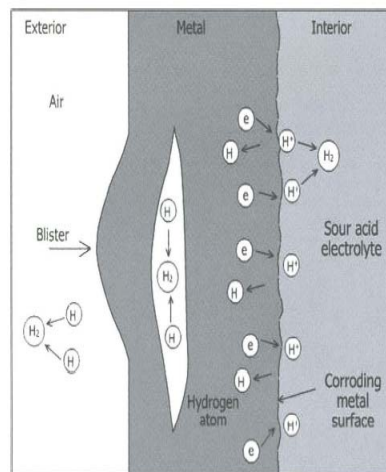


Fig. 11.11. Hydrogen embrittlement

Hydrogen may be dissolved in the metal or present as a gas outside.

Only ppm levels of H needed.

11.5.1.7.3. Liquid metal Embrittlement

Certain metals like Al and stainless steels undergo brittle failure when stressed in contact with liquid metals like Hg, Zn, Sn, Pb, Cd etc. Molten metal atoms penetrate the grain boundaries and fracture the metal.

11.5.2. Temperature corrosion

Generally corrosion rates increase with increases in temperature. This is due to several interrelated factors:

- i) Higher temperatures tend to promote the corrosion reaction kinetics. Therefore except in cases where oxygen is free to escape, higher temperatures boost the corrosion rate.
- ii) Corrosive by products will have a higher diffusion rate at higher temperatures and thus will be delivered to the corroding surface more efficiently.

11.5.2.1 High temperature corrosion

High temperature corrosion is a form of corrosion that does not require the presence of a liquid electrolyte. Sometimes, this type of damage is called "dry corrosion" or "scaling". The term oxidation is ambivalent since it can either refer to the formation of oxides or to the mechanism of oxidation of a metal, i.e. its change to a higher valence than the metallic state. Strictly speaking, high temperature oxidation is only one type of high temperature corrosion. In fact, oxidation is the most important high temperature corrosion reaction.

High temperature metals requires neither moisture nor dissolved electrolytes (salts, acids) to proceed.

11.5.2.2 Low temperature corrosion

Low-temperature corrosion appears in the boiler as well as on other surfaces where the temperature is under approx. 135 °C. It is caused by condensation of the acidic sulphur and chlorine-containing gases.

This type of corrosion is temperature-dependent. New plants are being designed differently in order to avoid low-temperature corrosion.

11.6. Causes of corrosion

The consequences of corrosion are many and varied and the effects of these on the safe, reliable and efficient operation of equipment or structures are often more serious than the simple loss of a mass of metal. Failures of various kinds and the need for expensive replacements may occur even though the amount of metal destroyed is quite small. Some of the major harmful effects of corrosion can be summarized as follows:

1. Reduction of metal thickness leading to loss of mechanical strength and structural failure or breakdown. When the metal is lost in localised zones so as to give a crack like structure, very considerable weakening may result from quite a small amount of metal loss.
2. Hazards or injuries to people arising from structural failure or breakdown (e.g. bridges, cars, aircraft).
3. Loss of time in availability of profile-making industrial equipment.
4. Reduced value of goods due to deterioration of appearance.
5. Contamination of fluids in vessels and pipes (e.g. beer goes cloudy when small quantities of heavy metals are released by corrosion).
6. Perforation of vessels and pipes allowing escape of their contents and possible harm to the surroundings. For example a leaky domestic radiator can cause expensive damage to carpets and decorations, while corrosive sea water may enter the boilers of a power station if the condenser tubes perforate.
7. Loss of technically important surface properties of a metallic component. These could include frictional and bearing properties, ease of fluid flow over a pipe surface, electrical conductivity of contacts, surface reflectivity or heat transfer across a surface.
8. Mechanical damage to valves, pumps, etc, or blockage of pipes by solid corrosion products.
9. Added complexity and expense of equipment which needs to be designed to withstand a certain amount of corrosion, and to allow corroded components to be conveniently replaced.
- 10) Buried gas or water supply pipes can suffer severe corrosion which is not detected until an actual leakage occurs, by which time considerable damage may be done.

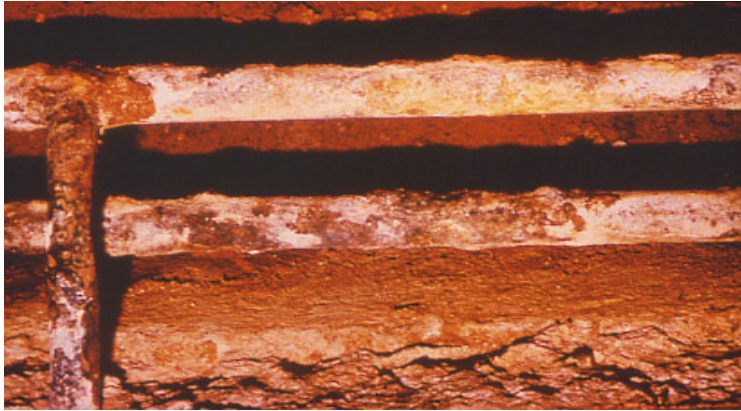


Fig .11.12. Corrosion of buried water supply pipe

11) In electronic equipment it is very important that there should be no raised resistance at low current connections. Corrosion products can cause such damage and can also have sufficient conductance to cause short circuits. These resistors form part of a radar installation.

12) The lower edge of this aircraft skin panel has suffered corrosion due to leakage and spillage from a wash basin in the toilet. Any failure of a structural component of an aircraft can lead to the most serious results.

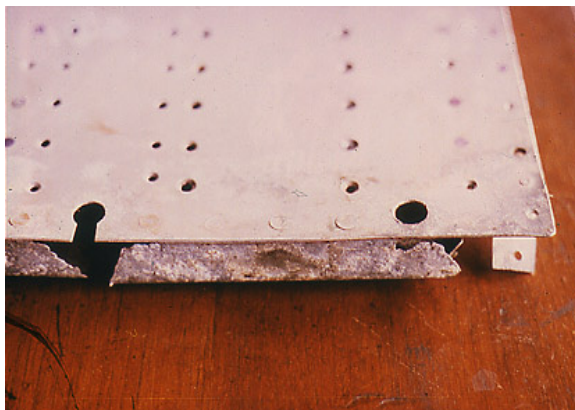


Fig . 11.13. Corrosion of Aircraft skin panel

13) Sea water is a highly corrosive electrolyte towards mild steel. This ship has suffered severe damage in the areas which are most buffeted by waves, where the protective coating of paint has been largely removed by mechanical action.



Fig . 11.14. Corrosion of ship by sea water

11.7. Prevention of corrosion

There are many methods of protecting metals against corrosion.

They are 1) barrier protection, 2) sacrificial protection, 3) cathodic protection.

11.7.1. Barrier protection

Here, a thin barrier is developed between the surface of iron and atmosphere by one of the following methods.

- i) Painting of the surface
- ii) Coating the surface with a thin film of oil or grease
- iii) Developing a thin layer of some non –corrosive metal like nickel, chromium copper etc., by electroplating.

11.7.2. Sacrificial protection

In this case, the surface of iron is covered with a more electropositive metal like zinc or aluminum. Since this metal loses electrons more readily than iron, rusting is prevented. As long as metal is present, iron does not get rusted. However, the metal atoms of the coating lose electrons and get consumed in due course of time. This type of protection is called ‘sacrificial production’. Zinc metal is generally coated on the surface of iron for this purpose. A coating of zinc is called ‘galvanization’. (Here zinc gradually gets lost as basic zinc carbonate $Zn(OH)_2 \cdot ZnCO_3$).

11.7.3. Cathodic protection (Electrical protection)

This method is especially used for underground iron pipes. Here, the iron pipe or tank is connected to a more electropositive metal like magnesium or aluminum. The more electropositive metal acts like anode (supplies electrons) and iron acts like cathode (receives electrons). Thus, iron is protected by turning it as a cathode. Hence, the method is called ‘cathodic protection’.

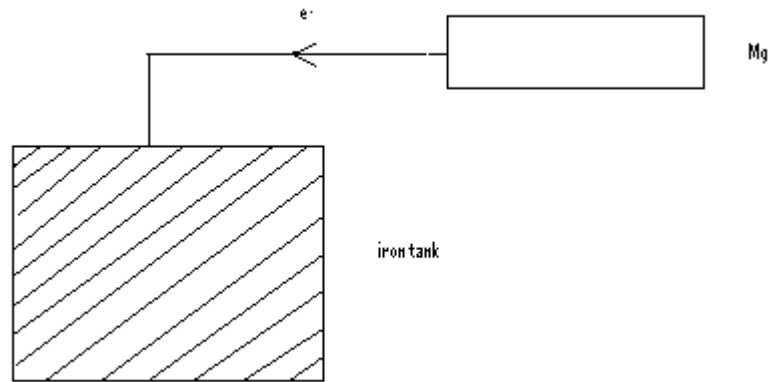


Fig. 11.15. Cathodic protection

11.7.4 Conditioning the metal

By retarding either the anodic or cathodic reactions the rate of corrosion can be reduced.

This can be achieved in several ways: This can be sub-divided into two main groups:

(a) Coating the metal, in order to prevent corrosion, resistant coating is made between metal and environment.

Metal coatings are applied by dipping, electroplating, spraying, cementation, and diffusion. The selection of a coating process for a specific application depends on several factors, including the corrosion resistance that is required, the anticipated life time of the coated material, the number of parts being produced, the production rate that is required, and environmental considerations.

i) Hot dipping

Hot dipping is carried out by immersing the metal on which the coating is to be applied, usually steel, in a bath of the molten metal that is to constitute the coating, most commonly zinc, but also aluminum and aluminum – zinc alloys. Hot dipping can be

either a continuous process, as in galvanizing steel sheet, or a batch process — for example, galvanizing fabricated parts, nuts, bolts etc.,

ii) Electroplating,

In electroplating the substrate, or base, metal is made the cathode in an aqueous electrolyte from which the coating is deposited. Although the primary purpose of electroplating coatings is to achieve corrosion resistance, these coatings can also be decorative, with a metallic luster after polishing. A wide of variety of coatings can be applied by electroplating for example, zinc, cadmium, chromium, copper, gold, nickel, tin, and silver, as well as alloys, such as tin – zinc, zinc – nickel, brass, bronze, gold alloys, and nickel alloys.

iii) In thermal spraying

Spraying of metal coatings, a gun is used that simultaneously melts and propels small droplets of metal onto the surface to be coated. There are several types of thermal spraying, with the three main variables in each type being the temperature of the flame, the velocity of the particles that are sprayed onto the substrate to form the coating, and the nature of the material that is to form the coating (i.e., powder, rod, wire, or liquid). The material that is to form the coating is called the “feedstock.” These coatings can be made adherent and of almost any desired thickness, and they can be applied on already fabricated structures. Sometimes, pores are filled with a thermoplastic resin in order to increase corrosion protection.

iv) Organic coatings

In organic coatings, such as resins, plastics, paints, enamel, oils and greases. The action of protective coatings is often more complex than simply providing a barrier between metal and environment. Paints may contain a corrosion inhibitor. Zinc coating in iron or steel confers cathodic protection

(b) Alloying the metal

Alloying the metal is to produce a more corrosion resistant alloy, e.g. stainless steel, in which ordinary steel is alloyed with chromium and nickel. Stainless steel is protected by an invisibly thin, naturally formed film of chromium sesquioxide Cr_2O_3 . The development of alloys for controlling corrosion in specific aggressive environments is certainly one of the great metallurgical developments.

In general, the corrosion behavior of alloys depends on the interaction of:

1. The alloy of specific chemical composition and metallurgical structure.
2. The film on the alloy surface.
3. The environment, whether it is sufficiently aggressive to break down the protectiveness of the surface film, thereby initiating localized corrosion.
4. The alloy/environment combination, controlling whether the film self repairs after breakdown and, if not, the type and rate of corrosion that propagates after initiation has occurred.

CHAPTER - 12

PROPERTIES AND PACKING PATTERNS OF SOLIDS

M. Anil Kumar

12.1. Introduction

The symmetry of crystals has fascinated people for thousands of years. Most solid objects are made of many tiny interlocking crystals. It is only occasionally that the individual crystals are large enough to catch our attention, as shown in **Fig. 12.1**.

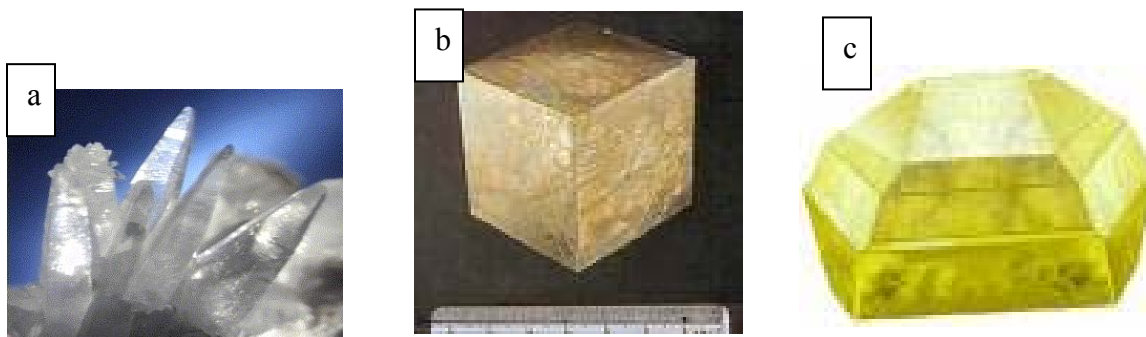


Fig. 12.1. Images of (a) Celestite, (b) Pyrite and (c) Sulphur

The atoms in a crystal are in a regular repeating pattern called the crystalline lattice. Although, the existence of this lattice known from many years, recently the Scanning Tunneling Microscope (STM) was invented. This allows us to see individual atoms. The STM image of platinum surface is shown in **Fig. 12.2**.

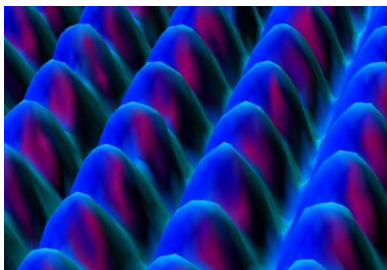


Fig. 12.2. STM image of a platinum surface

The properties of the solids are mainly influenced by their lattice. For example, if you consider diamond and graphite (**Fig. 12.3**), both contains the same atom-carbon. But the difference in their properties lies in how those atoms are arranged.

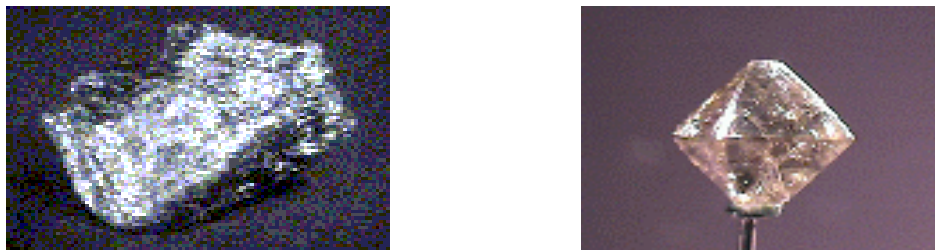


Fig. 12.3. Images of (a) Graphite and (b) diamond

Graphite is a black, soft and excellent lubricant. This suggests that it must be easy to separate atoms in graphite whereas diamond is a transparent, strong and very hard which suggests that the atoms are held very strongly (**Fig. 12.4**).

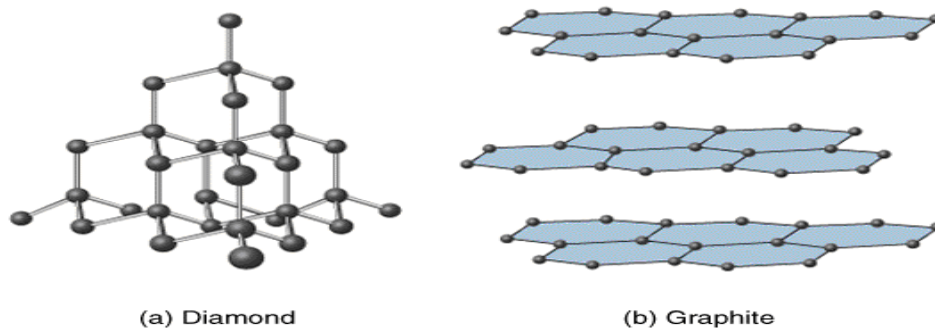


Fig.
12.4.

Structures of (a) Diamond and (b) graphite

Graphite consists of sheets of hexagonal rings. Each sheet is far from and weakly bound to the next (see figure. 4). The spaces between the layers allow other molecules to enter which gives the absorbing and catalytic properties to the graphite. Recently STM gives visual conformation of the structure of graphite (**Fig. 12.5**). STM clearly shows the interconnected 6-membered rings of graphite and the triangular geometry of each carbon atom.

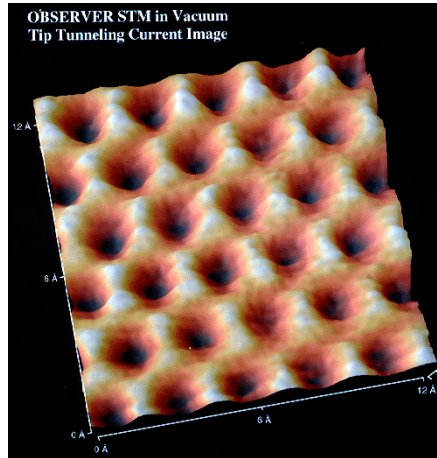


Fig. 12.5. STM image of graphite

12.2. Crystal lattices

A highly ordered 3-dimensional arrangement of atoms, ions or molecules is known as a crystal lattice. If the constituents of a crystal are denoted by points then a lattice may be regarded as an infinite set of points repeated regularly through space. A set of points repeated at a regular interval along a line is a one-dimensional lattice as shown in **Fig. 12.6.**

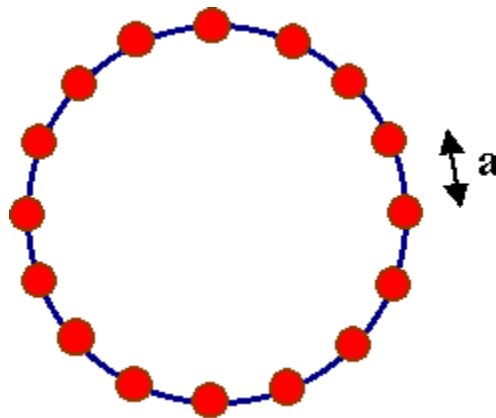


Fig. 12.6. One dimensional lattice

When a set of points are repeated regularly on a plane (along any two coordinate axes) it is called a two-dimensional lattice. The points in a two-dimensional plane can be arranged only in five different ways as shown in **Fig. 12.7.**

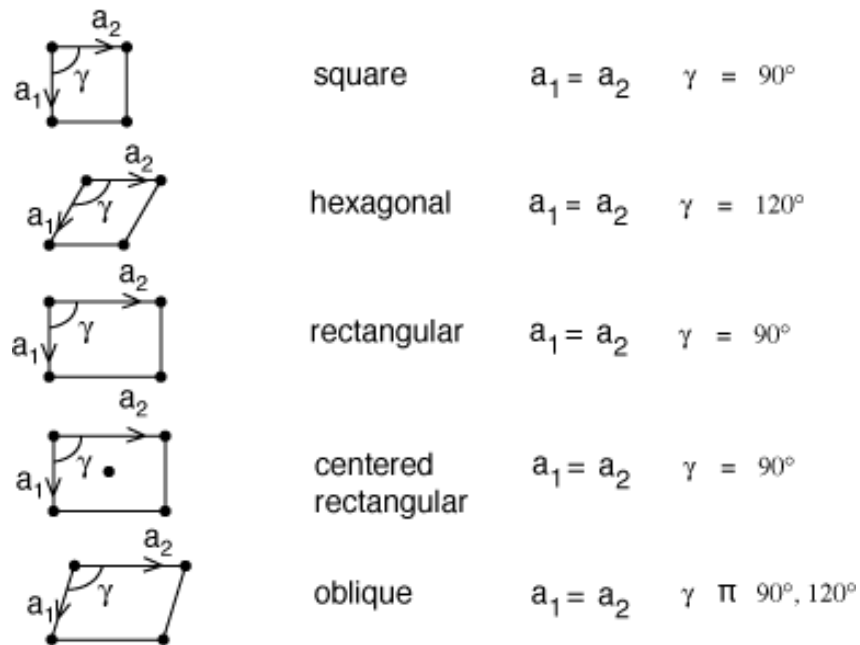


Fig. 12.7. Possible two dimensional lattices

Similarly, if the points are arranged in a regular, repeated manner along the three coordinate axes, it results in a three-dimensional lattice (**Fig. 12.8**) known as space lattice. The unit cell in a three dimensional lattice is characterized by the lengths a , b and c and the angles α , β and γ . These are known as the unit cell parameters.

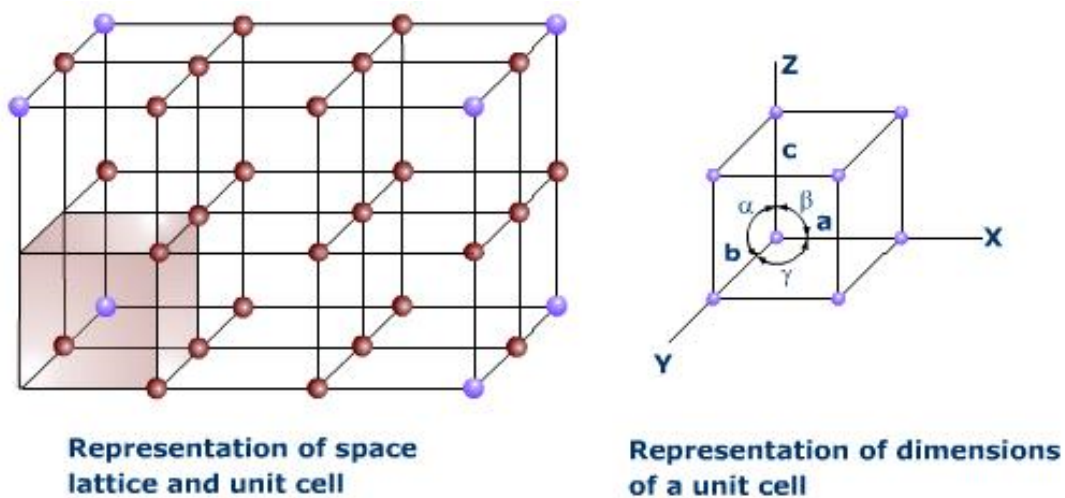


Fig. 12.8. A representative three dimensional lattice

12.3. Unit Cell

The smallest repeating unit with all the symmetry of a crystal is called as unit cell. Three dimensional stacking of unit cells is a crystal lattice.

12.3.1. There are an essentially infinite number of unit cells possible. For example, a square and hexagonal unit cells may contain any of the patterns as shown in **Fig. 12.9**.

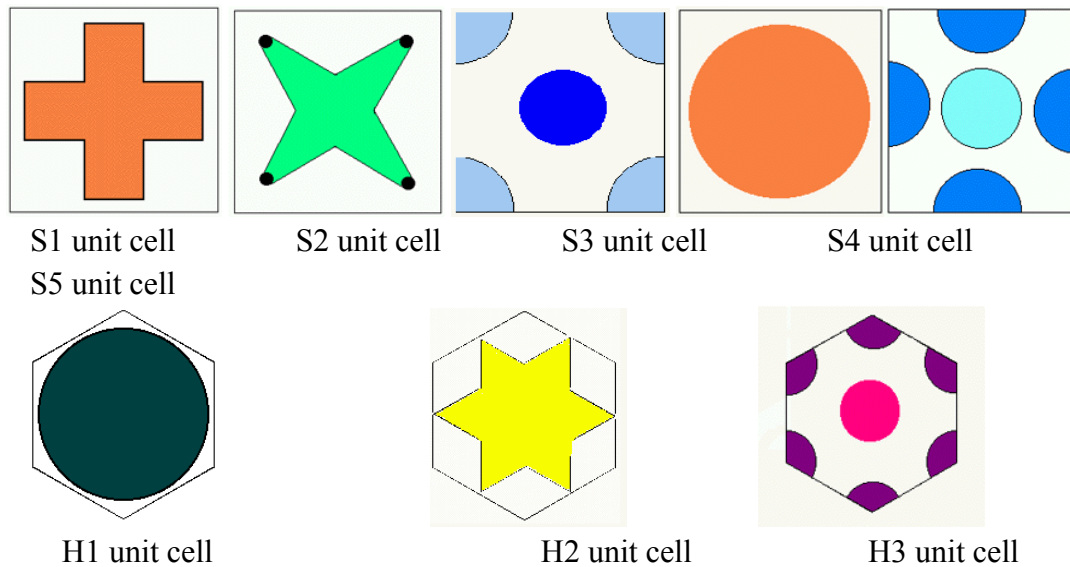


Fig. 12.9. Different possibilities in the patterns of square and hexagonal unit cells

The circles in S4 and H1 are the same. However, the empty space around the circle—which is also part of the unit cell—is different in the two unit cells. They will pack together differently; S4 in a square pattern and H1 in a hexagonal one

12.3.2. By stacking these unit cells, we can produce the corresponding lattices (figure. 10). For example,

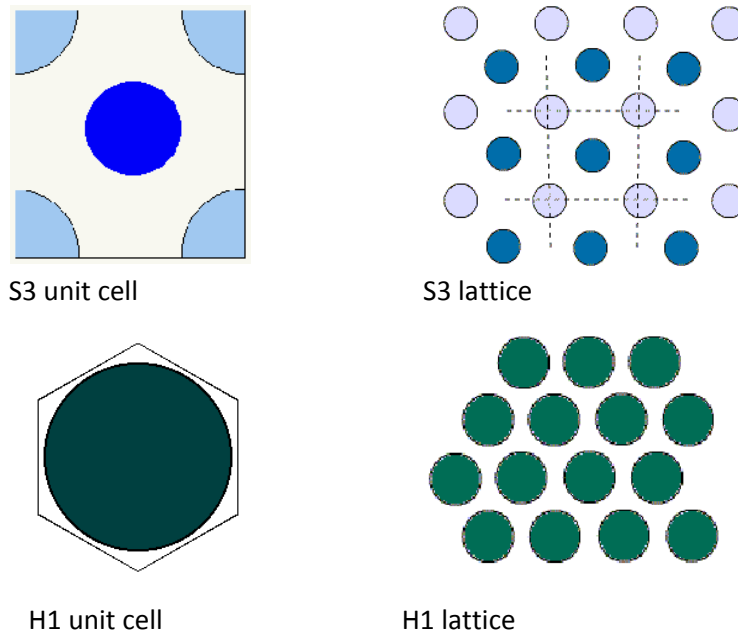


Fig. 12.10. Stacking of unit cells for producing lattices

12.3.3. If we start with the lattice, there is often more than one reasonable choice for unit cell. So, we have to choose the “best” unit cell which can fill the surface and form the lattice. Figure. 11 shows the possible unit cells in a given lattice.

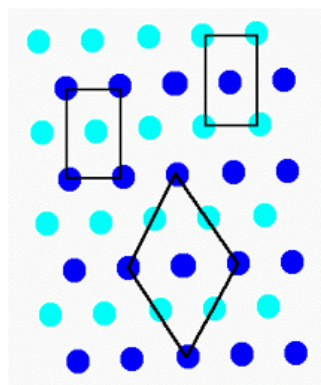


Figure. 12.11. Possible unit cells

12.3.4. Packing and geometry

The reason crystals form is the attraction between the atoms. Because they attract one another it is often favourable to have many neighbours. Thus, the coordination number, or number of adjacent atoms, is important.

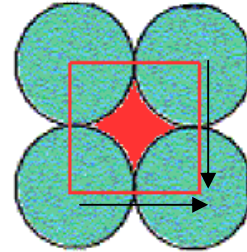
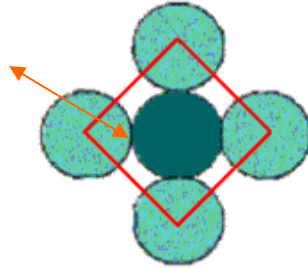
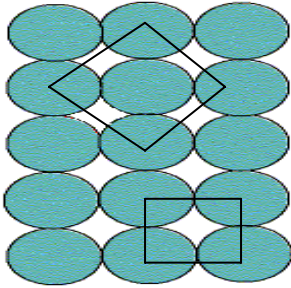


Fig. 12.12.1. Unit cells; **Fig. 12.12.2.** Unit cell; **Fig. 12.12.3.** Square Unit cells

For a square lattice, the coordination number is 4 (the number of circles touching any individual) and the coordination geometry is square.

The empty space between the atoms are interstitial sites (see figure. 12. 3). Since each is touched by 4 circles, the interstitial sites are also 4-coordinate, and the geometry is square. *The packing efficiency* is the fraction of the crystal (or unit cell) actually occupied by the atoms. It must always be less than 100% because it is impossible to pack spheres without having some empty space between them.

$$\text{P.E.} = (\text{area of circle}) / (\text{area of unit cell})$$

$$\text{Area of unit cell} = \text{length} \times \text{breadth} = 2r \times 2r = 4r^2$$

Regarding our square lattice of circles, we can calculate the packing efficiency (PE) for this particular lattice as follows:

$$\text{P.E.} = \frac{\pi r^2}{4r^2} = \pi/4 = 78.54 \%$$

The interstitial sites must occupy $100\% - 78.54\% = 21.46 \%$

Let us compare this with a hexagonal lattice of circles.

atomic coordination number = 6 , atomic coordination geometry = hexagonal

interstitial coordination number = 3, interstitial coordination geometry = triangular

packing efficiency = 90.69 %

interstitials = 9.31 %

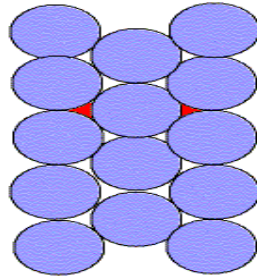


Figure. 12.13. Lattice with interstitial sites

By examining the **Fig. 12.13**, we can see that in this packing there are twice as many of these 3-coordinate interstitial sites as circles – for each circle there is one pointing right and another pointing left. Thus, these sites are much smaller than those of square lattice. The larger coordination number (more bonds) and greater packing efficiency suggests that this would be a more stable lattice than the square one.

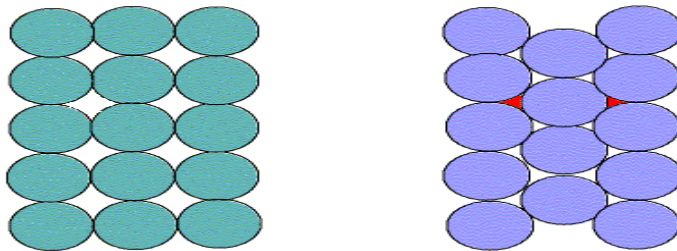


Fig 12.14. Comparison of the square and the hexagonal lattice

If we compare the square and hexagonal lattice, we see that both are made of columns of circles (**Fig. 12.14**). However, in the hexagonal lattice every other column shifted allowing the circles nestle in to the empty space. Thus, the higher packing efficiency.

12.4. Structure of solids

There are three common types of unit cells possible

i) Primitive cubic, in which atoms are at the corners of a simple cube (**Fig. 12.15.1**).

Each atom shared by 8 unit cells.

ii) Body centered cubic (bcc), in which atoms are at the corners of a cube plus one atom at the center of the body of a cube (**Fig. 12.15.2**).

Corner atoms shared by 8 unit cells and

Center atom completely enclosed in one unit cell

iii) Face centered cubic (fcc), in which atoms are at the corners of a cube plus one atom in the center of each face of the cube (**Fig. 12.15.3**).

Corner atoms shared by 8 unit cells and

Face atoms shared by 2 unit cells.

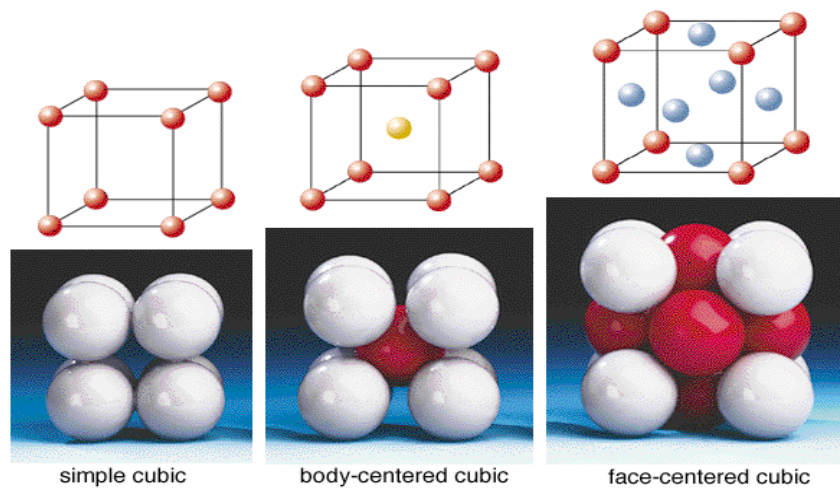


Fig. 12.15.1. Cubic; **Fig. 12.15.2.** BCC and **Fig. 12.15.3.** FCC lattices

Bravais showed that there are 14 different unit cells to account for the lattice points at the corners of the unit cell as well as those at the centers and on some of the faces. These 14 unit cells are known as the Bravais lattices (see **Fig. 12.16**).

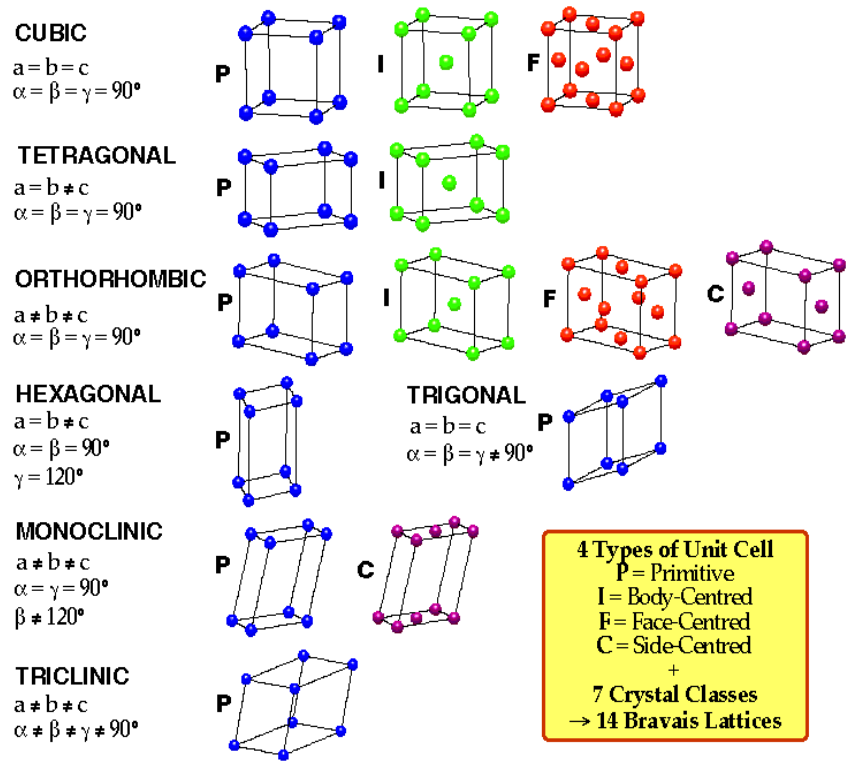


Fig. 12.16. The 14 Bravais lattices

12.4.1. Simple Cube

The simplest structure that a metal can adopt is simple cubic (SC) (**Fig. 12.17**).



Fig. 12.17. Simple cubic unit cell

In this unit cell, the atoms at the corners are cut because only a portion (in this case 1/8) belongs to that cell. The rest of the atom belongs to neighbouring cells.

The edge length of the cell is 2 X sphere radius = 2r.

In 3-D the packing efficiency is given by :

$$\text{P.E.} = (\text{volume of spheres})/(\text{volume of cell})$$

For a simple cubic lattice, this is:

$$\text{P.E.} = (8 \times 1/8)(4/3 \pi r^3) / (2r)^3 = \pi/6 = 52.35 \%$$

This low value is not surprising. Remember, that a 2-D square lattice uses space inefficiently. A simple cubic lattice is its 3-D analog, and also contains much empty space.

Coming to the empty space in the lattice as shown in figure. 18, each unit cell contains one large interstitial site in its center (47.65% of the volume). There are 8 atoms touching this space, so the **interstitial coordination number** is 8, and its geometry is **cubic** (a cube has 8 corners).

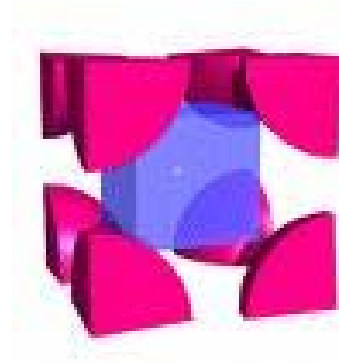


Figure. 12.18. Simple cubic unit cell with empty space

Since each unit cell contains one ($8 \times 1/8 =$) 1 atom and 1 interstitial site, the number of atoms and the interstitial sites is the same.

Examine the **Fig. 12.19**, which shows the arrangement about any single atom in the simple cubic lattice; not that each atom has 6 neighbours, so the **atomic coordination number is 6**. The coordination geometry is octahedral (an octahedron has 6 neighbours).

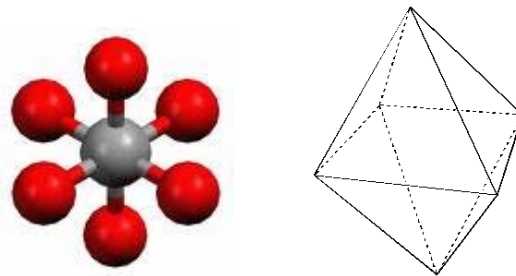


Figure. 12.19. An octahedron

Since both the coordination number and the packing efficiency are low, a simple cubic lattice uses space inefficiently. Very few examples of simple cubic lattices are known (**α -polonium** is one of the few known simple cubic lattices).

12.4.2 Face Centered Cubic (fcc) or Cubic Close Packed (ccp)

We can think of this cell as being made by inserting another atom into each face of the simple cubic lattice- hence the “face centered cubic” name (Fig. 12.20).

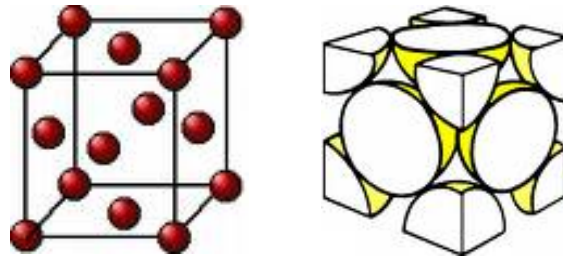


Fig. 12.20. Fcc unit cell

The corner atoms touch the atom in the center of the face. The name “close packed” refers to the packing efficiency of 74.05%. No other packing can exceed this efficiency.

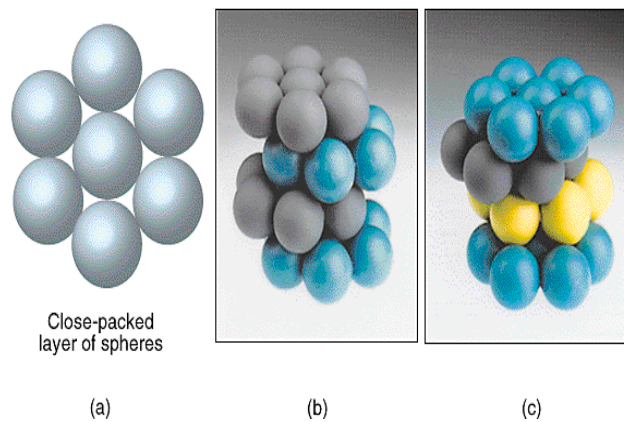
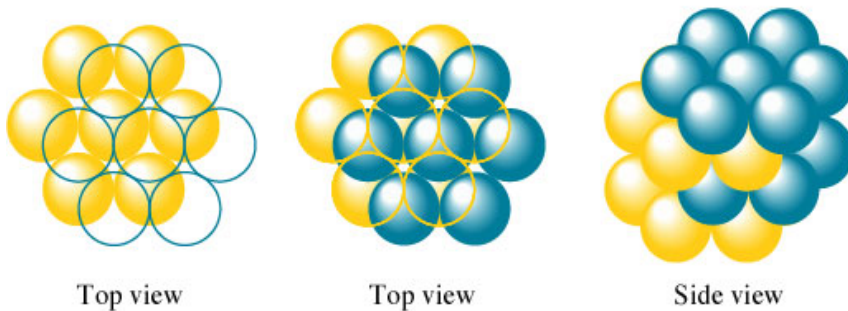


Fig. 12.21. (a) Close packed layer of spheres, (b) ABAB arrangement (hcp) and (c) ABCABC arrangement (ccp)

A crystal is built up by placing close packed layers of spheres on top of each other. There is only one place for the second layer of spheres. There are two choices for the third layer of spheres:

- i) Third layer eclipses the first (ABAB arrangement) (Fig. 12.21(b)). This is called hexagonal close packing (hcp);
- ii) Third layer is in a different position relative to the first (ABCABC arrangement). This is called cubic close packing (ccp) (Fig. 12.21(c)).

(a) *abab* — Closest packing



(b) *abca* — Closest packing

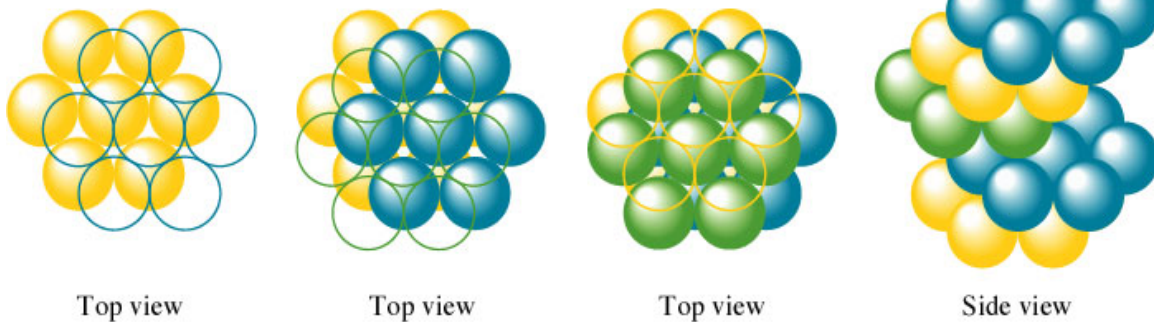


Fig . 12.22. The arrangements of layers in hcp and ccp structures

12.4.3. CCP(ABCABC)

We start with an hexagonal array of spheres (the “A” layer—close packed arrangement—no way to pack more spheres into a given area). Then place a second close pack layer (the “B” layer) atop the first layer, so they nestle into the left-pointing holes in the first. If we put another close packed layer on the interstices we generate a different layer, labelled

the “C” layer as shown in figure. 23. We can continue to stack these layers in any order, providing that no 2 identical layers are adjacent.

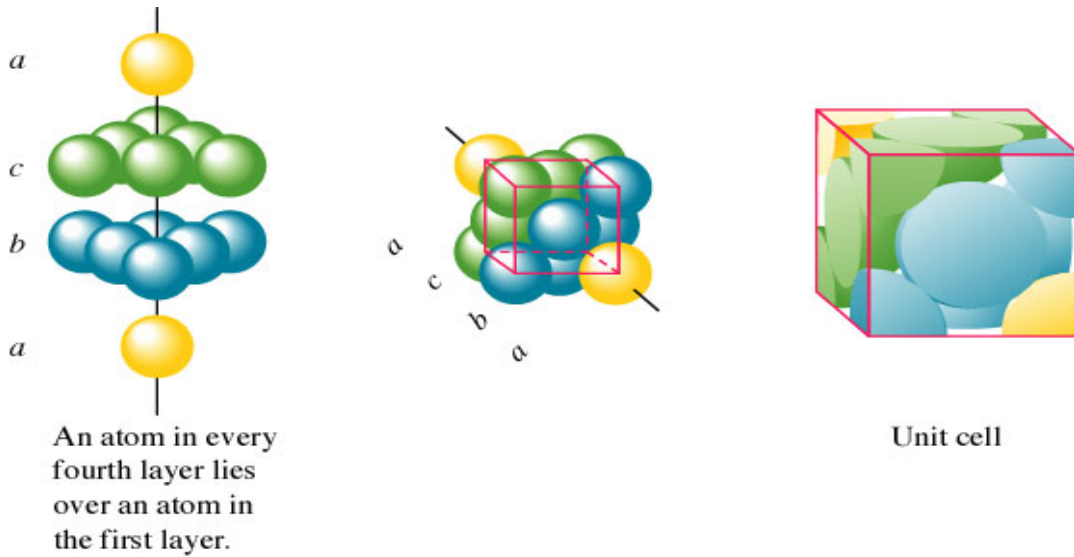


Fig. 12.23. Diagrammatic representation of packing of layers in ccp structure

Each sphere is surrounded by 12 other spheres (6 in one plane, 3 above and 3 below) as shown in figure. 24. Coordination number is the number of spheres directly surrounding a central sphere.

If unequally sized spheres are used, the smaller spheres are placed in the interstitial holes.

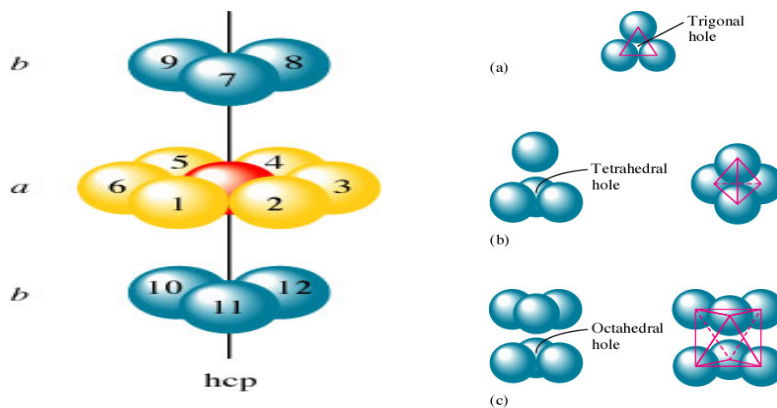


Fig. 12. 24. The holes that exist among closet packed uniform spheres

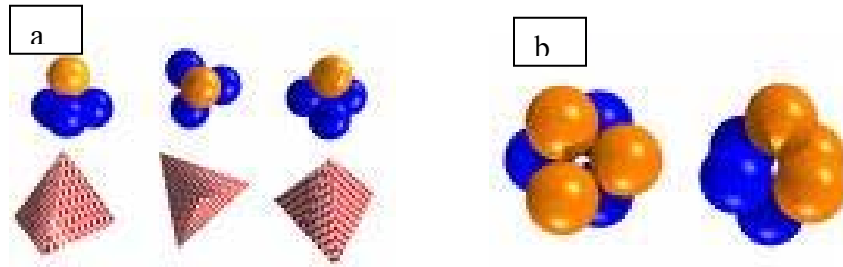


Fig. 12.25. (a) Tetrahedral interstitial sites (holes) and (b) octahedral interstitial sites (holes)

Examples of fcc/ccp includes nickel, silver, gold, copper and aluminium.

12.4.4. HCP(ABAB)

Another way of stacking these layers is to omit the third layer (C layer) altogether—simply alternate “A” and “B” (**Fig. 12.26**). This is also a close packed array, but the symmetry is different. It is called Hexagonal Close Packed (hcp). The hexagonal close packed structure can be made by piling the layers in the A-B-A-B----sequence. **Fig. 12.27.1** and **12.27.2** shows the full hcp lattice and its unit cell respectively.

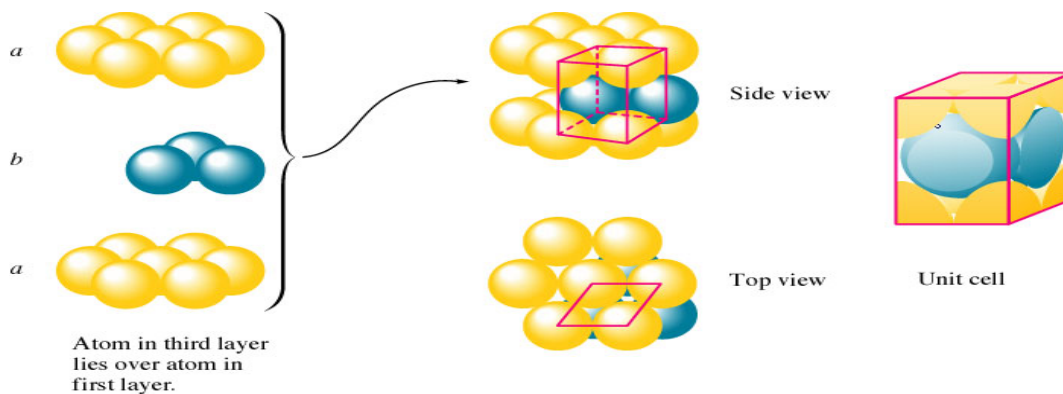
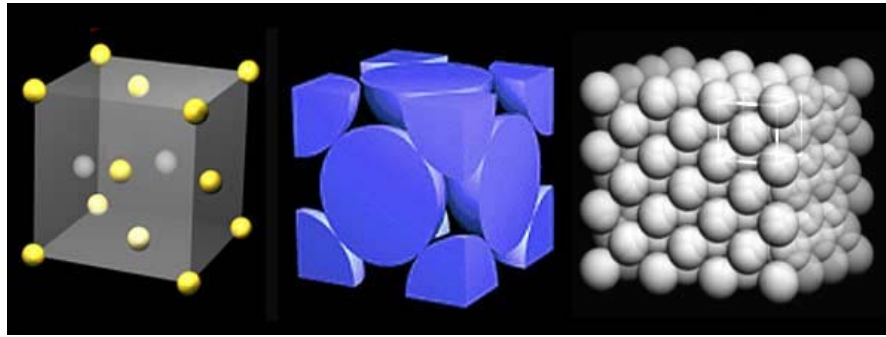


Fig. 12.26. Hexagonal close packing (HCP) in solids



HCP unit cell

HCP lattice

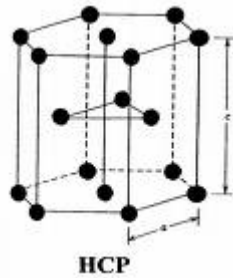


Fig. 12.27.1. Full HCP lattice

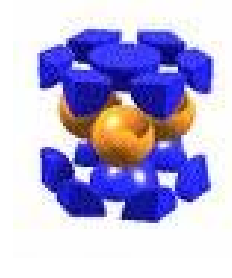


Fig. 12.27.2. Full HCP unit cell

Examples of hcp metals include zinc, titanium and cobalt

12.5. Comparison of fcc/ccp and hcp

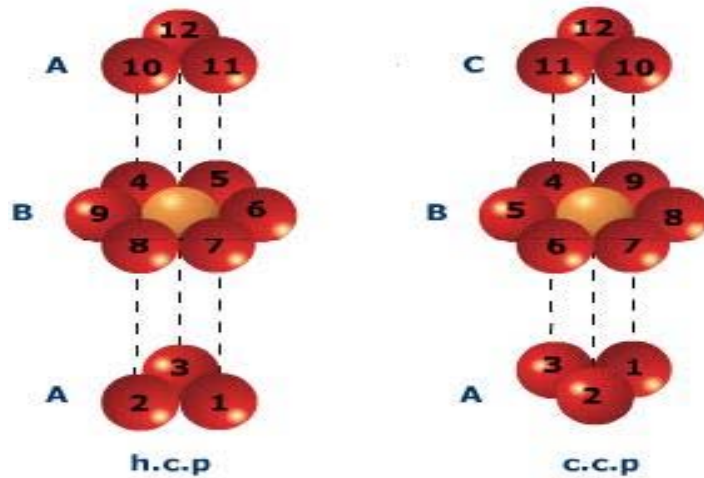


Fig. 12.28. The hexagonal and cubic close packed structures

Since both structures are composed of stacked hexagonal layers, we expect them to be similar- and they are. There are some subtle differences however. Both the structures have coordination number 12, while the arrangements are slightly different.

In hcp, top and bottom three are directly above one another. In ccp, they are staggered (as shown in **Fig. 12.28**).

Another difference arises from the packing order. In hcp there are never any atoms on the “right- pointing” holes. Thus if we see directly down on the structure we can see tiny channels through the hcp structure. These are absent in ccp (see figure. 29).

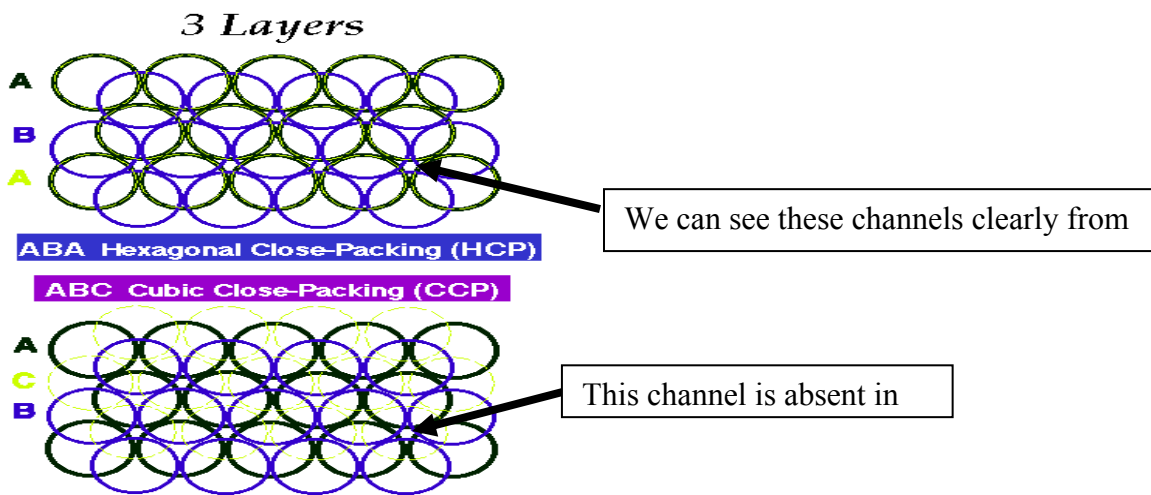


Fig. 12.29. Differences between the HCP and CCP

12.5.1. Body Centered Cubic structure

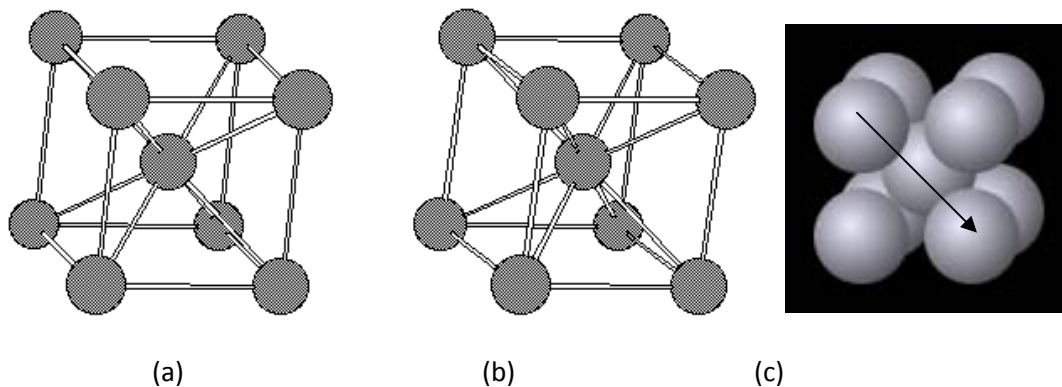
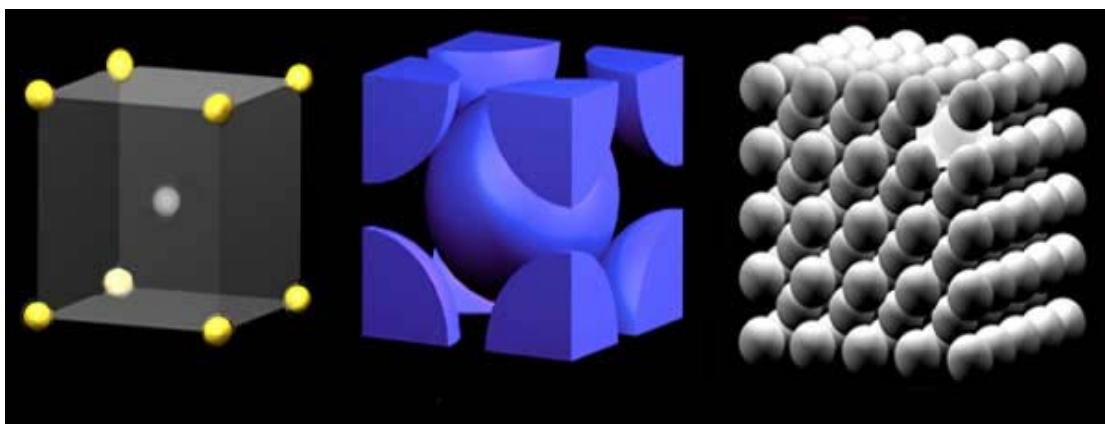


Fig. 12.30. Different representations of bcc unit cells

We can think of this unit cell as made by stuffing another atom into the center of the simple cubic lattice, slightly spreading the corners. Thus, the corner spheres no longer quite touch one another, but do touch the center (figure. 30 (a) & (b)). The diagonal through the body of the cube is $4 \times$ (sphere radius) (figure. 30 (c)).

The packing efficiency of a bcc lattice is considerably higher than that of a simple cubic: 69.02 %.

The coordination number and packing efficiency mean that this lattice uses space more efficiently than simple cubic.



BCC unit cells

BCC lattice formed by stacking of unit cells

Fig. 12.31. Representation of BCC unit cells and lattice

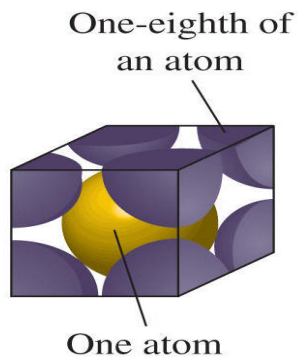


Fig. 12.32. Contribution of atoms in bcc unit cell

The body-centered cubic unit cell has atoms at each of the eight corners of a cube (like cubic unit cell) plus one atom at the center of the cube (**Fig.12.31**). Each of the corner

atoms is the corner of another cube so the corner atoms are shared among eight unit cells. It is said to have a coordination number of eight. The bcc unit cell consists of a net total of two atoms; one in the center and eight eighths from corners atoms as shown in **Fig. 12.32**.

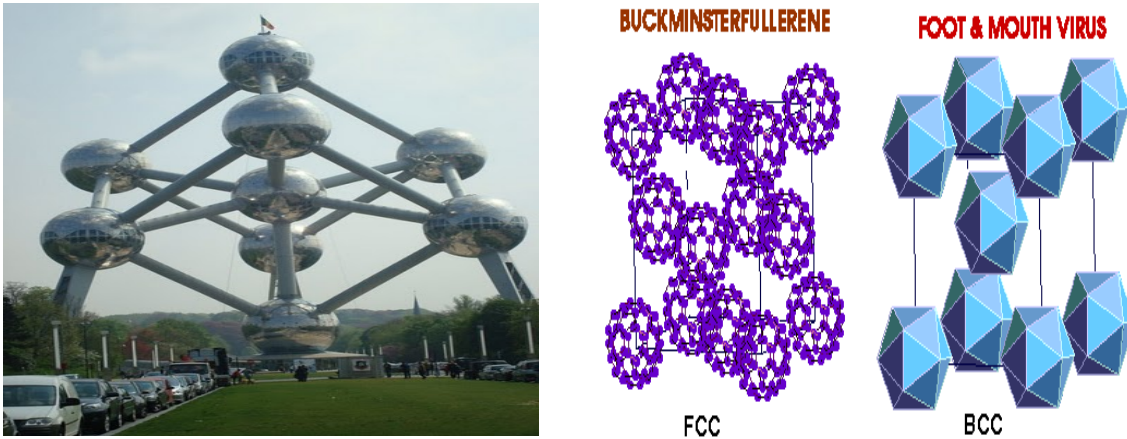


Fig. 12.33. Some examples of bcc structure (The famous Atomium...the BCC lattice of iron)

Some of the materials that have a bcc structure include lithium, sodium, potassium, chromium, barium, vanadium, alpha-iron and tungsten

12.6. Structures of ionic compounds

Ionic compounds generally have more complicated structures than metals. This is probably because:

- (1) There are now at least two kinds of particles in the lattice, generally of different sizes.
- (2) The cations attract the anions, but like ions repel one another. The structure must balance both types of forces.
- (3) Many ions (e.g. nitrate, carbonate, azide) are very non-spherical in shape. They will thus pack differently in different directions.

One simple ionic structure is CsCl.

12.6.1. Cesium Chloride

Cesium chloride crystallizes in a cubic lattice. The unit cell may be depicted as shown in **Fig. 12.34**.

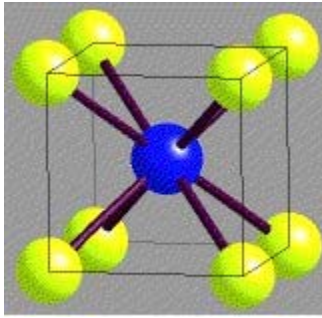


Fig. 12.34. CsCl unit cell

When these type of unit cells stacked into a lattice, they form a structure as shown in **Fig. 12.35**.

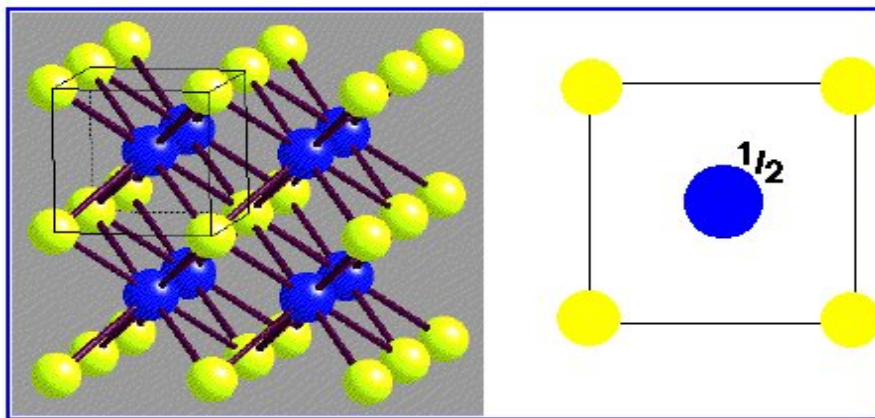


Fig. 12.35. Graphical representation of CsCl lattice

12.6.2. How the ions are arranged in cesium chloride?

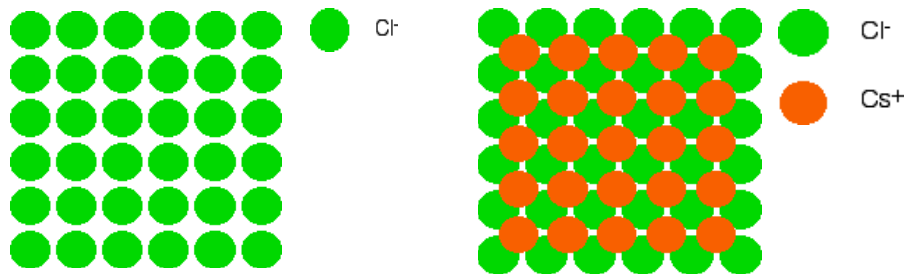


Fig. 12.36.1. Arrangement of Cl⁻ ions; **12.36.2.** Arrangement of Cs⁺ and Cl⁻ ions

Imagine a layer of chloride ions as shown in figure.36.1. The individual chloride ions aren't touching each other. That's really important - if they were touching, there would be repulsion.

Now let's place a similarly arranged layer of cesium ions on top of these as shown in **Fig. 12.36.2**.

Notice that the cesium ions aren't touching each other either, but that each cesium ion is resting on four chloride ions from the layer below. Now let's put another layer of chloride ions on, exactly the same as the first layer (**Fig.12.36.3**). Again, the chloride ions in this layer are NOT touching those in the bottom layer - otherwise you are introducing repulsion. Since we are looking directly down on the structure, you can't see the bottom layer of chloride ions any more, of course.

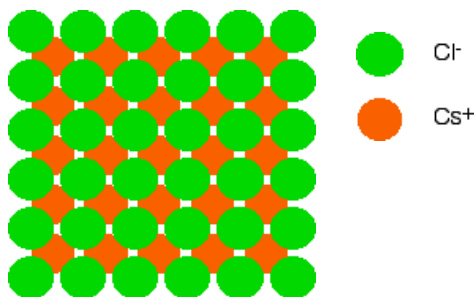


Fig. 12.36.3. CsCl structure

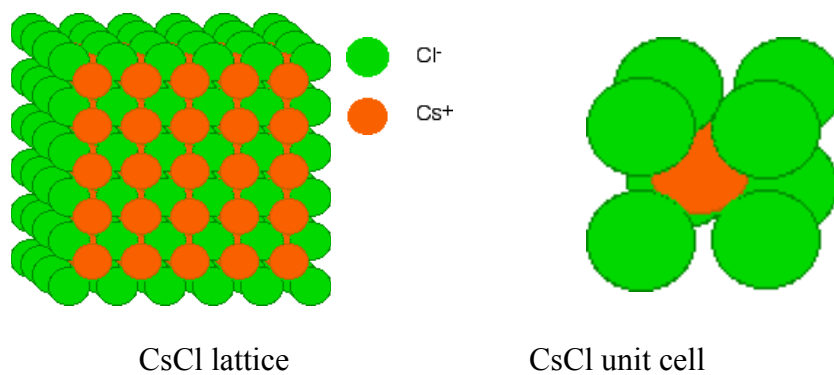


Fig. 12.36.4. Representation of the lattice and the unit cell of CsCl

If you now think about a cesium ion sandwiched between the two layers of chloride ions, it is touching four chloride ions in the bottom layer, and another four in the top one. Each cesium ion is touched by eight chloride ions. We say that it is 8-co-ordinated. If we added another layer of cesium ions, you could similarly work out that each chloride ion was touching eight cesium ions (**Fig. 36.4**). The chloride ions are also 8-co-ordinated. Overall, then, cesium chloride is **8:8-co-ordinated**.

The final diagram in this sequence takes a slightly tilted view of the structure so that you can see how the layers build up. These diagrams are quite difficult to draw without it looking as if ions of the same charge are touching each other. They aren't!

12.6.3. Sodium Chloride

Sodium chloride is taken as a typical ionic compound. Compounds like this consist of a giant (endlessly repeating) lattice of ions. So sodium chloride (and any other ionic compound) is described as having a **giant ionic structure**.

You should be clear that giant in this context doesn't just mean very large. It means that you can't state exactly how many ions there are.

There could be billions of sodium ions and chloride ions packed together, or trillions, or whatever - it simply depends how big the crystal is. That is different from, say, a water molecule which always contains exactly 2 hydrogen atoms and one oxygen atom - never more and never less.

Sodium chloride also crystallizes in a cubic lattice, but with a different unit cell.

A representation of a sodium chloride lattice looks like this:

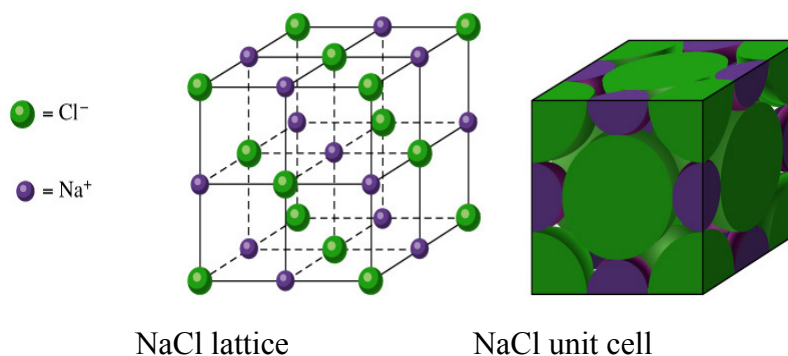


Fig. 12.37. Lattice and the unit cell of NaCl

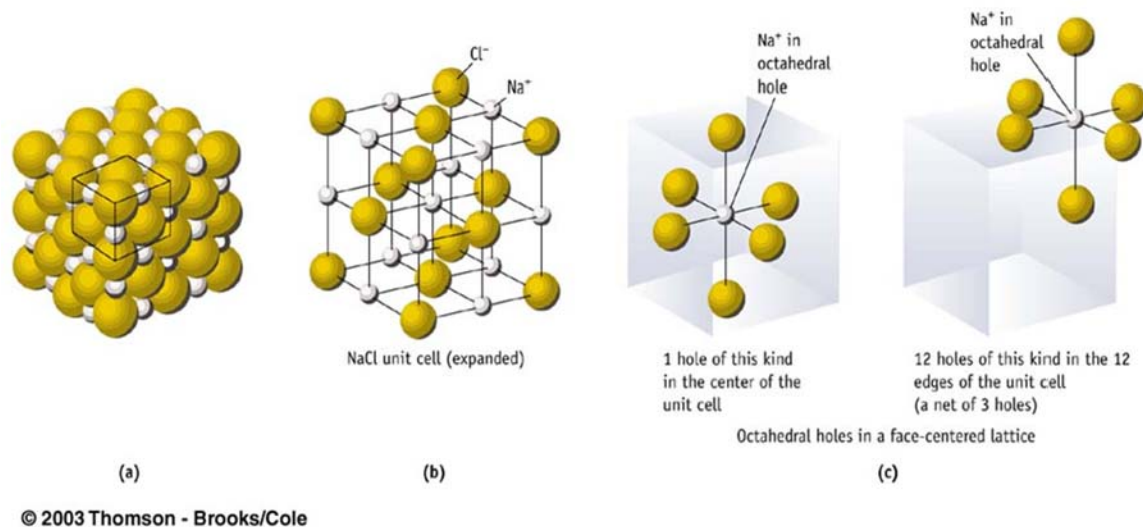


Fig. 12.38. The octahedral holes in fcc lattice

Only those ions joined by lines are actually touching each other. The sodium ion in the centre is being touched by 6 chloride ions. By chance we might just as well have centered the diagram around a chloride ion - that, of course, would be touched by 6 sodium ions. Sodium chloride is described as being **6:6-co-ordinated** (Fig. 12.38).

Fcc has one atom between the 4 atoms of each face. The number of face atoms per unit cell = $\frac{1}{2}$.

Total number of atoms for whole unit cell = $6 \times \frac{1}{2}$ (face atoms) + $8 \times \frac{1}{8}$ (corner atoms) = 4.

We can look at the NaCl as made up of fcc lattices interpenetrating. The Na's occupy the octahedral sites in the Cl sublattice, and the Cl's occupy the octahedral sites in the Na sublattice as shown in Fig. 12.38.

12.6.4. Why is sodium chloride 6:6-co-ordinated?

The more attraction there is between the positive and negative ions, the more energy is released. The more energy that is released, the more energetically stable the structure becomes.

That means that to gain maximum stability, you need the maximum number of attractions. So why does each ion surround itself with 6 ions of the opposite charge?

That represents the maximum number of chloride ions that you can fit around a central sodium ion before the chloride ions start touching each other. If they start touching, you introduce repulsions into the crystal which makes it less stable.

12.6.5. Why are the caesium chloride and sodium chloride structures different?

When attractions are set up between two ions of opposite charges, energy is released. The more energy that can be released, the more stable the system becomes. That means that the more contact there is between negative and positive ions, the more stable the crystal should become.

If you can surround a positive ion like cesium with eight chloride ions rather than just six (and vice versa for the chloride ions), then you should have a more stable crystal. So why doesn't sodium chloride do the same thing?

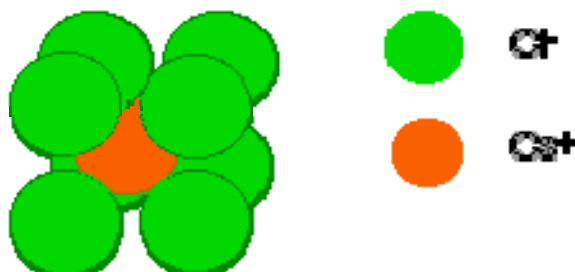


Fig. 12.39. CsCl unit cell

Now imagine what would happen if you replaced the cesium ion with the smaller sodium ion in **Fig. 12.39**. Sodium ions are, of course, smaller than cesium ions because they have fewer layers of electrons around them.

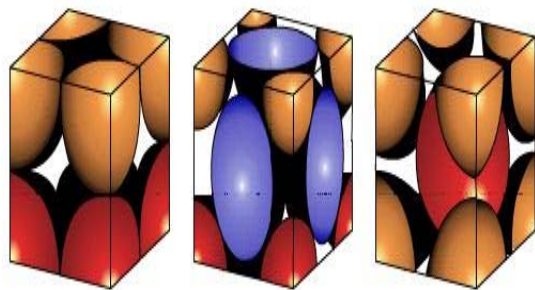
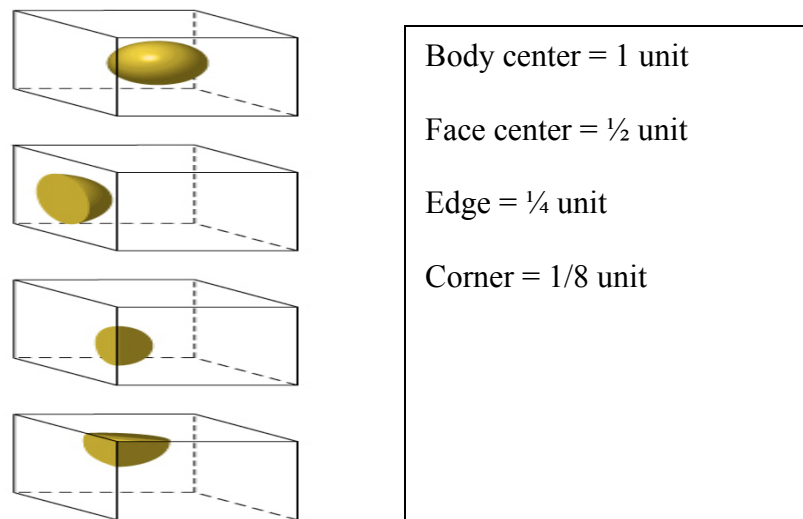
You still have to keep the chloride ions in contact with the sodium. The effect of this would be that the whole arrangement would shrink, bringing the chloride ions into contact with each other - and that introduces repulsion. Any gain in attractions because you have eight chlorides around the sodium rather than six is more than countered by the new repulsions between the chloride ions

themselves. When sodium chloride is 6:6-co-ordinated, there are no such repulsions - and so that is the best way for it to organise itself.

Which structure a simple 1:1 compound like NaCl or CsCl crystallises in depends on the *radius ratio* of the positive and the negative ions. If the radius of the positive ion is bigger than 73% of that of the negative ion, then 8:8-co-ordination is possible. Less than that (down to 41%) then you get 6:6-co-ordination.

In CsCl, the caesium ion is about 93% of the size of the chloride ion - so is easily within the range where 8:8-co-ordination is possible. But with NaCl, the sodium ion is only about 52% of the size of the chloride ion. That puts it in the range where you get 6:6-co-ordination

12.7. Calculation of Number of atoms per unit cell:



(a) Simple cubic (b) Face centred cubic (c) Body centred cubic

Three dimensional view showing the number of atoms per unit cell

Fig. 12.40. The contribution of atoms in the unit cell to the lattice

12.7.1. Simple cubic

In this type of unit cell, there are eight atoms at the corners and each such atom makes $1/8^{\text{th}}$ contribution to the unit cell (see figure. 40 (a)).

Hence, a simple cubic unit cell has,

$$8 \text{ (at corners)} \times 1/8 = 1 \text{ atom.}$$

12.7.2. Body centered cubic

This type of unit cell has eight atoms at corners and one at the body center. Each corner atom makes $1/8^{\text{th}}$ contribution and the atom at the body center belongs only to the particular unit cell (figure. 40 (c)).

Hence, a body centered cubic unit cell has,

$$8 \text{ (at corners)} \times 1/8 + 1 \text{ (at body center)} \times 1 = 2 \text{ atoms.}$$

12.7.3. Face centered cubic

A face centered cubic unit cell has one atom at each corner and one atom at each face center, being shared by two unit cells and making a contribution of only $1/2$ to a particular unit cell (figure. 40 (b)).

Hence, a face centered cubic unit cell has,

$$8 \text{ (at corners)} \times 1/8 + 6 \text{ (at face centers)} \times 1/2 = 4 \text{ atoms.}$$

12.8. Calculation of density of a unit cell:

The density of a unit cell and hence the density of a crystal is given by the formula.

$$d = \frac{Z \times M}{a^3 \times N_A \times 10^{-30}} \text{ gm / cm}^3$$

$$= \frac{Z \times M}{a^3 \times N_A} \text{ Kg / m}^3$$

Here, Z = Number of particles present per unit cell i.e., 1
for simple, 2 for Bcc, 4 for Fcc.

M = Atomic mass of element

a = Edge of the unit cell

N_A = Avogadro number.

for ionic crystals the formula used is same and the difference lies in –

- (1) Z = No. of formula units in one unit cell.
- (2) M = formula Mass (Molecular Mass) of the compound.
- (3) a = Edge which is 2 x distance between Na^+ and Cl^- in NaCl crystal.

12.9. Effect of ion size on crystal structure – Radius ratio:

In close packed arrangements of like charged ions, the oppositely charged ions touch one another. The difference in the crystal structure depends on the size of the ions. Larger the size of the given ion, greater will be the number of oppositely charged ions which can be packed around it. The geometrical requirement for a given structure in terms of the size of the two ions is expressed by radius ratio which is defined as:

$$R = r_c / r_a = r_+ / r_-$$

12.9.1. Radius ratio for three coordinate structures:

The tetrahedral angle, θ , is 109.5° so

$$\sin(\theta/2) = r_+ / (r_+ + r_-) \text{ So,}$$

$$\sin(54.7^\circ) = r_+ / (r_+ + r_-)$$

$$r_+ / r_- = 0.225$$

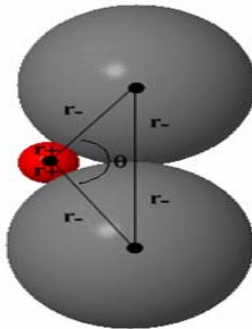


Fig. 12.41. Ions in a three coordinate structure

12.9.2. Radius ratio for six coordinate structures (NaCl structure):

The above structure shows the NaCl structure in which the Na^+ ion is surrounded by 6 Cl^- ions. As shown in the figure, along the cube edge, the Na^+ is touching two Cl^- ions so its length, a , is:

$$a = r_- + 2r_+ + r_- = 2r_+ + 2r_-$$

To get as close to the cation as possible, the anions must touch along the diagonal of a face of the cube. The diagonal has length, d , where:

$$d = r_- + 2r_- + r_- = 4r_-$$

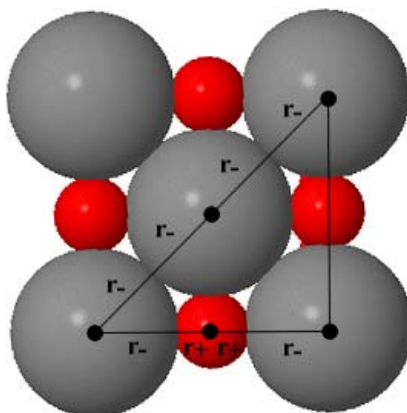


Fig. 12.42. Two dimensional view of packing around Na^+ in NaCl showing the face of the unit cell.

Using Pythagoras' theorem, the length of the side and face diagonal of a cube are related:

$$d^2 = a^2 + a^2 = 2a^2$$

$$d = (2)^{1/2}a$$

So,

$$4r_- = (2)^{1/2}(2r_+ + 2r_-)$$

$$r_+ / r_- = (2)^{1/2} - 1 = 0.414$$

As long as the radius of the cation is *no smaller* than 41% that of the anion, the NaCl structure is possible. If the cation is larger than this, the structure is stable as the anions do not need to touch but the CsCl structure is even more stable when the cation radius

reaches 73% that of the anion. If the cation radius is smaller than 41% that of the anion, the cation and anion will not be in contact. An even lower coordination number is then needed.

12.9.3. Radius ratio for eight coordination structures (CsCl structure)

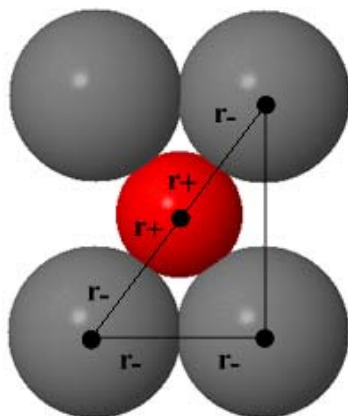


Fig. 12.43. Two dimensional view of packing around Cs^+ in CsCl showing two opposite edges of the unit cell

The above structure shows the CsCl structure in which the Cs^+ ion is surrounded by 8 Cl^- ions.

To get as close to the cation as possible, the anions must touch along the edge of the cube, as shown in the figure. The side of the cube has a length, a , where:

$$a = 2r.$$

Along the body diagonal, the Cs^+ is touching the two Cl^- ions on either end so its length, d , is:

$$d = r. + 2r_+ + r. = 2r_+ + 2r.$$

Using Pythagoras' theorem, the length of the side and the body diagonal of a cube are related:

$$d^2 = a^2 + a^2 + a^2 = 3a^2 = 3 \times 4r.^2 = 12r.^2$$

$$d = 2(3)^{1/2}r.$$

So,

$$2r. + 2r_+ = 2r(3)^{1/2}r.$$

$$r_+ / r. = (3)^{1/2} - 1 = 0.732$$

As long as the radius of the cation is *no smaller* than 73% that of the anion, the CsCl structure, with its high Madelung constant, is possible. If the cation is larger than this, the structure is stable as the anions do not need to touch. If the cation is smaller than this, the cation and anion will not be in contact. A lower coordination number is then needed

Table 12.1. The relation between the radius ratio and the coordination number

Radius Ratio	CN	Coordination
1.0	12	Cubic closest packed (CCP) Hexagonal closest packed (HCCP)
1.0–0.732	8	Cubic
0.732–0.414	6	Octahedral
0.414–0.225	4	Tetragonal
0.225–0.155	3	Triangular
<0.155	2	Linear

12.10. X-Ray Diffraction

- i) When waves are passed through a narrow slit they are diffracted.
- ii) When waves are passed through a diffraction grating (many narrow slits in parallel) they interact to form a diffraction pattern (areas of light and dark bands).
- iii) Efficient diffraction occurs when the wavelength of light is close to the size of the slits.
- iv) The spacing between layers in a crystal is 2 - 20 Å, which is the wavelength range for X-rays
- v) X-rays are passed through the crystal and are detected on a photographic plate.
- vi) The photographic plate has one bright spot at the center (incident beam) as well as a diffraction pattern (**Fig. 12.45**).
- vii) Each close packing arrangement produces a different diffraction pattern
- viii) Knowing the diffraction pattern, we can calculate the positions of the atoms required to produce that pattern.
- ix) We calculate the crystal structure based on knowledge of the diffraction pattern.

x) When waves of sufficient wavelength strikes the atom, waves reinforce each other when they are in phase (constructive interference, **Fig. 44(a)**) while they tend to cancel each other out when they are out of phase (destructive interference, **Fig. 44(b)**).

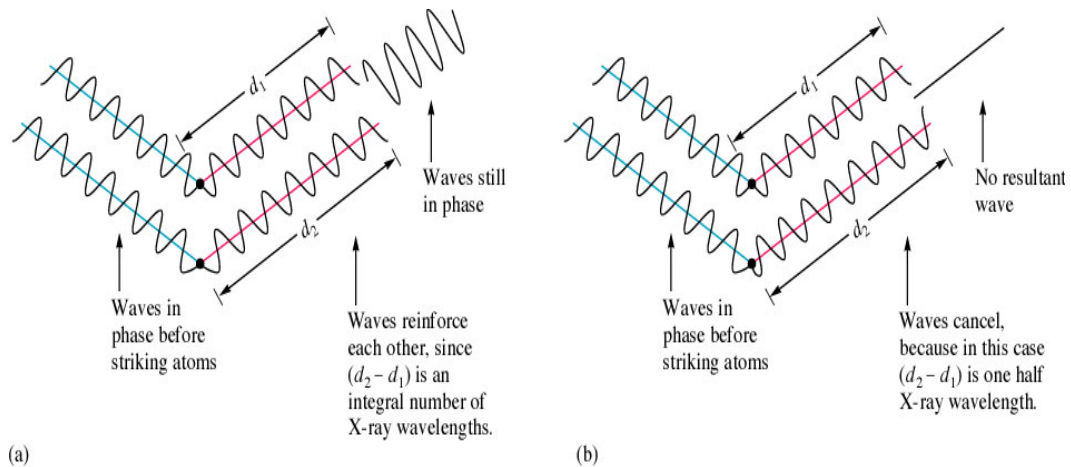


Fig. 12.44. Interference of light rays

The important discovery that a crystal could behave as a three dimensional diffraction grating to X- rays led W.H. Bragg and W.L. Brag to use X-ray for the purpose of studying the internal structure of the crystals.

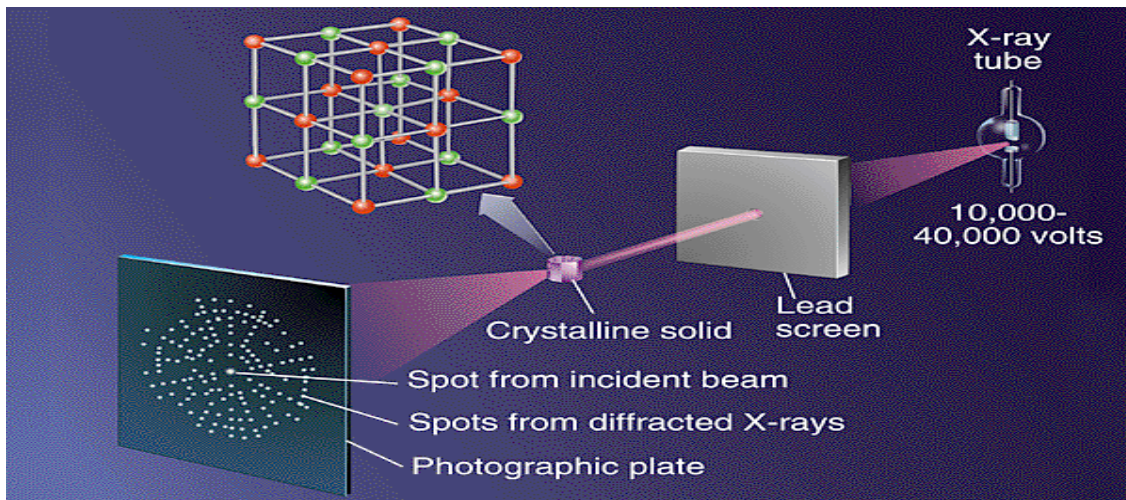


Fig. 12.45. Schematic representation of X-ray diffraction

12.10.1. The Bragg equation

Since a crystal may be regarded as consisting of a large numbers of parallel and equidistant atomic planes, Bragg considered that the diffraction effects observed for X-ray could be represented as reflection of X-ray by successive planes of atoms in the crystal. Thus when X rays are incident on a crystal face they penetrate into the crystal and are scattered by the atoms or ions.

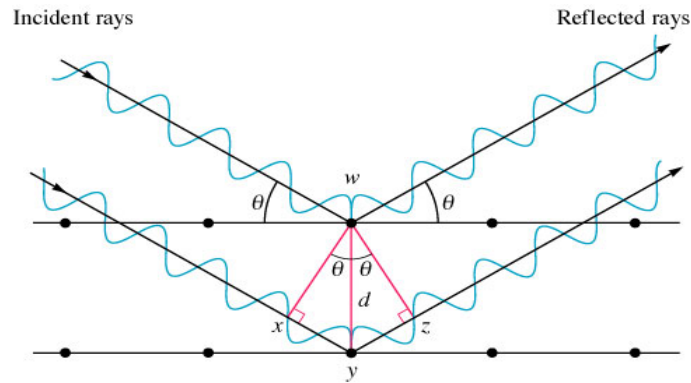


Fig. 12.46. Diagram to support the Bragg equation

If d is the interplanar spacing between the successive planes (see figure. 46), then both xy and yz are equal to $d \sin \theta$, since the angles xwy and ywz are each equal to θ . The total path difference is thus $2d \sin \theta$. For a reflection of maximum intensity this quantity must be an integral number (n) of wavelength (λ). Hence the condition of maximum reflection is,

$$n \lambda = 2d \sin \theta$$

12.11. Properties of Solids

Solids are classified into 3 groups namely,

- (i) *Conductors* with conductivity range of the order of 10^7 $(Wm)^{-1}$ e.g Metals.
- (ii) *Semiconductors* with conductivity range of the order of 10^{-6} - 10^4 $(Wm)^{-1}$ e.g. Semimetals.
- (iii) *Insulators* with conductivity range 10^{-10} - 10^{-2} $(Wm)^{-1}$ e.g. Non metals.

- In most of the solids conduction is through electron movement under an electric field, however, in some ionic solids the conduction is through ions.
- In metals conductivity strongly depends upon the no. of valence electrons available per atom. The atomic orbitals form molecular orbitals which are so close to each other as to form a BAND.
- The conductivity of solids can be better explained on the basis of energy gap present between the conduction band (HIGHER UNOCCUPIED BAND) and the valence band.

i) In metals the conduction band is almost overlapping with the valence band (see figure. 47) i.e., there is no energy gap present between these two bands or valence band is not completely filled. Then electrons can flow easily under the influence of electric field in both the cases.

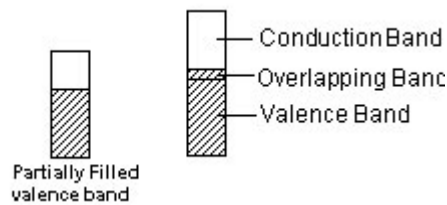


Fig. 12.47. Overlapping of the conduction band with the valence band

ii) In the case of semimetals the gap between valence band and conduction band is small and therefore some of the electrons may jump from valence band to conduction band and some conductivity is observed. The conductivity here increases in temperature. The reason for such an increase in lowering of energy gap shown below in the **Fig.. 12.48.**

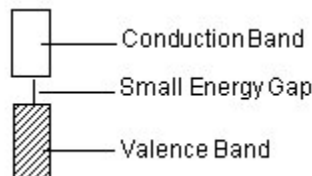


Fig. 12.48. Band picture of semimetals

The heat is actually responsible for ejection of electrons from their place thus leaving a (+)ve charge (positive hole). The crystal can now conduct electricity because on applying the electric field the electrons and holes migrate in opposite directions. This type of conductance is called INTRINSIC CONDUCTANCE: For Example Si, Ge etc.

Note:

(i) For practical purposes the conductivity of pure Si and Ge is very low at room temperature. In order to increase their conductance the pure substances are carefully doped (introduced with small amount of impurities in the form of elements of the 13 and 15 group of periodic table).

(ii) The group 15 elements have 1 electron excess to Si or Ge after forming 4 covalent bonds with group 14 member (Si or Ge). This excess free electron is responsible for electrical conductivity in them. Group 14 elements when doped with group 15 elements are called n-type semiconductors as shown in **Fig. 12.49**. Here n specifies that negative charge flows in them.

(iii) The group 13 elements have 1 electron short to Group 14 elements, thus giving rise to electron deficient band or a hole. Here such holes are responsible for electrical conductivity. Thus group 14 elements when doped with elements of group 13, these are called p-type semiconductors (**Fig. 12.48.1**). Here, p specifies that conduction is through positive holes in them.

(iv) Various combinations of n-type and p-type semiconductors are used to make electronic components. For example, diode is a combination of p and n-type semiconductors and used as rectifier, TRANSISTORS which are pnp or npn sandwich semiconductor are used to detect or amplify radio or audio signals.

(v) In the case of non metals (insulators) the energy gap between valence band and conduction band is so large that it cannot even be covered up by supplying energy in the form of heat as shown in **Fig. 12.49**.

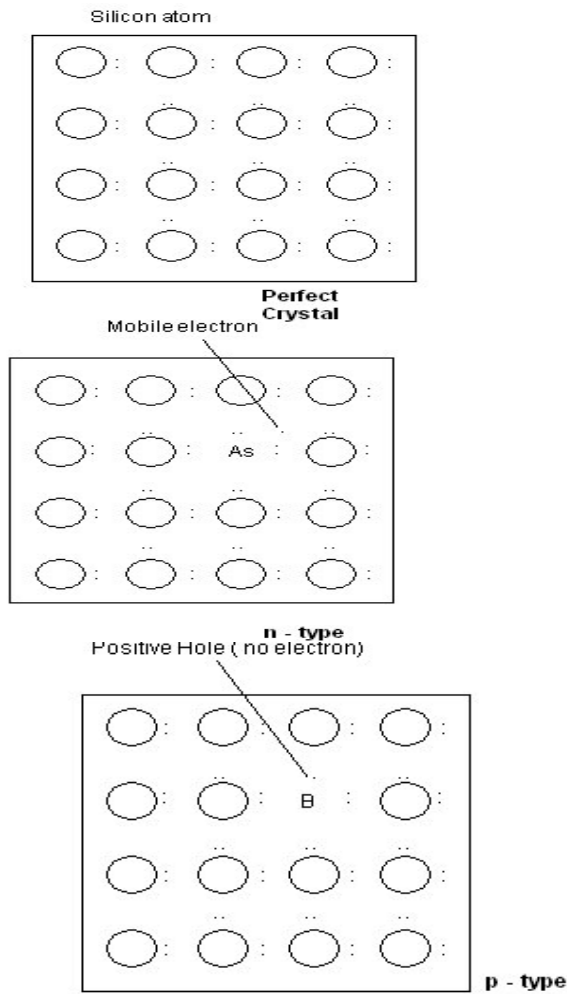


Fig. 12.48.1. Pictorial representation of the n-type and p-type semiconductors

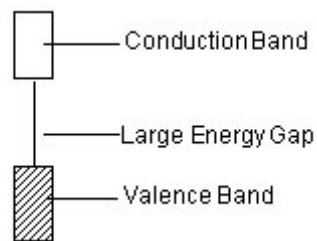


Fig. 12.49. Band picture of insulators

Besides conductivity solids also show magnetic properties and dielectric properties. On the basis of magnetic properties solids can be categorized to -
 (a) Diamagnetic i.e., which are feebly repelled by magnetic field. These have the

characteristic absence of unpaired electrons in them i.e., their all electrons are paired. For Example - Non metallic elements (except O₂ and S) inert gases and species with paired electrons e.g. TiO₂, V₂O₅, C₆H₆, NaCl etc.

(b) Paramagnetic i.e., which are attracted by magnetic field due to the presence of atoms, ions or molecules with unpaired electron in them (e.g., O₂, Cu²⁺, Fe³⁺ etc.). In magnetic field these tend to orient themselves parallel to the direction of magnetic field. These are used in electronic appliances.

(c) Ferromagnetic i.e., which show magnetism even in the absence of magnetic field, Fe, Co and Ni are 3 elements which show ferromagnetism at room temperature. A spontaneous alignment of magnetic moments in the same direction gives rise to ferromagnetism. The ferromagnetism is not seen above a temperature called CURIE TEMPERATURE.

(d) Antiferromagnetic i.e., those which have net magnetic moment zero due to compensatory alignment of magnetic moments. For example MnO, MnO₂, FeO, NiO, Cr₂O₃ etc.

The dielectric properties are seen in insulators, which, when are placed in on electric field, show generation of dipoles in them due to the pulling of electrons & nuclei of atoms or molecules in opposite directions. These dipoles-

(a) may align themselves in an ordered manner so that there is a net dipole moment in the crystal.

(b) may align themselves in such a manner that dipole moments may cancel each other

(c) It is also possible that there are no dipoles in the crystal but only ions are present.

□ The crystals where situation (a) is found exhibit PIEZOELECTRICITY or PRESSURE ELECTRICITY, which is production of electricity by a polar crystal when mechanical stress is applied to it. Piezoelectric crystals also show development of mechanical stress when electric field is applied to them, thus acting as a mechanical electrical transducers.

Note

1. Piezoelectric crystals with permanent dipoles are said to have ferroelectricity e.f. Rochelle's salt, BaTiO₃, KH₂PO₄ etc.

2. Piezoelectric crystals with zero dipole are said to have ANTIFERROELECTRICITY

3. Some piezoelectric crystals, when heated produce small electric potential or PYROELECTRICITY.

4. The phenomenon where electricity passes through a material without resistance is called SUPERCONDUCTIVITY. The material showing this property is said to be SUPERCONDUCTOR. It was KAMMERLINGH ONNES of Netherlands who first reported the case of Hg as superconductor at a very low temperature of 4.2 K. Afterwards, some metals alloys and certain organic solids have been reported to be superconducting but at very low temperatures. Now a days superconductors are also reported at comparatively higher temperatures for example $\text{YBa}_2\text{Cu}_3\text{O}_7$ at 90K, $\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_{10}$ at 105 K, and $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$ at 125 k etc.

Table 12.2. Crystallization of different metals in ccp, hcp and bcc with their corresponding lattice parameters in parenthesis

Cubic close packed, (a)	Hexagonal close packed (a, c)	Body centered cubic (a)
Cu (3.6147)	Be (2.2856, 3.5832)	Fe (2.8664)
Ag (4.0857)	Mg (3.2094, 5.2105)	Cr (2.8846)
Au (4.0783)	Zn (2.6649, 4.9468)	Mo (3.1469)
Al (4.0495)	Cd (2.9788, 5.6167)	W (3.1650)
Ni (3.5240)	Ti (2.506, 4.6788)	Ta (3.3026)
Pd (3.8907)	Zr (3.312, 5.1477)	Ba (5.019)
Pt (3.9239)	Ru (2.7058, 4.2816)	
Pb (4.9502)	Os (2.7353, 4.3191)	
	Re (2.760, 4.458)	

12.12. Problems

1. There are two types of closest packing of spheres: face-centered-cubic (fcc with the ABCABC... sequence) and the hexagonal closest packing (hcp with the ABAB... sequence) How many neighbors are there for a sphere in these packings?

2. If the radii of the spheres are 1.5 \AA , what will be the distance between centers of neighboring spheres?

3. If the radius of an atom is 123 pm, calculate the volume of the atom. Assume the atom to be a sphere.

4. The crystal structure of calcium is face centered cubic. Its cell edge is 557 pm.

Calculate the density of Ca in g /cm³

(Atomic mass, Ca, 40.08; Avogadro's number 6.022×10^{23})

5. The density of silver (atomic mass: Ag, 107.9) is 10.6 g/cm³, and it has a face centered cubic structure. Calculate the edge of the cubic unit cell in pm. (Avogadro's number 6.022×10^{23})

6. Consider a simple cubic (SC) unit cell and a simple hexagonal (SH) unit cell. For both of these cells, $Z = 1$ and $a = b = c = 2r$, where r is the radius of the host atoms which occupy the eight lattice points. Derive an exact mathematical expression for the ratio of cell volumes SC:SH.

7. An element occurs in bcc structure with a cell edge of 288 pm. The density of element is 7.2 g cm⁻³. How many atoms does 208 g of the element contain?

Solution:

$$\text{Volume of the unit cell} = (288 \times 10^{-10})^3 = 23.9 \times 10^{-24} \text{ cm}^3$$

$$\text{Volume of 208 g of the element} = 208 / 7.2 = 28.88 \text{ cm}^3$$

$$\text{Number of unit cell in } 28.88 \text{ cm}^3 = 28.88 / 23.9 \times 10^{-24} = 12.08 \times 10^{23} \text{ unit cells}$$

$$\text{So, total no. of atoms in } 12.08 \times 10^{23} \text{ unit cells} = 2 \times 12.08 \times 10^{23} \text{ [since each bcc unit cell contain 2 atoms]}$$

$$= 24.16 \times 10^{23}$$

8. Xenon crystallises in a face centred cubic lattice and the edge of the unit cell is 620 pm. Calculate the nearest neighbouring distance and the radius of the xenon atom?

Solution :

$$\text{Nearest neighbour distance (d)} = a / \sqrt{2} = 620 \text{ pm} / 1.4142 = 438.4 \text{ pm.}$$

$$\text{Radius of the xenon atom (r)} = a / 2\sqrt{2} = 620 \text{ pm} / 2 \times 1.4142 = 219.2 \text{ pm}$$

9. X-rays of wavelength 1.54 \AA strike a crystal and are observed to be deflected at an angle of 22.5° . Assuming that $n = 1$. Calculate the spacing between the planes of atoms that are responsible for this reflection.

Solution:

According to Bragg's law,

$$n\lambda = 2d \sin \theta$$

Given $n = 1$, $\lambda = 1.54 \text{ \AA}$, $\theta = 22.5^\circ$

$$d = 1.54 / 2 \sin 22.5^\circ = 1.54 / 2 \times 0.383 = 2.01 \text{ \AA}$$

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CHAPTER - 13

WAVE EQUATION AND ITS SIGNIFICANCE

Sandhya

13.1. Introduction to Atomic Structure

John Dalton (1809) regarded the atom as a hard, dense and smallest indivisible particle of matter, The emission of negatively and positively charged particles from radioactive elements as well as from gases on the passage of electricity through gases at very low pressures convinced that atom is not indivisible but consists of fundamental particles. The negatively charged material particles which constitute the cathode rays are called electrons.

J.J. Thomson determined the ratio e/m of electron by subjecting the beam of electrons produced in a discharge tube to magnetic as well as electric fields. The magnetic field is applied at right angles to the direction of the beam. Under the influence of magnetic force which is equal to Bev , the electron starts moving in the circular path of radius r . the centrifugal force mv^2/r arising from this circular motion is equal and opposite to the magnetic force,

$$Bev = mv^2/r ; \text{ or } e/m = v/(rB) \text{ -----(1)}$$

The electric force experienced by each electron is given by Ee . The magnetic and electric field are so adjusted as to produce equal and opposite effects in such a way that there is no deflection of the electron beam from its original position.

$$Bev = Ee$$

$$v = E/B$$

substituting v in eq (1)

$$e/m = E/(rB^2)$$

Robert Millikan determined the charge on electron by using oil drop technique. In this technique, an oil spray consisting of microscopic droplets of an oil produced by an atomizer is injected into a chamber containing air at a controlled pressure. The air is ionized by exposing to X-rays.

The electrons produced as a result of ionization of air get attached to oil droplets. The charged oil droplets move down under the action of gravity and acquire a constant

velocity U_1 when the force of gravity ($=Mg$) is balanced by the viscous resistance of air. The droplets enter a region in between two parallel plates held at suitable distance from each other. These plates can act as electrodes.

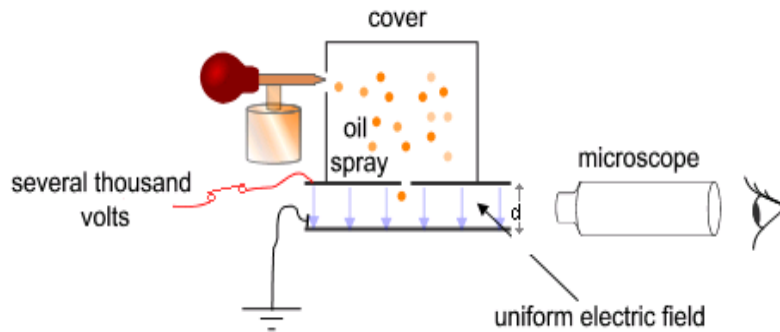


Fig. 13.1. Simplified scheme of Millikan's oil-drop experiment

An electric field of strength X is then applied through the two metal plates in such a way that it acts against the action of gravity. The total force which acts on the falling droplet would thus be $(Mg - Xe)$ where M is the mass and e is the charge on the droplet.

If the rate of the droplet is now U_2 , then

$$U_1/U_2 = Mg / (Mg - Xe)$$

When the droplets move only under the action of gravity, their velocity (U_1) is also given by the Stokes law, that is,

$$U_1 = \frac{2}{9} \frac{gr^2\rho}{\eta}$$

Where r , ρ , η are the radius of the droplet, the density of the droplet and the coefficient of viscosity of air. Assuming the particle is spherical, its mass $M = \frac{4}{3}\pi r^3 \rho$. Millikan carried out a number of experiments by varying the value of X and found that charge e was always equal to a simple multiple of 1.6022×10^{-19} coulomb.

13.2. The Rutherford Scattering Experiment

Ernest Rutherford directed a narrow beam of alpha particles obtained from polonium at an extremely thin sheet of a metal like silver and gold. After passing through the metal sheet, the α -particles were made to strike a fluorescent screen. Rutherford observed that:

1. Most of the α -particles pass through the metallic sheet without suffering any change in their path showing that the atom consists predominantly of empty space.
2. An extremely small number of α -particles get deflected through wider angles or even backwards showing the presence of a heavy positively charged body in each atom and that the volume of this body is only a minute fraction of the total volume of the atom.

Chadwick discovered in 1932, that when beryllium or boron is bombarded by alpha particles, new particles which carry no charge but have mass almost equal to that of a proton, are emitted. These particles are called neutrons.

13.2.1. The Rutherford Atomic Model

Based on his scattering experiments, Rutherford suggested the following model of the atom

- i) An atom consists of a minute positively charged body, located at its centre, called the nucleus. The nucleus though small, contains all the protons and neutrons.
- ii) An atom also consists of a sufficient number of extremely small negatively charged electrons distributed around the nucleus to balance the positive charge on the nucleus.

Rutherford proposed that the electrons are revolving round the nucleus at extremely high speeds at great distance from the nucleus. The centrifugal force arising from this motion balances the force of electrostatic attraction.

13.2.2. Objection to the Rutherford Model

Bohr argued that if an electron moved around the nucleus in an orbit, as in Rutherford's model, it should be subjected to acceleration due to continuous change in its direction of motion. The electron should, therefore, continuously emit radiation and lose energy. As a result, its orbit should become smaller and smaller and finally it should drop into the nucleus. This however does not happen. The solution to this difficulty on the basis of the quantum theory of radiation was put forth by Max Planck in 1901 to explain the observed distribution of energy in the spectrum of the heat radiation emitted by a hot body.

13.3. The Bohr Theory of Hydrogen atom

The Bohr postulates are

i) An atom consists of positively charged nucleus responsible for almost the entire mass of the atom.

ii) The electrons revolve round the nucleus in certain permitted circular orbits of definite radii.

iii) The permitted orbits are those for which the angular momentum of an electron is an integral multiple of $h/2\pi$ where h is the planck constant. If m is the mass and v is the velocity of the electron in a permitted orbit of radius r , then

$$L = mvr = n(h/2\pi); n = 1,2,3,\dots$$

where L is the orbital angular momentum.

iv) When electrons move in permitted discrete orbits, they do not radiate energy.

v) The energy is radiated when an electron jumps from higher to lower orbit and the energy is absorbed when it jumps from lower to higher orbit.

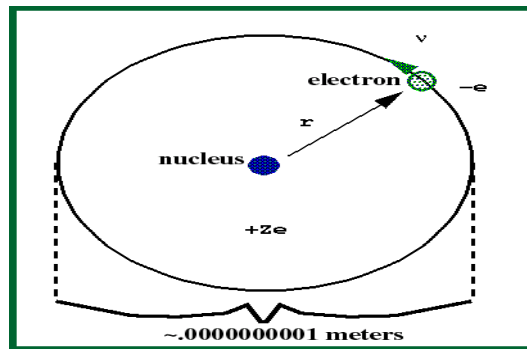


Fig. 13.2. The Hydrogen Atom

To calculate the energy of electron in the Bohr hydrogen atom:

The electron is held in a circular orbit by electrostatic attraction. The [centripetal force](#) is equal to the [Coulomb force](#).

$$\frac{m_e v^2}{r} = \frac{k_e e^2}{r^2}$$

where m_e is the mass, e is the charge of the [electron](#) and k_e is [Coulomb's constant](#). This determines the speed at any radius:

$$v = \sqrt{\frac{k_e e^2}{m_e r}}$$

It also determines the total energy at any radius:

$$E = \frac{1}{2}m_e v^2 - \frac{k_e e^2}{r} = -\frac{k_e e^2}{2r}$$

The total energy is negative and inversely proportional to r . This means that it takes energy to pull the orbiting electron away from the proton. For infinite values of r , the energy is zero, corresponding to a motionless electron infinitely far from the proton.

The [angular momentum](#) $L = m_e v r$ is an integer multiple of \hbar :

$$m_e v r = n \hbar$$

Substituting the expression for the velocity gives an equation for r in terms of n :

$$\sqrt{k_e e^2 m_e r} = n \hbar$$

so that the allowed orbit radius at any n is:

$$r_n = \frac{n^2 \hbar^2}{k_e e^2 m_e}$$

The smallest possible value of r is called the [Bohr radius](#) and is equal to:

$$r_1 = \frac{\hbar^2}{(k_e e^2) m_e} = 0.529 \times 10^{-10} \text{m}$$

The energy of the n -th level is determined by the radius:

$$E = -\frac{k_e e^2}{2r_n} = -\frac{(k_e e^2)^2 m_e}{2 \hbar^2 n^2} = \frac{-13.6 \text{eV}}{n^2}$$

An electron in the lowest energy level of hydrogen ($n = 1$) therefore has 13.6 [eV](#) less energy than a motionless electron infinitely far from the nucleus. The next energy level ($n = 2$) is -3.4 eV. The third ($n = 3$) is -1.51 eV, and so on. For larger values of n , these are also the binding energies of a highly excited atom with one electron in a large circular orbit around the rest of the atom.

13.4. The Sommerfeld Extension of the Bohr Theory

According to Sommerfeld, an electron revolving around a central positively charged nucleus is so influenced by the nuclear charge that it is set into motion in elliptical orbits with the nucleus situated at one of the foci.

Thus, while according to Bohr's theory, electrons move in circular orbits, according to Sommerfeld's modification electrons move in elliptical orbits. The electron

traveling in an elliptical orbit will have its angular momentum. This momentum, according to the quantum theory, must also be quantized and thus can have only a limited number of values given by the factor $kh/2\pi$, k is an integer known as azimuthal quantum number.

13.4.1. Objection to Bohr Model

Although Bohr's theory and its extension by Sommerfeld could explain atomic spectra of hydrogen, this model could not explain with mathematical exactness the spectra of atoms containing more than one electron.

The main objection to Bohr's model, however, originated from two additional sources.

i) In 1923, Louis de Broglie, suggested that electron like light, has a dual character. In Bohr's theory, there is no place for the wave character of electron.

ii) According to Heisenberg uncertainty principle it is not possible to determine simultaneously the exact position and the momentum of a small moving particle like an electron.

13.5. The particle Character of Electromagnetic Radiation

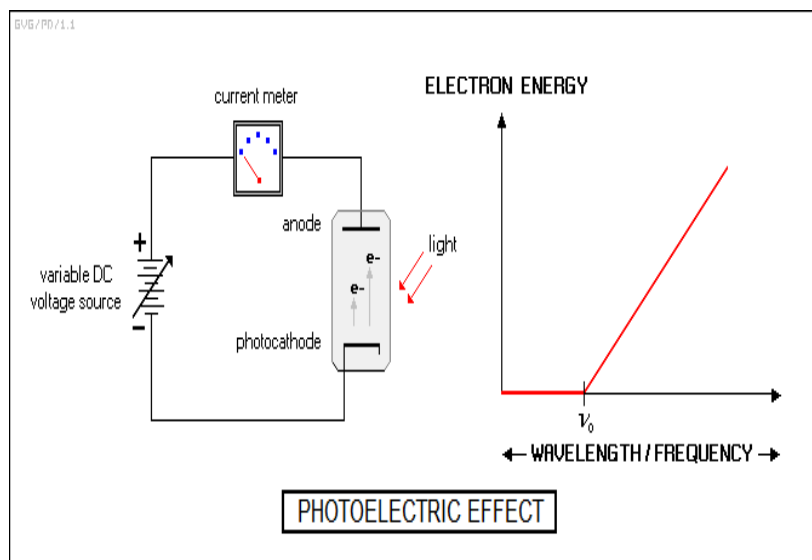


Fig. 13.3. Photoelectric effect

The evidence for the particle-like character of radiation comes from the measurement of the energies of electrons produced in the photoelectric effect. This effect is the ejection of electrons from metals when they are exposed to ultraviolet radiation. The experimental characteristics of the photoelectric effect are:

- i) No electrons are ejected, regardless of the intensity of the radiation, unless the frequency exceeds a threshold value characteristic of the metal.
- ii) The kinetic energy of the ejected electrons increases linearly with the frequency of the incident radiation but is independent of the intensity of the radiation.
- iii) Even at low light intensities, electrons are ejected immediately if the frequency is above threshold.

These observations strongly suggest that the photoelectric effect depends on the ejection of an electron when it is involved in a collision with a particle-like projectile that carries enough energy to eject the electron from the metal. If we suppose that the projectile is a photon of energy $h\nu$, where ν is the frequency of the radiation and the conservation of energy requires that the kinetic energy of the ejected electron should obey

$\frac{1}{2} m_e v^2 = h\nu - \Phi$, Φ is the characteristic of the metal called its work function, the energy required to remove an electron from the metal to infinity. Photon ejection cannot occur if $h\nu < \Phi$ because the photon brings insufficient energy.

13.6. Particle and Wave Character of Electron

Einstein had suggested, in 1905, that light has a dual character; as wave and also as particle. Louis de Broglie proposed that matter also has a dual character ; as wave and particle.

He derived an expression for calculating the wave length λ of a particle of mass m moving with velocity v according to

$$\lambda = h/mv \quad \text{-----}(2)$$

de Broglie equation can be derived using mass energy relationship

$$E = mc^2 \quad \text{-----}(3)$$

Equating this energy with the energy of photon,

$$h\nu = mc^2 \quad \text{-----(4)}$$

$$\nu = c/\lambda \quad \text{-----(5)}$$

hence $\lambda = h/mc$, replacing c by the velocity of electron we have,

$$\lambda = h/mv$$

13.7. The Davisson - Germer experiment

The de Broglie's hypothesis was experimentally supported by Davisson and Germer.

In this experiment, electrons were emitted from a hot filament and were accelerated by a potential ranging between 40 and 68 volts before striking a nickel plate, as shown in fig. 13.4.

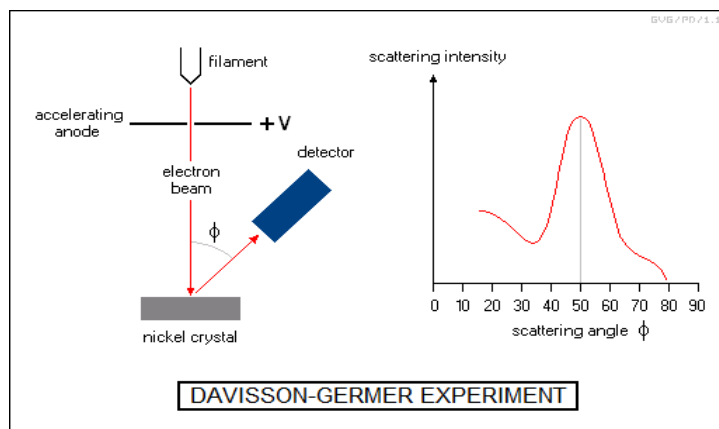


Fig. 13.4. Davison-Germer experiment

They found that the impact of electrons resulted in the production of diffraction patterns which were similar to those given by X-rays under similar conditions. Since X-rays possess wave character, the experiment gave direct evidence for wave character of electron as well.

13.8. The Heisenberg Uncertainty Principle

According to this principle, it is not possible to determine precisely both the position and the momentum of a small moving particle. It is appropriate to say that an electron is associated with a definite energy, i.e., it belongs to a definite energy level and not that it belongs to a particular orbit.

Heisenberg uncertainty principle is mathematically expressed as,

$$(\Delta x)(\Delta p) \geq h/4\pi$$

Where Δx is the uncertainty with regard to position and Δp is the uncertainty with regard to the momentum of the electron.

13.9. The failures of Classical Physics

13.9.1. Black Body Radiation

A hot object emits electromagnetic radiation. At high temperature, an appreciable proportion of short-wavelength blue light is generated as the temperature is raised. This behaviour is seen when a heated iron bar glowing red hot becomes white hot when heated further. The dependence is illustrated in Fig. 5, which shows how the energy output varies with wavelength at several temperatures. The curves are those of an ideal emitter called a black body, which is an object capable of emitting and absorbing all frequencies of radiation uniformly. The fig. 5 shows that the peak in the energy output shifts to shorter wavelengths as the temperature is raised. An analysis of the data led Wilhelm.

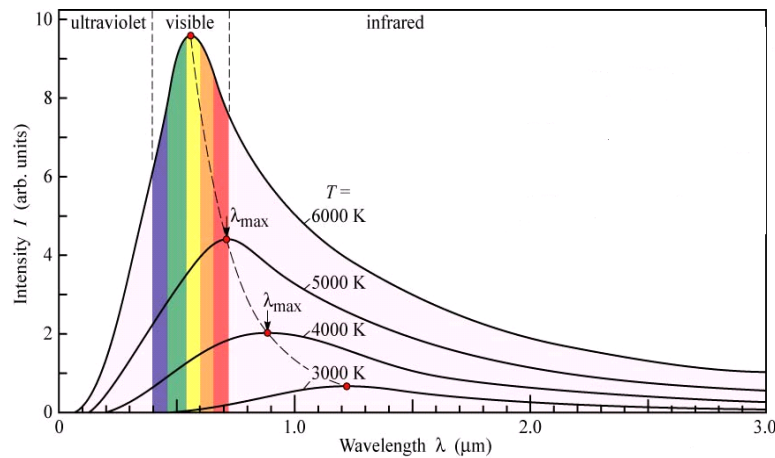


Fig. 13.5. The intensity distribution in a black body at different temperatures

Wien to formulate the Wien displacement law:

$$T\lambda_{\max} = 1/5 C_2; \quad C_2 = 1.44 \text{ cm K}$$

Where λ_{\max} is the wavelength corresponding to the maximum of the distribution at a temperature T . The constant C_2 is called the second radiation constant. Using its value, we can predict the $\lambda_{\max} \approx 2900 \text{ nm}$ at 1000 K .

A second feature of black body radiation had been noticed in 1879 by Josef Stefan, who considered the total energy density, \mathbf{E} the total electromagnetic energy in a region divided by the volume of the region ($\mathbf{E} = E/V$). This energy density of the electromagnetic field increases as the temperature increased, the Stefan-Boltzmann law states that,

$$E = aT^4$$

An alternative form of the law is in terms of excittance, M , the power emitted by a region of surface divided by the area of the surface, the excittance is a measure of the brightness of the emission. Since the excittance is proportional to the energy density, M is also proportional to T^4

$$M = \sigma T^4 \quad \sigma = 56.7 \text{ nW m}^{-2}\text{K}^{-4}$$

The constant σ is called the Stefan-Boltzmann constant.

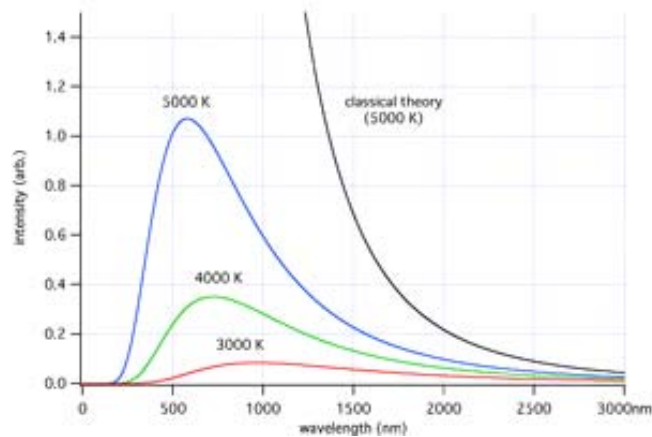


Fig. 13.6. The Rayleigh-Jeans law predicts an infinite energy density at short wavelengths

The Physicist Lord Rayleigh studied it theoretically from a classical viewpoint and thought of the electromagnetic field as a collection of oscillators of all possible frequencies. Rayleigh used the equipartition principle to calculate the average energy of each oscillator as kT . Then with the minor help from James Jeans he arrived at the Rayleigh Jeans law

$$dE = \rho d\lambda \quad \rho = 8\pi kT/\lambda^4$$

where ρ is the proportionality constant between $d\lambda$ and the energy density in that range of wavelengths; k is the Boltzmann's constant ($k = 1.381 \times 10^{-23} \text{ J K}^{-1}$).

Although Rayleigh Jeans law is successful at long wavelengths, it fails badly for short wavelengths (high frequencies). Thus, as λ decreases, ρ increases without going through a maximum.

The equation therefore predicts that oscillators of very short wavelength (corresponding to ultraviolet light, X-rays, and even γ -rays) are strongly excited even at room temperature. This absurd result, which implies that a large amount of energy, is called the ultraviolet catastrophe.

13.9.2. The Planck distribution

The German physicist Max Planck found that the energy of each electromagnetic oscillator is limited to discrete values and cannot be varied arbitrarily. This proposal is quite contrary in which all possible energies are allowed. The limitation of energy discrete values is called the quantization of energy. The permitted energies of an electromagnetic oscillator of frequency ν are integer multiples of $h\nu$

$$E = n h \nu \quad n = 0, 1, 2, \dots$$

where h is a fundamental constant known as Planck's constant.

On the basis of this assumption, Planck derived the Planck distribution

$$dE = \rho d\lambda \quad \rho = \frac{8\pi hc}{\lambda^5} (e^{hc/\lambda kT} - 1)^{-1}$$

The Planck distribution resembles the Rayleigh-Jeans law apart from the all important exponential factor in the denominator. For short wavelengths, $hc/\lambda kT \gg 1$ and $e^{hc/\lambda kT} \rightarrow \infty$ faster than $\lambda^5 \rightarrow 0$; therefore $\rho \rightarrow 0$ as $\lambda \rightarrow 0$ or $\nu \rightarrow \infty$. Hence, the energy density approaches zero at high frequencies. For long wavelengths, $hc/\lambda kT \ll 1$, and the denominator in the Planck distribution can be replaced by

$$e^{hc/\lambda kT} - 1 = \left(1 + \frac{hc}{\lambda kT} + \dots \right)^{-1} \approx \frac{hc}{\lambda kT}$$

When this approximation is substituted in Planck distribution, it reduces to Rayleigh-Jeans law.

13.10. Wave Mechanics – An Introduction to Quantum Mechanics

Classical mechanics, as formulated by Sir Isaac Newton in the seventeenth century, is obeyed by macroscopic particles such as planets and rigid bodies. However, since the microscopic particles such as electrons, protons, atoms and molecules show wave-particle duality, they do not obey Newtonian dynamics. They however, obey quantum mechanics a key feature of which is the quantization of energy and angular momentum.

The motion of a one-particle, one-dimensional classical system is governed by Newton's second law of motion, i.e, $F = ma = m d^2x/dt^2$. In order to obtain the position x , as a function of time, this differential equation must be integrated twice with respect to time. The first integration yields dx/dt and the second integration gives x . Each integration introduces an arbitrary integration constant. Hence, the integration of $F = ma$ gives an equation for x that contains two unknown constants c_1 and c_2 .

$$\text{Thus } x = f(t, c_1, c_2)$$

where f is some function. To evaluate c_1 and c_2 we require two pieces of information about the system. If we know that at a certain time t_0 , the particle is at the position x_0 and has speed v_0 , then c_1 and c_2 can be calculated from the equations

$$x_0 = f(t_0, c_1, c_2)$$

$$\text{and } v_0 = f'(t_0, c_1, c_2),$$

where f' is the derivative of f with respect to t . Thus, if we know the force F and the initial position and velocity of the particle, we can use Newton's second law of motion to predict the position of the particle at any future time.

Classical mechanics is a deterministic theory in that it allows us to predict the exact paths taken by the particles of the system and tells us where they will be at a future time. In contrast, quantum mechanics gives the probabilities of finding the particles at various locations in space.

In quantum mechanics, the state of a system is defined by the state function or wave function ψ , which is a function of the coordinates of the particles of the system and is also a function of time. Thus, for a two-particle system, the wave function can be written as

$$\Psi = f(x_1, y_1, z_1, x_2, y_2, z_2, t)$$

where x_1, y_1, z_1 are the coordinates of particle 1, etc. For an n-particle system, the equation governing the time-dependence of ψ is given by

$$\sum_{i=1}^n -\frac{\hbar^2}{2m_i} \left(\frac{d^2\psi}{dx_i^2} + \frac{d^2\psi}{dy_i^2} + \frac{d^2\psi}{dz_i^2} \right) + v(x_i, y_i, z_i, t)\Psi = i\hbar \frac{d\Psi}{dt}$$

where m_i is the mass and V is the potential energy of the particle. The above equation, known as the Schrodinger wave equation.

13.10.1. The Schrodinger Wave Equation

Erwin Schrodinger's wave model of an atom, the discrete energy levels or orbits proposed by Bohr are replaced by mathematical functions, ψ , which are related to the probability of finding, electrons at various places around the nucleus.

Consider a simple wave motion as that of the vibration of a stretched string. Let y be the amplitude of this vibration at any point whose coordinate is x at time t . The equation for such a wave motion may be expressed as

$$d^2y/dx^2 = (1/v^2) \times (d^2y/dt^2) \text{ ----- (6)}$$

where v is the velocity with which the wave is propagating. There are two variables, x and t , in the above differential equation, i.e., the amplitude y depends upon two variables x and t .

In order to solve the above differential equation, it is necessary to separate the two variables. Thus, y may be expressed as

$$y = f(x) g(t) \text{-----(7)}$$

where $f(x)$ is a function of the coordinate x only and $g(t)$ is a function of the time t only. For stationary waves, such as occur in a stretched string, the function $g(t)$ be represented by the expression

$$g(t) = A \sin(2\pi vt) \text{-----(8)}$$

where v is the vibrational frequency and A is a constant known as the maximum amplitude. Hence, for stationary waves, the equation for y may be written as

$$y = f(x) A \sin(2\pi vt) \text{-----(9)}$$

$$\text{Hence } d^2y/dt^2 = -f(x) 4\pi^2 v^2 A \sin(2\pi vt) \text{-----(10)}$$

$$= -4\pi^2 v^2 f(x) g(t) \text{-----(11)}$$

Similarly it follows from Eq.(9) that

$$d^2y/dt^2 = \{d^2f(x)/dx^2\} \times \{g(t)\} \text{-----(12)}$$

combining equation 11 and 12,

$$d^2f(x)/dx^2 = \{-4\pi^2v^2/\lambda^2\} \times \{f(x)\} \text{----- (13)}$$

As is well known, the frequency of the vibrations v is related to the velocity u by the expression $v = u/\lambda$ hence equation 13 becomes

$$d^2f(x)/dx^2 = \{-4\pi^2/\lambda^2\} \times \{f(x)\} \text{---- (14)}$$

Equation 14 is for the wave motion in one dimension only. We may now extend it to three dimensions represented by the coordinates x, y and z . Evidently, $f(x)$ will then be replaced by the amplitude function for the three coordinates, $\psi(x, y, z)$. For the sake of simplicity, it may be put as ψ . Hence Eq. 14 takes the form

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} = -\frac{4\pi^2}{\lambda^2}\psi \text{-----(15)}$$

Following de Broglie's ideas, E.Schrodinger, applied the above treatment to material waves associated with all particles including electrons, atoms and photons.

Incorporating de Broglie's relationship, viz, $\lambda = h/mv$ in eq (15) we have

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} = -\frac{4\pi^2m^2v^2}{h^2}\psi \text{-----(16)}$$

where m is the mass and v is the velocity of the particle.

The Kinetic energy of the particle given by $\frac{1}{2}mv^2$ is equal to the total energy E minus the potential energy V of the particle, i.e.,

$$\begin{aligned} \frac{1}{2}mv^2 &= E - V \\ mv^2 &= 2(E - V) \text{----- (17)} \end{aligned}$$

combining this result with Eq. 16 we get,

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2m(E-V)}{h^2}\psi = 0 \text{-----(18)}$$

Eq. 18 is the Schrodinger wave equation proposed by him in 1926. It is customarily written in the following form

or
$$\left[-\frac{\hbar^2}{2m} \nabla^2 + v \right] \Psi = E\Psi \text{ -----(20)}$$

$$\left[-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + v \right] \Psi = E\Psi \text{ -----(19)}$$

where ∇^2 is the laplacian operator, defined as

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \text{ -----(21)}$$

Defining the Hamiltonian operator as

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + v \text{ -----(22)}$$

Eq. 22 becomes

$$\hat{H}\Psi = E\Psi \text{ -----(23)}$$

E.Schrodinger shared the 1933 Physics Nobel prize with the British physicist P.A.M. Dirac for formulating the quantum theory of matter.

The acceptable wave function must satisfy the following conditions

i) The wave function ψ is single valued, i.e., for each value of the variables x, y, z there is only one value of ψ . Suppose one of the variables is an angle θ , then, single value of ψ requires that

$$\Psi(\theta) = \psi(\theta + 2n\pi) \text{ where } n \text{ is an integer.}$$

ii) The wave function ψ and its first derivative with respect to its variables must be continuous, i.e., there must not be any sudden change in ψ when its variables are changed.

iii) For bound states, ψ must vanish at infinity. If ψ is a complex function, then $\psi^* \psi$ must vanish at infinity (ψ^* is the complex conjugate of ψ). Satisfying the above conditions, the Schrodinger equation yields significant solutions for certain definite values of the total energy E. These values are called eigen values. Eq. 23 is thus an eigenequation and we can write it as

$$\hat{H}\Psi_n = E_n\Psi_n \text{ (} n = 1, 2, \dots \text{) -----(24)}$$

where n is the quantum number. In equation 24 ψ_n are the Eigenfunctions and E_n are the eigenvalues. For an atom, these eigenvalues correspond to discrete sets of energy values postulated by Bohr.

- The eigenfunctions are said to be orthonormal if

$$\int \Psi_n \Psi_m d\tau = \begin{cases} 0, n \neq m \\ 1, n = m \end{cases} \text{-----(24)}$$

$$= \delta_{mn}$$

i.e., they are orthogonal when

$$\int \Psi_n^* \Psi_m d\tau = 0 \text{-----(25)}$$

And normalized when

$$\int \Psi_n^* \Psi_n d\tau = 1 \text{-----(26)}$$

The Significance of Wavefunction

The Schrodinger equation for a particle of mass m free to move parallel to the x -axis with zero potential energy is obtained from equation 20 by setting $v = 0$

$$\frac{\hbar}{2m} \frac{d^2\Psi}{dx^2} = E\Psi \text{-----(27)}$$

The solution of this equation have the form

$$\Psi = Ae^{ikx} + Be^{-ikx} \quad E = k^2\hbar^2/2m \text{-----(28)}$$

Where A and B are constants

13.10.1.1. The Probability density

Suppose that $B = 0$ in Eq. 28 then the wavefunction is

$$\Psi = Ae^{ikx} \text{-----(29)}$$

The square modulus of the form give the probability density.

$$|\Psi|^2 = (Ae^{ikx})^*(Ae^{ikx}) = (A^*e^{-ikx})(Ae^{ikx}) = |A|^2 \text{-----(30)}$$

The probability is independent of x ; If the wavefunction of the particle is given by Eq. 29 then we cannot predict where we will find the particle. The same would be true if the wavefunction in Eq. 28 had $A = 0$; then the probability density would be $|B|^2$, a constant.

If $A = B$ in the wavefunction, then eq.28 becomes

$$\Psi = A(e^{ikx} + e^{-ikx}) = 2A \cos kx \quad \text{-----(31)}$$

The probability density now has the form

$$|\Psi|^2 = (2A \cos kx) * (2A \cos kx) = 4|A|^2 \cos^2 kx \quad \text{-----(32)}$$

The probability density periodically varies between 0 and $4|A|^2$. The locations where the probability density is zero correspond to nodes in the wavefunction. Particles will never be found at the nodes. The probability density never passes through zero as it cannot be negative.

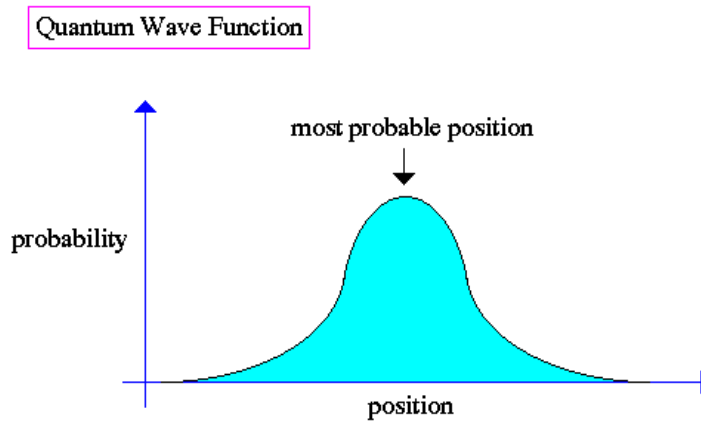


Fig. 13.7. Quantum wave distribution

13.10.1.2. Eigenvalues and Eigenfunctions

Because the total energy of the particle is its kinetic energy, $p^2/2m$, it follows from Eq. 28 that

$$p = \hbar k$$

This value is independent of the values of A and B. The schrodinger equation may be written in the succinct form

$$H\Psi = E \Psi \quad \text{-----(33)}$$

The quantity H is an operator, something that carries out a mathematical operation on the function Ψ . The Hamiltonian operator is the operator corresponding to the total energy of the system. When the Schrodinger equation is written as in Eq. 33, it is seen to be an eigenvalue equation, an equation of the form

$$(\text{operator})(\text{function}) = (\text{constant factor}) \times (\text{same function})$$

If we denote by a general operator by Ω and a constant factor by ω , an eigenvalue equation has the form $\Omega\psi = \omega\psi$

The factor ω is called the eigenvalue of the operator Ω . The eigenvalue in eq.33 is the energy. The function ψ is called an eigenfunction and is different for each eigenvalue.

13.10.1.3. Operators

Observables, Ω are represented by operators, $\hat{\Omega}$, built from the following position and momentum operators:

$$\hat{x} = xX \quad \hat{p}_x = \frac{\hbar}{i} \frac{d}{dx} \quad \text{-----(34)}$$

That is, the operator for location along x axis is multiplication by x and the operator for linear momentum parallel to the x-axis is proportional to taking the derivative (of the wavefunction) with respect to x.

The definition in Eq.34 is used to construct operators for other spatial observables. For example, suppose we wanted the operator for a potential energy of the form

$$V = \frac{1}{2} kx^2 \quad \text{-----(35)}$$

With k a constant. Then it follows from Eq. 34 that the operator corresponding to V is multiplication by x^2 :

$$\hat{V} = \frac{1}{2} kx^2x \quad \text{-----(36)}$$

In normal practice, the multiplication sign is omitted. To construct the operator for kinetic energy, we make use of the classical relation between kinetic energy and linear momentum, which in one dimension is

$$E_k = p_x^2/2m \quad \text{-----(37)}$$

Then using the operator for p_x , in equation 34,

$$\hat{E}_k = \frac{1}{2m} \left(\frac{\hbar}{i} \frac{d}{dx} \right) \left(\frac{\hbar}{i} \frac{d}{dx} \right) = - \frac{\hbar^2}{2m} \frac{d^2}{dx^2} \quad \text{-----(38)}$$

It follows that the operator for the total energy, the Hamiltonian operator, is

$$\hat{H} = \hat{E}_k + \hat{V} = - \frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \hat{V} \quad \text{-----(39)}$$

The expression for the kinetic energy operator, Eq. 38 gives another clue to the qualitative interpretation of a wavefunction and the structure of the Schrodinger equation. In mathematics, the second derivative of a function is a measure of its curvature: a large second derivative indicates a sharply curved function. It follows that a sharply curved wavefunction is associated with a high kinetic energy and one with a low curvature is associated with a low kinetic energy.

13.11. Solutions of Schrodinger equation for some simple systems

The Schrodinger equation can be solved exactly for the following simple systems

- (a) Particle in a One-Dimensional box
- (b) Particle in a Three-Dimensional box
- (c) One-Dimensional Simple Harmonic Oscillator
- (d) The Rigid Rotor
- (e) The Hydrogen atom

Problems

- (1) Show that $e^{\alpha x}$ is an eigenfunction of the operator d^2/dx^2 . What is the eigenvalue?

$$\begin{aligned} f(x) &= e^{\alpha x} & \hat{A} &= d^2/dx^2 \\ d^2/dx^2(e^{\alpha x}) &= \alpha d/dx (e^{\alpha x}) \\ &= \alpha^2 e^{\alpha x} \end{aligned}$$

Thus $e^{\alpha x}$ is the eigenfunction of the given operator d^2/dx^2 . α^2 is the eigenvalue.

- (2) Show that e^{ikx} is an eigenfunction of a operator

$$\begin{aligned} F(x) &= e^{ikx} & \hat{P}_x &= -i\hbar \frac{\partial}{\partial x} \\ &= -i\hbar \frac{\partial}{\partial x} e^{ikx} \\ &= -i^2 \hbar k^2 e^{ikx} \\ &= \hbar k^2 e^{ikx} \end{aligned}$$

Thus e^{ikx} is an eigenfunction

(2) For the wavefunction $\psi(\phi) = Ae^{im\phi}$, where m is an integer. Calculate A so that the wavefunction is normalized.

$$\begin{aligned} \int \psi_n^*(x) \psi_n(x) dx &= 1 \\ \int Ae^{im\phi} Ae^{-im\phi} d\phi &= 1 \\ = A^2 \int e^{im\phi} e^{-im\phi} d\phi &= 1 \\ = A^2 \phi &= 1 \end{aligned}$$

Thus $A = 1/\sqrt{\phi}$

(4) For the wavefunction of $\psi(x) = B \sin n\pi x/a$, Evaluate B so that the wavefunction is normalized. The permitted values of x are $0 \leq x \leq a$.

$$\begin{aligned} \int_0^a \psi_x \psi_x^* &= 1 \\ \int_0^a (B \sin n\pi x/a) (B \sin n\pi x/a) dx &= 1 \\ B^2 \int_0^a \sin^2(n\pi x/a) dx &= 1 \\ \frac{B^2 a}{2n\pi} \int_0^{n\pi} 1 - \cos 2z dx &= 1 \\ \frac{B^2 a}{2n\pi} [x - \sin 2z/2]_0^{n\pi} &= 1 \quad \text{Hence } B = \sqrt{2} / a \end{aligned}$$

(5) Show that the wavefunction $\psi_1 x = \sin n\pi x/a$ and $\psi_2 x = \cos n\pi x/a$ where n and a constant are orthogonal. The permitted values of x are $0 \leq x \leq a$.

$$\begin{aligned} \int_0^a (\sin n\pi x/a) (\cos n\pi x/a) dx &= 0 \\ \frac{a}{2n\pi} \int_0^{n\pi} \sin 2z dz &= 0 \\ \frac{a}{2n\pi} \int_0^{n\pi} \sin z \cos z dz &= 0 \\ = - \frac{a}{4n\pi} [\cos 2z]_0^{n\pi} &= 0 \end{aligned}$$

$$= 0$$

Thus the wavefunctions are orthogonal

(6) Examine if d^2/dx^2 is a Hermitian operator for the functions $\psi = e^{ix}$ and $\phi = \sin x$

since

$$\int \psi (\hat{A} \phi) d\tau = \int (\hat{A} \psi) \phi d\tau$$

$$\int e^{ix} \hat{A} \sin x$$

$$= \int e^{ix} d^2/dx^2 \sin x dx$$

$$= e^{ix}(-\sin x) dx \text{ -----(1)}$$

$$\int d^2/dx^2 e^{ix}(\sin x)$$

$$= -e^{ix}(\sin x) dx \text{ -----(2)}$$

Thus from (1) and (2) the functions $\psi = e^{ix}$ and $\phi = \sin x$ are Hermitian operators

CHAPTER - 14

PETROLEUM AND PETROCHEMICALS

V. Nithya

14.1. Introduction

Industrial organic chemistry today can be divided roughly into four major areas. In order of their current economic importance they are polymers, petrochemicals, synthetic materials (other than polymers), and miscellaneous organic materials lumped together under the general heading of "fine chemicals". The historic development and present industrial structure of each of these areas are different.

Most modern industrial organic materials are derived from petroleum, whose modern production dates from about 1860, or from natural gas. Less important sources include coal tar, wood, and agricultural waste materials. Oil refineries are generally large installations having some flexibility in both input and output, and traditionally switch output between fuel, lubricating oils, and petrochemicals depending on prices and markets.

Much of what we take for granted in today's world simply would be possible, without petroleum and the extensive range of products that come from it. Formed from decayed organic matter now buried below the Earth's surface, it is the result of millions of years of changing geological and chemical processes. Today, technology and industrial processes have enabled humans to refine it to produce fuels, plastics, solvents and a myriad of other hydrocarbon compounds, which are integral to everyday life.

Petroleum is a major source of fuels and various raw materials. It is the major input in the production of polymers (plastics). The uses of petroleum are restricted unless it is refined and broken down and changed into a variety of hydrocarbons.

14.2. What is Petroleum?

Our society is highly depending on petroleum for its activities. About 90% is used as an energy source for transportation and for generation of heat and electricity and the remaining as feed stocks in the chemical Industry.

Petroleum oil or Crude oil (derived from Greek word Petra-rock, Oleum-oil; color-dark greenish brown viscous liquid) is a naturally occurring volatile flammable

liquids, consists of lower to higher molecular weights hydrocarbon and various organic compounds of very great complexity.

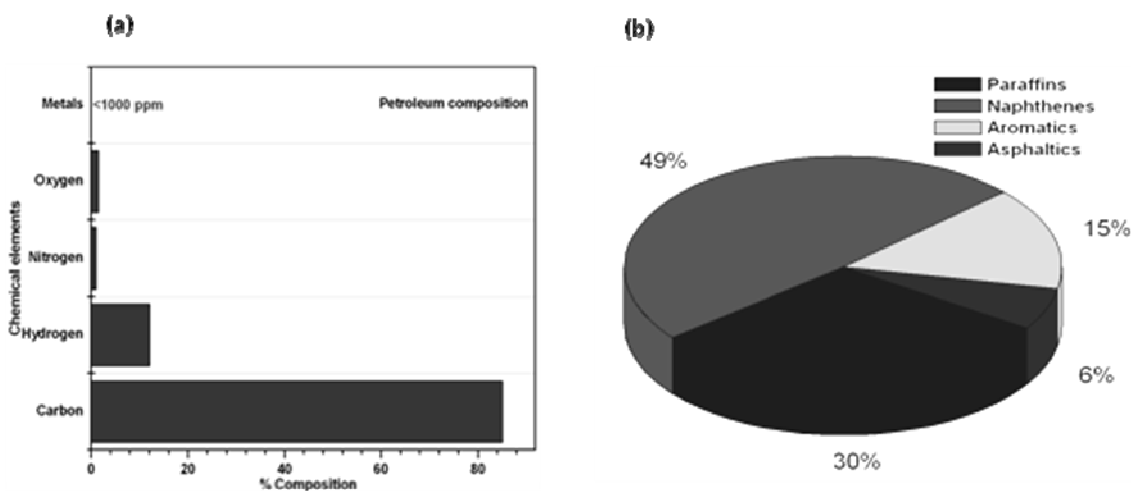
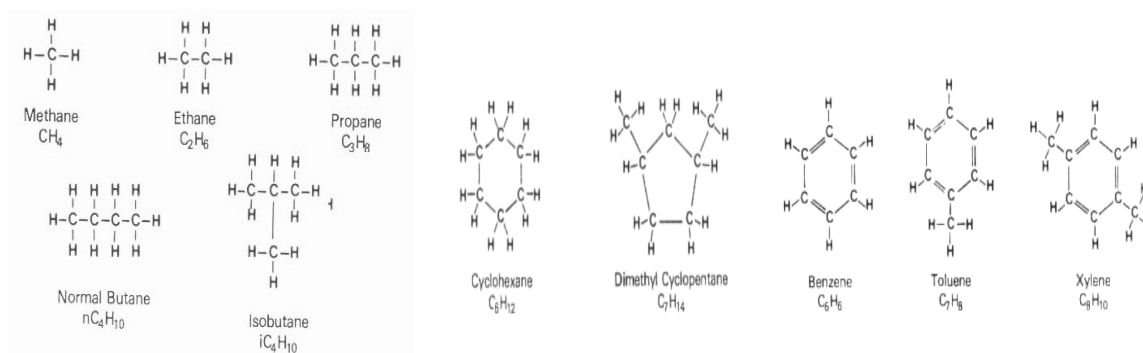


Fig. 14.1. (a) Elemental composition and (b) Different hydrocarbon composition of crude Oil

(a) Paraffins



The hydrocarbons composed of mainly alkanes, cycloalkanes and various aromatic hydrocarbons whereas the other organic compounds contain nitrogen, oxygen and sulfur, and trace amounts of metals such as iron, nickel, copper and vanadium. The exact molecular composition varies widely from formation to formation. The proportions of chemical elements and different hydrocarbon compositions of crude oil were shown in Fig. 14.1. and the structure of compounds from crude oil were shown in below.

Crude oil can be divided into three types such as light distillates (LPG, gasoline, naphtha), middle distillates (kerosene, diesel), heavy distillates and residuum (heavy fuel oil, lubricating oils, wax, asphalt). This classification is based on the way crude oil is distilled and separated into fractions (called distillates and residuum).

While there are a few surface seepages, the vast majority of petroleum is found well below the surface of the earth and can be reached only drilling. Oil wells tap into pools of oil, or into porous rock containing the oil, called reservoirs or fields. The oil is sometimes found under sufficiently high pressure to flow to the surface without pumping, but for most wells pumping is required. The amount of oil recoverable from a field by pumping may be only 5%, more frequently 25-30%, of the oil believed to be present. Addition of liquids to the field down wells, often salt water from brine wells or local fresh surface water with a small amount of surfactant added, is used to provide enhanced recovery of oil. In fields where the oil is very heavy steam injection may be used. Complete removal of the oil from a field is not possible even with enhanced recovery methods.

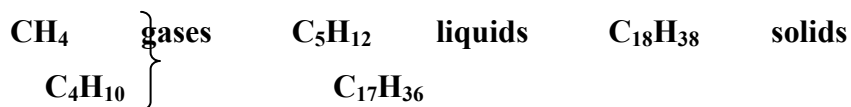
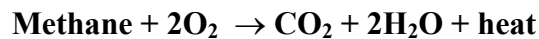
Crude oil is found in many parts of the world. Major producing areas include the southern United States, western Canada, Mexico, Venezuela, the Middle East, the eastern Soviet Union, Rumania, Nigeria, and Indonesia. Crude oil can be transported economically long distances overland by pipeline and overseas in very large tanker vessels. Refineries are located on seacoasts with tanker docks or are connected to the production areas or tanker ports by pipeline.

14.3. What are hydrocarbons?

Hydrocarbons mainly composed of hydrogen and carbon. May have single, double or triple (strong covalent bonds: atoms share one or more number of electrons) bonds between carbon and hydrogen atoms. Hydrocarbons can form large molecules via chain, branched and rings. The primary compounds present in petroleum. Hydrocarbon easily burn in air and can produce carbon dioxide, and water with heat (exothermic reaction).

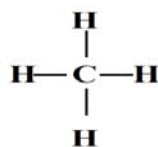
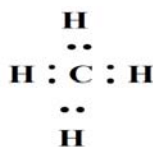
The physical properties vary with length of the hydrocarbon chain. Hydrocarbons -along with NO_x and sunlight - contribute to the formation of tropospheric ozone and

greenhouse gases. The hydrocarbons can be divided into four types such as alkanes, alkenes, alkynes and aromatic compounds.

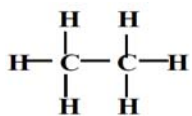


14.3.1. Structure and formula of alkanes?

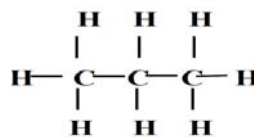
In alkanes, carbon atom attached with hydrogen (or another carbon) atom with single covalent bond and forms symmetrical tetrahedral structure with any bond angle between two hydrogen atom is 109.5° . General formula for hydrocarbon formation is $\text{C}_n\text{H}_{2n+2}$. Simplest alkane is **methane**.



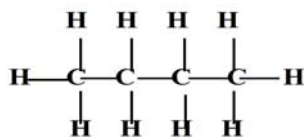
The alkanes also have a linear and branched hydrocarbon depends on the structure. For example methane, ethane and propane can only forms linear chain hydrocarbons.



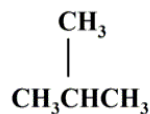
Ethane



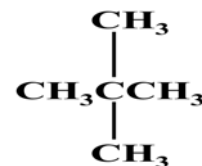
Propane



n- butane



Methyl propane



Pentane

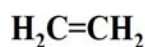
2-methyl butane

2,2-dimethyl propane

Whereas, further alkanes (Number of carbons from 4, 5, 6, 7, etc.,) can form linear and branched (isomer) structures. For example the structure of butane, pentane, hexane, etc.,

14.3.2. Structure and formula of alkenes?

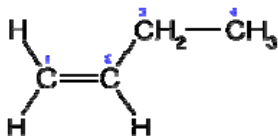
In alkenes, at least one carbon-carbon double bonds must be present. The simplest alkene can have only one double bond, and no other functional groups, form a homologous series of hydrocarbons with the general formula of C_nH_{2n} . The simplest alkene is ethylene.



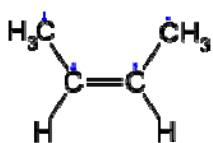
Whereas, further alkenes (Number of carbons from 3, 4, 5, 6, etc.,) can form various isomers. For example the structure of propene, butene, pentene, etc.,



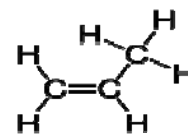
1-Propene (Propylene)



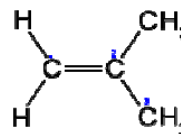
1-Butene (Butylene)



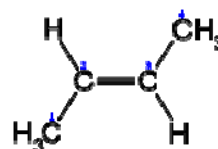
Cis-butene



1-methyl propene (Iso-propene)



2-methyl propene (Iso-butene)



Trans-butene

In the same way further alkenes, can form various structures depend on their carbon atom. The location of carbon-carbon double bonds can be altered and forms various structural isomers.

14.4. Saturated and unsaturated compounds

A saturated compound has no double or triple bonds. Saturated hydrocarbons can be linear alkanes. Alkanes, also known as paraffins, are chemical compounds that consist only of the elements carbon and hydrogen (i.e., hydrocarbons), wherein these atoms are linked together exclusively by single bonds (i.e., they are saturated compounds) without any cyclic structure.

There is no limit to the number of carbon atoms that can be linked together, the only limitation being that the molecule is acyclic, is saturated, and is a hydrocarbon. Saturated oils and waxes are examples of larger alkanes where the number of carbons in the carbon backbone tends to be greater than 10.

Saturated hydrocarbons can also combine any of the linear, cyclic (e.g., polycyclic) and branching structures, and they are still alkanes (no general formula) as long as they are acyclic (i.e., having no loops).

Unsaturated are used where the carbon contains double or triple bonds. Alkenes (carbon-carbon double bonds) are olefin, or olefine which is also known as unsaturated chemical compound. The degree of unsaturation defines the amount of hydrogen that a compound can bind. Examples of unsaturated compounds are alkenes.

14.4.1. Hydrocarbon rings

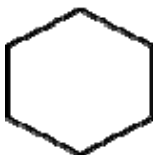
Alkanes and alkenes also forms ring structure. For example, cyclopentane (C_5H_{10}), cyclopentane (C_5H_8), cyclohexane (C_6H_{12}), cyclohexene (C_6H_{10}), benzene (C_6H_6).



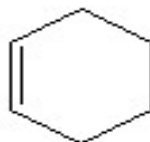
(C_5H_{10})



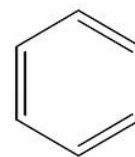
(C_5H_8)



(C_6H_{12})



(C_6H_{10})



(C_6H_6)

14.5. How were fossil fuels formed?

Oil and natural gas are fossil fuels. They formed from microscopic decayed plants, algae and bacteria in oceans over hundreds of millions of years ago. When the microscopic plants and algae died, they sank to the bottom and were covered by layers of sediment (oxygen diffusion environment). Many deposits formed during the Jurassic dinosaur

period, about 150 million years ago. They are called hydrocarbons because they are mainly made of hydrogen (about 12%) and carbon (about 85%). As more layers of sediment covered the fossil remains, they were changed by the extra pressure and heat into petroleum.

The oil and gas moved upwards through the sedimentary rock until they either escaped at the surface or were trapped by a layer of impermeable rock. The layer that traps the oil and gas is called a cap rock. The oil, gas and sea water occur in porous rock, not big hollows like caves in the rock. About 84% of petroleum is used for fuel; the other 16% is used for products such as fertilizers, pesticides and plastics. The formation of fossil fuel is shown in Fig. 14.2.

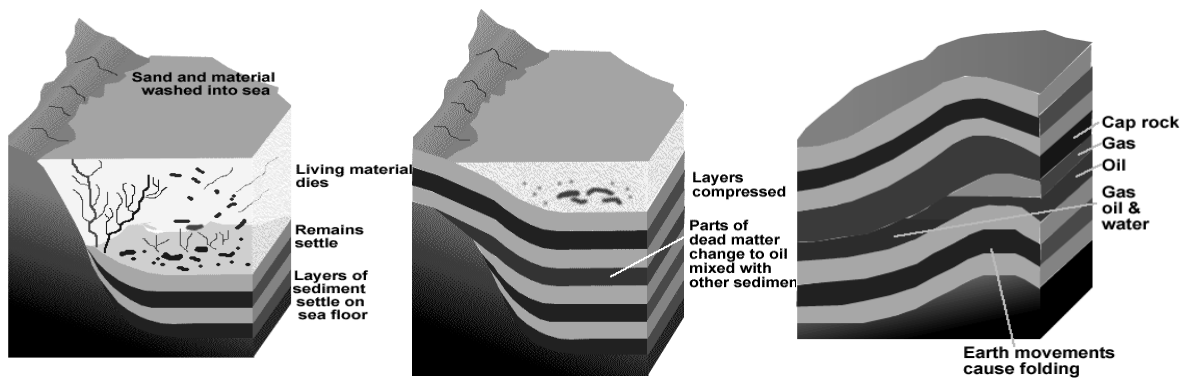


Fig. 14.2. Fossil fuel formation from the Earth (reproduced from ref. 6)

14.6. Extraction and transport of crude oil

The extraction starts with locating the oil field. It is done by seismic surveys, gravimeters and magnetometers. Then the oil well is created by drilling a hole into the earth with an oil rig. If the underground pressure in the oil reservoir is sufficient to force the oil to the surface all that is necessary is to place a complex arrangement of valves on the well head to connect the well to a pipeline network for storage and processing. The oil is thicker or heavier than steam is applied into a well at a temperature of 300-340 °C to force the oil to the surface. Typical extraction method of oil from Earth's surface is shown in fig. 14.3.

The heavy crude oil or crude bitumen extracted from oil sands is a viscous, solid or semisolid form that does not easily flow at normal oil pipeline temperatures, making it difficult to transport to market and expensive to process into gasoline, diesel fuel, and

other products. Despite the difficulty and cost, oil sands are now being mined by energy companies on a vast scale to extract the bitumen, which is then converted into synthetic oil (syncrude) by bitumen upgraders, or refined directly into petroleum products by specialized refineries.

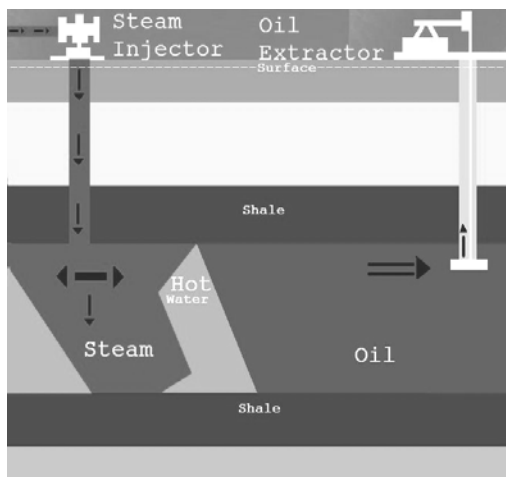


Fig. 14.3. Extraction of petroleum oil from Earth's surface (reproduced from ref. 7)

14.7. What is Petroleum refining?

An oil refining or petroleum refining is an industrial process where crude oil is processed and refined into more useful petroleum products, such as gasoline, diesel fuel, asphalt base, heating oil, kerosene, and liquefied petroleum gas. The extracted crude oil is converted into various fractions using fractional distillation followed by secondary processes which involves cracking and reforming. For the fractional distillation of Crude oil, various heating furnaces are used. The distillation tower holds the heavier fractions at the bottom and those in the lighter form, in gaseous state gets settled at the top inside the distillation tower. Petroleum refining products and their properties were shown in Table. 14.1.

Crude oil fractionation mainly follows the principle of boiling point in which molecules with strong interaction or bond with each other through a variety of intermolecular forces cannot move easily or rapidly and therefore, do not achieve the kinetic energy necessary to escape the liquid state. Therefore, molecules with strong intermolecular forces will have higher boiling points. This is a consequence of the

increased kinetic energy needed to break the intermolecular bonds so that individual molecules may escape the liquid as gases.

Table 14.1. Petroleum refining products and their properties

Name	Major product	Approximate boiling range (°C)
LPG; liquified petroleum gas	C ₄ and some C ₃ hydrocarbons	below 0
Petrol (gasoline)	C ₅ to C ₉ aromatic rich	30 to 160
Kerosene/ Aviation turbine fuel (ATF)	C ₁₀ to C ₁₅ alkane rich	150 to 270
Diesel	C ₁₄ to C ₁₉ alkane rich	260 to 360
Lubricating oils	C ₂₀ to C ₄₀ non aromatic and	300 to 550
Non n-paraffinic wax	C ₂₀ to C ₄₀ n-alkanes	> 300

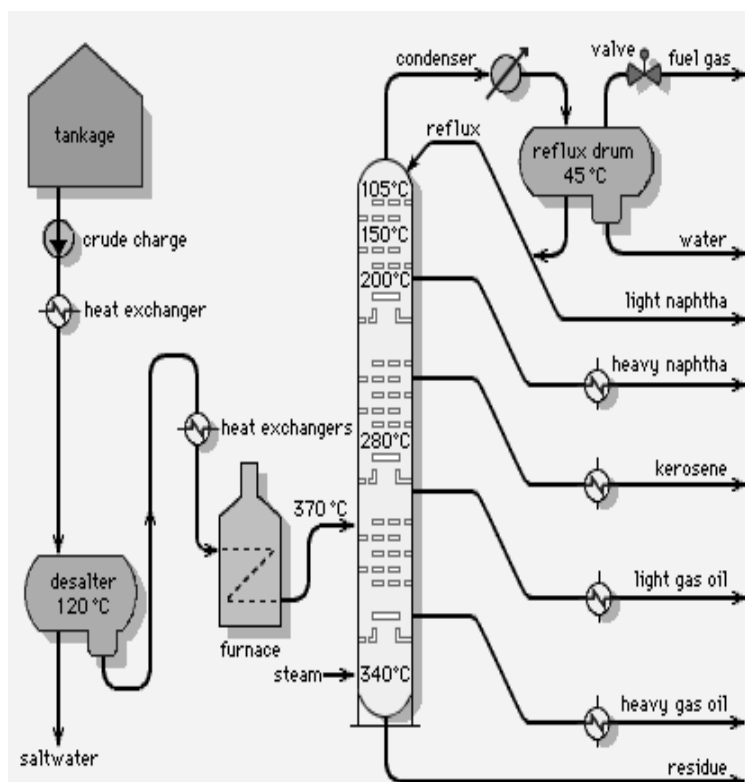


Fig. 14.4. Typical pictorial diagram of fractional distillation unit in petroleum refining (reproduced from ref. 5)

From the above principle, the crude oil is separated. It contains longer carbon chain, so higher temperature is needed to which the compounds will boil. The crude petroleum is heated and changed into a gas. The gases are passed through a distillation column which becomes cooler as the height increases. When a compound in the gaseous state cools below its boiling point, it condenses into a liquid. The liquids may be drawn off the distilling column at various heights. The typical crude oil distillation diagram is shown in fig. 14.4.

The obtained fractions were further treated into various processes such as cracking of hydrocarbons and reforming the compounds by alkylation and Isomerization in order to produce desired products for domestic use. Generally, the petrochemical refineries are mainly based on the catalysts technology in all process. The most common catalysts used in petroleum refinery are Zeolite and based metal catalysts.

14.8. Uses of Petroleum products

Petroleum products are indispensable because of its variety of applications. The obtained products compositions varied depend on the quality of crude oil. The obtained products compositions were shown in fig. 14.5.

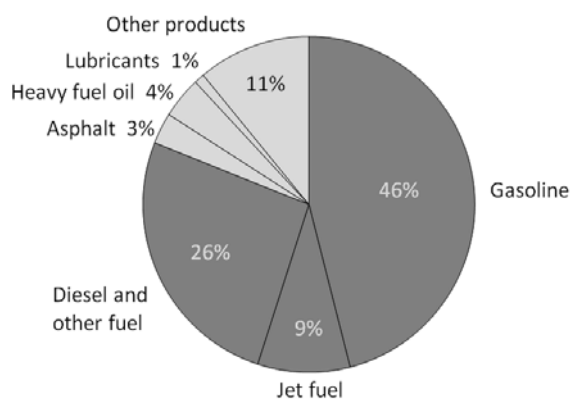


Fig. 14.5. The various product composition of petroleum refining (reproduced from ref. 7)

Fossil fuels are mainly used as domestic fuel, fuel for running automobiles, fuel for producing electric power, and also give various petrochemical products. The general uses of different fraction products are:

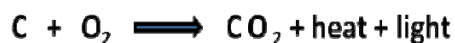
- i) **Petroleum gas:** Gaseous fuel. Raw material for making petrochemicals
- ii) **Gasoline:** As a motor fuel and as a jet engine fuel
- iii) **Kerosene:** As domestic fuel
- iv) **Diesel:** Fuel for heavy vehicles
- v) **Residue:** As fuel-oil in industry; used to obtain lubricating oils, waxes and bitumen

14.8.1. Energy Production

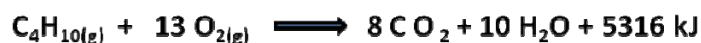
When the fossil fuels or even biomass fuels are burnt heat is produced. Thus, the combustion of fossil fuels and biomass fuels reaction is 'Exothermic reaction'. So, the produced heat can be converted into other forms of energy. For example, in the production of electricity, the heat is used to convert water into steam, which in turns runs a turbine that generates electricity. The transformation of stored chemical energy into other forms is shown below;

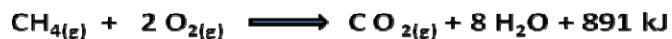


Energy from fuel such as coal, petroleum and natural gas, which undergo combustion (burnt in air either alone or after mixing with another substance) and release energy are needed for the working of machines. The energy released keeps the machines working. More is the energy released, better is the fuel. Coal, petroleum, natural gas, etc. are regarded as fuels for many machines and industrial processes. Carbon is the combustible component of coal. When, it burns in air to give heat and light.



Similarly LPG, which contains butane and biogas, CNG which contains methane combust releasing energy as follows:

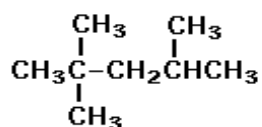




14.8.1.1. Quality of gasoline and LPG

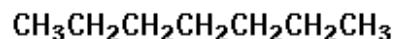
Gasoline is a complex mixture of over 500 hydrocarbons that may have between 5 to 12 carbons. Smaller amounts of alkane cyclic and aromatic compounds are present. Virtually no alkenes or alkynes are present in gasoline. Its best quality is mainly depends on their octane number. The octane number of gasoline is a measure of its resistance to knock. The **octane number** is determined by comparing the characteristics of a gasoline to isooctane (2, 2, 4-trimethylpentane) and heptane. Isooctane is assigned an octane number of 100. It is a highly branched compound that burns smoothly, with little knock. On the other hand, heptane, a straight chain, unbranched molecule is given an octane rating of zero because of its bad knocking properties.

isooctane or 2,2,4-trimethylpentane



Octane number: 100

heptane



Octane number: 0

Straight-run gasoline (directly from the refinery distillation column) has an octane number of about 70. In other words, straight-run gasoline has the same knocking properties as a mixture of 70% isooctane and 30% heptane. Many of these compounds are straight chain alkanes. Cracking, isomerization, and other refining processes can be used to increase the octane rating of gasoline to about 90. Anti-knock agents may be added to further increase the octane rating. Octane rating versus type of compound;

- i) Octane ratings decrease with increasing carbon chain length.
- ii) Octane ratings increase with carbon chain branching.
- iii) Octane ratings increase in aromatics with same number of carbons

LPG is a mixture of gaseous hydrocarbons, primarily propane and butane, derived during natural gas and oil extraction as well as during refining. At ambient conditions, propane is a gas, while butane can be either a gas or a liquid. LPG is easily liquefied under modest pressure. The best quality LPG must have the composition of propane, butane and their

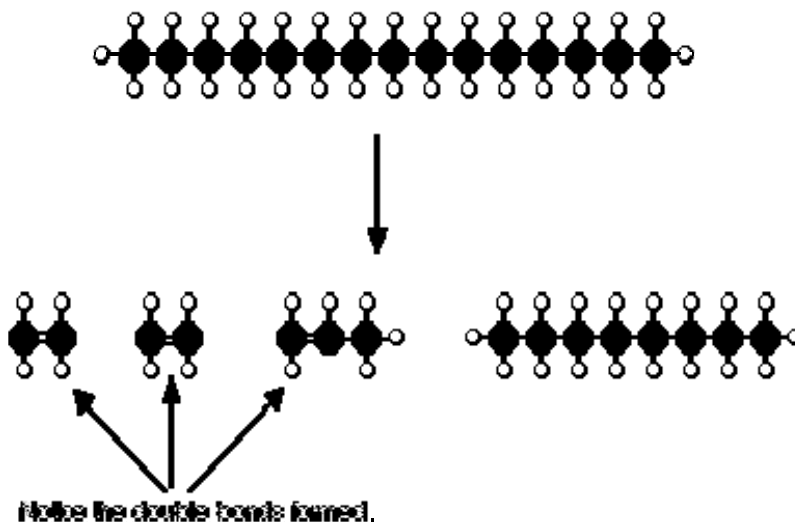
physical parameters such as vapour pressure, moisture and sulfur content, free water and residue. The various compositions were shown in table. 14.2.

Table 14.2. The quality of LPG properties

	Propane	Butane
Composition (liq. volume %)		
Propane	95 minimum	
Butane +	2.5 maximum	95 min
Pentane		2.0 max
Vapour pressure(kPa @ 37°C)	1434 max	483 max
Copper strip	No 1	No 1
Volatile sulfur (ppm/ wt)	30 max	30 max
Residue (ml/ 100ml)	< 0.05	< 0.05
Free water		Nil
Moisture content	pass	

14.9. Cracking

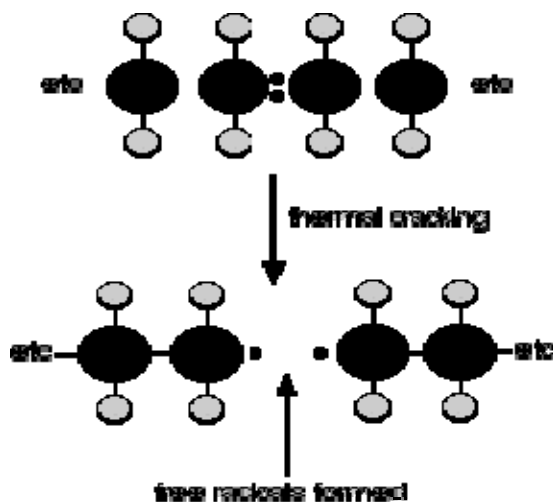
Cracking which means heavier or larger chain hydrocarbon fractions are converted into smaller and other useful chemicals. Some of the obtained products also contain carbon-carbon double bonds. The obtained compounds from cracking further alkylated or isomerize to attain particular octane number by using the catalysts. The simple cracking reactions were shown in below;



This can be done by three different ways;

14.9.1. Thermal Cracking

The ancient method of hydrocarbon cracking, which can be usually done by higher temperature (450-750°C) and pressure (70 atm). The lighter elements produced from this process can be made into distillate fuels and petrol. This follows free radical mechanism. For example, the two C-C bond have two electrons in a covalent bond. During the thermal cracking, the two carbon atom shares each one electron and that can combine with another hydrocarbon which is already shared their one electron (free radical) to another molecule. Finally, the two free radical hydrocarbon combines and forms new hydrocarbon. The formation of free radical was shown below;



14.9.2. Catalytic Cracking

The modern cracking reactions in petroleum are called catalytic cracking. Catalysts – change in the rate of reaction. This reaction can be done by lower temperature (450-500°C) and moderately low pressure when compared to thermal cracking. The catalysts used for catalytic cracking is Zeolites. It is also called as aluminosilicates, which consists of aluminium, silicon and oxygen atom. The cracking reactions yield petrol, LPG,

unsaturated olefin compounds, cracked gas oils, a liquid residue called cycle oil, light gases and a solid coke residue.

14.9.3. Hydrocracking

Hydrocracking is done by using catalysts and also the presence of hydrogen. It produces only light oils. This cracking reaction will increase the yield of petrol. The use extra hydrogen will saturate or hydrogenate the chemical bonds of the cracked hydrocarbons and forms the desired isomers. This also used to treat contaminants like sulfur and nitrogen in order to remove them. The favourable catalysts for this process is Ni-W (used when sulfide and other poisons are high) supported on amorphous silica-alumina or a noble metal like Pt or Pd (to get gasoline as a desired product) supported on highly active Zeolite materials.

14.10. Reforming

The major objective of this process is to convert low-octane naphtha into a high-octane reformat for gasoline blending and/or to provide aromatics (benzene, toluene, and xylene) for petrochemical plants. Reforming also produces high purity hydrogen for hydrotreating processes. Reforming reactions occur in chloride promoted fixed catalyst beds; or continuous catalyst regeneration (CCR) beds where the catalyst is transferred from one stage to another, through a catalyst regenerator and back again. Hydrocracking of paraffins is undesirable due to increased light-ends make. Desired reactions include;

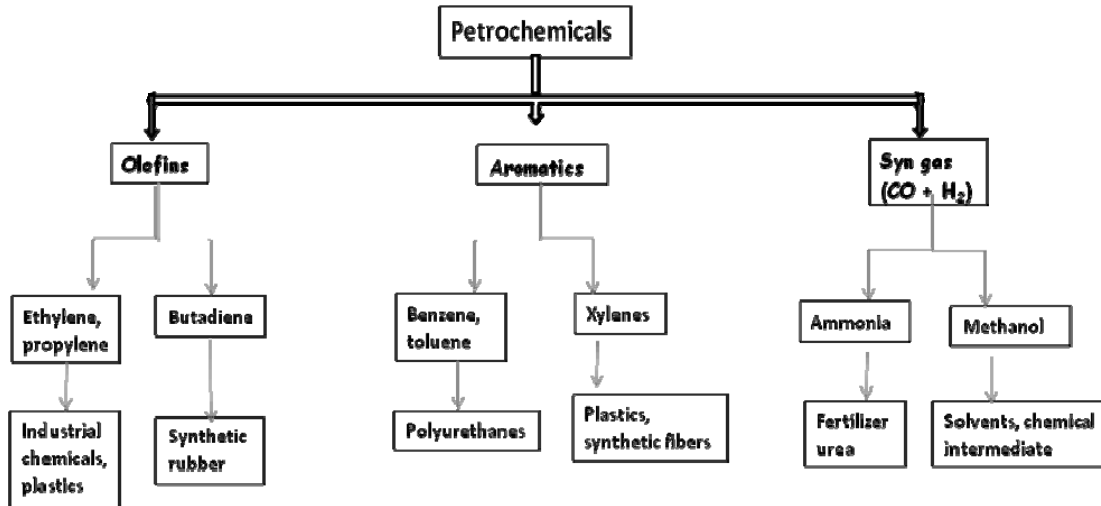
- i) Dehydrogenation of naphthenes to form aromatics;
- ii) Isomerization of naphthenes;
- iii) Dehydrocyclization of paraffins to form aromatics; and
- iv) Isomerization of paraffins.

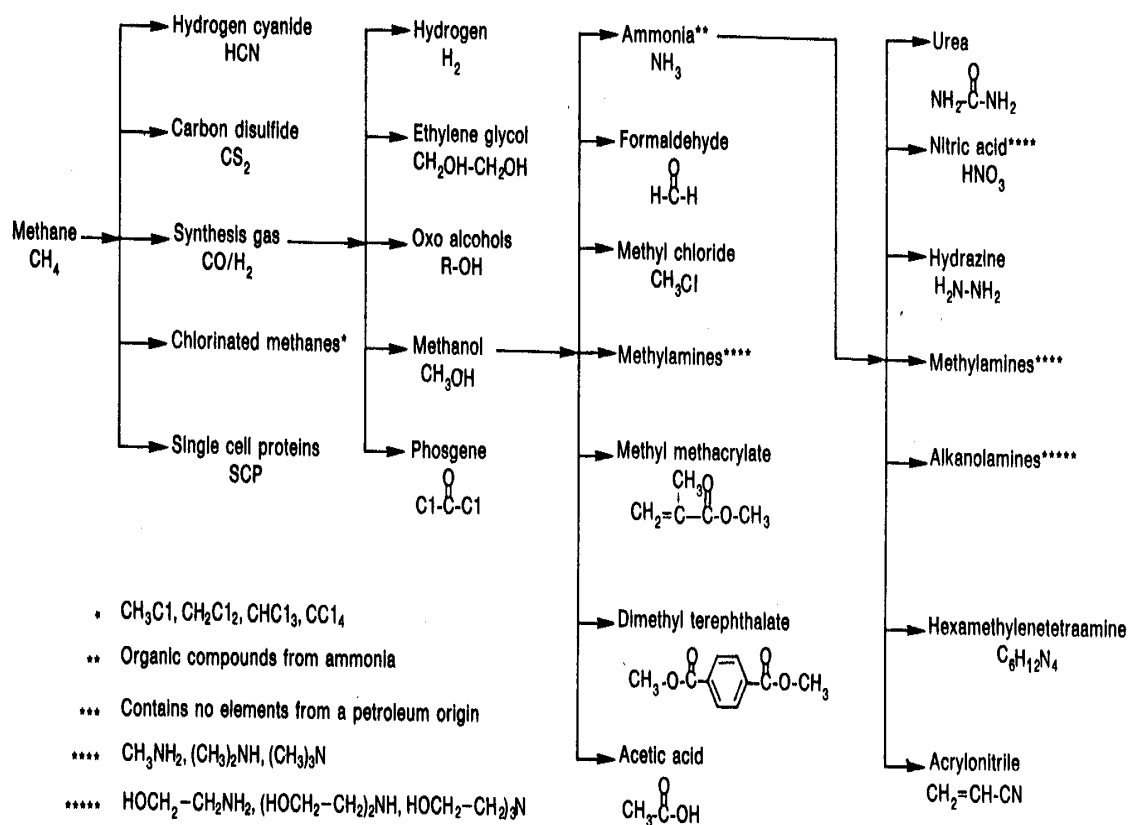
14.11. Petrochemicals

Petrochemicals are chemical products derived from petroleum. Some chemical compounds made from petroleum are also obtained from other fossil fuels such as coal or natural gas. There are two class of petrochemicals are olefins such as ethylene, propylene

and aromatics such as benzene, toluene, oxylene isomers. Primary petrochemicals are divided into three groups depending on their chemical structure;

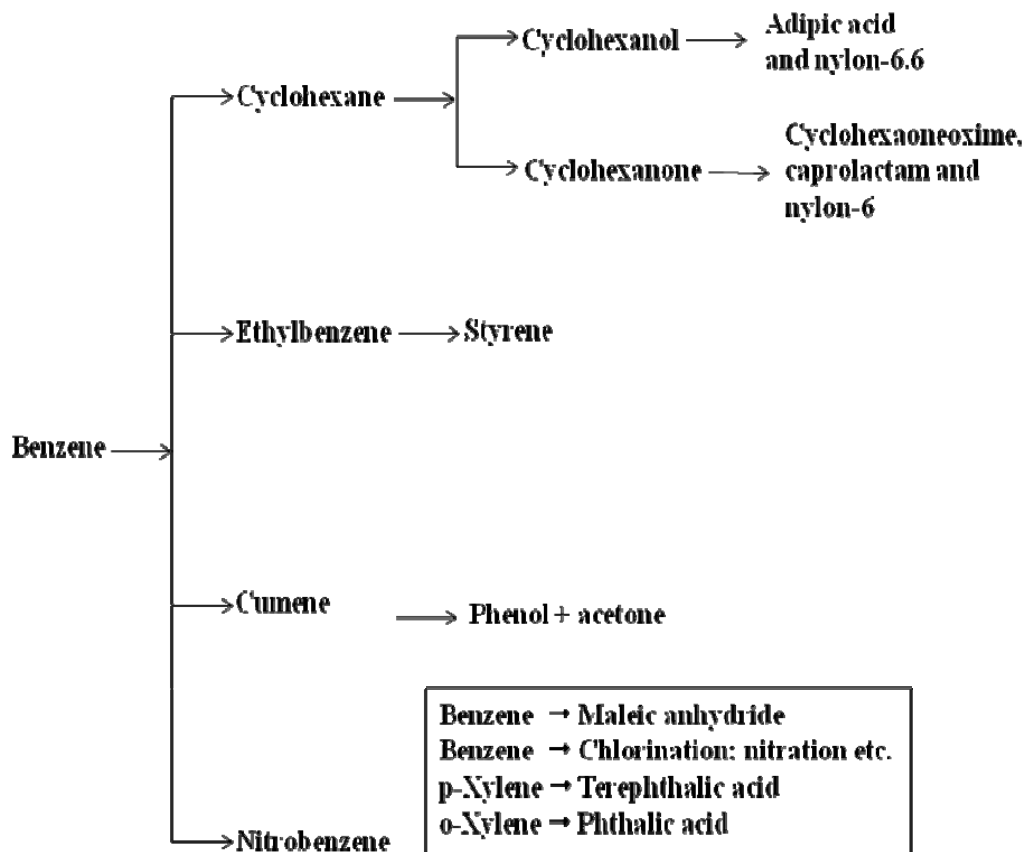
The natural gas obtained from petroleum oil is nearly 80% of methane, which is used to produce variety of petrochemicals. The products are shown in below,



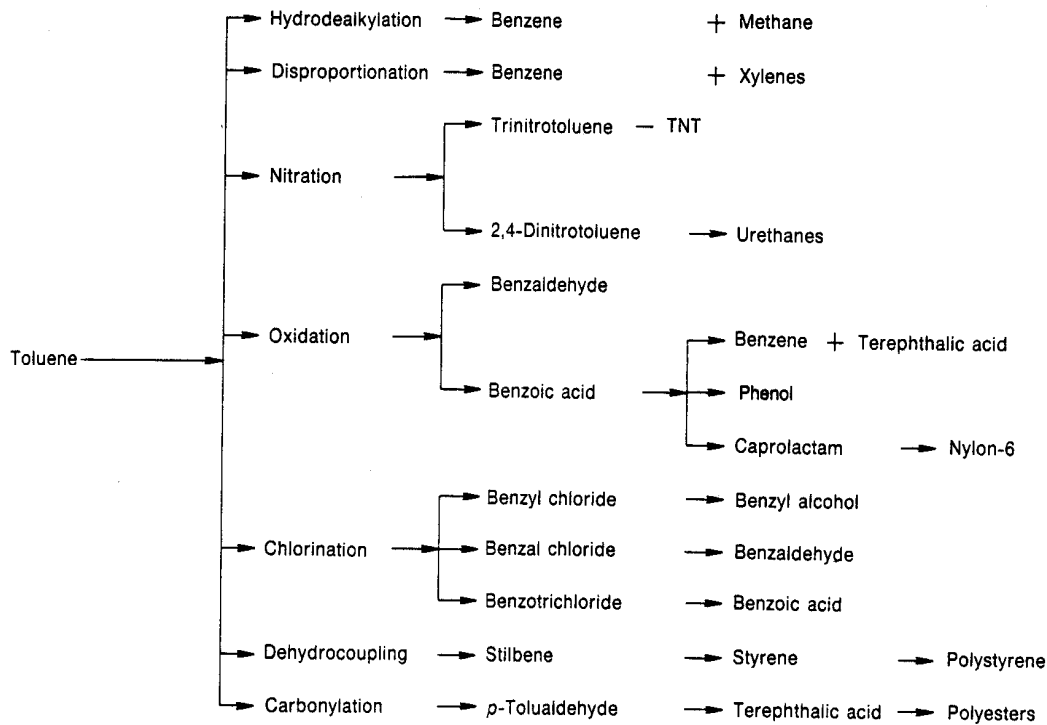


In addition the other gases produced from petroleum refining is ethylene, propylene and butenes. Ethylenes are used to produce ethylene oxide, ethylene glycol, acetic acid, ethanol, vinyl chloride, etc., the propylene is found to produce propylene oxide, propylene glycol, acrylic acid and acrylonitrile, allyl chloride, epichlorohydrin, etc., and the butenes are mainly used to produce maleic anhydride.

The obtained primary aromatic petrochemicals like benzene and toluene found to be more useful for the preparation of their derivatives and other chemicals. The list of chemicals obtained from benzene and toluene were shown in below,



All chemicals were produced from different fraction units by various processes using catalysts technology. For example, olefins are produced by fluid catalytic cracking and steam cracking of natural gas liquids like ethane and propane. Aromatic compounds were produced by fluid catalytic cracking and also catalytic reforming of naphtha. These hydrocarbon compounds and their derivatives are seems to be more useful in various applications such as, solvents, detergents, adhesives, fertilizers, polymers and variety of applications. Most importantly, olefins are primary basis for the production of polymers and oligomers which are used to prepare plastics, resins, fibers, elastomers, lubricants and gels.



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