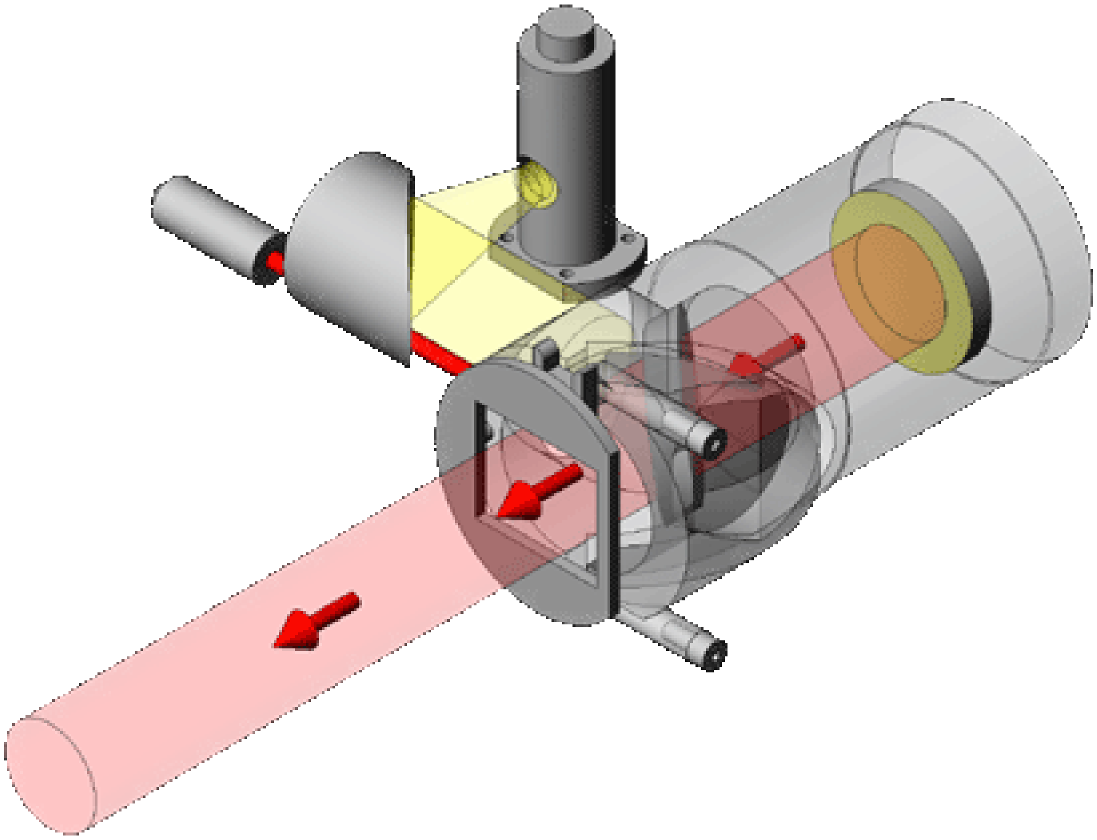
CHAPTER

1

BASIC CONCEPTS



Animation 1.1: Spectrometer
Source & Credit: gascell

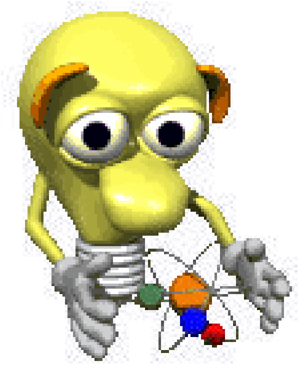
1.1 ATOM

Long time ago, it was thought that matter is made up of simple, indivisible particles. Greek philosophers thought that, matter could be divided into smaller and smaller particles to reach a basic unit, which could not be further sub-divided. Democritus (460-370 B.C.) called these particles atomos, derived from the word “atomos” means indivisible. However, the ideas of Greek philosophers were not based on experimental evidences.

In the late 17th century, the quantitative study of the composition of pure substances disclosed that a few elements were the components of many different substances. It was also investigated that how, elements combined to form compounds and how compounds could be broken down into their constituent elements.

In 1808, an English school teacher, John Dalton, recognized that the law of conservation of matter and the law of definite proportions could be explained by the existence of atoms. He developed an atomic theory; the main postulate of which is that all matter is composed of atoms of different elements, which differ in their properties.

Atom is the smallest particle of an element, which can take part in a chemical reaction. For example, He and Ne, etc. have atoms, which have independent existence while atoms of hydrogen, nitrogen and oxygen do not exist independently.



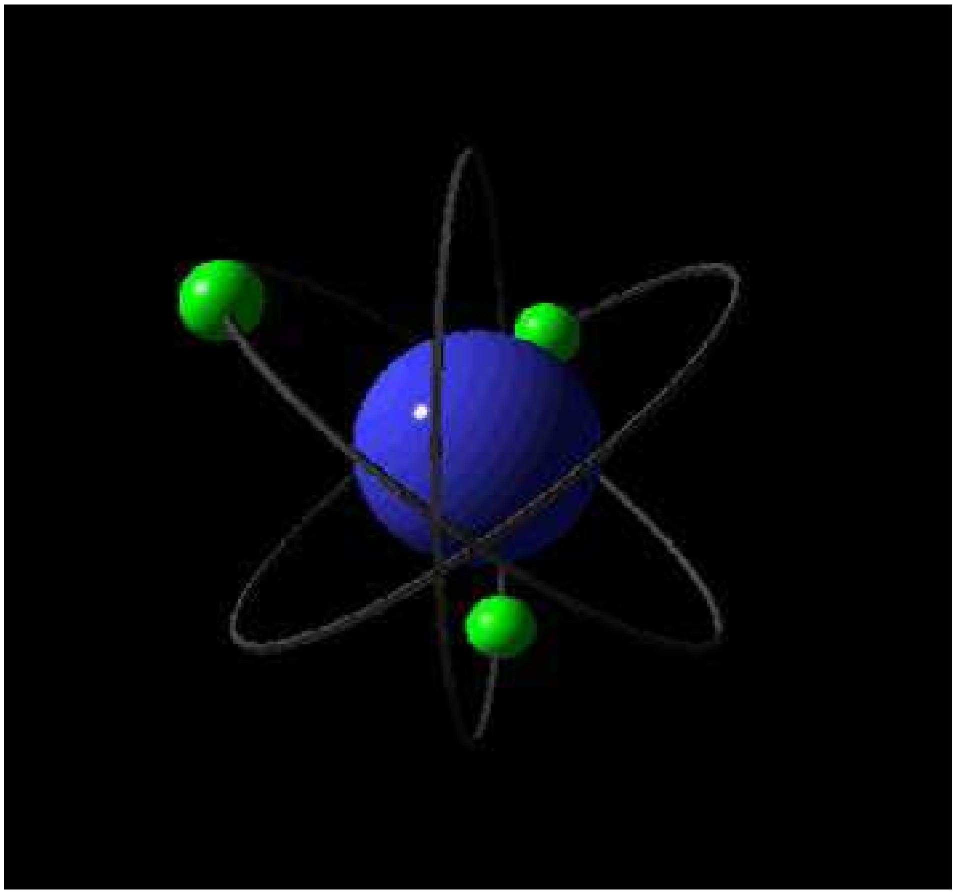
Animation 1.2: Atom
Source & Credit: 123gifs

The modern researches have clearly shown that an atom is further composed of subatomic particles like electron, proton, neutron, hypron, neutrino, anti-neutrino, etc. More than 100 such particles are thought to exist in an atom. However, electron, proton and neutron are regarded as the fundamental particles of atoms.

A Swedish chemist J. Berzelius- (1779-1848) determined the atomic masses of elements. A number of his values are close to the modern values of atomic masses. Berzelius also developed the system of giving element a symbol.

1.1.1 Evidence of Atoms

It is not possible actually to see the atoms but the nearest possibility to its direct evidence is by using an electron microscope. A clear and accurate image of an object that is smaller than the wavelength of visible light, cannot be obtained. Thus an ordinary optical microscope can measure the size of an object upto or above 500 nm (lnm = 10^{-9}m). However, objects of the size of an atom can be observed in an electron microscope. It uses beams of electrons instead of visible light, because wavelength of electron is much shorter than that of visible light.



Animation 1.3:Made of Atom
Source & Credit: imgur

Fig. (1.1) shows electron microscopic photograph of a piece of a graphite which has been magnified about 15 millions times. The bright band in the figure are layers of carbon atoms.
In the 20th century, X-ray work has shown that the diameter of atoms are of the order $2x10^{-10}$ m which is 0.2 nm. Masses of atoms range from 10^{-27} to 10^{-25} kg. They are often expressed in atomic mass units (amu) when 1 amu is = 1.661×10^{-27} kg. The students can have an idea about the amazingly small size of an atom from the fact that a full stop may have two million atoms present in it.

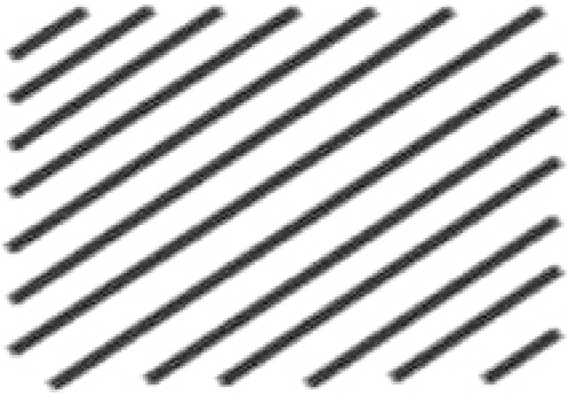


Fig (1.1) Electron microscopic photograph of graphite

1.1.2 Molecule

A molecule is the smallest particle of a pure substance which can exist independently. It may contain one or more atoms. The number of atoms present in a molecule determines its atomicity. Thus molecules can be monoatomic, diatomic and triatomic, etc., if they contain one, two and three atoms respectively. Molecules of elements may contain one, two or more same type of atoms. For example, He, Cl_2, O_3, P_4, S_8. On the other hand, molecules of compounds consist of different kind of atoms. For example, HCl, NH_3, H_2SO_4,$C_6H_{12}O_6$.
The sizes of molecules are definitely bigger than atoms. They depend upon the number of atoms present in them and their shapes. Some molecules are so big that they are called macromolecules. Haemoglobin is such a macromolecule found in blood. It helps to carry oxygen from our lungs to all parts of our body. Each molecule of haemoglobin is made up of nearly 10,000 atoms and it is 68,000 times heavier than a hydrogen atom.

1.1.3 Ion

Ions are those species which carry either positive or negative charge. Whenever an atom of an element loses one or more electrons, positive ions are formed.

A sufficient amount of energy is to be provided to a neutral atom to ionize it.

$$A \rightarrow A^+ + e^-$$

This A^+ is called a cation. A cation may carry +1, +2, +3, etc.charge or charges. The number of charges present on an ion depends upon the number of electrons lost by the atom. Anyhow, energy is always required to do so. Hence the formation of the positive ions is an endothermic process. The most common positive ions are formed by the metal atoms such as Na^+, K^+, Ca^{2+}, Mg^{2+} , Al^{3+}, Fe^{3+}, Sn^{4+}, etc. The chapter on chemical bonding will enable us to understand the feasibilities of their formation. When a neutral atom picks up one or more electrons, a negative ion is produced, which is called an anion.

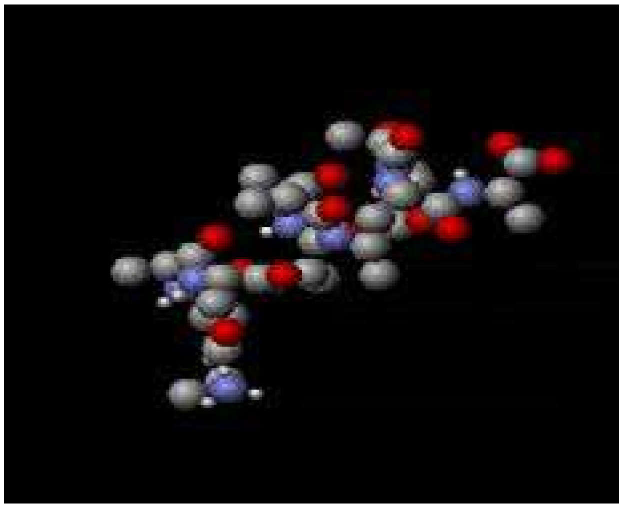
$$B + e^- \rightarrow B^-$$

Energy is usually released when an electron is added to the isolated neutral atom, Therefore, the formation of an uninegative ion is an exothermic process.The most common negative ions are F^-, Cl^-, Br^-, S^{2-} etc.

The cations and anions possess altogether different properties from their corresponding neutral atoms. There are many examples of negative ions which consist of group of atoms like OH^-, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}, MnO_4^{1-}, $Cr_2O_7^{2-}$ etc. The positive ions having group of atoms are less common e.g. NH_4^+ and some carbocations in organic chemistry.

1.1.4 Molecular Ion

When an atom loses or gains an electron, it forms an ion. Similarly, a molecule may also lose or gain an electron to form a molecular ion, e.g., CH_4^+, CO^+, N_2^+ Cationic molecular ions are more abundant than anionic ones. These ions can be generated by passing high energy electron beam or α-particles or X-rays through a gas. The break down of molecular ions obtained from the natural products can give important information about their structure.



Animation 1.4: Molecules
Source & credit: wikimedia

1.2 RELATIVE ATOMIC MASS

Relative atomic mass is the mass of an atom of an element as compared to the mass of an atom of carbon taken as 12.
The unit used to express the relative atomic mass is called atomic mass unit (amu) and it is 1/12 th of the mass of one carbon atom, On carbon -12 scale, the relative atomic mass of ${}^{12}_{6}C$ is 12.0000 amu and the relative atomic mass of ${}^{1}_{1}H$ is 1.008 amu. The masses of the atoms are extremely small. We-don't have any balance to weigh such an extremely small mass, that is why we use the relative atomic mass unit scale.
The relative atomic masses of some elements are given in the following Table (1.1).

Table (1.1) Relative atomic masses of a few elements

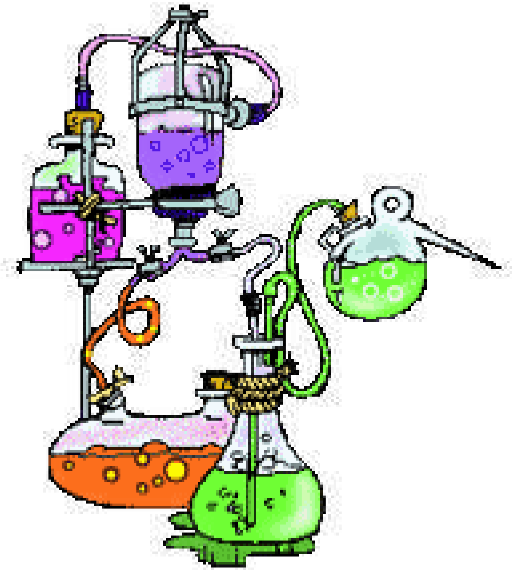
Element	Relative Atomic Mass (amu)	Element	Relative Atomic Mass (amu)
H	1.008	Cl	35.453
O	15.9994	Cu	63.546
Ne	20.1797	U	238.0289

These element have atomic masses in fractions and will be explained in the following article on isotopes.

1.3 ISOTOPES

In Dalton's atomic theory, all the atoms of an element were considered alike in all the properties including their masses. Later on, it was discovered that **atoms of the same element can possess different masses but same atomic numbers. Such atoms of an element are called isotopes**. So isotopes are different kind of atoms of the same element having same atomic number, but different atomic masses. The isotopes of an element possess same chemical properties and same position in the periodic table. This phenomenon of isotopy was first discovered by Soddy. Isotopes have same number of protons and electrons but they differ in the number of neutrons present in their nuclei.

Carbon has three isotopes written as ${}^{12}_{6}C$, ${}^{13}_{6}C$, ${}^{14}_{6}C$ and expressed as C-12, C-13 and C-14. Each of these have 6-protrons and 6 electrons. However, these isotopes have 6, 7 and 8 neutrons respectively. Similarly, hydrogen has three isotopes ${}^{1}_{1}H$, ${}^{2}_{1}H$, ${}^{3}_{1}H$ called protium, deuterium and tritium. Oxygen has three, nickel has five, calcium has six, palladium has six, cadmium has nine and tin has eleven isotopes.



Animation 1.5: Basic Concepts
Source & Credit: pixshark

1.3.1 Relative Abundance of Isotopes

The isotopes of all the elements have their own natural abundance. The properties of a particular element, which are mentioned in the literature, mostly correspond to the most abundant isotope of that element. The relative abundance of the isotopes of elements can be determined by mass spectrometry.

Table (1.2) shows the natural abundance of some common isotopes.

Table (1.2) Natural abundance of some common isotopes.

Element	Isotope	Abundance (%)	Mass (amu)
Hydrogen	^{1}H, ^{2}H	99.985, 0.015	1.007825, 2.01410
Carbon	^{12}C, ^{13}C	98.893, 1.107	12.0000, 13.00335
Nitrogen	^{14}N, ^{15}N	99.634, 0.366	14.00307 15.00011
Oxygen	^{16}O, ^{17}O, ^{18}O	99.759, 0.037, 0.204	15.99491, 16.99914, 17.9916
Sulphur	^{32}S, ^{33}S, ^{34}S, ^{36}S	95.0, 0.76, 4.22, 0.014	31.97207, 32.97146, 33.96786, 35.96709
Chlorine	^{36}Cl, ^{37}Cl	75.53, 24.47	34.96885, 36.96590
Bromine	^{79}Br, ^{81}Br	50.54, 49.49	78.918, 80.916

We know at present above 280 different isotopes occur in nature. They include 40 radioactive isotopes as well. Besides these about 300 unstable radioactive isotopes have been produced through artificial disintegration. The distribution of isotopes among the elements is varied and complex as it is evident from the Table (1.2). The elements like arsenic, fluorine, iodine and gold, etc have only a single isotope. They are called mono-isotopic elements.

In general, the elements of odd atomic number almost never possess more than two stable isotopes. The elements of even atomic number usually have larger number of isotopes and isotopes whose mass numbers are multiples of four are particularly abundant. For example, ^{16}O, ^{24}Mg, ^{28}Si, ^{40}Ca and ^{56}Fe form nearly 50% of the earth's crust. Out of 280 isotopes that occur in nature, 154 have even mass number and even atomic number.

1.3.2 Determination of Relative Atomic Masses of Isotopes by Mass Spectrometry

Mass spectrometer is an instrument which is used to measure the exact masses of different isotopes of an element. In this technique, a substance is first volatilized and then ionized with the help of high energy beam of electrons. The gaseous positive ions, thus formed, are separated on the basis of their mass to charge ratio (m/e) and then recorded in the form of peaks. Actually mass spectrum is the plot of data in such a way that (m/e) is plotted as abscissa (x-axis) and the relative number of ions as ordinate (y-axis).

First of all, Aston’s mass spectrograph was designed to identify the isotopes of an element on the basis of their atomic masses. There is another instrument called Dempster’s mass spectrometer. This was designed for the identification of elements which were available in solid state.

The substance whose analysis for the separation of isotopes is required, is converted into the vapour state. The pressure of these vapours is kept very low, that is, 10^{-6} to 10^{-7} torr. These vapours are allowed to enter the ionization chamber where fast moving electrons arc thrown upon them. The atoms of isotopic element present in the form of vapours, are ionized. These positively charged ions of isotopes of an element have different masses depending upon the nature of the isotopes present in them.

The positive ion of each isotope has its own (m/e) value. When a potential difference (E) of 500-2000 volts is applied between perforated accelerating plates, then these positive ions are strongly attracted towards the negative plate. In this way, the ions are accelerated.

These ions are then allowed to pass through a strong magnetic field of strength (H), which will separate them on the basis of their (m/e) values. Actually, the magnetic field makes the ions to move in a circular path. The ions of definite m/e value will move in the form of groups one after the other and fall on the electrometer.

The mathematical relationship for (m/e) is

$$m/e = H^2r/2E$$

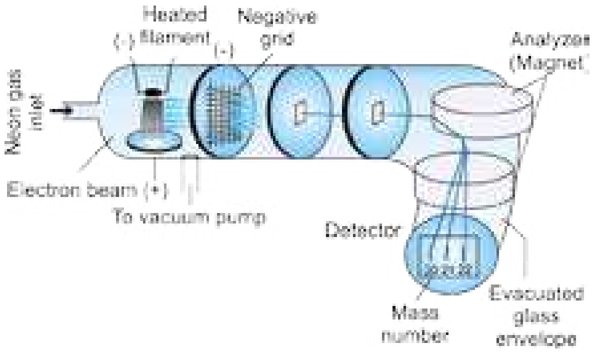
Where H is the strength of magnetic field, E is the strength of electrical field, r is the radius of circular path. If E is increased, by keeping H constant then radius will increase and positive ion of a particular m/e will fall at a different place as compared to the first place. This can also be done by changing the magnetic field. Each ion sets up a minute electrical current.

Electrometer is also called an ion collector and develops the electrical current. The strength of the current thus measured gives the relative abundance of ions of a definite m/e value.

Similarly, the ions of other isotopes having different masses are made to fall on the collector and the current strength is measured. The current strength in each case gives the relative abundance of each of the isotopes. The same experiment is performed with C-12 isotope and the current strength is compared.

This comparison allows us to measure the exact mass number of the isotope Fig. (1.2), shows the separation of isotopes of Ne. Smaller the (m/e) of an isotope, smaller the radius of curvature produced by the magnetic field according to above equation.

In modern spectrographs, each ion strikes a detector, the ionic current is amplified and is fed to the recorder. The recorder makes a graph showing the relative abundance of isotopes plotted against the mass number.



Fig(1.2) Diagram of a simple Mass Spectrometer

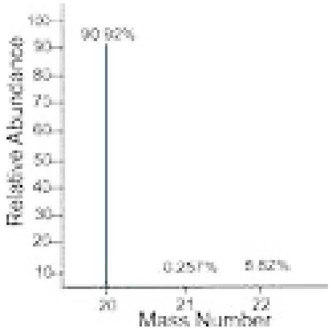


Fig (1.3) Computer plotted graph for the isotopes of neon

The above Fig (1.3) shows a computer plotted graph for the isotopes of neon.

The separation of isotopes can be done by the methods based on their properties. Some important methods are as gaseous diffusion, thermal diffusion, distillation, ultracentrifuge, electromagnetic separation and laser separation.

1.3.3 Average Atomic Masses

Table (1.1) of atomic masses of elements shows many examples of fractional values. Actually the atomic masses depend upon the number of possible isotopes and their natural abundance. Following solved example will throw light on this aspect.

Example (1):

A sample of neon is found to consist of ${}^{20}_{10}\mathrm{Ne}$, ${}^{21}_{10}\mathrm{Ne}$ and ${}^{22}_{10}\mathrm{Ne}$ in the percentages of 90.92%, 0.26%, 8.82% respectively. Calculate the fractional atomic mass of neon.

Solution:

The overall atomic mass of neon, which is an ordinary isotopic mixture, is the average of the determined atomic masses of individual isotopes. Hence

Average atomic mass = $\dfrac{20\mathrm{x}90.92+21\mathrm{x}0.26+22\mathrm{x}8.82}{100}=20.18\,Answer$

Hence the average atomic mass of neon is 20.18 amu

It is important to realize that no individual neon atom in the sample has a mass of 20.18 amu. For most laboratory purposes, however, we consider the sample to consist of atoms with this average mass.

1.4 ANALYSIS OF A COMPOUND - EMPIRICAL AND MOLECULAR FORMULAS

Before we go into the details of empirical and molecular formulas of a compound, we should be interested to know the percentage of each element in the compound. For this purpose all the elements present in the compound are first identified.

This is called qualitative analysis. After that the compound is subjected to quantitative analysis in which the mass of each element in a sample of the compound is determined. From this we determine the percentage by mass of each element. The percentage of an element in a compound is the number of grams of that element present in 100 grams of the compound.

$$\text{Percentage of an element} = \frac{\text{Mass of the element in the compound}}{\text{mass of the compound}} \text{ x } 100$$

Example (2):

8.657 g of a compound were decomposed into its elements and gave 5.217 g of carbon, 0.962 g of hydrogen, 2.478 g of oxygen. Calculate the percentage composition of the compound under study.

Solution:

Applying the formula

$$\text{Percentage of carbon} = \frac{\text{Mass of carbon}}{\text{Mass of the compound}} \text{ x } 100 = \frac{5.217g}{8.657g} \text{ x } 100 = 60.28 \text{ Answer}$$

$$\text{Percentage of hydrogen} = \frac{\text{Mass of hydrogen}}{\text{Mass of the compound}} \text{ x } 100 = \frac{0.962g}{8.657g} \text{ x } 100 = 11.11 \text{ Answer}$$

$$\text{Percentage of oxygen} = \frac{\text{Mass of oxygen}}{\text{Mass of the compound}} \text{ x } 100 = \frac{2.478g}{8.657g} \text{ x } 100 = 28.62 \text{ Answer}$$

The above results tell us that in one hundred grams of the given compound, there are 60.26 grams of carbon, 11.11 grams of hydrogen and 28.62 grams of oxygen.

Percentage composition of a compound can also be determined theoretically if we know the formula mass of the compound. The following equation can be used for this purpose.

$$\text{Percentage of an element} = \frac{\text{Mass of the element in one mole of the compound}}{\text{Formula mass of the compound}} \text{ x } 100$$

1.4.1 Empirical Formula

It is the simplest formula that gives the small whole number ratio between the atoms of different elements present in a compound. In an empirical formula of a compound, A_xB_y, there are x atoms of an element A and y atoms of an element B.

The empirical formula of glucose ($C_6H_{12}O_6$) is CH_2O and that of benzene (C_6H_6) is CH.

Empirical formula of a compound can be calculated following the steps mentioned below:

1. Determination of the percentage composition.
2. Finding the number of gram atoms of each element. For this purpose divide the mass of each element (% of an element) by its atomic mass.
3. Determination of the atomic ratio of each element. To get this, divide the number of moles of each element (gram atoms) by the smallest number of moles.
4. If the atomic ratio is simple whole number, it gives the empirical formula, otherwise multiply with a suitable digit to get the whole number atomic ratio.

Example (3):

Ascorbic acid (vitamin C) contains 40.92% carbon, 4.58% hydrogen and 54.5% of oxygen by mass. What is the empirical formula of the ascorbic acid?

Solution:

From the percentages of these elements, we believe that in 100 grams of ascorbic acid, there are 40.92 grams of carbon, 4.58 grams of hydrogen and 54.5 grams of oxygen.

Divide these masses of the elements (or percentages) by their atomic masses to get the number of gram atoms.

$$\text{No. of gram atoms of hydrogen} = \frac{4.58\text{g}}{1.008\ \text{gmol}^{-1}} = 4.54\ \text{gram atoms}$$

$$\text{No. of gram atoms of oxygen} = \frac{54.5\text{g}}{16\ \text{gmol}^{-1}} = 3.406\ \text{gram atoms}$$

$$\text{No. of gram atoms of carbon} = \frac{40.92\text{g}}{12.0\ \text{gmol}^{-1}} = 3.41\ \text{gram atoms}$$

Atomic ratio is obtained by dividing the gram atoms with 3.406, which is the smallest number.

$$\text{C:H:O} = \frac{3.41}{3.406} : \frac{4.54}{3.406} : \frac{3.406}{3.406}$$

$$\text{C:H:O} = 1 : 1.33 : 1$$

To convert them into whole numbers, multiply with three

$$\text{C:H:O} = 3(1 : 1.33 : 1) = \boxed{3 : 4 : 3}\ \text{Answer}$$

This whole number ratio gives us the subscripts for the empirical formula of the ascorbic acid i.e.,$C_3H_4O_3$.

1.4.2 Empirical Formula from Combustion Analysis

Those organic compounds which simply consist of carbon, hydrogen and oxygen can be analyzed by combustion. The sole products will be CO_2 and H_2O. These two products of combustion are separately collected.

Combustion Analysis

A weighed sample of the organic compound is placed in the combustion tube. This combustion tube is fitted in a furnace. Oxygen is supplied to burn the compound. Hydrogen is converted to H_2O and carbon is converted to CO_2. These gases are absorbed in $Mg(ClO_4)_2$ and 50% KOH respectively. (Fig 1.4). The difference in the masses of these absorbers gives us the amounts of H_2O and CO_2 produced. The amount of oxygen is determined by the method of difference.

Fig(1.4) Combustion analysis

Following formulas are used to get the percentages of carbon, hydrogen and oxygen, respectively.

$$\text{\% of carbon} = \frac{\text{Mass of } CO_2}{\text{Mass of organic compound}} \times \frac{12.00}{44.00} \times 100$$

$$\text{\% of hydrogen} = \frac{\text{Mass of } H_2O}{\text{Mass of organic compound}} \times \frac{2.016}{18} \times 100$$

The percentage of oxygen is obtained by the method of difference.

% of oxygen = 100 - (% of carbon + % of hydrogen) .

Example (4):

A sample of liquid consisting of carbon, , hydrogen and oxygen was subjected to combustion analysis. 0.5439 g of the compound gave 1.039 g of CO_2, 0.6369. g of H_2O.
Determine the empirical formula of the compound.

Solution:

Mass of organic Compound = 0.5439 g
Mass of carbon dioxide = 1.039g
Mass of water = 0.6369 g

Element	%	No. of Gram atoms	Atomic Ratio	Empirical formula
C	$\frac{1.039\,\text{g}}{0.543g}\text{x}\frac{12.00}{44.00}\text{x}100$ $=52.108$	$\frac{52.108}{12}=4.34$	$\frac{4.34}{2.17}=2$	C_2H_6O
H	$\frac{0.6369\,\text{g}}{0.5439g}\text{x}\frac{2.016}{18}\text{x}100$ $=13.11$	$\frac{13.11}{1.008}=13.01$	$\frac{13.01}{2.17}=6$	
O	$100-(52.108+13.11)$ $=34.77$	$\frac{34.77}{16.00}=2.17$	$\frac{2.17}{2.17}=1$	

1.4.3 Molecular Formula

That formula of a substance which is based on the actual molecule is called molecular formula. It gives the total number of atoms of different elements present in the molecule of a compound. For example, molecular formula of benzene is C_6H_6 while that of glucose is $C_6H_{12}O_6$.

The empirical formulas of benzene and glucose are CH and CH_2O respectively, so for these compounds the molecular formulas are the simple multiple of empirical formulas. Hence

Molecular formula = n (Empirical formula)

Where 'n' is a simple integer. Those compounds whose empirical and molecular formulae are the same are numerous. For example, H_2O, CO_2, NH_3 and $C_{12}H_{22}O_{11}$ have same empirical and molecular formulas. Their simple multiple 'n' is unity. Actually the value of 'n' is the ratio of molecular mass and empirical formula mass of a substance.

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}}$$

Example (5):

The combustion analysis of an organic compound shows it to contain 65.44% carbon, 5.50% hydrogen and 29.06% or oxygen. What is the empirical formula of the compound? If the molecular mass of this compound is 110.15 g.mol^{-1}. Calculate the molecular formula of the compound.

Solution:

First of all divide the percentage of each element by its atomic mass to get the number of gram atoms or moles.

$$\text{No of gram atoms of C} = \frac{65.44 \text{ g of C}}{12 \text{ g / mol}} = 5.45 \text{ gram atoms of C}$$

$$\text{No of gram atoms of hydrogen} = \frac{5.50 \text{ g of H}}{1.008 \text{ g / mol}} = 5.46 \text{ gram atoms of H}$$

$$\text{No of gram atoms of oxygen} = \frac{29.06 \text{ g of O}}{16.00 \text{ g / mol}} = 1.82 \text{ gram atoms of O}$$

Molar ratio:

$$\begin{array}{ccccc} \text{C} & : & \text{H} & : & \text{O} \\ 5.45 & : & 4.46 & : & 1.82 \end{array}$$

Divide the number of gram atoms by the smallest number i.e 1.82

$$\begin{array}{ccccc} \text{C} & : & \text{H} & : & \text{O} \\ \frac{5.45}{1.82} & : & \frac{5.46}{1.82} & : & \frac{1.82}{1.82} \\ 3 & : & 3 & : & 1 \end{array}$$

Carbon, hydrogen and oxygen are present in the given organic compound in the ratio of 3:3:1. So the empirical formula is C_3H_3O.

In order to determine the molecular formula, first calculate the empirical formula mass.

Empirical formula mass = **12 x 3 + 1.008 x 3 + 16 x 1 = 55.05 g/mol**
Molar mass of the compound = **110.15g.mol^{-1}**

$$n = \frac{\text{Molar mass of the compound}}{\text{Empirical formula mass}} = \frac{110.15}{55.05} = 2$$

Molecular formula **= n (empirical formula)**
= 2 (C_3H_3O) =$C_6H_6O_2$ Answer

There are many possible structures for this molecular formula.

1.5 CONCEPT OF MOLE

We know that atom is an extremely small particle. The mass of an individual atom is extremely small quantity. It is not possible to weigh individual atoms or even small number of atoms directly. That is why, we use the atomic mass unit (amu) to express the atomic masses.

For the sake of convenience, the atomic mass may be given in any unit of measurement i.e. grams, kg, pounds, and so on.

When the substance at our disposal is an element then the atomic mass of that element expressed in grams is called one gram atom. It is also called one gram mole or simply a mole of that element.

$$\text{Number of gram atoms or moles of an element} = \frac{\text{Mass of an element in grams}}{\text{Molar mass of an element}}$$

For example

1 gram atom of hydrogen = 1.008 g
1 gram atom of carbon = 12.000 g
and 1 gram atom of uranium = 238.0 g

It means that one gram atom of different elements have different masses in them. One mole of carbon is 12 g, while 1 mole of magnesium is 24g. It also shows that one atom of magnesium is twice as heavy as an atom of carbon.

The molecular mass of a substance expressed in grams is called gram molecule or gram mole or simply the mole of a substance.

$$\text{Number of gram molecules or moles of a molecular substance} = \frac{\text{Mass of molecular substance in grams}}{\text{Molar mass of the substance}}$$

For example

1 gram molecule of water = 18.0 g

1 gram molecule of H_2SO_4 = 98.0 g

and 1 gram molecule of sucrose = 342.0 g

It means that one gram molecules of different molecular substances have different masses.

The formula unit mass of an ionic compound expressed in grams is called gram formula of the substance. Since ionic compounds do not exist in molecular form therefore the sum of atomic masses of individual ions gives the formula mass. The gram formula is also referred to as gram mole or simply a mole.

$$\text{Number of gram formulas or moles of a substance} = \frac{\text{Mass of the ionic substance in grams}}{\text{Formula mass of the ionic substance}}$$

1 gram formula of NaCl = 58.50 g

1 gram formula of Na_2CO_3 = 106 g

1gram formula of $AgNO_3$ = 170g

It may also be mentioned here that ionic mass of an ionic species expressed in grams is called one gram ion or one mole of ions.

$$\text{Number of gram ions or moles of an species} = \frac{\text{Mass of the ionic species in grams}}{\text{Formula mass of the ionic species}}$$

For example

1 g ion of OH^- = 17g

1 g ion of SO_4^{2-}=96g

1 g ion of CO_3^{2-} =60g

So, t**he atomic mass, molecular mass, formula mass or ionic mass of the substance expressed in gram is called molar mass of the substance.**

Example (6):

Calculate the gram atoms (moles) in

(a) 0.1 g of sodium.

(b) 0.1 kg of silicon.

Solution

$$\text{(a) No. of gram atoms} = \frac{\text{Mass of element in gram}}{\text{Molar mass}}$$

Mass of sodium = 0.1 g

Molar mass = 23 g/mol

$$\text{Number of gram atoms of sodium} = \frac{0.1\text{g}}{23\ \text{gmol}^{-1}} = 0.0043\ \text{mol}$$

$$= \boxed{4.3 \times 10^{-3}\ \text{mol}}$$ Answer

(b) First of all convert the mass of silicon into grams.

Mass of silicon = 0.1 kg = 0.1 x 1000 = 100 g

Molar mass = 28.086 gmol^{-1}

$$\text{Number of gram atoms of silicon} = \frac{100\ \text{g}}{28.086\ \text{gmol}^{-1}} = \boxed{3.56\ \text{moles}}\ \text{Answer}$$

Example (7):

Calculate the mass of 10^{-3} moles of $MgSO_4$.

Solution:

$MgSO_4$ is an ionic compound. We will consider its formula mass in place of molecular mass.

$$\text{Number of gram formula or mole of a substance} = \frac{\text{Mass of the ionic substance}}{\text{Formula mass of the ionic substance}}$$

Formula mass of $MgSO_4$ = 24 + 96 = 120 $gmol^{-1}$

Number of moles of $MgS0_4$ = 10^{-3}moles

Applying the formula

$$10^{-3} = \frac{\text{Mass of MgSO}_4}{120\ \text{gmol}^{-1}}$$

Mass of $MgSO_4$ = 10^{-3} moles x 120$gmol^{-1}$

= 120 x 10^{-3} = $\boxed{0.12\ \text{g}}$ Answer

1.5.1 Avogadro's Number

Avogadro's number is the number of atoms, molecules and ions in one gram atom of an element, one gram molecule of a compound and one gram ion of a substance, respectively.

To understand Avogadro's number let us consider the following quantities of substances.

1.008 g of hydrogen = 1 mole of hydrogen = 6.02 x 10^{23} atoms of H

23 g of sodium = 1 mole of Na = 6.02 x$1O^{23}$ atoms of Na

238 g of uranium = 1 mole of U = 6.02x10^{23} atoms of U

This number, 6.02 x 10^{23} is the number of atoms in one mole of the element. It is interesting to know that different masses of elements have the same number of atoms. An atom of sodium is 23 times heavier than an atom of hydrogen. In order to have equal number of atoms sodium should be taken 23 times greater in mass than hydrogen. Magnesium atom is twice heavier than carbon; i.e. 10 g of Mg and 5 g of C contain the same number of atoms.

18 g of H_2O =1 mole of water =6.02x10^{23} molecules of water

180 g of glucose = 1 mole of glucose = 6.02 x 10^{23} molecules of glucose

342 g of sucrose = 1 mole of sucrose = 6.02 x 10^{23} molecules of sucrose

Hence, one mole of different compounds has different masses but has the same number of molecules.

When we take into consideration the ions, then

96 g of SO_4^{2-} = 1 mole of SO_4^{2-} = 6.02 x 10^{23} ions of SO_4^{2-}

62 g of NO_3^- = 1 mole of NO_3^- = 6.02 x 10^{23} ions of NO_3^-

From the above discussion, we reach the conclusion that the number 6.02 X 10^{23} is equal to one mole of a substance. This number is called Avogadro's number and it is denoted by N_A.
Following relationships between amounts of substances in terms of their masses and the number of particles present in them, are useful

1) $$\text{Number of atoms of an element} = \frac{\text{Mass of the element x } N_A}{\text{Atomic mass}}$$

2) $$\text{Number of molecules of a compound} = \frac{\text{Mass of the compound x } N_A}{\text{Molecular mass}}$$

3) $$\text{Number of ions of an ionic species} = \frac{\text{Mass of the ion x } N_A}{\text{Ionic mass}}$$

When we have compounds of known mass we can calculate the number of atoms from their formulas. In 18 g of water there are present 6.02 x 10^{23} molecules of H_2O, 2 x 6.02 x 10^{23} atoms of hydrogen and 6.02 x 10^{23} atoms of oxygen. Similarly, in 98g of H_2SO_4, it has twice the Avogadro's number of hydrogen atoms, four times the Avogadro's number of oxygen atoms and the Avogadro's number of sulphur atoms.
Some substances ionize in suitable solvents to yield cations and anions. The number of such ions, their masses, number of positive and negative charges can be easily calculated from the known amount of the substance dissolved. Let us dissolve 9.8 g of H_2SO_4 in sufficient quantity of H_2O to get it completely ionized. It has 0.1 moles of H_2SO_4. It will yield 0.2 mole or 0.2 x 6.02 x 10^{23} H^+ and 0.1 moles or 0.1 x 6.02 x 10^{23} SO_4^{2-} etc. Total positive charges will be 0.2 x 6.02 x 10^{23} and the total negative charges will be 0.2 x 6.02 x 10^{23} (because each SO_4^{2-}, has two negative charges). The total mass of H^+ is (0.2 x 1.008)g and that of SO_4^{2-} is (0.1 x 96) g.

Example (8):

How many molecules of water are there in 10.0 g of ice? Also calculate the number of atoms of hydrogen and oxygen separately, the total number of atoms and the covalent bonds present in the sample.

Solution:

Mass of ice (water) = 10.0 g
Molar mass of water =18gmol^{-1}

$$\text{Number of molecules of water} = \frac{\text{Mass of water in gram}}{\text{Molar mass of water in g mol}^{-1}} \text{ x Avogadro's number}$$

$$= \frac{10}{18 \text{ g mol}^{-1}} \text{ x } 6.02 \text{ x } 10^{23}$$

Number of molecules of water = 0.55 x 6.02 x 10^{23} = $\boxed{3.31\ x\ 10^{23}}$ Answer
One molecule of water contain hydrogen atoms = 2
3.31 x 10^{23} molecules of water contain hydrogen atoms = 2 x 3.31 x 10^{23}
= $\boxed{6.68\ x\ 10^{23}}$ Answer
One molecule of water contains oxygen atom = 1
3.31 x 10^{23} molecules of water contain oxygen atoms = $\boxed{3.31\ x\ 10^{23}}$ Answer
One molecule of water contains number of covalent bonds =2
3.31 x 10^{23} molecules of water contain number of covalent bonds = 2 x 3.31 x 10^{23}
= $\boxed{6.68\ x\ 10^{23}}$ Answer
Total number of atoms of hydrogen and oxygen = 6.68 x 10^{23} + 3.31 x 10^{23}
= $\boxed{9.99\ x\ 10^{23}}$ Answer

Example (9):

10.0 g of H_3PO_4 has been dissolved in excess of water to dissociate it completely into ions. Calculate,

a) Number of molecules in 10.0 g of H_3PO_4.
b) Number of positive and negative ions in case of complete dissociation in water.
c) Masses of individual ions.
d) Number of positive and negative charges dispersed in the solution.

Solution:

(a) Mass of H_3PO_4 =10 g
Molar mass of H_3PO_4 =3 + 31 + 64 = 98
No. of molecules of H_3P0_4 = $= \dfrac{\text{Mass of } H_3PO_4}{\text{Molar mass of } H_3PO_4} \text{ x } 6.02 \text{ x } 10^{23}$

$$= \frac{10}{98\text{ g } mol^{-1}} \text{ x } 6.02 \text{ x } 10^{23}$$

$= 0.102 \text{ x } 6.02 \text{ x } 10^{23}$

$= 0.614 \text{ x } 10^{23}$

$= \boxed{6.14 \text{ x } 10^{22}}$ Answer

(b) H_3PO_4 dissolves in water and ionizes as follows

H_3PO_4 □ $3H^+ \quad +PO_4^{3-}$

According to the balanced chemical equation

H_3PO_4 : H^+

1 : 3

$6.14 \text{ x } 10^{22}$: $3 \text{ x } 6.14 \text{ x } 10^{22}$

$6.14 \text{ x } 10^{22}$: $1.842 \text{ x } 10^{23}$

Hence, the number of H^+ will be $1.842 \text{ x } 10^{23}$

H_3PO_4 : PO_4^{3-}

1 : 1

$6.14 \text{ x } 10^{22}$: $6.14 \text{ x } 10^{22}$

Hence, the number of PO_4^{3-} will be $\boxed{6.14 \text{ x } 10^{22}}$ Answer

(c) In order to calculate the mass of the ions, use the formulas

$$\text{Number of } H^+ = \frac{\text{Total mass of } H^+}{\text{Ionic mass of } H^+} \text{ x } 6.02 \text{ x } 10^{23}$$

$$1.842 \text{ x } 10^{23} = \frac{\text{Total mass of } H^+}{1.008} \text{ x } 6.02 \text{ x } 10^{23}$$

$$\text{Total mass of } H^+ = \frac{1.842 \text{ x } 10^{23} \text{ x } 1.008}{6.02 \text{ x } 10^{23}} = 0.308 \text{ g}$$

$$\text{No. of } PO_4^{3-} = \frac{\text{Total mass of } PO_4^{3-}}{\text{Ionic mass of } PO_4^{3-}} \text{ x } 6.02 \text{ x } 10^{23} \text{ molecules}$$

$$6.14 \text{ x } 10^{22} = \frac{\text{Total mass of } PO_4^{3-}}{95} \text{ x } 6.02 \text{ x } 10^{23}$$

$$\text{Total mass of } PO_4^{3-} = \frac{6.14 \text{ x } 10^{22} \text{ x } 95}{6.02 \text{ x } 10^{23}} = \boxed{9.689\text{g}} \text{ Answer}$$

(d) One molecule of H_3PO_4 gives three positive charges in the solution

$6.14 \text{ x } 10^{22}$ molecules of H_3PO_4 will give $=3 \text{ x } 6.14 \text{ x } 10^{22}$

$= \boxed{1.842 \text{ x } 10^{23} \text{ positive charges}}$ Answer

Number of positive and negative charges are always equal. So the number of negative charges dispersed in the solution = $1.842 \text{ x } 10^{23}$

1.5.2 Molar Volume

One mole of any gas at standard temperature and pressure (STP) occupies a volume of 22.414 dm^3. This volume of 22.414 dm^3 is called molar volume and it is true only when the gas is ideal (the idea of the ideality of the gas is mentioned in chapter three).

With the help of this information, we can convert the mass of a gas at STP into its volume and vice versa.

Hence we can say that

2.016 g of H_2 = 1 mole of H_2 = 6.02 x 10^{23} molecules of H_2 = 22.414 dm^3 of H_2 at S.T.P

16g of CH_4 = 1 mole of CH_4 = 6.02 x 10^{23} molecules of CH_4= 22.414 dm^3 of CH_4 at S.T.P.

It is very interesting to know from the above data that 22.414 dm^3 of each gas has a different mass but the same number of molecules. The reason is that the masses and the sizes of the molecules don't affect the volumes. Normally, it is known that in the gaseous state the distance between molecules is 300 times greater than their diameters.

Example (10):

A well known ideal gas is enclosed in a container having volume 500 cm^3 at S.T.P. Its mass comes out to be 0.72g.What is the molar mass of this gas.

Solution:

We can calculate the number of moles of the ideal gas at S.T.P from the given volume.

$$\text{22.414 dm}^3\text{or 22.414 cm}^3\text{of the ideal gas at S.T.P} = 1\text{ mole}$$

$$\text{1 cm}^3\text{of the ideal gas at S.T.P} = \frac{1}{22414}\text{ mole}$$

$$\text{500 cm}^3\text{of the ideal gas at S.T.P} = \frac{1}{22414}\text{ x 500}$$

$$= 0.0223\text{ moles}$$

We know that

$$\text{Number of moles of the gas} = \frac{\text{Mass of the gas}}{\text{Molar of the gas}}$$

$$\text{Molar mass of the gas} = \frac{\text{Mass of the gas}}{\text{Number of moles of the gas}}$$

$$\text{Molar mass of the gas} = \frac{0.72\text{ g}}{0.0223\text{ mole}} = \boxed{32\text{ g mol}^{-1}}\text{ Answer}$$

1.6 STOICHIOMETRY

With the knowledge of atomic mass, molecular mass, the mole, the Avogadro's number and the molar volume, we can make use of the chemical equations in a much better way and can get many useful information from them.

Chemical equations have certain limitations as well. They do not tell about the conditions and the rate of reaction. Chemical equation can even be written to describe a chemical change that does not occur. So, when stoichiometeric calculations are performed, we have to assume the following conditions.

1. All the reactants are completely converted into the products.
2. No side reaction occurs.

Stoichiometry is a branch of chemistry which tells us the quantitative relationship between reactants and products in a balanced chemical equation.

While doing calculations, the law of conservation of mass and the law of definite proportions are obeyed.

The following type of relationships can be studied with the help of a balanced chemical equation.

1) Mass-mass Relationship

If we are given the mass of one substance, we can calculate the mass of the other substances involved in the chemical reaction.

2) Mass-mole Relationship or Mole-mass Relationship

If we are given the mass of one substance, we can calculate the moles of other substance and vice-versa.

3) Mass-volume Relationship

If we are given the mass of one substance, we can calculate the volume of the other substances and vice-versa.Similarly, mole-mole calculations can also be performed.

Example (11):

Calculate the number of grams of K_2SO_4 and water produced when 14 g of KOH are reacted with excess of H_2SO_4. Also calculate the number of molecules of water produced.

Solution:

For doing such calculations, first of all convert the given mass of KOH into moles and then compare these moles with those of K_2SO_4 with the help of the balanced chemical equation.

Mass of KOH = 14.0 g
Molar mass of KOH = 39 + 16 + 1 = 56 g/mol

$$\text{Number of moles of KOH} = \frac{14.0\ \text{g}}{56\ \text{g mol}^{-1}} = 0.25$$

Equation: $$2KOH(aq) + H_2SO_4(aq) \longrightarrow K_2SO_4(aq) + 2H_2O(l)$$

To get the number of moles of K_2SO_4, compare the moles of KOH with those of K_2SO_4.

KOH : K_2SO_4
2 : 1
1 : $\frac{1}{2}$
0.25 : 0.125

So, 0.125 moles of K_2SO_4 is being produced from 0.25 moles of KOH

Molar mass of K_2SO_4 = 2 x 39 + 96
= 174 g/mol

Mass of K_2SO_4 produced = No. of moles x molar mass
= 0.125 moles x 174 g mol^{-1}
=21.75g

To get the number of moles of H_2O, compare the moles of KOH with those of water

KOH : H_2O
2 : 2
1 : 1
0.25 : 0.25

So, the number of moles of water produced is 0.25 from 0.25 moles of KOH

Mass of water produced = 0.25 moles x 18 g mol^{-1}
= 4.50 g

Number of molecules of water = No. of moles x 6.02 x 10^{23}
= 0.25 moles x 6.02 x 10^{23} molecules per mole
= $\boxed{1.50 \text{ x } 1023 \text{ molecules}}$ Answer

Example (12):

Mg metal reacts with HCl to give hydrogen gas. What is the minimum volume of HCl solution (27% by weight) required to produce 12.1g of H_2. The density of HCl solution is 1.14g/cm^3.

$$Mg(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2(g)$$

Solution:

Mass of H_2 produced = 12.1 g
Molar mass of H_2 = 2.016 g mol^{-1}

$$\text{Moles of } H_2 = \frac{\text{Mass of } H_2}{\text{Molar mass of } H_2} = \frac{12.1\text{g}}{2.016 \text{ g mol}^{-1}} = 6.0 \text{ moles}$$

To calculate the number of moles of HCl, compare the moles of H_2 with those of HCl

H_2 : HCl
1 : 2
6 : 12

So, 12 moles of HCl are being consumed to produce 6 moles of H_2.

Mass of HCl =Moles of HCl x Molar mass of HCl
= 12 moles x 36.5 g mol^{-1}
= 438 grams

We know that HCl solution is 27% by weight, it means that
27 g of HCl are present in HCl solution = 100 g

$$\text{1 g is present in HCl solution} = \frac{100}{27}$$

$$\text{438 g are present in HCl solution} = \frac{100}{27} \times 438 = 1622.2 \text{ g}$$

$$\text{Density of HCl solution} = 1.14 \text{ g/cm}^3$$

$$\text{Volume of HCl} = \frac{\text{Mass of HCl solution}}{\text{Density of HCl}}$$

$$= \frac{1622.2g}{1.14gcm^{-3}} = \boxed{1423 \text{ cm}^3} \text{ Answer}$$

1.7 LIMITING REACTANT

Having completely understood the theory of stoichiometry of the chemical reactions, we shift towards the real stoichiometric calculations. Real in the sense that we deal with such calculations very commonly in chemistry. Often, in experimental work, one or more reactants is/are deliberately used in excess quantity. The quantity exceeds the amount required by the reaction's stoichiometry. This is done, to ensure that all of the other expensive reactant is completely used up in the chemical reaction. Sometimes, this strategy is employed to make reactions occur faster. For example, we know that a large quantity of oxygen in a chemical reaction makes things burn more rapidly. In this way excess of oxygen is left behind at the end of reaction and the other reactant is consumed earlier. This reactant which is consumed earlier is called a limiting reactant. In this way, the amount of product that forms is limited by the reactant that is completely used. Once this reactant is consumed, the reaction stops and no additional product is formed. **Hence the limiting reactant is a reactant that controls the amount of the product formed in a chemical reaction due to its smaller amount.**

The concept of limiting reactant is analogous to the relationship between the number of "kababs" and the "slices" to prepare "sandwiches". If we have 30 "kababs" and five breads "having 58 slices", then we can only prepare 29 "sandwiches". One "kabab" will be extra (excess reactant) and "slices" will be the limiting reactant. It is a practical problem that we can not purchase exactly sixty "slices" for 30 "kababs" to prepare 30 "sandwiches".

Consider the reaction between hydrogen and oxygen to form water.

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(\ell)$$

When we take 2 moles of hydrogen (4g) and allow it to react with 2 moles of oxygen (64g), then we will get only 2 moles (36 g) of water. Actually, we will get 2 moles (36g) of water because 2 moles (4g) of hydrogen react with 1 mole (32 g) of oxygen according to the balanced equation. Since less hydrogen is present as compared to oxygen, so hydrogen is a limiting reactant. If we would have reacted 4 moles (8g) of hydrogen with 2 moles (64 g) of oxygen, we would have obtained 4 moles (72 g) of water.

Identification of Limiting Reactant

To identify a limiting reactant, the following three steps are performed.

1. Calculate the number of moles from the given amount of reactant.
2. Find out the number of moles of product with the help of a balanced chemical equation.
3. Identify the reactant which produces the least amount of product as limiting reactant.

Following numerical problem will make the idea clear.

Example (13):

NH_3 gas can be prepared by heating together two solids NH_4Cl and $Ca(OH)_2$. If a mixture containing 100 g of each solid is heated then

(a) Calculate the number of grams of NH_3 produced.

(b) Calculate the excess amount of reagent left unreacted.

$$2NH_4Cl\,(s) + Ca\,(OH)_2\,(s) \longrightarrow CaCl_2(s) + 2NH_3\,(g) + 2H_2O(\ell)$$

Solution:

(a) Convert the given amounts of both reactants into their number of moles.

Mass of NH_4Cl = 100g

Molar mass of NH_4C1 = 53.5g mol^{-1}

Mass of NH_4Cl $= \dfrac{100g}{53.5\text{g mol}^{-1}} = 1.87$

Mass of $Ca(OH)_2$ = $100g$

Molar mass of $Ca(OH)_2$ = 74 g mol^{-1}

Moles of $Ca(OH)_2$ $= \dfrac{100g}{74\text{ g mol}^{-1}} = 1.35$

Compare the number of moles of NH_4Cl with those of NH_3

NH_4Cl : NH_3
2 : 2
1 : 1
1.87 : 1.87

Similarly compare the number of moles of $Ca(OH)_2$ with those of NH_3.

$Ca(OH)_2$: NH_3
1 : 2
1.35 : 2.70

Since the number of moles of NH_3 produced by l00g or 1.87 moles of NH_4Cl are less, so NH_4Cl is the limiting reactant. The other reactant, $Ca(OH)_2$ is present in excess. Hence

Mass of NH_3 produced = 1.87 moles x 17 g mol^{-1}

= $\boxed{31.79\text{ g}}$ Answer

(b) Amount of the reagent present in excess

Let us calculate the number of moles of $Ca(OH)_2$ which will completely react with 1.87 moles of NH_4Cl with the help of equation. For this purpose, compare NH_4Cl and $Ca(OH)_2$

NH_4Cl : $Ca(OH)_2$
2 : 1
1 : $\frac{1}{2}$
1.87 : 0.935

Hence the number of moles of $Ca(OH)_2$ which completely react with 1.87 moles of NH_4Cl is 0.935 moles.

No. of moles of $Ca(OH)_2$ taken =1.35
No. of moles of $Ca(OH)_2$ used = 0.935
No. of moles of $Ca(OH)_2$ left behind = 1.35 - 0.935 = 0.415

Mass of $Ca(OH)_2$ left unreacted (excess) = 0.415x74 = $\boxed{30.71\ g}$ Answer

It means that we should have mixed 100 g of NH_4Cl with 69.3 g (100 - 30.71) of $Ca(OH)_2$ to get 1.87 moles of NH_3.

1.8 YIELD

The amount of the products obtained in a chemical reaction is called the actual yield of that reaction. The amount of the products calculated from the balanced chemical equation represents the theoretical yield. The theoretical yield is the maximum amount of the product that can be produced by a given amount of a reactant, according to balanced chemical equation.

In most chemical reactions the amount of the product obtained is less than the theoretical yield. There are various reasons for that. A practically inexperienced worker has many shortcomings and cannot get the expected yield. The processes like filtration, separation by distillation, separation by a separating funnel, washing, drying and crystallization if not properly carried out, decrease the actual yield. Some of the reactants might take part in a competing side reaction and reduce the amount of the desired product. So in most of the reactions the actual yield is less than the theoretical yield.

A chemist is usually interested in the efficiency of a reaction. The efficiency of a reaction is expressed by comparing the actual and theoretical yields in the form of percentage (%) yield.

$$\%\ \text{yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$

Example (14):

When lime stone ($CaCO_3$) is roasted, quicklime (CaO) is produced according to the following equation. The actual yield of CaO is 2.5 kg, when 4.5 kg of lime stone is roasted. What is the percentage yield of this reaction.

$$CaCO_3\ (s) \longrightarrow CaO(s) + CO_2(s)$$

Solution:

Mass of limestone roasted = 4.5 kg = 4500 g

Mass of quick lime produced (actual yield) = 2.5 kg = 2500 g

Molar mass of $CaCO_3$ = 100 g mol^{-1}

Molar mass of CaO = 56 g mol^{-1}

According to the balanced chemical equation

100 g of $CaCO_3$ should give CaO = 56 g

1g of $CaCO_3$ should give CaO = 56 / 100

4500 g of $CaCO_3$ should give CaO = 56 / 100 x 4500

= 2520 g

Theoretical yield of CaO = 2520 g

Actual yield of CaO = 2500 g

$$\%\ \text{yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100 = \frac{2500g}{2520g} \times 100$$

$$= \boxed{99.2\ \%}\ \text{Answer}$$

KEY POINTS

1. Atoms are the building blocks of matter. Atoms can combine to form molecules. Covalent compounds mostly exist in the form of molecules. Atoms and molecules can either gain or lose electrons, forming charged particles called ions. Metals tend to lose electrons, becoming positively charged ions. Non-metals tend to gain electrons forming negatively charged ions. When X-rays or α -particles are passed through molecules in a gaseous state, they are converted into molecular ions.
2. The atomic mass of an element is determined with reference to the mass of carbon as a standard element and is expressed in amu. The fractional atomic masses can be calculated from the relative abundance of isotopes. The separation and identification of isotopes can be carried out by mass spectrograph.
3. The composition of a substance is given by its chemical formula. A molecular substance can be represented by its empirical or a molecular formula. The empirical and molecular formula are related through a simple integer.
4. Combustion analysis is one of the techniques to determine the empirical formula and then the molecular formula of a substance by knowing its molar mass.
5. A mole of any substance is the Avogadro's number of atoms or molecules or formula units of that substance.
6. The study of quantitative relationship between the reactants and the products in a balanced chemical equation is known as stoichiometry. The mole concept can be used to calculate the relative quantities of reactants and products in a balanced chemical equation.
7. The concept of molar volume of gases helps to relate solids and liquids with gases in a quantitative manner.
8. A limiting reactant is completely consumed in a reaction and controls the quantity of products formed.
9. The theoretical yield of a reaction is the quantity of the products calculated with the help of a balanced chemical equation. The actual yield of a reaction is always less than the theoretical yield. The efficiency of a chemical reaction can be checked by calculating its percentage yield.

EXERCISE

Q1 Select the most suitable answer from the given ones in each question.

(i) Isotopes differ in

(a) properties which depend upon mass
(b) arrangement of electrons in orbitals
(c) chemical properties
(d) the extent to which they may be affected in electromagnetic field.

(ii) Select the most suitable answer from the given ones in each question.

(a) Isotopes with even atomic masses are comparatively abundant.
(b) Isotopes with odd atomic masses are comparatively abundant.
(c) Isotopes with even atomic masses and even atomic numbers are comparatively abundant.
(d) Isotopes with even atomic masses and odd atomic numbers are comparatively abundant.

(iii) Many elements have fractional atomic masses. This is because

(a) the mass of the atom is itself fractional.
(b) atomic masses are average masses of isobars.
(c) atomic masses are average masses of isotopes.
(d) atomic masses are average masses of isotopes proportional to their relative abundance.

(iv) The mass of one mole of electrons is

(a) 1.008 mg (b) 0.55 mg (c) 0.184 mg (d)1.673mg

(v) 27 g of A1 will react completely with how much mass of O_2 to produce Al_2O_3.

(a) 8 g of oxygen (b) 16 g of oxygen (c) 32 g of oxygen (d) 24 g of oxygen

(vi) The number of moles of CO_2 which contain 8.0 g of oxygen.

(a) 0.25 (b) 0.50 (c) 1.0 (d)1.50

(vii) The largest number of molecules are present in

(a) 3.6g of H_2O (b) 4.8g of C_2H_5OH (c) 2.8g of CO (d) 5.4g of N_2O_5

(viii) One mole of SO_2 contains

(a) $6.02x10^{23}$ atoms of oxygen (b) 18.1 x 10^{23} molecules of SO_2
(c) $6.02x10^{23}$ atoms of sulphur (d) 4 gram atoms of SO_2

(ix) The volume occupied by 1.4 g of N_2 at S.T.P is

(a) 2.24 dm^3 (b) 22.4 dm^3 (c) 1.12 dm^3 (d) 112 cm^3

(x) A limiting reactant is the one which

(a) is taken in lesser quantity in grams as compared to other reactants.
(b) is taken in lesser quantity in volume as compared to the other reactants.
(c) gives the maximum amount of the product which is required.
(d) gives the minimum amount of the product under consideration.

Q 2. Fill in the blanks

(i) The unit of relative atomic mass is________________.

(ii) The exact masses of isotopes can be determined by_______________ spectrograph.

(iii) The phenomenon of isotopy was first discovered by .___________________

(iv) Empirical formula can be determined by combustion analysis for those compounds which have ______ and _________in them.

(v) A limiting reagent is that which controls the quantities of___________

(vi) 1 mole of glucose has________ atoms of carbon, _________ of oxygen and ______of hydrgen.

(vii) 4g of CH_4 at 0°C and 1 atm pressure has ____________molecules of CH_4

(viii) Stoichiometric calculations can be performed only when _______________ is obeyed.

Q3. Indicate true or false as the case may be:

(i) Neon has three isotopes and the fourth one with atomic mass 20.18 amu.

(ii) Empirical formula gives the information about the total number of atoms present in the molecule.

(iii) During combustion analysis $Mg(ClO_4)_2$ is employed to absorb water vapours.

(iv) Molecular formula is the integral multiple of empirical formula and the integral mutiple can never be unity.

(v) The number of atoms in 1.79 g of gold and 0.023 g of sodium are equal.

(vi) The number of electrons in the molecules of CO and N_2 are 14 each, so 1 g of each gas will have same number of electrons.

(vii) Avogadro’s hypothesis is applicable to all types of gases i.e. ideal and non-ideal.

(viii) Actual yield of a chemical reaction may be greater than the theoretical yield.

Q.4 What are ions? Under what conditions are they produced?

Q.5 (a) What are isotopes? How do you deduce the fractional atomic masses of elements from the relative isotopic abundance? Give two examples in support of your answer.

(b) How does a mass spectrograph show the relative abundance of isotopes of an elment?

(c) What is the justification of two strong peaks in the mass spectrum for bromine; while for iodine only one peak at 127 amu is indicated?

Q.6 Silver has atomic number 47 and has 16 known isotopes but two occur naturally i.e. Ag-107 and Ag-109. Given the following mass spectrometric data, calculate the average atomic mass of silver.

Isotopes	Mass (amu)	Percentage abundance
^{107}Ag	106.90509	51.84
^{109}Ag	108.90476	48.16

Q.7 Boron with atomic number 5 has two naturally occurring isotopes. Calculate the percentage abundance of ^{10}B and ^{11}B from the following informations.

Average atomic mass of boron = 10.81 amu
Isotopic mass of ^{10}B = 10.0129 amu
Isotopic mass of ^{11}B =11.0093amu (Ans: 20.002%, 79.992)

Q.8 Define the following terms and give three examples of each.

1. Gram atom
2. Gram molecular **mass**
3. Gram formula
4. Gram ion
5. Molar volume
6. Avogadro's number
7. Stoichiometry
8. Percentage yield

Q.9 Justify the following statement!:

1. 23 g of sodium and 238 g of uranium have equal number of atoms in them.
2. Mg atom is twice heavier than that of carbon atom.
3. 180 g of glucose and 342 g of sucrose have the same number of molecules but different number of atoms present in them.
4. 4.9 g of H_2SO_4 when completely ionized in water, have equal number of positive and negative charges but the number of positively charged ions are twice the number of negatively charged ions.
5. One mg of K_2CrO_4 has thrice the number of ions than the number of formula units when ionized in water.
6. Two grams of H_2, 16 g of CH_4 and 44 g of CO_2 occupy separately the volumes of 22.414 dm^3, although the sizes and masses of molecules of three gases are very different from each other.

Q.10 Calculate each of the following quantities.

a) Mass in grams of 2.74 moles of $KMnO_4$.	• (Ans: 432.92g)
b) Moles of O atoms in 9.00g of $Mg\ (N0_3)_2$.	• (Ans: 0.36 mole)
c) Number of O atoms in 10.037g of $CUSO_4.5H_2O$.	• (Ans: 2.18 x 10^{23} atoms)
d) Mass in kilograms of 2.6x10^{20} molecules of SO_2.	• (Ans: 2.70x10^{-5} kg)
e) Moles of Cl atoms in 0.822 g $C_2H_4Cl_2$.	• (Ans: 0.0178 moles)
f) Mass in grams of 5.136 moles of Ag_2CO_3.	• (Ans: 1416.2 g)
g) Mass in grams of 2.78 x 10^{21} molecules of CrO_2Cl_2.	• (Ans: 0.7158 g)
h) Number of moles and formula units in 100g of $KClO_3$.	• (Ans: 0.816 moles, 4.91 x 10^{23} formula units)
i) Number of K^+ ions, ClO^-_3 ions, Cl atoms, and O atoms in (h).	• (Ans:4.91 x 10^{23} K^+, 4.91 x 10^{23} ClO_3^{-1}, 4.91 x 10^{23} Cl^{-1}, 1.47x 10^{24} O atoms)

Q.11 Aspartame, the artificial sweetner, has a molecular formula of $C_{14}H_{18}N_2O_5$.

a) What is the mass of one mole of aspartame? (Ans: 294 g mol^{-1})

b) How many moles are present in 52 g of aspartame? (Ans: 0.177mole)

c) What is the mass in grams of 10.122 moles of aspartame? (Ans: 2975.87

d) How many hydrogen atoms are present in 2.43 g of aspartame?(Ans: 8.96 x 10^{22} atoms of H)

Q.12 A sample of 0.600 moles of a metal M reacts completely with excess of fluorine to form 46.8 g of MF_2.

a) How many moles of F are present in the sample of MF_2 that forms? (Ans: 1.2 moles)

b) Which element is represented by the symbol M? (Ans:calcium)

Q.13 In each pair, choose the larger of the indicated quantity, or state if the samples are equal.

a) Individual particles: 0.4 mole of oxygen molecules or 0.4 mole of oxygen atoms.
(Ans: both are equal)

b) Mass: 0.4 mole of ozone molecules or 0.4 mole of oxygen atoms. (Ans: ozone)

c) Mass: 0.6 mole of C_2H_4 or 0.6 mole of I_2. (Ans: I_2)

d) Individual particles: 4.0 g N_2O_4 or 3.3 g SO_2. (Ans: SO_2)

e) Total ions: 2.3 moles of $NaClO_3$ or 2.0 moles of $MgCl_2$. (Ans: $MgCl_2$)

f) Molecules: 11.0 g H_2O or 11.0 g H_2O_2. (Ans:H_2O)

g) Na^+ ion: 0.500 moles of NaBr or 0.0145 kg of NaCl. (Ans: NaBr)

h) Mass: 6.02 x 10^{23} atoms of ^{235}U or 6.02 x 10^{23} atoms of ^{238}U. (Ans: U^{238})

Q.14 a) Calculate the percentage of nitrogen in the four important fertilizers i.e.,

(i) NH_3 (ii) NH_2CONH_2(urea) (iii) $(NH_4)_2SO_4$ (iv) NH_4NO_3.

(Ans: 82.35%, 46.67%, 21.21%, 35%)

b) Calculate the percentage of nitrogen and phosphorus in each of the following:
(i) $NH_4H_2PO_4$ (ii) $(NH_4)_2HPO_4$ (iii) $(NH_4)_3PO_4$

(Ans: (i)N=12.17%,P=26.96% (ii)N=21.21%,P=23.48% (iii)N=28.18%,P=20.81%)

Q.15 Glucose $C_6H_{12}O_6$ is the most important nutrient in the cell for generating chemical potential energy. Calculate the mass % of each element in glucose and determine the number of C, H and O atoms in 10.5 g of the sample.

(Ans: C=40%, H=6.66%, 0 =53.33%, C=2.107×10^{23}, H=4.214×10^{23}, O=2.107×10^{23})

Q.16 Ethylene glycol is used as automobile antifreeze. It has 38.7% carbon, 9.7 % hydrogen and 51.6% oxygen. Its molar mass is 62.1 grams mol^{-1}. Determine its empirical formula.?

(Ans: CH_3O)

Q.17 Serotenin (Molar mass = 176g mol^{-1}) is a compound that conducts nerve impulses in brain and muscles. It contains 68.2 % C.6.86 % H, 15.09 % N, and 9.08 % O. What is its molecular formula.

(Ans: $C_{10}H_{12}N_2O$)

Q.18 An unknown metal M reacts with S to form a compound with a formula M_2S_3. If 3.12 g of M reacts with exactly 2.88 g of sulphur, what are the names of metal M and the-compowad M_2S_3?

(Ans: Cr; Cr_2S_3)

Q.19 The octane present in gasoline burns according to the following equation.

$$2C_8H_{18}\ (l) + 25O_2\ (g) \longrightarrow 16CO_2\ (g) + 18H_2O(l)$$

a) How many moles of O_2 are needed to react fully with 4 moles of octane?

(Ans: 50 moles)

b) How many moles of CO_2 can be produced from one mole of octane?

(Ans: 8 moles)

c) How many moles of water are produced by the combustion of 6 moles of octane?

(Ans: 54 moles)

d) If this reaction is to be used to synthesize 8 moles of CO_2 how many grams of oxygen are needed? How many grams of octane will be used?

(Ans: 400 g: 114 g)

Q.20 Calculate the number of grams of Al_2S_3 which can be prepared by the reaction of 20 g of Al and 30 g of sulphur. How much the non-limiting reactant is in excess?

(Ans: 46.87g; 3.125g)

Q.21 A mixture of two liquids, hydrazine N_2H_4 and N_2O_4 are used in rockets. They produce N_2 and water vpours. How many grams of N_2 gas will be formed by reacting 100 g of N_2H_4 and 200g of N_2O_4. (Ans: 131.04g)

$$2N_2H_4 + N_2O_4 \longrightarrow 3N_2 + 4H_2O$$

Q.22 Silicon carbide (SiC) is an important ceramic material. It is produced by allowing sand (SiO_2) to react with carbon at high temperature.

$$SiO_2 + 3C \longrightarrow SiC + 2CO$$

When 100 kg sand is reacted with excess of carbon, 51.4 kg of SiC is produced. What is the pecentage yield of SiC? (Ans: 77%)

Q.23 a. What is stoichiometry? Give its assumptions? Mention two important laws, which help to perform the stoichiometric calculations?

b. What is a limiting reactant? How does it control the quantity of the product formed? Explain with three examples?

Q.24 a. Define yield. How do we calculate the percentage yield of a chemical reaction?

b. What are the factors which are mostly responsible for the low yield of the products in chemical reactions?

Q.25 Explain the following with reasons.

i) Law of conservation of mass has to be obeyed during stoichiometric calculations.

ii) Many chemical reactions taking place in our surrounding involve the limiting reactants.

iii) No individual neon atom in the sample of the element has a mass of 20.18 amu.

iv) One mole of H_2SO_4 should completely react with two moles of NaOH. How does Avogadro's number help to explain it.

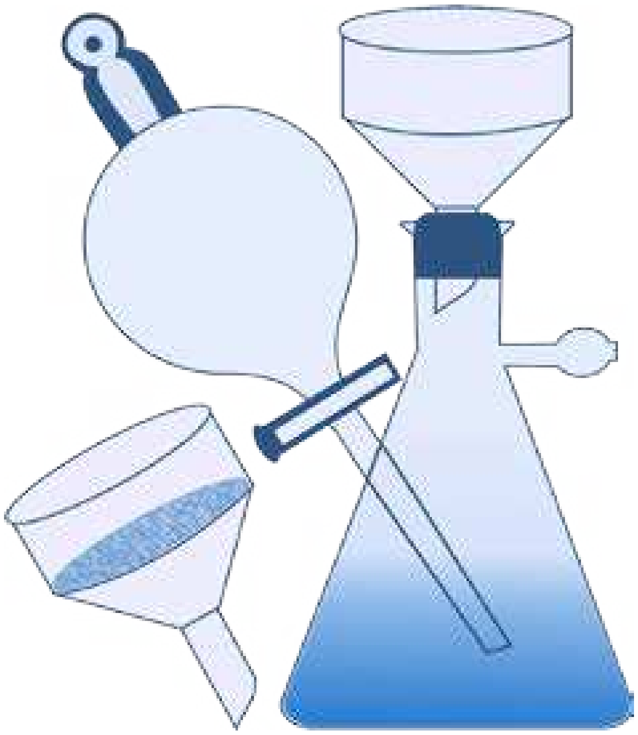
v) One mole of H_2O has two moles of bonds, three moles of atoms, ten moles of electrons and twenty eight moles of the total fundamental particles present in it.

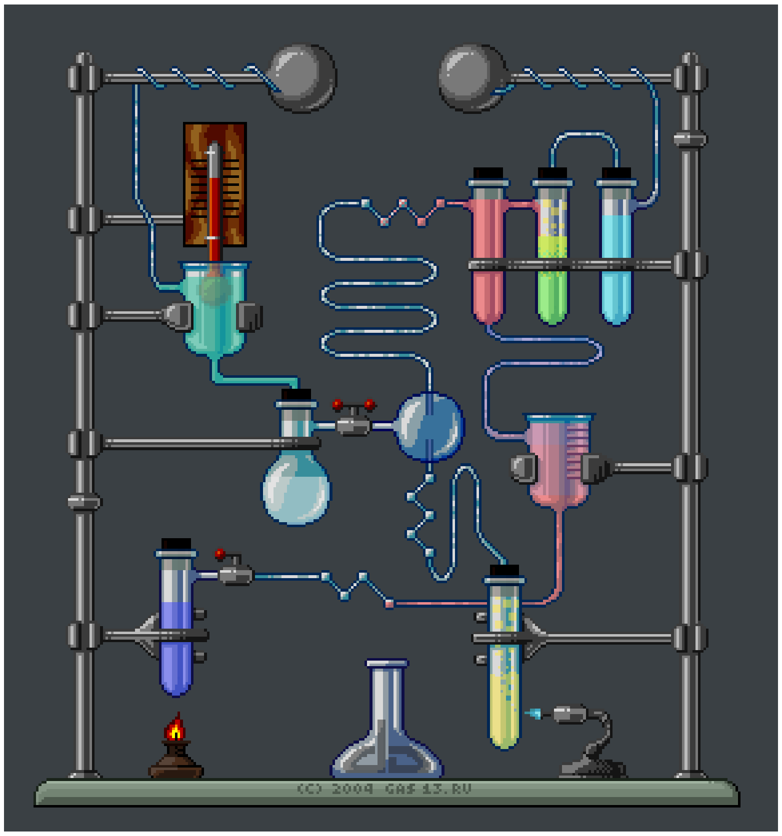
vi) N_2 and CO have the same number of electrons, protons and neutrons.

CHAPTER

2

EXPERIMENTAL TECHNIQUES IN CHEMISTRY





Animation 2.1 :Basic Concepts
Source & Credit: chem.ucsb

Analytical chemistry is the science of chemical characterization. A complete chemical characterization of a compound must include both qualitative and quantitative analyses. In qualitative analysis, the chemist is concerned with the detection or identification of the elements present in a compound. Whereas in quantitative analysis, the relative amounts of the elements are determined. A complete quantitative determination generally consists of four major steps (i) Obtaining a sample for analysis (ii) Separation of the desired constituent (iii) Measurement, and calculation of results (iv) Drawing conclusion from the analysis. In this chapter, we will restrict ourselves to only important techniques of separation. The students will practice these techniques during their laboratory work whereas their theoretical treatment is given here.

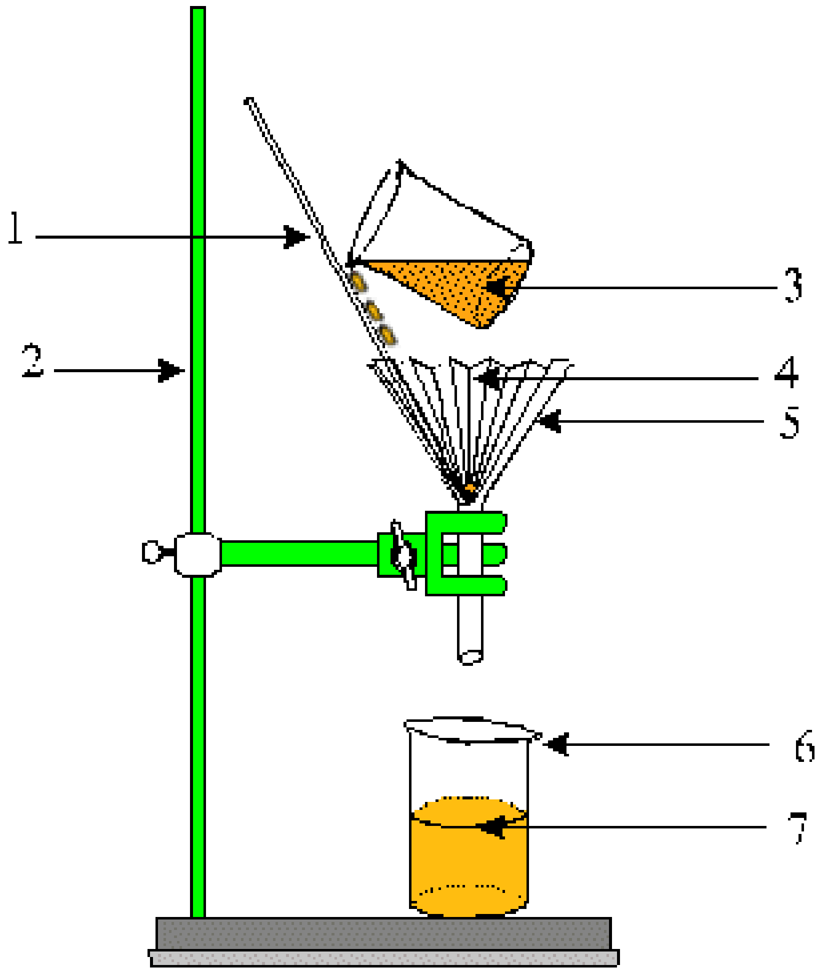
2.1 FILTRATION

The process of filtration is used to separate insoluble particles from liquids. It can be performed with several types of filter media. Nature of the precipitate and other factors dictate which filter medium must be used. The most convenient ways of filtration are either through a filter paper or through a filter crucible.

Animation 2.2: Filtration Assembly
Source & Credit:eLearn.punajb

2.1.1 Filtration Through Filter Paper

Filtration by a glass funnel and filter paper is usually a slow process. As the mixture is poured onto the filter paper, the solvent (water) passes through leaving behind the suspended particles on the filter paper. Filter papers are available in a variety of porosites (pore sizes) . Which pore size is to be used, depends upon the size of particles in the precipitate. The filter paper should be large enough so that it is one-fourth to one-half full of precipitate at the end of filtration. The funnel should, in turn, be large enough for its rim to extend 1 to 2 cm above the top circumference of the paper. If the process of filtration is to run smoothly, the stem of the funnel should remain continuously full of liquid as long as there is liquid in the conical portion.



Animation 2.3: filtration
Source & Credit:shermanqmatrangas

The stem of the funnel should be several inches long so that it can extend a few centimeters down into the receiving beaker, and the tip should touch the side of the beaker. In this way, the filtrate runs down the side of beaker without splashing. A complete filter paper assembly is shown in Fig(2.1).

Folding of Filter Paper

The folding of filter paper is important and the following points should be kept in mind. The paper should be folded twice. The first fold should be along the diameter of the paper.The second fold should be such that edges do not quite match.

The paper should be opened on the slightly larger section. This provides a cone with three fold thickness halfway around and one thickness the other halfway around, and an apex angle very slightly greater than 60 degrees.

The paper may then be inserted into 60 degree funnel, moistened with water and firmly pressed down. The filtering operation could be very time consuming if it were not aided by a gentle suction as liquid passes through the stem. This suction cannot develop unless the paper fits tightly all around its upper circumference.

Fig. (2.1)Filtration assembly

Fluted Filter Paper

The rate of filtration through conical funnel can be considerably increased using a **Fluted Filter Paper.** For preparation of such a paper ordinary filter paper is folded in such a way that a fan like arrangement with alternate elevations and depressions at various folds is obtained Fig (2.2).

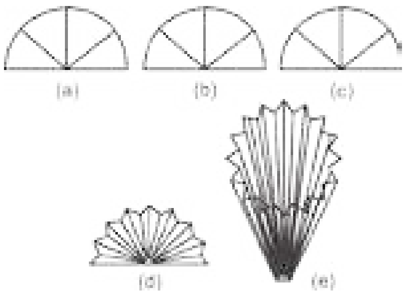


Fig. (2.2) Fluted filter paper

2.1.2 Filtration Through Filter Crucibles

Another convenient way to filter a precipitate is by suction through a crucible. Two types of crucibles are generally used.

Gooch Crucible

It is made of porcelain having a perforated bottom which is covered with paper pulp or a filter paper cut to its size Fig (2.3 a). Quick filtration can be done by placing the Gooch crucible in a suction filtering apparatus. It is useful for the filtration of precipitates, which need to be ignited at high temperature. If its perforations are covered with asbestos mat then it may be used to filter solutions that react with paper e.g. concentrated HCl and $KMnO_4$ solutions.

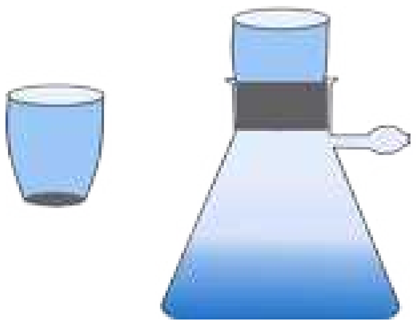


Fig. (2.3a) Gooch Crucible with filtering apparatus

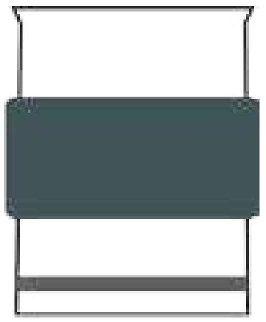


Fig. (2.3b) Sintered glass Crucible

Sintered glass crucible

Sintered glass crucible is a glass crucible with a porous glass disc sealed into the bottom. It is very convenient to use because no preparation is needed as with the Gooch crucible Fig (2.3b)

2.2 CRYSTALLIZATION

Crystallization is the removal of a solid from solution by increasing its concentration above the saturation point in such a manner that the excess solid separates out in the form of crystals.

The preparation of a chemical compound usually affords a crude product and there is a need to purify it by crystallization from a suitable solvent. The basic principle of crystallization is the fact that the solute should be soluble in a suitable solvent at high temperature and the excess amount of the solute is thrown out as crystals when it is cooled. The process of crystallization involves the following steps.

Animation 2.4: crystilization
Source & Credit: evilforalltime

2.2.1 Choice of a Solvent

The solvent is chosen on hit and trial basis and it is necessary to try a number of solvents before arriving at a conclusion. An ideal solvent should have the following features.

i. It should dissolve a large amount of the substance at its boiling point and only a small amount at the room temperature.
ii. It should not react chemically with the solute.
iii. It should either not dissolve the impurities or the impurities should not crystallize from it along with the solute.
iv. On cooling it should deposit well-formed crystals of the pure compound.
v. It should be inexpensive.
vi. It should be safe to use and should be easily removable.

The solvents which are mostly used for crystallization are, water, rectified spirit (95% ethanol), absolute ethanol, diethyl ether, acetone, chloroform, carbon tetrachloride, acetic acid and petroleum ether. If none of the solvents is found suitable for crystallization, a combination of two or more miscible solvents may be employed. If the solvent is inflammable then precaution should be taken while heating the solution so that it does not catch fire. In such cases, water bath is used for heating purpose.

2.2.2 Preparation of the Saturated Solution

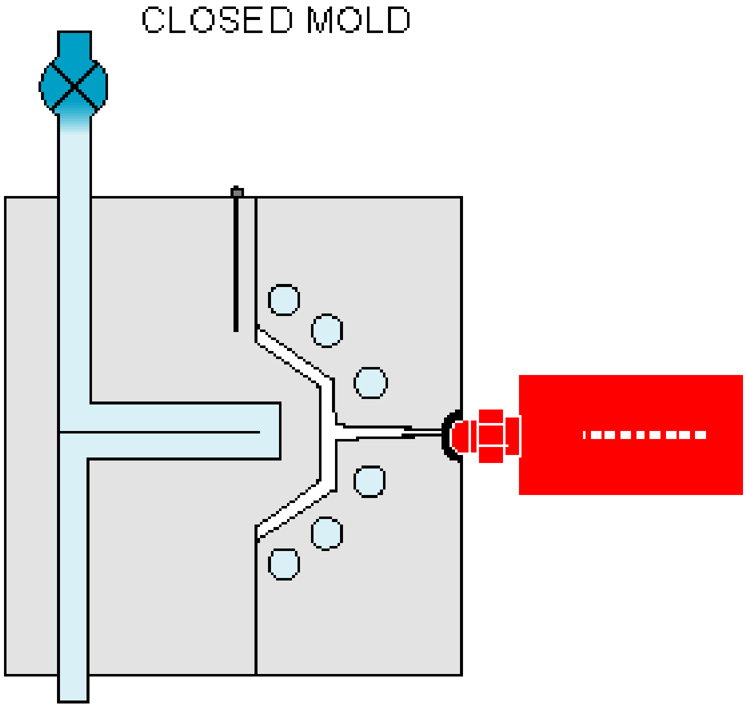
After selecting a suitable solvent, the substance is then dissolved in a minimum amount of solvent and is heated directly or on a water bath with constant stirring. Add more solvent to the boiling solution if necessary until all the solute has dissolved.

2.2.3 Filtration

The insoluble impurities in the saturated solution are then removed by filtering the hot saturated solution, through a normal or a fluted filter paper. This avoids the premature crystallization of the solute on the filter paper or in the funnel stem. If necessary hot water funnel should be used for this purpose.

2.2.4 Cooling

The hot filtered solution is then cooled at a moderate rate so that medium sized crystals are formed. Slow cooling yields bigger crystals which are likely to include considerable amount of solvent carrying impurities with it and complicating the drying process.



Animation 2.5: Cooling
Source & Credit: Pulsecooling

2.2.5 Collecting the Crystals

When the crystallization is complete, the mixture of crystals and the mother liquor is filtered through a Gooch crucible using a vacuum pump. Full suction is applied in order to drain the mother-liquor from the crystals as effectively as possible. When the filter cake is rigid enough it is pressed firmly with a cork to drain the left-over liquid. The crystals are then washed with a small portion of cold solvent and the process is repeated several times. The mother liquor is quite often concentrated by evaporation and cooled to obtain a fresh crop of crystals. The process of crystallization appears to be very simple yet the success of operation lies in the amount or the percentage of crystallized product obtained from the crude substance.

2.2.6 Drying of the Crystallized Substance

Pressing it between several folds of filter papers and repeating the process several times dries the crystallized substance. This process has the disadvantage that the crystals are crushed to a fine powder and sometimes the fibres of filter paper contaminate the product. Alternatively,the crystals are dried in an oven provided the substance does not melt or decompose on heating at 100° C.
A safe and reliable method of drying crystals is through a vacuum desiccator. In this process the crystals are spread over a watch glass and kept in a vacuum desiccator for several hours. The drying agents used in a desiccator are $CaCl_2$, silica gel or phosphorus pentaoxide.

2.2.7 Decolourization of Undesirable Colours

Sometimes during the preparation of a crude substance, the colouring matter or resinous products affect the appearance of product and it may appear coloured. Such impurities are conveniently removed by boiling the substance in the solvent with the sufficient quantity of finely powdered animal charcoal and then filtering the hot solution.

The coloured impurities are adsorbed by animal charcoal and the pure decolourized substance crystallizes out from the filtrate on cooling.

2.3 SUBLIMATION

It is a process in which a solid, when heated, vapourizes directly without passing through the liquid phase and these vapours can be condensed to form the solid again. It is frequently used to purify a solid. Examples of such solids are ammonium chloride, iodine, naphthalene, benzoic acid, etc. To carry out the process, the substance is taken in a watch-glass covered with an inverted funnel. The substance is then heated slowly over a sand-bath and the funnel is cooled with wet cotton. The pure solid deposits on the inner side of the funnel Fig (2.4).

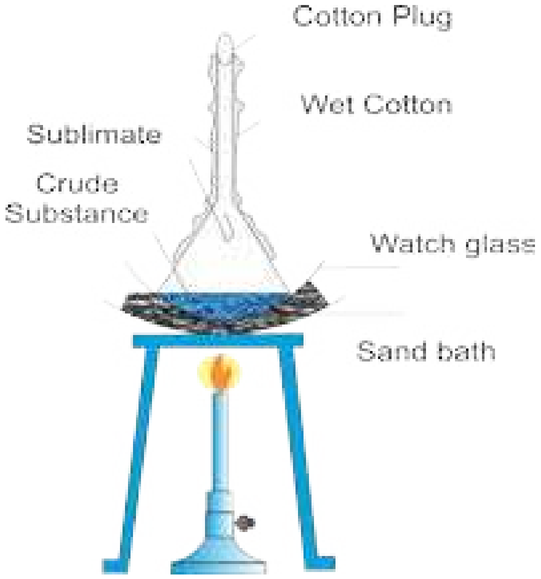
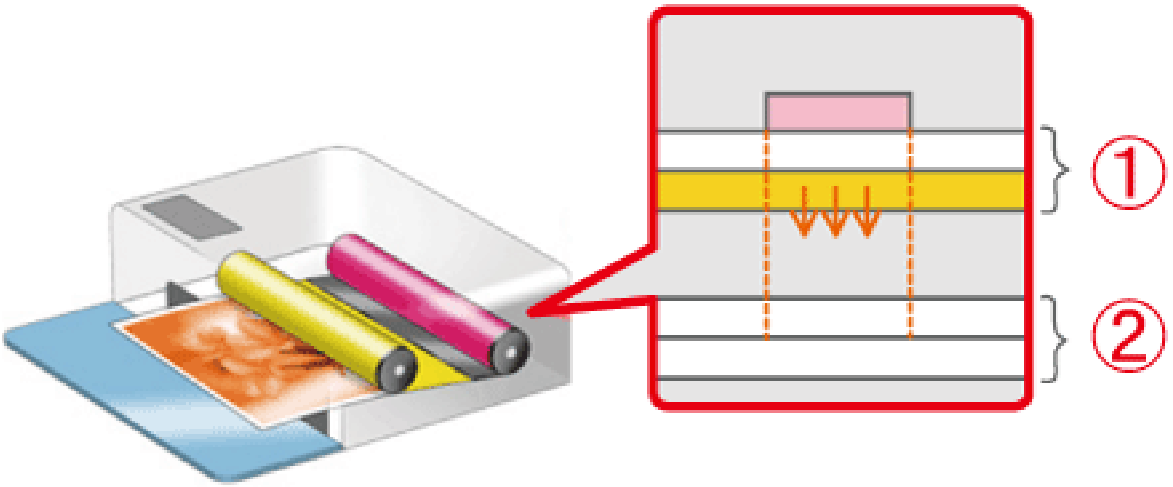


Fig (2.4) SUBLIMATION

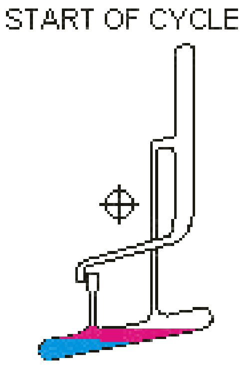


Animation 2.6: SUBLIMATION
Source & Credit: support-th

2.4 SOLVENT EXTRACTION

Solvent extraction is an important technique in chemical analysis. According to this technique a solute can be separated from a solution by shaking the solution with a solvent in which the solute is more soluble and the added solvent does not mix with the solution. Usually it is done by placing the solution and the second liquid into a separating funnel Fig (2.5). The funnel is stoppered and the two liquids are shaken together.

The most common laboratory example of solvent extraction is ether extraction. This is used to separate the products of organic synthesis from water. In a typical organic synthesis, the aqueous solution containing the organic product is shaken up with ether in a separating funnel and allowed to separate.



Animation 2.7: Solvent extraction
Source & Credit: chem

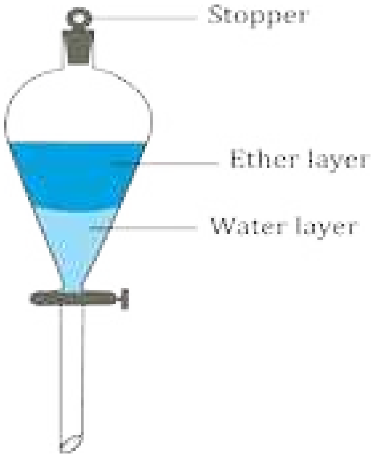


Fig.(2.5) Separating funnel

The inorganic impurities remain in aqueous phase whereas the organic compound goes to the ether layer. The ether layer is separated and the organic product is obtained by evaporating the ether. Repeated extractions using small portions of solvent (ether) are more efficient than using a single but larger volume of solvent. The technique is particularly useful when the product is volatile or thermally unstable.

Solvent extraction is an equilibrium process and follows the distribution law or partition law. This law states that a solute distributes itself between two immiscible liquids in a constant ratio of concentrations irrespective of the amount of solute added.

The law is based on experimental evidence. Consider, for example, the distribution of iodine between two immiscible solvents, water in the presence of KI and carbon tetrachloride. Iodine reacts with iodide ion to produce tri-iodide ion in a reversible reaction.

The following dynamic equilibrium is established.

$$I_2 + I^-(aq) \rightleftharpoons I_3^-(aq)$$

soluble in CCl_4 soluble in water

At this point the rate at which iodine passes from CCl_4 to water equals the rate at which it passes from water to CCl_4.

So, if we add CCl_4 to an aqueous solution of I_3^- ions, the iodine will transfer from the aqueous layer into the organic layer. As a result, the brown colour of the tri-iodide ions fades and the purple colour of free iodine molecules appears in organic phase. To achieve a good separation, the two liquids are gently shaken to increase their area of contact and improve the chances of transferring iodine molecules. No matter how much iodine is used, the ratio of the final concentrations at equilibrium is constant. The constant is called distribution coefficient, K and is given by

$$K=[I_2(CCl_4)]/[I^-_{3(aq)}]$$

2.5 CHROMATOGRAPHY

Another important application of the distribution phenomenon is chromatography. The word chromatography originates from the Greek word "Khromatos" meaning colour writing.

Chromatography is a method used primarily for the separation of a sample of mixture. It involves the distribution of a solute between a stationary phase and a mobile phase. The stationary phase may be a solid or a liquid supported as a thin film on the surface of an inert solid. The mobile phase flowing over the surface of the stationary phase may be a gas or a liquid.

In chromatography, substances are separated due to their relative affinities for the stationary and mobile phases. The distribution of the components of a mixture between the two phases is governed by distribution coefficient K.

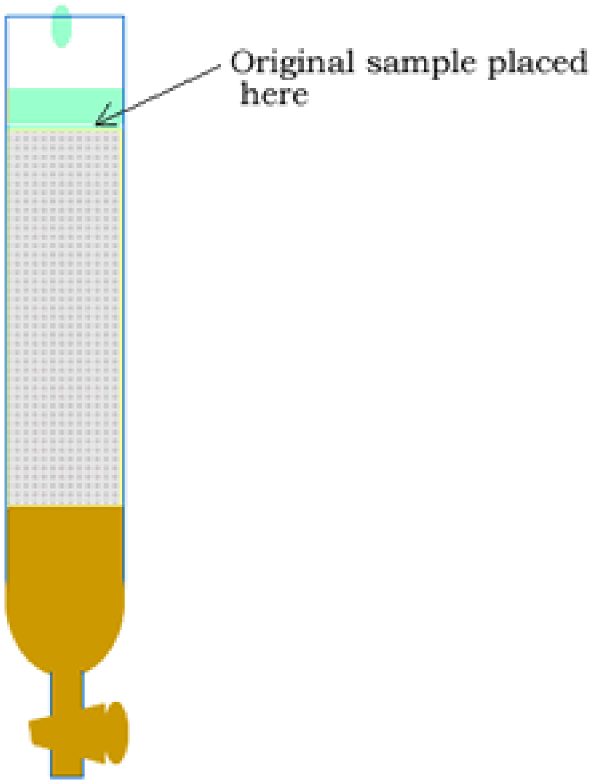
$$K= \frac{\text{Concentration of a component in the moving phase}}{\text{Concentration of that component in the Stationary phase}}$$

The component of a mixture with a small value of K mostly remains in the stationary phase as the moving phase flows over it. The component with a greater value of K remains largely dissolved in the mobile phase and passes over the stationary phase quickly.

Chromatography in which the stationary phase is a solid, is classified as adsorption chromatography. In this type, a substance leaves the mobile phase to become adsorbed on the surface of the solid phase.

Chromatography in which the stationary phase is a liquid, is called partition chromatography. In this type, the substances being separated are distributed throughout both the stationary and mobile phases.

There are various techniques of chromatography. One such technique namely paper chromatography is discussed below.



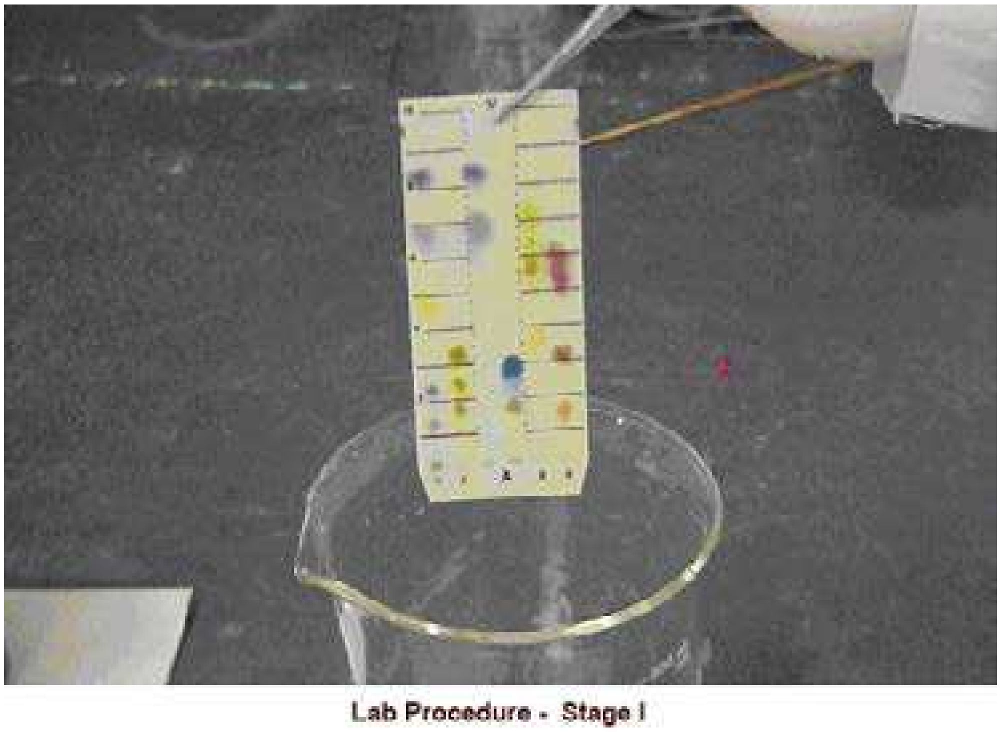
Animation 2.8:Chromatography
Source & Credit: Support-th

2.5.1 PAPER CHROMATOGRAPHY

It is a technique of partition chromatography. Here the stationary phase is a liquid (say H_2O) adsorbed on paper. The adsorbed water behaves as an immiscible liquid towards the mobile phase, which passes over the paper. The mobile phase is usually an organic liquid.

There are three common ways of carrying out paper chromatography namely (i) ascending (ii) descending (iii) radial/circular. Only the ascending type will be discussed here. In this technique the solvent is in a pool at the bottom of a vessel in which the paper is supported and the solvent travels upwards by capillary action.

A solvent mixture, specially composed in accordance with the sample to be separated, is poured into the chromatographic tank Fig (2.6). Cover the tank to homogenise its inner atmosphere. Take about 20 cm strip of Whatmann's chromatographic paper No.1 and draw on it a thin pencil line about 2.5 cm from one end. Spot a point, on the pencil line, with the sample mixture solution. To facilitate identification of the components of the mixture, spots of the known compounds may also be placed alongside.



Animation 2.9: PAPER CHROMATOGRAPHY
Source & Credit: chem

When the spots have dried, suspend the paper with clips so that the impregnated end dips into solvent mixture to a depth of 5-6 mm. Cover the tank. As the solvent front passes the spots, the solutes begin to move upward. The rate at which they move depends on their distribution coefficients. When the solvent front has risen to about 3/4 th of the length of the paper, remove the strip, mark the solvent front with a pencil and allow the strip to dry.

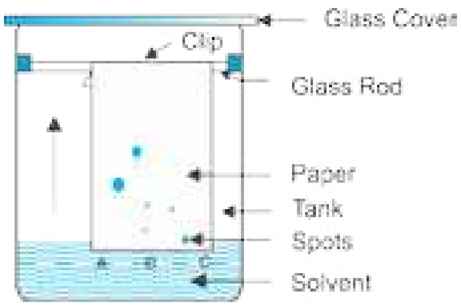


Fig. (2.6) Paper chromatography

Once the paper is dried, the pattern on the paper is called a chromatogram. The different components of the mixture, if coloured, can visually be identified. If colourless, the chromatogram has to be developed by chemical methods or physical techniques used to identify the spots. Each component has a specific retardation factor called R_f value. The R_f value is related to its distribution coefficient and is given by:

$$R_f = \frac{\text{Distance travelled by a component from the original spot}}{\text{Distance travelled by solvent from the original spot}}$$

With reference to Fig 2.7 the chromatogram shows that the sample A contains both components B and C. The R_f values for B and C are given by:

$$R_f(B) = x/y$$
$$R_f(C) = z/y$$

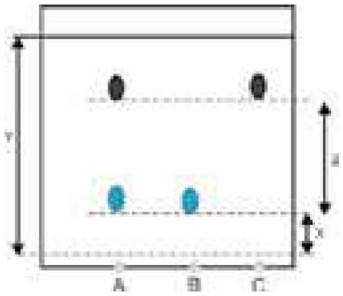
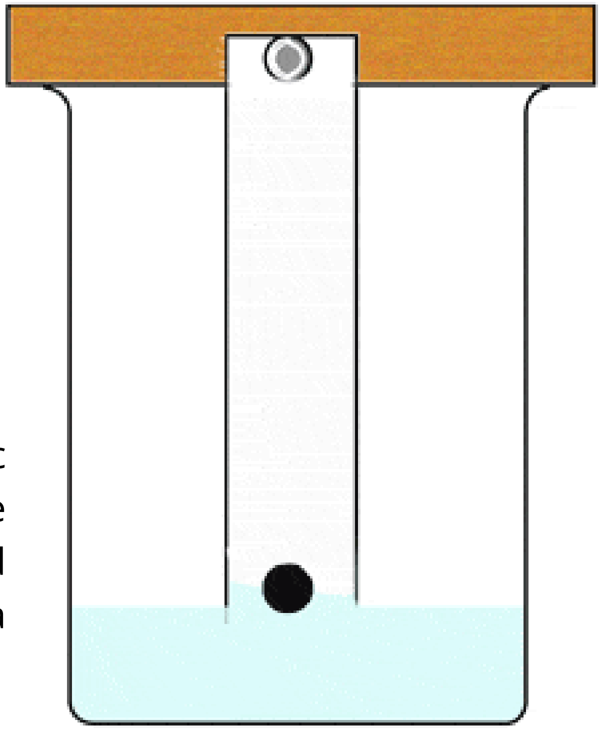


Fig. (2.7) Chromatogram

Uses of Chromatography

The techniques of chromatography are very useful in organic synthesis for separation, isolation and purification of the products. They are equally important in qualitative and quantitative analyses and for determination of the purity of a substance.



Animation 2.10: Uses of Chromatography
Source & Credit: Dynamicscience

KEY POINTS

1. A complete characterization of a compound must include both qualitative and quantitative analyses.
2. A complete quantitative analysis of a compound generally involves four major steps.
3. The process of filtration is used to separate insoluble particles from liquids and it can be performed with several types of filter media.
4. If the process of filtration with the filter paper is to run smoothly, the stem of the funnel should remain continuously full of liquid as long as there is liquid in the conical portion.
5. The filtering operation with the filter paper could be very time consuming if it were not aided by a gentle suction as liquid passes through the stem. This suction cannot develop unless the paper fits tightly all around the upper circumference of the funnel.
6. The rate of filtration can be considerably increased using a fluted filter paper.
7. A solid compound is purified by crystallization from a suitable solvent. A solvent for crystallization should be able to dissolve the solute at high temperature and the maximum amount of the solute should be thrown out by the solvent when the solution is cooled. The process of crystallization involves many steps.
8. The process of sublimation involves converting a solid directly into vapours and these vapours are then condensed to form solid again. It is frequently used to purify a solid.
9. Solvent extraction technique involves the separation of a solute from a solution by shaking it with an immiscible solvent in which the solute is more soluble. The technique is mostly applied to separate organic compounds from water.
10. Repeated extractions using small portions of solvent are more efficient than using a single extraction but large volume of solvent.
11. Solvent extraction is an equilibrium process and it is controlled by distribution law. The technique is particularly useful when the compound to be separated is volatile or thermally unstable.
12. Chromatography is a technique used for separating the components of a mixture. These components are distributed between a stationary and a mobile phase. The stationary phase may be a solid or a liquid supported on a solid. It adsorbs the mixture under separation. The mobile phase may be a liquid or a gas and while passing over the stationary phase, competes with it for the constituents of the mixture.
13. In paper chromatography, the stationary phase is water adsorbed on paper. The mobile phase is usually an organic liquid.
14. The techniques of chromatography are very useful in organic synthesis for separation, isolation and purification of the products.

EXERCISE

Q.1 Multiple choice questions.

(i) A filtration process could be very time consuming if it were not aided by a gentle suction which is developed:
- (a) if the paper covers the funnel upto its circumference.
- (b) if the paper has got small sized pores in it.
- (c) if the stem of the funnel is large so that it dips into the filtrate.
- (d) if the paper fits tightly.

(ii) During the process of crystallization, the hot saturated solution:
- (a) is cooled very slowly to get large sized crystals.
- (b) is cooled at a moderate rate to get medium sized crystals.
- (c) is evaporated to get the crystals of the product.
- (d) is mixed with an immiscible liquid to get the pure crystals of the product.

(iii) Solvent extraction is an equilibrium process and it is controlled by.
- (a) law of mass action. (b) the amount of solvent used.
- (c) distribution law. (d) the amount of solute.

(iv) Solvent extraction method is a particularly useful technique for separation when the product to be separated is:
- (a) non-volatile or thermally unstable. (b) volatile or thermally stable.
- (c) non-volatile or thermally stable. (d) volatile or thermally unstable.

(v) The comparative rates at which the solutes move in paper chromatography, depend on:
- (a) the size of paper (b) R values Of solutes.
- (c) temperature of the experiment. (d) size of the chromatographic tank used.

Fill in the blanks.

1. A complete chemical characterization of a compound must include_________.
2. During filtration the tip of the stem of the funnel should touch the side of the beaker to avoid_________.
3. A fluted filter paper is used to_________ the process of filtration.
4. A solvent used for crystallization is required to dissolve of the substance at its boiling point and_______ at the room temperature.
5. Repeated solvent extractions using small portions of solvent are_________________ than using a single extraction with larger volume of the solvent.

Q.3 Tick the correct sentences. If the sentence is incorrect, write the correct statements.

(i) A qualitative analysis involves the identification of elements present in a compound.

(ii) If the process of filtration is to run smoothly, the stem of the funnel should remain empty.

(iii)If none of the solvents is found suitable for crystallization a combination of two or more immiscible solvents may be used.

(iv) A solute distributes itself between two immiscible liquids in a constant ratio of concentrations depending upon the amount of solvent added.

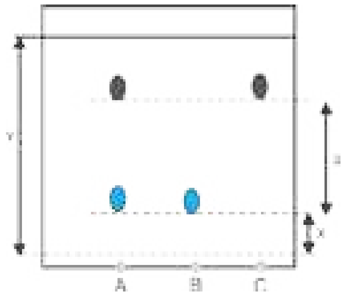
(v) Paper chroma tography is a technique of partition chromatography.

Q.4 Why is there a need to crystallize the crude product?

Q.5 A water insoluble organic compound aspirin is prepared by the reaction of salicylic acid with a mixture of acetic acid and acetic anhydride. How will you separate the product from the reaction mixture?

Q.6 A solid organic compound is soluble in water as well as in chloroform. During its preparation, it remains in aqueous layer. Describe a method to obtain from this layer.

Q.7 The following figure shows a developed chromatogram on paper with five spots.



(i) Unknown mixture X
(ii) Sample A
(iii) Sample B
(iv) Sample C
(v) Sample D

Find out (i) the composition of unknown mixture X

(ii) which sample is impure and what is its composition.

Q.8 In solvent extraction technique, why repeated extraction using small portions of solvent are more efficient than using a single extraction but larger volume of solvent?

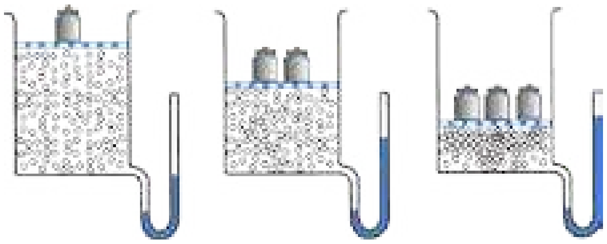
Q.9 Write down the main characteristics of a solvent selected for crystallization of a compound.

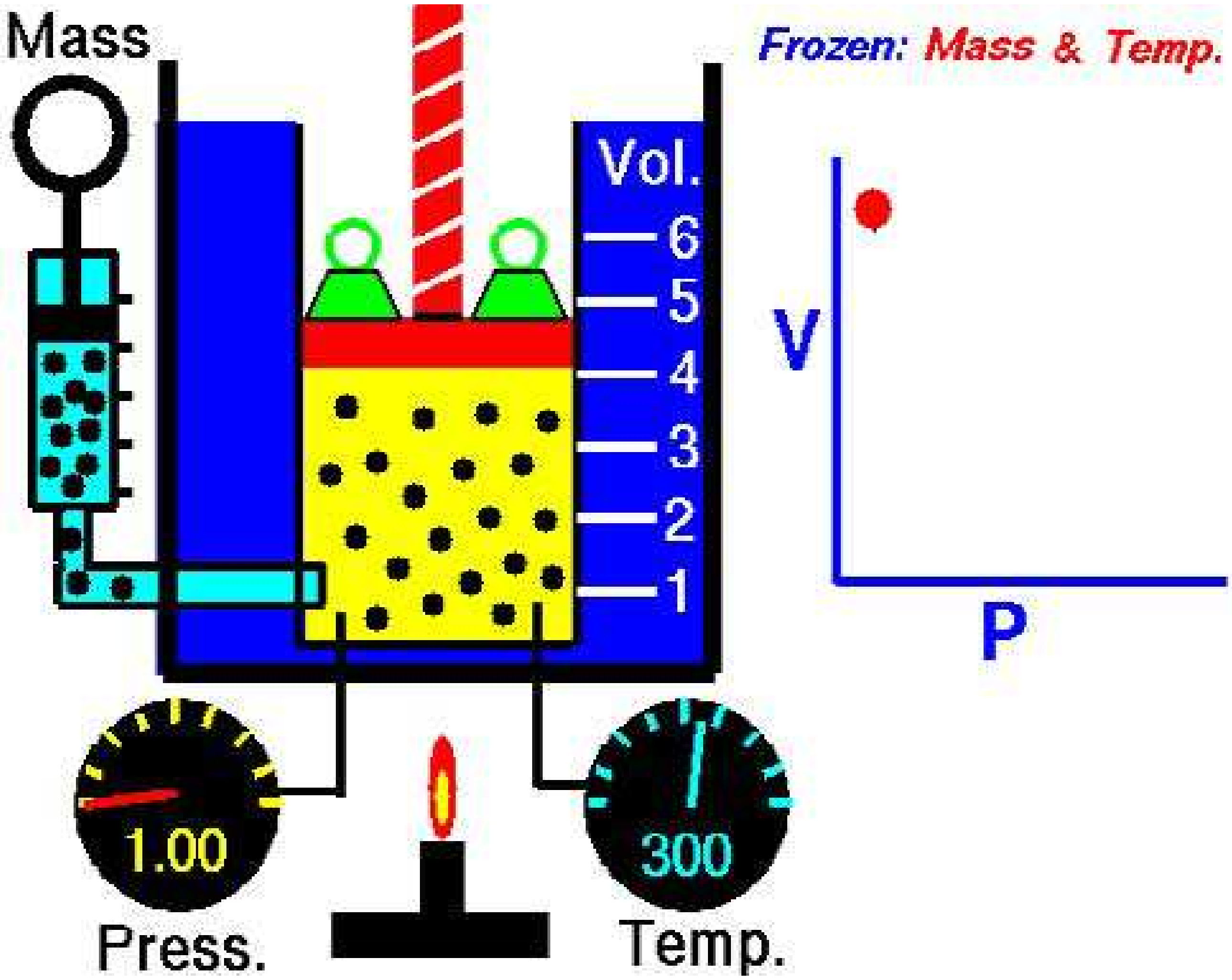
Q.10 You have been provided with a mixture containing three inks with different colours. Write down the procedure to separate the mixture with the help of paper chromatography.

CHAPTER

3

GASES





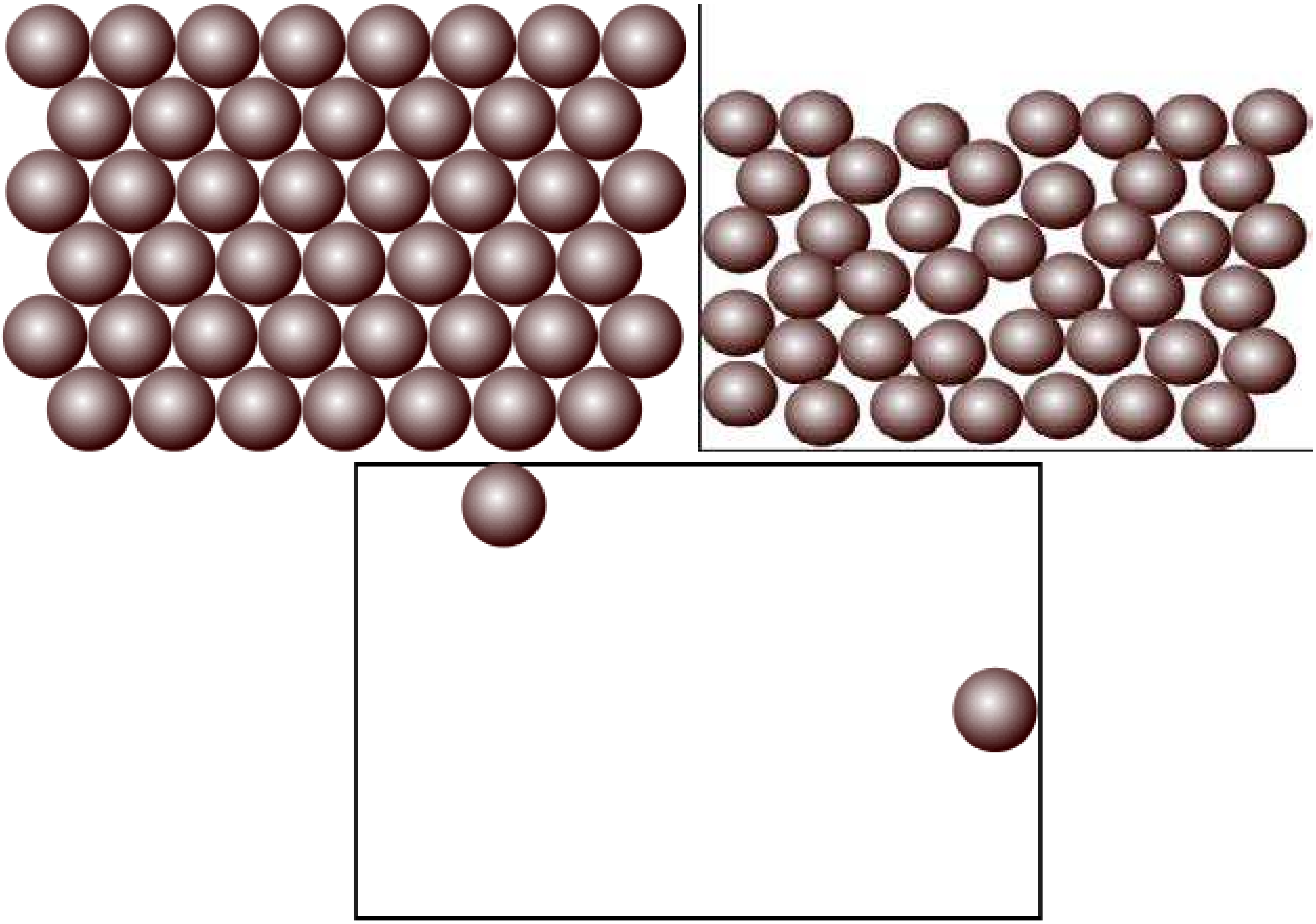
Animation 3.1: Boyle's Law
Source & credit: wikipedia

3.1 STATES OF MATTER

Matter exists in four states i.e., solid, liquid, gas and plasma. The simplest form of matter is the gaseous state and most of matter around us is in the solid state.

Liquids are less common than solids, gases and plasmas. The reason is that the liquid state of any substance can exist only within a relatively narrow range of temperature and pressure.

Let us look at the general properties of gases, liquids and solids. Kinetic molecular theory of gases can help us understand their properties.



Animation 3.2.: States of Matter

Source & Credit: knockhardy

3.1.1 Properties of Gases

1. Gases don’t have a definite volume and occupy all the available space. The volume of a gas is the volume of the container.
2. They don’t have a definite shape and take the shape of the container just like liquids.
3. Due to low densities of gases, as compared to those of liquids and solids, the gases bubble through liquids and tend to rise up.
4. Gases can diffuse and effuse. This property is negligible in solids but operates in liquids as well.
5. Gases can be compressed by applying a pressure because there are large empty spaces between their molecules.
6. Gases can expand on heating or by increasing the available volume. Liquids and solids, on the other hand, do not show an appreciable increase in volume when they are heated.
7. When sudden expansion of gases occurs cooling takes place, it is called Joule Thomson effect.
8. Molecules of gases are in a constant state of random motion They can exert a certain pressure on the walls of the container and this pressure is due to the number of collisions.
9. The intermolecular forces in gases are very weak.

3.1.2 Properties of Liquids

6. Liquids don’t have a definite shape but have a definite volume. Unlike solids they adopt the shape of the container.
7. Molecules of liquids are in a constant state of motion. The evaporation and diffusion of liquid molecules is due to this motion.
8. The densities of liquids are much greater than those of gases but are close to those of solids.
9. The spaces among the molecules of liquids are negligible just like solids.
10. The intermolecular attractive forces in liquids are intermediate between gases and solids. The melting and boiling points of gases, liquids and solids depend upon the strength of such forces.
11. Molecules o f liquids possess kinetic energy due to their motion. Liquids can be converted into solids on cooling i.e., by decreasing their kinetic energy. Molecules of liquids collide among themselves and exchange energy but those of solids can not do so.

3.1.3 Properties of Solids

1. The particles present in solid substances are very close to each other and they are tightly packed. Due to this reason solids are non-compressible and they cannot diffuse into each other.
2. There are strong attractive forces in solids which hold the particles together firmly and for this reason solids have definite shape and volume.
3. The solid particles possess only vibrational motion.

3.1.4 Units of Pressure:

The pressure of air that can support 760 mmHg column at sea level, is called one atmosphere. It is the force exerted by 760mm or 76cm long column of mercury on an area of $1cm^2$ at 0°C.It is the average pressure of atmosphere at sea level 1mmHg=1torr. The S.I. unit of pressure is expressed in Nm^{-2}. One atmospheric pressure i.e 760 torr is equal to 101325 Nm^{-2}.
1pascal=1 Nm^{-2}. So, 760 torr = 101325Pa = 101.325 kilopascals (kpa is another unit of pressure)
The unit pounds per square inch (psi) is used most commonly in engineering work, and 1 atm = 760 torr=14.7 pounds $inch^{-2}$. The unit millibar is commonly used by meteorologists.

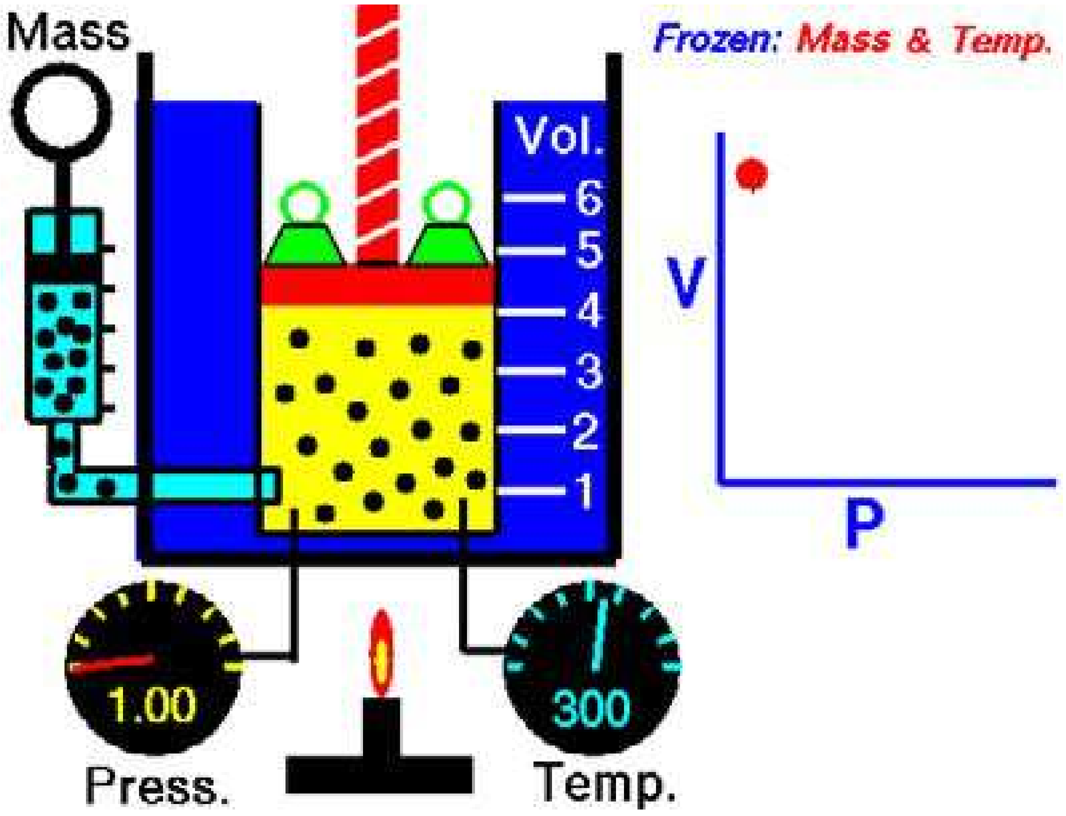
3.2 GAS LAWS

It is a matter of common observation that when external conditions of temperature and pressure are changed, the volume of a given quantity of all gases is affected. This effect is nearly the same irrespective of the nature of the gas. So gases show a uniform behaviour towards the external conditions. The gas laws describe this uniform behaviour of gases. The relationships between volume of a given amount of gas and the prevailing conditions of temperature and pressure are called the gas laws. Different scientists, like Boyle, Charles, Graham and Dalton have given their laws relating to the properties of gases.

3.2.1 Boyle's Law

In Boyle's law the pressure and volume are variables while the temperature and quantity of a gas remains constant. Boyle's law is stated as follows:-

The volume of a given mass of a gas at constant temperature is inversely proportional to the pressure applied to the gas.



Animation 3.3: Boyle's Law
Source & credit: wikipedia

So

$V \alpha 1/P$ (when the temperature and number of moles are constant)

or $V=k/p$

$PV = k$ (when T and n are constant) (1)

'k' is proportionality constant. The value of k is different for the different amounts of the same gas. According to the equation (1), Boyle's law can also be defined as **The product of pressure and volume of a fixed amount of a gas at constant temperature is a constant quantity.**

So $P_1V_1 = k$ and $P_2V_2 = k$

Hence $P_1V_1 = P_2V_2$

P_1V_1 are the initial values of pressure and volume, while P_2V_2 are the final values of pressure and volume.

3.2.2 Experimental Verification of Boyle's Law

The following diagram Fig. (3.1) indicates that at constant temperature say at 25^{0}C,the volume of a given quantity of a gas is reduced in proportion to the increase in pressure. Let us take a gas in a cylinder having a moveable piston.

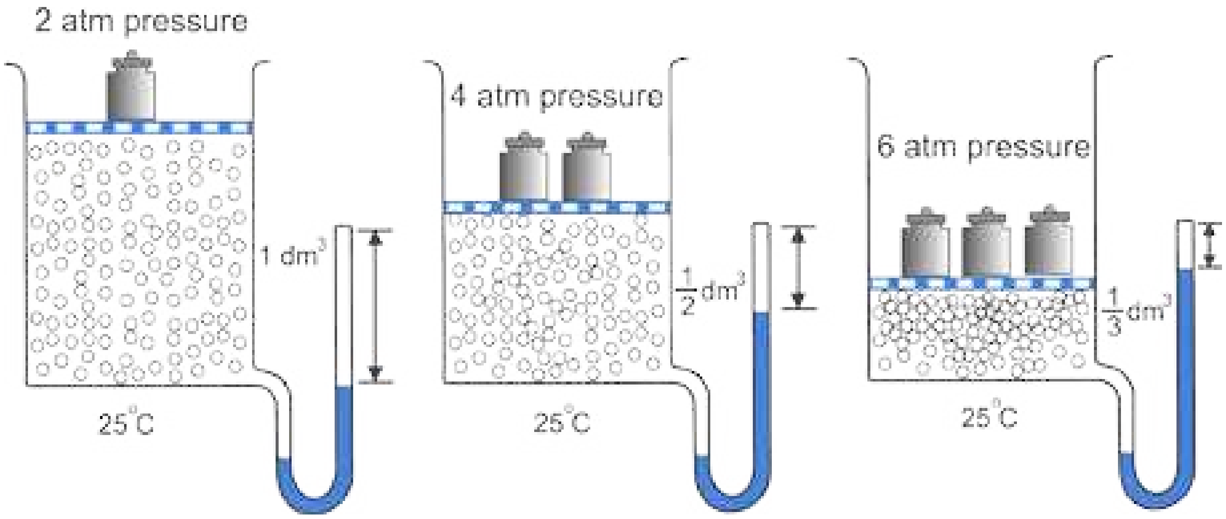


Fig (3.1) Verification of Boyle's Law

The cylinder is also attached with a manometer to read the pressure of the gas directly. Let the initial volume of gas is 1 dm^3 and its pressure is 2 atmospheres when the piston has one weight on it. When the piston is pressed twice with the help of two equal weights, the pressure becomes four atmospheres.

Similarly, when the piston is loaded with a mass three times greater, then the pressure becomes six atmospheres. The initial volume of the gas at two atmospheres is 1 dm^3 it is reduced to 1/2 dm^3 and then 1/3 dm^3 with increase of weights, respectively Fig (3.1).

$$P_1V_1 = 2 \text{ atm} \times 1 \text{ dm}^3 = 2 \text{ dm}^3 \text{ atm} = k$$
$$P_2V_2 = 4 \text{ atm} \times 1/2 \text{ dm}^3 = 2 \text{ dm}^3 \text{ atm} = k$$
$$P_3V_3 = 6 \text{ atm} \times 1/3 \text{ dm}^3 = 2 \text{ dm}^3 \text{ atm} = k$$

Hence Boyle's law is verified.

The value of k will remain the same for the same quantity of a gas at the same temperature.

Example 1

A gas having a volume of 10 dm^3 is enclosed in a vessel at 0^0C and the pressure is 2.5 atmospheres. This gas is allowed to expand until the new pressure is 2 atmospheres. What will be the new volume of this gas, if the temperature is maintained at 273 K.

Solution

Initial volume of gas (V_1) = 10 dm^3
Initial temperature (T_1) = 0^0C + 273 K = 273 K
Initial pressure (P_1) = 2.5 atm
Final pressure (P_2) = 2 atm
Final temperature (T_2) = 273 K
Final volume (V_2) = ?

Since the temperature is constant ($T_1 = T_2$) Boyle's law is applicable

$$P_1V_1 = P_2V_2 \text{ (when T and n are constant)}$$

$$V_2 = \frac{P_1V_1}{P_2}$$

$$V_2 = \frac{2.5 \text{ atm} \times 10 \text{ dm}^3}{2 \text{ atm}}$$

$$= 12.5 \text{ dm}^3 \text{ Answer}$$

3.2.3 Graphical Explanation of Boyle's Law

Let us take a particular amount of a gas at a constant temperature say 0^0C and enclose it in a cylinder having a piston in it. When the pressure of the gas is varied, its volume changes. Increase in pressure decreases the volume. If a graph is plotted between pressure on the x-axis (abscissa) and volume on the y-axis (ordinate), then a curve is obtained as shown in the Fig (3.2). This curve is called isotherm 'iso' means same, "therm" means heat. Now increase the temperature of the gas to 25°C.

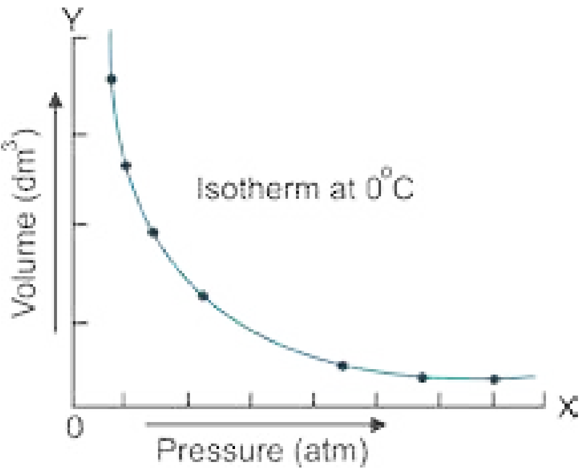


Fig (3.2) Isotherm of a gas at 0 °C.

Keep this temperature constant and again vary the pressure and volume, and plot the isotherm. It goes away from both the axes Fig (3.3). The reason is that at higher temperature, the volume of the gas has increased. Similarly, if we increase the temperature further, make it constant and plot another isotherm, it further goes away from the axis.

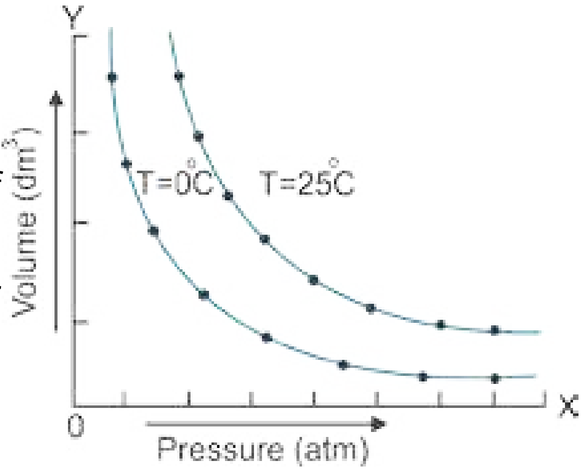


Fig (3.3) Isothermes o f a gas at different temperatures.

If a graph is plotted between 1/V on x-axis and the pressure P on the y-axis then a straight line is obtained as shown in the Fig (3.4). This shows that the pressure and inverse of volume are directly proportional to each other. This straight line will meet at the origin which means that when the pressure is very close to zero, then the volume is so high that its inverse is very close to zero.

By increasing the temperature of the same gas from T_1 to T_2 and keeping it constant, one can vary pressure and volume. The graph of this data between P and 1/V will give another straight line. This straight line at T_2 will be closer to the pressure-axis Fig (3.4).

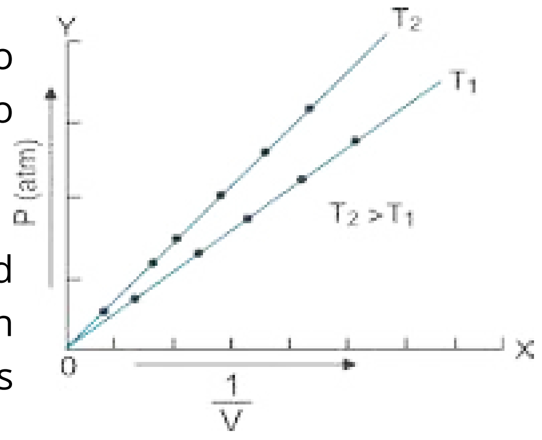


Fig (3.4) A plot between P and $\frac{1}{V}$

Now, plot a graph between pressure on x-axis and the product PV on Y-axis. A straight line parallel to the pressure axis is obtained Fig(3.5). This straight line indicates that 'k' is a constant quantity.
At higher constant temperature, the volume increase and value of product PV should increase due to increase of volume at same pressure, but PV remains constant at this new temperature and a straight line parallel to the pressure axis is obtained. This type of straight line will help us to understand the non-ideal behaviour of gases. Boyle's law is applicable only to ideal gases.

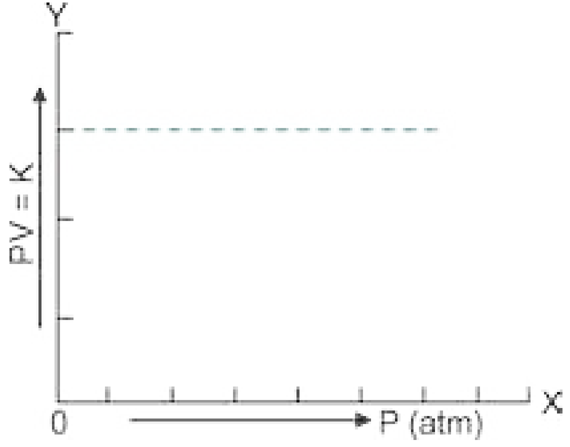


Fig (3.5) A plot between pressure and product of P V

3.2.4 Charle s 's Law

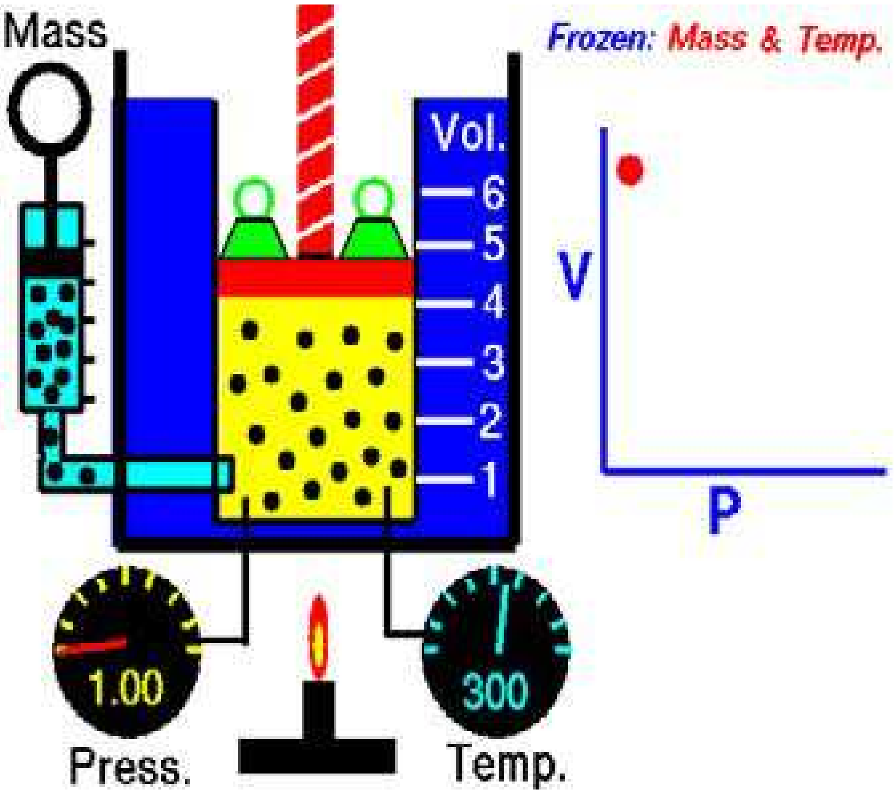
It is a quantitative relationship between temperature and volume of a gas and was given by French scientist J.

Charles in 1787. According to this law, **the volume of the given mass of a gas is directly proportional to the absolute temperature when the pressure is kept constant.**

$V \propto T$ (when pressure and number of moles are constant)

$V = kT$

$V/T = k$



Animation 3.4: Charle s 's Law
Source & Credit: docsity

If the temperature is changed from T_1 to T_2 and volume changes from V_1 to V_2, then

$V_1/T_1 = k$ and $V_2/T_2 = k$

So, **$V_1/T_1 = V_2/T_2$** **................................. (2)**

The ratio of volume to temperature remains constant for same amount of gas at same pressure.

3.2.5 Experimental Verification of Charles ‘s Law

Let us consider a certain amount of a gas enclosed in a cylinder fitted with a movable piston. The volume of the gas is **V_1** and its temperature is **T_1**. When the gas in the cylinder is heated both volume and the temperature of the gas increase.

The new values of volume and temperature are **V_2** and **T_2** respectively Fig(3.6). Experiment shows that

$$V_1/T_1 = V_2/T_2$$

Hence Charles's law is verified.

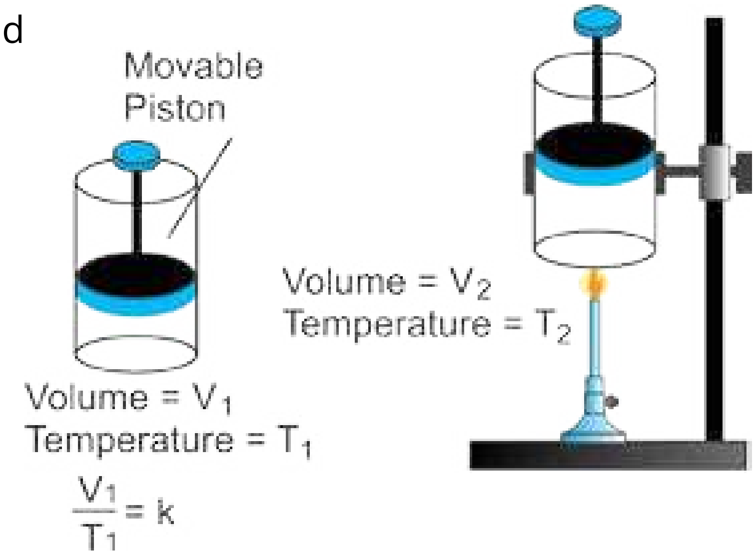


Fig (3.6) Verification of Charles's law

Example 2

250 cm^3 of hydrogen is cooled from 127°C to -27°C by maintaining the pressure constant Calculate the new volume of the gas at low temperature.

Solution

Pressure has been kept constant so this gas is obeying the Charles's law.
Initial volume (V_1) = 250 cm^3 = 0.25 dm^3
Initial temperature (T_1) = 127 °C + 273 K = 400 K
Final temperature (T_2) = -27 °C + 273K - 246 K
Final volume (V_2) = ?
According to Charles's law

$$V_1/T_1 = V_2/T_2 \text{ (when pressure and number of moles are constant)}$$

$$V_2 = \frac{V_1 x\ T_2}{T_1}$$

$$V_2 = \frac{0.25\ dm^3\ x\ 246K}{400\ K} = 0.153\ dm^3 = 153\ cm^3 \text{ Answer}$$

So by decreasing the temperature the volume of the gas has decreased at constant pressure.

3.2.6 Derivation of Absolute Zero

In order to derive absolute zero of temperature, consider the following quantitative definition of Charles's law.

At constant pressure, the volume of the given mass of a gas increases or decreases by 1/273 of its original volume at 0°C for every 1 °C rise or fall in temperature respectively.

In order to understand the above statement, look at the Table (3.1) of temperature volume data of a hypothetical gas. At 0 °C the volume of the gas taken is 546 cm^3 It is twice 273cm^3, and is being supposed for the sake of convenience of understanding. At 273 °C, the volume of the gas has doubled (1092 cm^3) and it should become practically zero at -273°C. The general equation to know the volumes of the gas at various temperatures is

$$V_t = V_o\left(1+\frac{t}{273}\right) \text{ .... (3)}$$

Where V_t = volume of gas at temperature T

V_o = Volume of gas at 0°C

t = Temperature on centigrade or celsius scale

If a gas is warmed by 1°C, it expands by $\frac{1}{273}$ of its original volume at 0°C. Since original volume is 546 cm^3 ,so, for 1°C rise in temperature, 2 cm^3 increase in volume will take place. 2cm^3 is the $\frac{1}{273}$ of 546 cm^3. Similarly, for 100 °C rise in temperature, a change of 200 cm^3 will take place. The Table (3.1) shows that the volume does not increase corresponding to increase in temperature on celsius scale. For example, the increase in temperature from 10 °C to 100 °C, increases the volume from 566cm^3 to 746cm^3.

Applying Charles's law

$$\frac{V_1}{T_1}=\frac{V_2}{T_2}$$

$$\frac{566}{10}\neq\frac{746}{100}$$

The two sides of equation are not equal. So, Charles's law is not being obeyed when temperature is measured on the Celsius scale.

For this reason a new temperature scale has been developed. It starts from 273 °C (more precisely -273.16 °C) which is called zero Kelvin or zero absolute. Let us now explain how the new temperature scale has been developed. The best way is to plot a graph between the variables of Charles's law.

Table(3.1) volume-Temperature data for a given amount of a gas at constant pressure

Volumes (cm^3)	Celsius Temperature (°C)	Temperature (K)	$\frac{V}{T}$ = k = cm^{3}K^{-1}
1092	273	546	2
846	150	423	2
746	100	373	2
646	50	323	2
566	10	283	2
548	1	274	2
546	0	273	2
544	-1	272	2
526	-10	263	2
400	-73	200	2
346	-100	173	2
146	-200	73	2
0	-273	0	

Graphical Explanation

If we plot a graph between temperature on x-axis and the volume of one mole of an ideal gas on y-axis, we get a straight line which cuts the temperature axis at -273.16 °C. This can be possible only if we extrapolate the graph upto -273.16 °C. This temperature is the lowest possible temperature, which would have been achieved if the substance remains in the gaseous state Fig (3.7). Actually, all the gases are converted into liquids above this temperature.

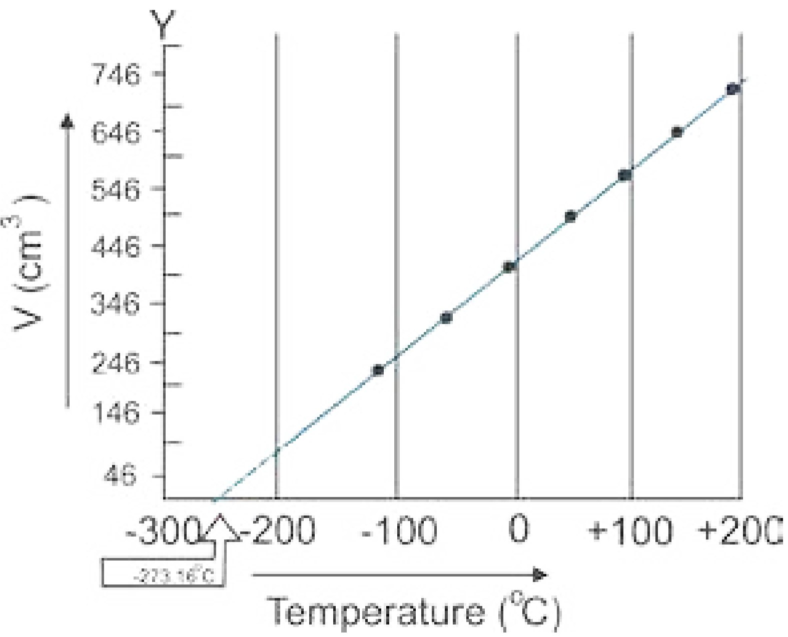


Fig (3.7) The graph between volume and temperature for a gas according to Table (3.1).

Charles's law is obeyed when the temperature is taken on the Kelvin scale. For example, at 283 K (10 °C) the volume is 566 cm^3, while at 373 K (100 °C) the volume is,746cm^3 Table (3.1). According to Charles's law.

$$\frac{V_1}{T_1}=\frac{V_2}{T_2}=K$$

$$\frac{566}{283}=\frac{746}{373}=2=K$$

Greater the mass of gas taken, greater will be the slope of straight line. The reason is that greater the number of moles greater the volume occupied. All these straight lines when extrapolated meet at a single point of -273.16 °C (0 Kelvin). It is apparent that this temperature of -273.16 °C will be attained when the volume becomes zero. But for a real gas the zero volume is impossible which shows that this temperature can not be attained for a real gas. This is how we recognize that -273.16 °C must represent the coldest temperature.

3.2.7 Scales of Thermometry

There are three scales of thermometery which are used for temperature measurements.

(a) Centigrade Scale: It has a zero mark for the temperature of ice at one atmospheric pressure. The mark 100°C indicates the temperature of boiling water at 1 atmospheric pressure. The space between these temperature marks is divided into 100 equal parts and each part is 1°C.

(b) Fahrenheit Scale: The melting point of ice at 1 atmospheric pressure has a mark 32°F and that of boiling water is 212 °F. The space between these temperature marks is divided into 180 equal parts and each part is 1 °F.

(c) Absolute or Kelvin Scale: The melting Point of ice at 1 atmospheric pressure is 273K. The water boils at 373K or more precisely at 373.16K.
Temperature on Kelvin scale = Temperature °C + 273.16
Following relationships help us to understand the interconversion of various scales of temperatures.

$$K = {}^\circ C + 273.16$$

$$^\circ C = 5/9[^\circ F-32]$$

$$^\circ F = 9/5(^\circ C)+32$$

3.3 GENERAL GAS EQUATION

While describing Boyle's and Charles's laws, some of the variables are held constant during the changes produced in the gases. According to Boyle's law.

$$V \propto \frac{1}{P}$$ (when 'n' and 'T' are held constant)

According to Charles's law

$$V \propto T$$ (when n and P are held constant)

It is a well known fact that volume of the given gas at constant temperature and pressure is directly proportional to the number of moles (Avogadro's law).

$$V \propto n$$ (when Pand T a re held constant)

If we think for a moment that none of the variables are to be kept constant then all the above three relationships can be joined together.

$$V \propto \frac{nT}{P}$$

$$V = \text{Constant}\ \frac{nT}{P}$$

The constant suggested is R which is called general gas constant.

$$V = R\frac{nT}{P}$$

$$PV = nRT \ \ldots\ldots\ldots\ldots (4)$$

The equation (4) is called an ideal gas equation. It is also known as general gas equation. This equation shows that if we have any quantity of an ideal gas then the product of its pressure and volume is equal to the product of number of moles, general gas constant and absolute temperature. This equation is reduced to Boyle's law, Charles's law and Avogadro's law, when appropriate variables are held constant.

PV = nRT, when T and n are held constant, PV = k (Boyle's law)

$V = R\ \frac{nT}{P}$, when P and n are held constant, V = kT (Charles's law)

$V = R\ \frac{nT}{P}$, when P and T are held constant V = kn (Avogadro's law)

For one mole of a gas, the general gas equation is

$$PV = RT \text{ or } \frac{PV}{T} = R$$

It means that ratio of PV to T is a constant quantity (molar gas constant)

Hence

$$\frac{P_1V_1}{T_1} = R \qquad \frac{P_2V_2}{T_2} = R$$

Therefore,

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \qquad \ldots\ldots\ldots\ldots \qquad (5)$$

3.3.1 Ideal Gas Constant R

The values and units of R can be calculated by Avogadro's principle very easily. Its value depends upon the units chosen for pressure, volume and temperature. The volume of one mole of an ideal gas at STP (one atmospheric pressure and 273.16 K) is 22.414 dm^3.
Putting these values in the general gas equation will give the value of R.

$$R= \frac{PV}{nT}$$

Putting their values, alongwith units

$$R= \frac{1 \text{ atm x } 22.414 \text{ dm}^3}{1 \text{ mole x } 273.16 \text{ K}}$$

$$R = 0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$$

When the pressure is in atmospheres, volume in dm^3, then the value of R, used should be 0.0821 dm^3 atm K^{-1} mol^{-1}
The physical meanings of this value is that, if we have one mole of an ideal gas at 273.16 K and one atmospheric pressure and its temperature is increased by 1 K, then it will absorb 0.0821 dm^3 -atm of energy, dm^3 -atm is the unit of energy in this situation. Hence, the value of R is a universal parameter for all the gases. It tells us that the Avogadro’s number of molecules o f all the ideal gases have the same demand of energy.

If the pressure is expressed in mm of mercury or torr and the volume of the gas in cm^3 then values of R are,

$R = 0.0821\ dm^3\ atm\ K^{-1}\ mol^{-1}$

$= 0.0821 \times 760\ dm^3\ mm\ Hg\ K^{-1}\ mol^{-1}$

$= 62.4\ dm^3\ mm\ Hg\ K^{-1}\ mol^{-1}$ Since, (1 mm o f Hg = 1 to rr)

$= 62.4\ dm^3\ torr\ K^{-1}\ mol^{-1}$

$= 62400\ cm^3\ torr\ K^{-1}\ mol^{-1}$ As, ($1\ dm^3 = 1000$ cm)

Using SI units of pressure, volume and temperature in the general equation, the value of R is calculated as follows. The SI units of pressure are Nm^{-2} and of volume are m^3. By using Avogadro's principle

$1\ atm = 760\ torr = 101\ 325\ Nm^{-2}$

$Im^3 = 1000\ dm^3$

n = 1 mole

T = 273.16 K

$P = 1\ atm = 101325\ Nm^{-2}$

$V = 22.414\ dm^3 = 0.022414\ m^3$

Putting their values, alongwith units.

$$R = \frac{PV}{nT} = \frac{101325\ N\ m^{-2}\ x\ 0.0224l\ m^3}{1\ mol\ x\ 273.16\ K}$$

$R = 8.3143\ Nm\ K^{-1}\ mol^{-1} = 8.3143\ J\ K^{-1}\ mol^{-1}$ (1 Nm = 1J)

Since 1cal. = 4.18 J

$$\text{so } R = \frac{8.3143}{4.18} = 1.989 cal\ K^{-1}\ mol^{-1}$$

Keep in mind that, wherever the pressure is given in Nm^{-2} and the volume in m^3, then the value of R used must be $8.3143\ JK^{-1}\ mol^{-1}$.

3.3.2 Density of an ideal Gas

For calculating the density of an ideal gas, we substitute the value of number of moles (n) of the gas in terms of the mass (m), and the molar mass (M) of the gas.

$$n = \frac{m}{M}$$

$$PV = \frac{m}{M} RT \quad \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Equation (6) is an other form of general gas equation that may be employed to calculate the mass of a gas whose P, T, V and molar mass are known. Rearranging equation (6)

$$PM = \frac{m}{V} RT$$

$$PM = d\,RT \qquad (d= \frac{m}{V})$$

$$d= \frac{PM}{RT} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(7)}$$

Hence the density of an ideal gas is directly proportional to its molar mass. Greater the pressure on the gas, closer will be the molecules and greater the density. Higher temperature makes the gases to expand, hence density falls with the increase in temperature. With the help of equation (7), one can calculate the relative molar mass (M) of an ideal gas if its temperature, pressure and density are known.

Example 3

A sample of nitrogen gas is enclosed in a vessel of volume 380 cm^3 at 120 °C and pressure of 101325 Nm^{-2} .This gas is transferred to a 10 dm^3 flask and cooled to 27°C. Calculate the pressure in Nm^{-2} exerted by the gas at 27°C.

Solution

All the three parameters of this gas have been changed, so we can solve this problem

by using the general gas equation of the form $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

Preferably, convert the volume to dm^3 and temperature to Kelvin scale.

Initial volume of the gas (V_1) = 380 cm^3 = 0.38 dm^3
Initial temperature (T_1) = 120 °C + 273 K = 393 K
Initial pressure (P_1) = 101325 N m^{-2}
Final temperature (T_2) = 27°C + 273 K = 300 K
Final volume (V_2) = 10 dm^3
Final pressure (P_2) = ?

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$P_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{V_2}$$

$$p_2 = \frac{101325Nm^{-2} \times 0.38dm^3 \times 300K}{393K \times 10dm^3}$$

$$=2938.4Nm^{-2} \text{ Answer}$$

Example 4

Calculate the density of CH_4 (g) at 0 °C and 1 atmospheric pressure. What will happen to the density if (a)temperature is increased to 27 °C, (b) the pressure is increased to 2 atmospheres at 0 °C.

Solution

Temperature of the gas = 0°C + 273 K - 273 K
Pressure of the gas = 1atm
Molecular mass of the gas =16g mol^{-1}
Gas constant (R) = 0.0821 dm^3 atm K^{-1} mol^{-1}

Formula for density of a gas at any temperature and pressure

$$d = \frac{PM}{RT}$$

Putting values $d = \frac{1\,atm\, x\, 16\, g\, mol^{-1}}{0.0821\, dm^3\, atm\, K^{-1}\, mol^{-1}\, x\, 273\, K}$

Simplifying the units $d = = \frac{1\, x\, 1\, 6}{0.0821\, x\, 273}\, g\, dm^{-3}$

$$d = \boxed{0.7138\, g\, dm^{-3}}\ Answer$$

It means that under the given conditions 1 dm^3 of CH_4 gas has a mass of 0.7138 g.

(a) Density at 27 °C

Temperature = 27 + 273 = 300 K

Putting values in the equation of density and simplifying the units.

$$d = \frac{PM}{RT} = \frac{1\ \text{atm x } 16\ \text{g mol}^{-1}}{0.0821\ \text{dm}^3\ .\text{atm.K}^{-1}\ .\text{mol}^{-1}\ \text{x } 300\ \text{K}} = 0.649\ \text{g dm}^{-3}$$

So, by increasing the temperature from 0°C to 27°C the density of gas has decreased from 0.7138 g dm^{-3} to 0.649 g dm^{-3}. The increase of temperature makes the molecules of a gas to move away from each other.

(b) Density at 2 atmospheric pressure and 0°C

T = 0 + 273 = 273 K

P = 2 atm

Putting values in the equation and simplifying the units.

$$d = \frac{PM}{RT} = \frac{2\ \text{atm x } 16\ \text{g mol}^{-1}}{0.0821\ \text{dm}^3\ .\text{atm.K}^{-1}\ .\text{mol}^{-1}\ \text{x } 273\ \text{K}} = 1\ .427\ \text{g dm}^{-3}$$

The increase of pressure has increased the density of CH_4. The density has almost doubled by doubling the pressure. The reason is that increase of pressure makes the molecules to come close to each other.

Example 5

Calculate the mass of 1 dm^3 of NH_3 gas at 30 °C and 1000 mm Hg pressure, considering that NH_3 is behaving ideally.

Solution

Pressure of the gas $= 1000\ \text{mm Hg} = \frac{1000}{760} = 1.315\ \text{atm}$

Volume of the gas = 1dm^3

Temperature of the gas = 30°C + 273 K = 303 K

Molecular mass of the gas = 17 g mol^{-1}

General gas equation PV $= \frac{m}{M}RT$ can be used to calculate the mass (m) of the gas.

Rearranging m $= \frac{PVM}{RT}$

Putting values along with units

$$\text{Mass of NH}_3 = \frac{1.315 \text{ atm} \times 1 \text{ dm}^3 \times 17 \text{ g mol}^{-1}}{0.0821 \text{ dm}^3 \text{ atm K}^{-1}\text{mol}^{-1} \times 303 \text{ K}}$$

Simplifying the units

$$\text{Mass of NH}_3 = \frac{1.315 \times 1 \times 17\text{g}}{0.0821 \times 303} = \boxed{0.907 \text{ g}} \text{ Answer}$$

This is the mass of 1 dm^3 of NH$_3$ under the given conditions. In other words, it is the density of NH$_3$, if it is acting as an ideal gas.

3.4 AVOGADRO'S LAW

According to this law, **"equal volumes of all the ideal gases at the same temperature and pressure contain equal number of molecules".** This statement is indirectly the same as has been used for evaluating the general gas constant R i.e., one mole of an ideal gas at 273.16K and one atm pressure has a volume of 22.414 dm^3. Since one mole of a gas has Avogadro's number of particles, so 22.414 dm^3 of various ideal gases at S T P will have Avogadro's number of molecules i.e. 6.02 x 10^{23}. 22.414 dm^3 of a gas at 273.16 K and one atmospheric pressure has number of molecules = 6.02 x1O^{23}.

In other words, if we have one dm^3 of each of H$_2$, He, N$_2$, O$_2$, and CO in separate vessels at STP, then the number of molecules in each will be 2.68 x 10^{22} This is obtained by dividing 6.02x 10^{23} with 22.414 dm^3 .

Similarly, when the temperature or pressure are equally changed for these four gases, then the new equal volumes i.e. 1dm^3 each will have the same number of molecules i.e. 2 . 6 8 x 10^{22}.

No doubt, one dm^3 of H$_2$ at STP weighs approximately 0.0899 grams and one dm^3 of O$_2$ at STP weighs 1.4384 g, but their number of molecules are the same. Although, oxygen molecule is 16 times heavier than hydrogen, but this does not disturb the volume occupied, because molecules of the gases are widely separated from each other at STP One molecule is approximately at a distance of 300 times its own diameter from its neighbour at room temperature.

3.5 DALTON'S LAW OF PARTIAL PRESSURES

John Dalton studied the mixtures o f gases and gave his law of partial pressures. According to this law, **the total pressure exerted by a mixture of non-reacting gases is equal to the sum of their individual partial pressures.** Let the gases are designated as 1,2,3, and their partial pressures are p_1, p_2, p_3.The total pressure (P) of the mixture of gases is given by

$$P_t = p_1 + p_2 + p_3$$

The partial pressure of a gas in a mixture of gases is the pressure that it would exert on the walls of the container, if it were present all alone in that same volume under the same temperature.

Let us have four cylinders of same volume, i.e., 10 dm^3 each and three gases H_2, CH_4 and O_2 are separately enclosed in first three of them at the same temperature. Let their partial pressures be 400 torr, 500 torr and 100 torr respectively.

All these gases are transferred to a fourth cylinder of capacity 10 dm^3 at the same temperature. According to Dalton's law

$$P_t = p_{H_2} + p_{CH_4} + p_{O_2} = (400 + 500 + 100)\ \text{torr}$$
$$P_t = 1000\ \text{torr}$$

These three non-reacting gases are behaving independently under the normal conditions. The rapidly moving molecules of each gas in a mixture have equal opportunities to collide with the walls of the container. Hence, each gas exerts a pressure independent of the pressure of other gases. The total pressure is the result of total number of collisions per unit area in a given time.

Molecules of each gas move independently, so the general gas equation (PV = nRT) can be applied to the individual gases in the gaseous mixture.

$$p_{H_2}V = n_{H_2}RT \qquad p_{H_2} = n_{H_2}\frac{RT}{V} \qquad p_{H_2}\ \alpha\ n_{H_2}$$

$$p_{CH_4}V = n_{CH4}RT \qquad p_{CH_4} = n_{CH_4}\frac{RT}{V} \qquad p_{CH_2}\ \alpha\ n_{CH_4}$$

$$p_{O_2}V = n_{O_2}RT \qquad p_{O_2} = n_{O_2}\frac{RT}{V} \qquad p_{O_2}\ \alpha\ n_{O_2}$$

$\frac{RT}{V}$ is a constant factor for each gas.

All these gases have their own partial pressures. Since volumes and temperatures are the same, so their number of moles will be different and will be directly proportional to their partial pressures. Adding these three equations

$$P_t = p_{H_2} + p_{CH_4} + p_{O_2}$$

$$P_t = (n_{H_2} + n_{CH_4} + n_{O_2})\frac{RT}{V}$$

$$P_t = n_t\frac{RT}{V} \qquad \text{where} \quad n_t = n_{H_2} + n_{CH_4} + n_{O_2}$$

$$P_tV = n_tRT \qquad \text{................ (8)}$$

According to equation (8), the total pressure of the mixture of gases depends upon the total number of moles of the gases.

3.5.1 Calculation of Partial Pressure of a Gas

The partial pressure of any gas in a mixture of gases can be calculated, provided one knows the mass of that gas or its number of moles alongwith the total pressure and the total number of moles present in the mixture.

In order to have a relationship, let us suppose that we have a mixture of gas A and gas B. This mixture is enclosed in a container having volume (V). The total pressure is one atm.

The number of moles of the gases A and B are n_A and n_B respectively. If they are maintained at temperature T, then

$P_tV = n_tRT$ .... (equation for the mixture of gases)

$p_AV = n_ART$ .... (equation for gas A)

$p_BV = n_BRT$ .... (equation for gas B)

Divide the first two equations

$$\frac{p_AV}{P_tV} = \frac{n_ART}{n_tRT}$$

$$\frac{p_A}{P_t} = \frac{n_A}{n_t} \qquad \text{.......... (9)}$$

$$p_A = \frac{n_A}{n_t}\,P_t \qquad \text{.......... (10)}$$

$$p_A = x_A\,P_t \qquad (x_A \text{ is mole fraction of gas A})$$

$$p_B = x_B\,P_t$$

Similarly

Partial pressure of a gas is the mole fraction of that gas multiplied by the total pressure of the mixture. Remember that mole fraction of anyone of the gases in the mixture is less than unity. Moreover, the sum of mole fractions is always equal to unity.

Example 6

There is a mixture of hydrogen, helium and methane occupying a vessel of volume 13 dm^3 at 37 °C and pressure of 1 atmosphere. The masses of H_2 and He are 0.8 g and 0.12 g respectively. Calculate the partial pressures in torr of each gas in the mixture.

Solution

Volume of the mixture of gases $= 13\ dm^3$
Temperature of the mixture $= 37 + 273 = 310\ K$
Pressure of the mixture $= 1\ atm$

Firstcalculatethetotalnumberofmolespresentinthemixtureofgasesbyapplyingthegeneralgasequation. Since

$$PV = nRT$$

or

$$n = \frac{PV}{RT}$$

Putting values along with the units and simplifying

$$n = \frac{1\ \text{atm x } 13\ \text{dm}^3}{0.0821\ \text{dm}^3\ \text{atm. K}^{-1}\ \text{mol}^{-1}\ \text{x } 310\ \text{K}} = 0.51\ \text{moles}$$

So, the total number of moles of H_2, He and CH_4 = 0.51 moles

Mass of H_2 $= 0.8$ g

Number of moles of H_2 $= \dfrac{\text{mass of } H_2}{\text{molar mass}} = \dfrac{0.8 \text{ g}}{2.0 \text{ g mol}^{-1}} = 0.40$

Mass of He $= 0.12$ g

Number of moles of He $= \dfrac{\text{mass of He}}{\text{molar mass}} = \dfrac{0.12 \text{ g}}{4 \text{ g mol}^{-1}} = 0.03$

Number of moles of CH_4 = total moles - moles of H_2 - moles of He

$= 0.51 - 0.396 - 0.03$

$= 0.084$

Mole fraction of $H_2 \left(X_{H_2} \right)$ $= \dfrac{\text{no of moles of } H_2}{\text{total number of moles}} = \dfrac{0.40}{0.51} = 0.784$

Mole fraction of He$\left(X_{He} \right)$ $= \dfrac{\text{no of moles of He}}{\text{total number of moles}} = \dfrac{0.03}{0.51} = 0.058$

Mole fraction of $CH_4 \left(X_{CH_4} \right)$ $= \dfrac{\text{no of moles of } CH_4}{\text{total number of moles}} = \dfrac{0.084}{0.51} = 0.164$

(Being a ratio mole fraction has no units.)

$Partial\ pressure\ of\ H_2\ \left(p_{H_2} \right) = X_{H_2} P$

$== 0.776\ x\ 1.00 \quad 0.776\ atm$

$== 0.776 x 760 \quad 589.76\ torr$

$Partial\ pressure\ of\ He\ \left(p_{He} \right) = X_{He}\ \mathrm{P}$

$== 0.058\ x\ 1.00 \quad 0.058\ atm$

$== 0.058\ x\ 760 \quad 44.08\ torr$

$Partial\ pressure\ of\ CH_4\ \left(p_{CH_4} \right) = X_{CH_4}\ \mathrm{P}$

$== 0.164 x\ 1.00 \quad 0.164\ atm$

$== 0.164\ x\ 760 \quad \boxed{124.64\ mm\ of\ Hg} \quad Answer$

The sum of individual pressures i.e. 589.76.44.08 and 124.64 is almost 760 mm of Hg, i.e. total pressure of the mixture.

3.5.2 Applications of Dalton's Law of Partial Pressures

Following are the four important applications of Dalton's Law of partial pressures.

1. Some gases are collected over water in the laboratory. The gas during collection gathers water vapours and becomes moist. The pressure exerted by this moist gas is, therefore, the sum of the partial pressures of the dry gas and that of water vapours.

The partial pressure exerted by the water vapours is called aqueous tension.

$$P_{moist} = p_{dry} + p_{w.vap}$$
$$P_{moist} = p_{dry} + \text{aqueous tension}$$
$$p_{dry} = P_{moist} - \text{aqueous tension}$$

While solving the numericals the aqueous tension is subtracted from the total pressure (P_{moist}).

2. Dalton's law finds its applications during the process of respiration. The process of respiration depends upon the difference in partial pressures. When animals inhale air then oxygen moves into lungs as the partial pressure of oxygen in the air is 159 torr, while the partial pressure of oxygen in the lungs 116 torr. CO_2 produced during respiration moves out in the opposite direction, as it's partial pressure is more in the lungs than that in air.

3. At higher altitudes, the pilots feel uncomfortable breathing because the partial pressure of oxygen in the un-pressurized cabin is low, as compared to 159 torr, where one feels comfortable breathing.

4. Deep sea divers take oxygen mixed with an inert gas say He and adjust the partial pressure of oxygen according to the requirement. Actually, in sea after every 100 feet depth, the diver experiences approximately 3 atm pressure, so normal air cannot be breathed in depth of sea. Moreover, the pressure of N_2 increases in depth of sea and it diffuses in the blood.

3.6 DIFFUSION AND EFFUSION

Diffusion

According to the kinetic molecular theory of gases, the molecules of the gases move haphazardly. They collide among themselves, collide with the walls of the vessel and change their directions. In other words the molecules of gases are scattered after collisions.

This spontaneous intermingling of molecules of one gas with another at a given temperature and pressure is called diffusion.

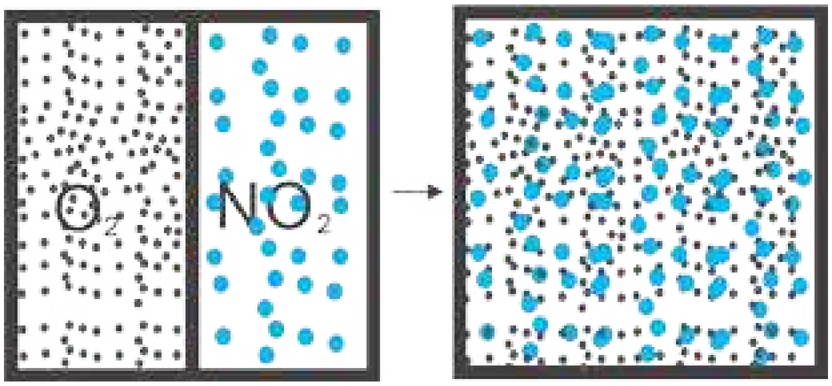


Fig (3.8) Diffusion

The spreading of fragrance of a rose or a scent is due to diffusion. When two gases diffuse into each other, they wish to make their partial pressures same every where. Suppose NO_2, a brown coloured gas and O_2, a colourless gas, are separated from each other by a partition Fig (3.8).When the partition is removed, both diffuse into each other due to collisions and random motion.

A stage reaches when both gases generate a homogeneous mixture and partial pressures of both are uniform throughout the mixture.

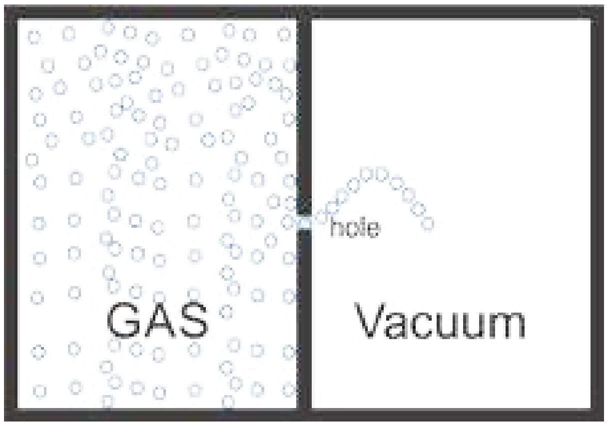


Fig (3.9) Escape of gas molecules through a hole is effusion.

Effusion

The effusion of a gas is it's movement through an extremely small opening into a region of low pressure. This spreading of molecules is not due to collisions, but due to their tendency to escape one by one. Actually, the molecules of a gas are habitual in colliding with the walls of the vessel. When a molecule approaches just in front of the opening it enters the other portion of the vessel. **This type of escape of molecules is called of effusion Fig(3.9).**

3.6.1 Graham 's Law of Diffusion

Thomas Graham (1805 -1869), an English scientist, found that the rate of diffusion or effusion of a gas is inversely proportional to the square root of it's density at constant temperature and pressure.

$$\text{Rate of diffusion} \propto \frac{1}{\sqrt{d}} \qquad (\text{at constant temperature and pressure})$$

$$\text{Rate of diffusion} = \frac{k}{\sqrt{d}}$$

$$\text{Rate of diffusion x } \sqrt{d} = k$$

$$\text{or Rate x } \sqrt{d} = k$$

The constant k is same for all gases, when they are all studied at the same temperature and pressure. Let us have two gases 1 and 2, having rates of diffusion as r_1 and r_2 and densities as d_1 and d_2 respectively. According to Graham's law

$$r_1 \text{ x } \sqrt{d_1} = k$$

$$r_2 \text{ x } \sqrt{d_2} = k$$

Divide the two equations and rearrange

$$\frac{r_1}{r_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}} \qquad \text{..........(11)}$$

Since the density of a given gas is directly proportional to its molecular mass. Graham's law of diffusion can also be written as follows.

$$\frac{r_1}{r_2} = \frac{\sqrt{M_2}}{\sqrt{M_1}} \qquad \text{.........(12)}$$

Where M_1 and M_2 are the molar masses of gases.

Demonstration of Graham's Law

This law can also be very easily verified in the laboratory by noting the rates of diffusion of two gases in a glass tube, when they are allowed to move from opposite ends Fig (3.10). Two cotton plugs soaked in HCl and NH_3 solutions are introduced in the open ends of 100 cm long tube simultaneously. HCl molecules travel a distance of 40.5 cm while NH_3 molecules cover 59.5 cm in the same duration. They produce dense white fumes of ammonium chloride at the point of junction. So

$$\frac{r_{NH_3}}{r_{HCl}} = \frac{\sqrt{M_{HCl}}}{\sqrt{M_{NH_3}}}$$

$$\frac{59.5}{40.5} = \frac{\sqrt{36.5}}{\sqrt{17}}$$

Fig (3.10) Verification of Graham's law of diffusion

$$1.46 = 1.46$$

Hence the law is verified.

Example 7

250 cm³ of the sample of hydrogen effuses four times as rapidly as 250 cm³ of an unknown gas. Calculate the molar mass of unknown gas.

Solution

Let the unknown gas is given the symbol X

$$\text{Rate of effusion of unknown gas } (r_x) = 1$$
$$\text{Rate of effusion of hydrogen gas } (r_{H_2}) = 4$$

$$\text{Molar mass of } H_2 \text{ gas} (M_{H_2}) = 2 \text{ g mol}^{-1}$$
$$\text{Molar mass of unknown gas } (M_x) = ?$$

$$\frac{r_{H_2}}{r_x} = \sqrt{\frac{M_x}{M_{H_2}}}$$

$$\frac{4}{1} = \sqrt{\frac{M_x}{2}}$$

$$\frac{M_x}{2} = \frac{16}{1}$$

$$M_x = 16 \, x \, 2 = \boxed{32 \text{ g mol}^{-1}} \text{ Answer}$$

3.7 KINETIC MOLECULAR THEORY OF GASES

The behaviour of gases has already been discussed in gas laws. These laws were based on experimental observations quite independent of nature of a gas. In order to illustrate the behaviour of gases quantitatively, Bernoulli (1738) put forward kinetic molecular theory of gases. This theory lead Clausius (1857) to derive the kinetic equation and deduced all the gas laws from it. The theory was later on elaborated and extended by Maxwell, who gave the law of distribution of velocities. According to this law,molecules are in the form of groups having definite velocity ranges. Boltzmann also Contributed and studied the distribution of energies among the gas molecules. Among some other names Van der Waal is the prominent scientist in this field.

Following are the fundamental postulates of this kinetic theory of gases.

1. Every gas consists of a large number of very small particles called molecules. Gases like He, Ne, Ar have monoatomic molecules.
2. The molecules of a gas move haphazardly, colliding among themselves and with the walls of the container and change their directions.
3. The pressure exerted by a gas is due to the collisions of its molecules with the walls of a container. The collisions among the molecules are perfectly elastic.
4. The molecules of a gas are widely separated from one another and there are sufficient empty spaces among them.
5. The molecules of a gas have no forces of attraction for each other.
6. The actual volume of molecules of a gas is negligible as compared to the volume of the gas.
7. The motion imparted to the molecules by gravity is negligible as compared to the effect of the continued collisions between them.
8. The average kinetic energy of the gas molecules varies directly as the absolute temperature of the gas.

Keeping in view the basic assumptions given above, R.J Clausius deduced an expression for the pressure of an ideal gas. Actually, pressure on the walls of the vessel is due to collisions. Whenever the molecules move they collide among themselves and with the walls of the container. Due to these collisions, a force is exerted on the walls of the container. This force when divided by the area of the vessel gives force per unit area, which is called pressure. In this way, the final form of kinetic equation is as follows.

$$PV = \frac{1}{3} mN\overline{c^2} \qquad \text{.........} (13)$$

Where,

P = pressure
V = volume
m = mass of one molecule of the gas
N = number of molecules of gas in the vessel
$\overline{c^2}$ = mean square velocity

The idea of the mean square velocity is important. All the molecules of a gas under the given conditions don't have the same velocities. Rather different velocities are distributed among the molecules. To understand it study Maxwell's law of distribution of velocities. If there are n_1 molecules with velocity c_1, n_2 molecules with velocity c_2, and so on then,

$$\overline{c^2} = \frac{c_1^{\ 2} + c_2^{\ 2} + c_3^{\ 2} + \ldots\ldots}{n_1 + n_2 + n_3 + \ldots\ldots} \qquad \ldots\ldots\ldots \quad (14)$$

In this reference $n_1+n_2+n_3$ ....=N

$\overline{c^2}$ is the average of the squares of all the possible velocities. When we take the square root of this $\overline{c^2}$, then it is called root mean square velocity (C_{rms}). So, (C_{rms}) = $\sqrt{\overline{c^2}}$

The expression for the root mean square velocity deduced from the kinetic equation is written as follows.

$$C_{rms} = \sqrt{\frac{3RT}{M}} \qquad \ldots\ldots\ldots \quad (15)$$

Where, C_{rms} = root mean square velocity
M = molar mass of the gas
T = temperature

This equation (15) is a quantitative relationship between the absolute temperature and the velocities of the gas molecules. According to this equation, higher the temperature of a gas, greater the velocities. Kinetic equation can be used to explain gas laws.

3.7.1 Explanation of Gas Laws from Kinetic Theory of Gases

Kinetic theory of gases gives birth to kinetic equation of gases, which can be employed to justify the gas laws. In other words, it proves that gas laws get their explanation from kinetic theory of gases

(a) Boyle's Law

According to one of the postulates of kinetic theory of gases, the kinetic energy is directly proportional to the absolute temperature of the gas. The kinetic energy of N molecules is $\frac{1}{2}mN\overline{c^2}$

so

$$\frac{1}{2}mN\overline{c^2} \propto T$$

$$\frac{1}{2}mN\overline{c^2} = kT \qquad \ldots\ldots\ldots\ldots \quad (16)$$

Where k is the proportionality constant. According to the kinetic equation of gases

$$PV=\frac{1}{3}\,mN\overline{c^2}$$

Multiplying and dividing by 2 on right hand side

$$PV=\frac{2}{3}\left(\frac{1}{2}mN\overline{c^2}\right) \qquad \ldots\ldots\ldots \qquad (17)$$

Putting equation (16) into equation (17).

$$PV=\frac{2}{3}\,kT \qquad \ldots\ldots\ldots \qquad (18)$$

If the temperature (T) is constant then right hand side of equation (18) $\frac{2}{3}$ kT is constant. Let that constant be k'.

So, PV = k' (which is Boyle's law)

Hence at constant temperature and number of moles, the product PV is a constant quantity.

(b) Charles's law

Consider the equation (18) which has just been derived

Or

$$PV=\frac{2}{3}\,kT$$

$$V=\frac{2}{3}\,\frac{kT}{P}=\left(\frac{2k}{3P}\right)T$$

At constant pressure,

Therefore,

$$\frac{2}{3}\frac{k}{P}=k'' \text{ (a new constant)}$$

or

$$V=k''T$$

$$\frac{V}{T}=k'' \text{ (which is Charles's law)}$$

(c) Avogadro's Law

Consider two gases 1 and 2 at the same pressure P and having the same volume V.Their number of molecules are N_1 and N_2 , masses of molecules are m_1 and m_2 and mean square velocities are $\overline{c_1^{\,2}}$ and $\overline{c_2^{\,2}}$ respectively.

Their kinetic equations can be written as follows:

$$PV=\frac{1}{3}\ m_1N_1\overline{c_1^{\ 2}} \quad \text{for gas(1)}$$

$$PV=\frac{1}{3}\ m_2N_2\overline{c_2^{\ 2}} \quad \text{for gas(2)}$$

$$\text{Equalizing} \quad \frac{1}{3}\ m_1N_1\overline{c_1^{\ 2}} = \frac{1}{3}\ m_2N_2\overline{c_2^{\ 2}}$$

$$\text{Hence,} \quad m_1N_1\overline{c_1^{\ 2}} = m_2N_2\overline{c_2^{\ 2}} \qquad \ldots\ldots\ldots \quad (19)$$

When the temperature of both gases is the same, their mean kinetic energies per molecule will also be same, so

$$\frac{1}{2}\ m_1\overline{c_1^{\ 2}} = \frac{1}{2}\ m_2\overline{c_2^{\ 2}}$$

$$m_1\overline{c_1^{\ 2}} = m_2\overline{c_2^{\ 2}} \qquad \ldots\ldots\ldots \quad (20)$$

Divide equation (19) by (20)

$$N_1 = N_2$$

Hence equal volumes of all the gases at the same temperature and pressure contain equal number of molecules, which is Avogadro's law.

(d) Graham's Law of Diffusion

$$PV = \frac{1}{3}\ mN\overline{c^2} \qquad \ldots\ldots\ldots\ldots \quad (13)$$

Applying the kinetic equation

$$PV = \frac{1}{3}\ mN_A\overline{c^2}$$

If we take one mole of a gas having Avogadro's number of molecules ($N = N_A$) then the equation (13) can be written as:

$$PV = \frac{1}{3}\ M\overline{c^2} \quad (M = mN_A) \qquad \ldots\ldots\ldots \quad (21)$$

or

$$\overline{c^2} = \frac{3PV}{M}$$

where M is the molecular mass of the gas

Taking square root

$$\sqrt{\overline{c^2}} = \sqrt{\frac{3PV}{M}}$$

$$\sqrt{\overline{c^2}} = \sqrt{\frac{3P}{M/V}} = \sqrt{\frac{3P}{d}} \quad (\frac{M}{V} = d)$$

'V' is the molar volume of gas at given conditions. Since the root mean square velocity of the gas is proportional to the rate of diffusion of the gas.

so

$$\sqrt{\overline{c^2}} \propto r$$

$$r \propto \sqrt{\frac{3P}{d}}$$

At constant pressure

$$r \propto \sqrt{\frac{1}{d}}$$

which is Graham’s law of diffusion

3.8 KINETIC INTERPRETATION OF TEMPERATURE

According to kinetic molecular theory of gases the molecules of a gas move randomly. They collide among themselves, with the walls of the vessels and change their directions. The collisions are elastic and the pressure of the gas is the result of these collisions with the walls of the container. Let us rewrite the kinetic equation of gases (13) as already mentioned

$$PV = \frac{1}{3} mN\overline{c^2} \quad .... \quad (13)$$

Here m is the mass o f one molecule of the gas, N is the number of molecules in the vessel and $\overline{c^2}$ is their mean square velocity. The average kinetic energy associated with one molecule o f a gas due to its translational motion is given by the following equation.

$$E_k = \frac{1}{2} m\overline{c^2} \qquad \ldots\ldots\ldots \quad (22)$$

Remember that E_k is the average translational kinetic energy of gas molecules.
Equation (13) can be rewritten as:

$$PV = \frac{2}{3} N \left(\frac{1}{2} m\overline{c^2} \right) \qquad \ldots\ldots\ldots \quad (23)$$

Putting equation (22) into (23)

So

$$PV = \frac{2}{3} N E_k \qquad \ldots\ldots\ldots\ldots \quad (24)$$

Equation (24) gives an important insight into the meaning of temperature. To understand it, consider one mole of a gas.
So

$$N = N_A$$

$$PV = \frac{2}{3} N_A E_k \qquad \ldots\ldots\ldots\ldots \quad (25)$$

According to the general gas equation for 1 mole of a gas

$$PV = RT \qquad \ldots\ldots\ldots\ldots \quad (4)$$

Comparing equation (4) and (25)

$$\frac{2}{3} N_A E_k = RT \qquad \ldots\ldots\ldots\ldots \quad (26)$$

$$E_k = \frac{3R}{2N_A} T \qquad \ldots\ldots\ldots\ldots \quad (27)$$

The equation (27) gives a new definition of temperature according to which the kelvin temperature of a gas is directly proportional to the average translational kinetic energy of its molecules. This suggests that a change in temperature means change in the intensity of molecular motion. When heat flows from one body to another, the molecules in the hotter body give up some of their kinetic energy through collisions to molecules in the colder body. This process of flow of heat continues until the average translational kinetic energies of all the molecules become equal. This equalises the temperature of both bodies.

In gases and liquids, temperature is the measure of average translational kinetic energies of molecules. In solids, where molecules cannot move freely temperature becomes a measure of vibrational kinetic energy.

Keeping in view this kinetic interpretation of temperature, w e have a way of looking at absolute zero of temperature. It is that temperature at which the molecular motions cease. The absolute zero is unattainable. Anyhow, current attempts have resulted in temperature as low as 10^{-5}K.

3.9 LIQUEFACTION OF GASES

3.9.1 General Principle of Liquefaction

The conversion of a gas into a liquid requires high pressure and low temperature. High pressure brings the molecules of a gas close to each other. Low temperature deprives the molecules from kinetic energy and attractive forces start dominating.

For every gas there exists a temperature above which the gas cannot be liquefied, no matter how much pressure is applied. **The highest temperature at which a substance can exist as a liquid, is called its critical temperature (T_c).** There is a corresponding pressure which is required to bring about liquefaction at this critical temperature (T_c). This is called critical pressure (P_c).

The critical temperature and the critical pressure of the substances are very important for the workers dealing with the gases. These properties provide us the information about the condition under which gases liquefy. For example, O_2 has a critical temperature 154.4 K (-118.75 °C). It must be cooled below this temperature before it can be liquefied by applying high pressure. Ammonia is a polar gas. Its critical temperature is 405.6 K (132.44 °C), so it can be liquefied by applying sufficient pressure close to room temperature.

Table (3.2) shows the critical parameters of some common substances. Non- polar gases of low polarizability like Ar have a very low critical temperature. The substances like H_2O vapours and NH_3 gas are among the polar gases and they have better tendencies to be liquefied CO_2, can not be liquefied above 31.1 °C, no matter how much the pressure is applied. Anyhow, if temperature of CO_2 is maintained below 31.1 °C, then lower pressure than critical pressure is required to liquefy it. The value of the critical temperature of a gas depends upon its size, shape and intermolecular forces present in it.

When a gas is measured at its critical temperature and critical pressure, then at that stage volume of 1 mole of gas is called critical volume which is represented by V_c. The critical volume of O_2 is 74.42 $cm^3\ mol^{-1}$, of CO_2 , is 95.65 $cm^3\ mol^{-1}$ and that of H_2 is 64.51 $cm^3\ mol^{-1}$.

Table (3.2) Critical Temperatures and Critical Pressures of Some Substances

Substance	Critical Temperature T_c (K)	Critical Pressure P_c (atm)
Water vapours, H_2O	647.6 (374.44 °C)	217.0
Ammonia, NH_3	405.6 (132.44 °C)	111.5
Freon-12 , CCl_2F_2	384.7 (111.54 °C)	39.6
Carbon dioxide, CO_2	304.3 (31.142 °C)	73.0
Oxygen, O_2	154.4 (-118.75 °C)	49.7
Argon, Ar	150.9 (-122.26 °C)	48
Nitrogen, N_2	126.1 (-147.06 °C)	33.5

3.9.2 Methods of Liquefaction of Gases

There are various methods to liquefy a gas . One of them is Linde's method. It is based on Joule-Thomson effect.

Joule Thomson Effect

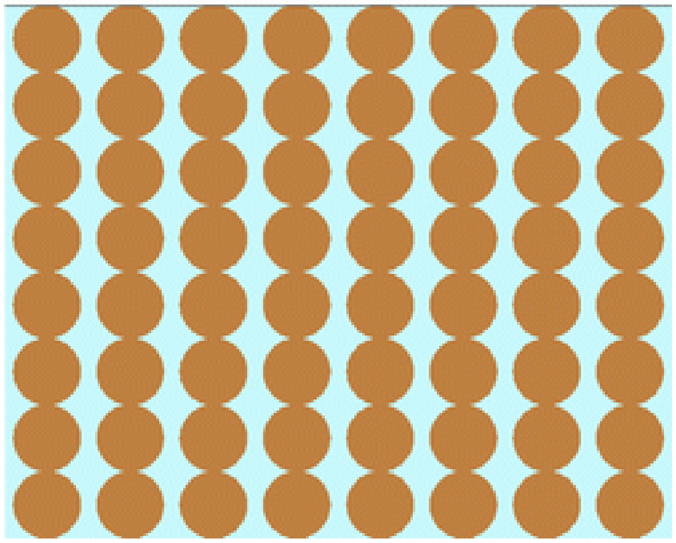
Low temperature can be achieved by Joule-Thomson effect, according to which when a compressed gas is allowed to expand into a region of low pressure it gets cooled.

The molecules of the compressed gas are very close to each other and appreciable attractive forces are present among them. When a gas is allowed to undergo sudden expansion through the nozzle of a jet, then the molecules move apart. In this way energy is needed to overcome the intermolecular attractions. This energy is taken from the gas itself, which is cooled.

Linde's Method of Liquefaction of Gases

Linde has employed Joule-Thomson effect as the basis for liquefaction. The apparatus designed for this purpose is shown in the Fig (3.11).

For the liquefaction of air, it is compressed to about 200 atmospheres, and then passed though a water cooled pipe where the heat of compression is removed. It is then allowed to pass through a spiral pipe having a jet at the end. When the air comes out of the jet the expansion takes place from 200 atm. to 1 atm. In this way, considerable fall of temperature occurs.



Animation 3.5.: Liquefaction
Source& Credit: wikipedia

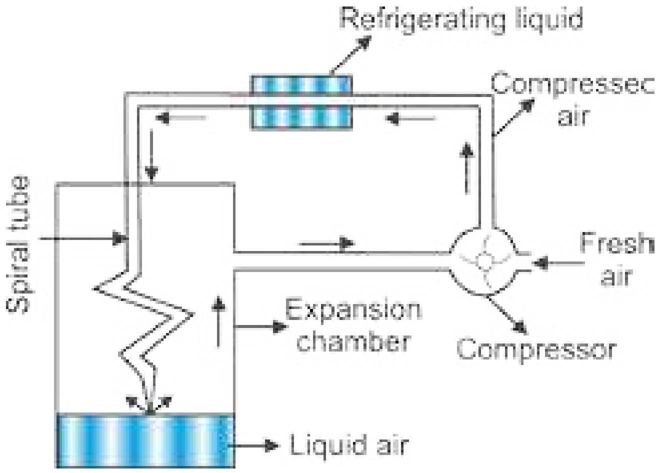


Fig (3.11) Linde's method for the liquefaction of air

This cooled air goes up and cools the incoming compressed air. It returns to the compression pump. This process is repeated again and again. The liquid air is collected at the bottom of the expansion chamber. All gases except H_2, and He can be liquefied by the above procedure.

3.10 NON-IDEAL BEHAVIOUR OF GASES

Whenever, we discuss gas laws it.is proposed that ideal gases obey them. Particularly an ideal gas obeys Boyle's law, Charles's law and the general gas equation under all conditions of temperature and pressure. Let us try to understand the behaviour of a few real gases like H_2, He, N_2 and CO_2 at °C.keeping in view the variation of the pressure on the gas and consequently the change in its volume.

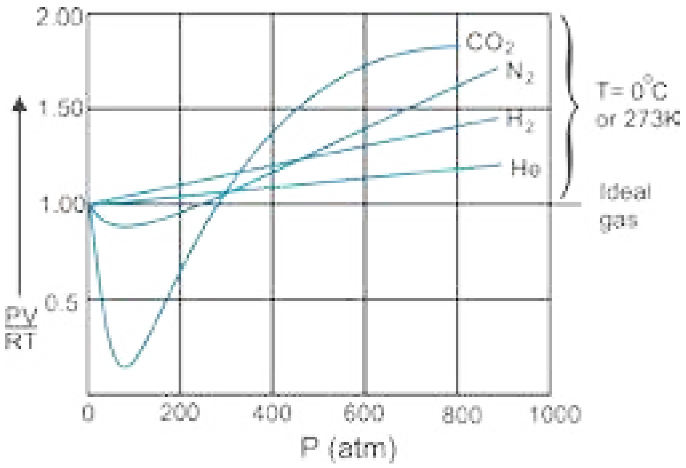


Fig (3.12 a) Non-ideal behaviour of gases at 0 °C

For this purpose, first of all plot a graph between pressure on x-axis and the $\frac{PV}{nRT}$ on Y-axis for an ideal gas.

The factor $\frac{PV}{nRT}$ is called the compressibility factor. Its value is unity under all conditions for an ideal gas. Since the increase of pressure decreases the volume in such a way that $\frac{PV}{nRT}$ remains constant at a constant temperature, so a straight line is obtained parallel to the pressure axis. This is shown in the Figs (3.12 a, b). All the real gases have been found to show marked deviations from this behaviour. It is observed that the graph for helium gas goes along with the expected horizontal dotted line to some extent but goes above this line at very high pressures.

It means that at very high pressure the decrease in volume is not according to general gas equation and the value of $\frac{PV}{RT}$ has increased from the expected values. With this type of behaviour, we would say that the gas is non-ideal.

In the case of H_2 the deviation starts even at low pressure in comparison to He. N_2 shows a decrease in $\frac{PV}{RT}$ value at the beginning and shows marked deviation even at low pressure than H_2. CO_2 has a very strange behaviour as it is evident from the graph.

The extent of deviation of these four gases shows that these gases have their own limitations for obeying general gas equation. It depends upon the nature of the gas that at which value of pressure, it will start disobeying.

When we study the behaviour of all these four gases at elevated temperature i.e., 100°C then the graphs come closer to the expected straight line and the deviations are shifted towards higher pressure. This means that the increase in temperature makes the gases ideal Fig (3.12 b).

This discussion on the basis of experimental observations, convinces us that

(i) Gases are ideal at low pressure and non-ideal at high pressure

(ii) Gases are ideal at high temperature and non-ideal at low temperature.

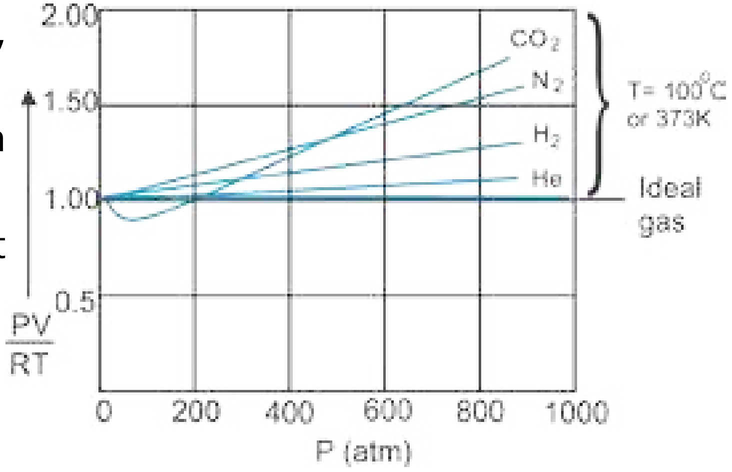
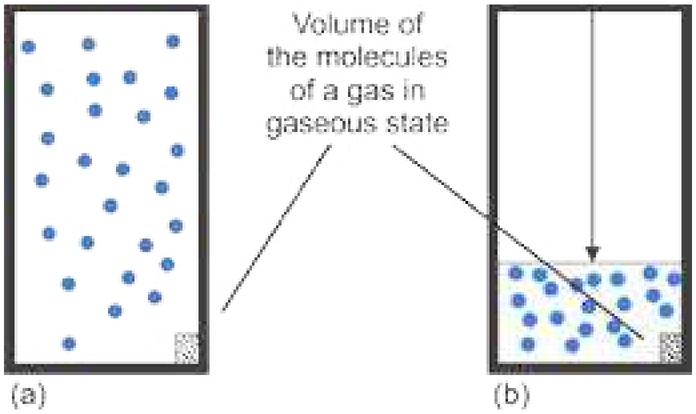


Fig (3.12 b) Non-ideal behaviour of gases at 100 °C.

3.10.1 Causes for Deviations from Ideality



Fig(3.13.a) A gas at low pressure when actual volume is negligible.

Kig(3.13.b) A gas at high pressure when actual volume is not negligible.

It was van der Waals (1873) who attributed the deviation of real gases from ideal behaviour to two of the eight postulates of kinetic molecular theory of gases.
These postulates are as under.
(i) There are no forces of attraction among the molecules of a gas.
(ii) The actual volume of gas molecules is negligible as compared to the volume of the vessel.
When the pressure on a gas is high and the temperature is low then the attractive forces among the molecules become significant, so the ideal gas equation PV = nRT does not hold. Actually, under these conditions, the gas does not remain ideal.The actual volume of the molecules of a gas is usually very small as compared to the volume of the vessel and hence it can be neglected. This volume, however, does not remain negligible when the gas is subjected to high pressure. This can be understood from the following Figs (3.13 a, b).

3.10.2 van der Waals Equation for Real Gases

Keeping in view the above discussion, van der Waals pointed out that both pressure and volume factors in ideal gas equation needed correction in order to make it applicable to the real gases.

Volume Correction

When a gas is compressed, the molecules are pushed so close together that the repulsive forces operate between them. When pressure is increased further it is opposed by the molecules themselves. Actually the molecules have definite volume, no doubt very small as compared to the vessel, but it is not negligible. So van der Waals postulated that the actual volume of molecules can no longer be neglected in a highly compressed gas. If the effective volume of the molecules per mole of a gas is represented by b, then the volume available to gas molecules is the volume of the vessel minus the volume of gas molecules.

$$V_{free} = V_{vessel} - b \qquad \text{..........} \qquad (28)$$

V_{free} is that volume which is available to gas molecules. The factor b is termed as the excluded volume which is constant and characteristic of a gas. It's value depends upon the size of gas molecules. Table (3.3) shows the b values for some important gases. It is interesting to know that the excluded volume b is not equal to the actual volume of gas molecules. In fact, it is four times the actual volume of molecules.

$$b = 4V_m$$

Where V_m is the actual volume of one mole of gas molecules, 'b' is effective volume or excluded volume of one mole of a gas. It is that volume of gas which is occupied by 1 mole of gas molecules in highly compressed state, but not in the liquid state.

Pressure Correction

A molecule in the interior of a gas is attracted by other molecules on all sides, so these attractive forces are cancelled out. However, when a molecule strikes the wall of a container, it experiences a force of attraction towards the other molecules in the gas. This decreases the force of its impact on the wall. Consider the molecule "A" which is unable to create pressure on the wall due to the presence of attractive forces due to 'B' type molecules Fig (3.14). Let the observed pressure on the wall of the container is P. This pressure is less than the actual pressure P_i, by an amount P', so

$$P = P_i - P'$$

P_i is the true kinetic pressure, if the forces of attractions would have been absent. P' is the amount of pressure lessened due to attractive forces. Ideal pressure P_i is

$$P_i = P + P'$$

It is suggested that a part of the pressure P for one mole of a gas used up against intermolecular attractions should decrease as volume increases. Consequently, the value of P' in terms of a constant 'a' which accounts for the attractive forces and the volume V of vessel can be written as

$$P' = \frac{a}{V^2}$$

How to prove it

P' is determined by the forces of attraction between molecules of type A, which are striking the wall of the container and molecules of type B, which are pulling them inward. The net force of attraction is proportional to the concentrations of A type and B type molecules.

$$\therefore \quad P' \propto C_A \cdot C_B$$

Let n is the number of moles of A and B separately and total volume of both types of molecules is 'V' .The n/V is moles dm^{-3} of A and B, separately.

$$P' \propto \frac{n}{V} \cdot \frac{n}{V}$$

$$P' \propto \frac{n^2}{V^2}$$

$$P' \propto \frac{an^2}{V^2}$$

('a' is a constant of proportionality)

If, n = 1 (one mole of gas)

then $$P' = \frac{a}{V^2} \quad \ldots\ldots. (29)$$

Greater the attractive forces among the gas molecules, smaller the volume of vessel, greater the value of lessened pressure P'.

This 'a' is called co-efficient of attraction or attraction per unit volume. It has a constant value for a particular real gas. Thus effective kinetic pressure of a gas is given by P_i, which is the pressure if the gas would have been ideal.

$$P_i = P + \frac{a}{V^2} \quad \ldots\ldots. \quad (30)$$

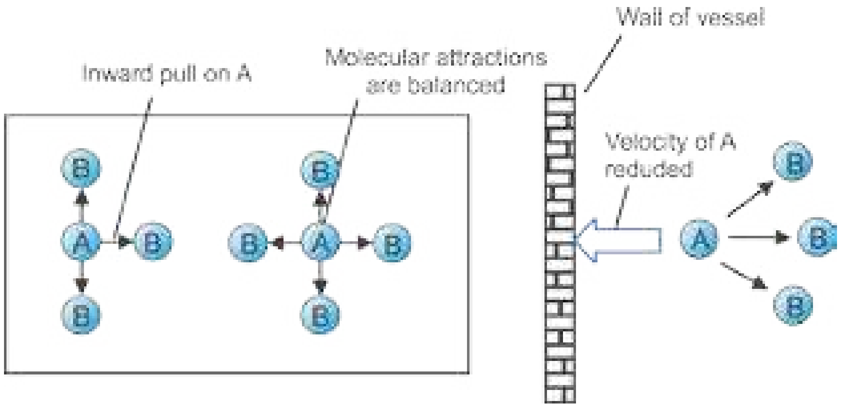


Fig (3.14) Forces of attraction and pressure correction

Once the corrections for pressure and volume are made, the kinetic equation for one mole of a gas can be constructed by taking pressure as $(P + \frac{a}{V^2})$ and volume as (V - b) for one mole of a gas.

$$(P + \frac{a}{V^2})(V - b) = RT \quad \ldots\ldots\ldots \quad (31)$$

For 'n' moles of a gas $$(P + \frac{n^2a}{V^2})(V - nb) = nRT \quad \ldots\ldots\ldots \quad (32)$$

This is called van der Waal's equation, 'a' and 'b' are called van der Waal's constants.

Units of 'a'.

Since,

$$P' = \frac{n^2a}{V^2}$$

So

$$a = \frac{P'V^2}{n^2}$$

$$a = \frac{atm \times (dm^3)^2}{(mol)^2}$$

$$a = atm\ dm^6\ mol^{-2}$$

In S.I. units, pressure is in Nm^{-2} and volume in m^3

or $$a = \frac{Nm^{-2} \times (m^3)^2}{(mol)^2}$$

or $$a = Nm^{+4}\ mol^{-2}$$

Units o f 'b': b' is excluded or incompressible volume /mol^{-1} of gas. Hence its units should be $dm^3\ mol^{-1}$ or $m^3\ mol^{-1}$

The values of 'a' and 'b' can be determined by knowing the values of P, V and T of a gaseous system under two different conditions. Following Table (3.3) gives the values of 'a' and 'b' for some common gases.

Table(3.3) van der Waals Constant for Some Common Gases

Gas	'a' (atm dm^6 mol^{-2})	'b' (dm^3 mol^{-1})
Hydrogen	0.245	0.0266
Oxygen	1.360	0.0318
Nitrogen	1.390	0.0391
Carbon dioxide	3.590	0.0428
Ammonia	4.170	0.0371
Sulphur dioxide	6.170	0.0564
Chlorine	6.493	0.0562

The presence of intermolecular forces in gases like Cl_2 and SO_2 increases their 'a' factor.The least value of 'a' for H_2 is due to its small size and non-polar character. The 'b' value of H_2 is 0.0266 dm^3 mol^{-1}. It means that if 2.016g (1mole) of H_2 is taken, then it will occupy 0.0266 dm^3 or 266cm^3 of volume at closest approach in the gaseous state.

Example 8

One mole of methane gas is maintained at 300 K. Its volume is 250 cm^3. Calculate the pressure exerted by the gas under the following conditions.
(i) when the gas is ideal
(ii) when the gas is non-ideal

a = 2.253 atm dm^6 mol^{-2} , b = 0.0428 dm^3 mol^{-1}

Solution

(i) When the gas is ideal, general gas equation is applied i.e.,
PV = nRT
V = 250 cm^3 = 0.25 dm^3 1 dm^3 = 1000 cm^3

$$n = 1 \text{ mole}$$
$$T = 300 \text{ K}$$
$$R = 0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$$
$$P = \frac{nRT}{V}$$

Putting the values alongwith units

$$P = \frac{1 \text{ mol x } 0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1} \text{ x } 300 \text{ K}}{0.25\ dm^3}$$

$$P = \boxed{98.5 \text{ atm}} \text{ (Answer)}$$

If CH_4 gas would have been ideal, under the given conditions, 98.5 atm. pressure would have been exerted.

(ii) When the gas is behaving as non-ideal, we should use the van der Waals equation

$$\left(P + \frac{n^2a}{V^2}\right)(V\text{-}nb) = n\,R\,T$$

By rearranging the equation and taking the pressure on L.H.S.

$$P + \frac{n^2a}{V^2} = \frac{n\,R\,T}{V\text{-}nb}$$

or

$$P = \frac{n\,R\,T}{V\text{-}nb} - \frac{n^2a}{V^2}$$

Substituting the following values (ignore the units for sake of simplicity)

$n = 1$ mol, $R = 0.0821$ dm^3 atm K^{-1} mol^{-1},

$V = 0.25$ dm^3, $T = 300$ K, $a = 2.253$ dm^6 atm mol^{-2}, $b = 0.0428$ dm^3 mol^{-1}

$$\frac{1 \text{ x } 0.0821 \text{ x } 300}{0.25\text{-}1(0.0428)} - \frac{1 \text{ x } 2.253}{(0.25)} = \frac{24.63}{0.207} - \frac{2.253}{0.0625}$$

$$P = 118.985 - 36.048 = 82.85 \text{ atm.}$$

In the non-ideal situation the pressure has lessened upto

$$98.5 - 82.85 = \boxed{15.65 \text{ atm.}} \text{ Answer}$$

Conclusion:

The difference of these two pressures shows that this gas is non-ideal. Actually CH_4 is thought to be ideal near 1 atm, but around 100 atmospheres, it develops non-ideal attitude. This difference of ideal and non-ideal pressure goes on decreasing when gas is considered at low pressures.

3.11 PLASMA STATE

What is plasma?

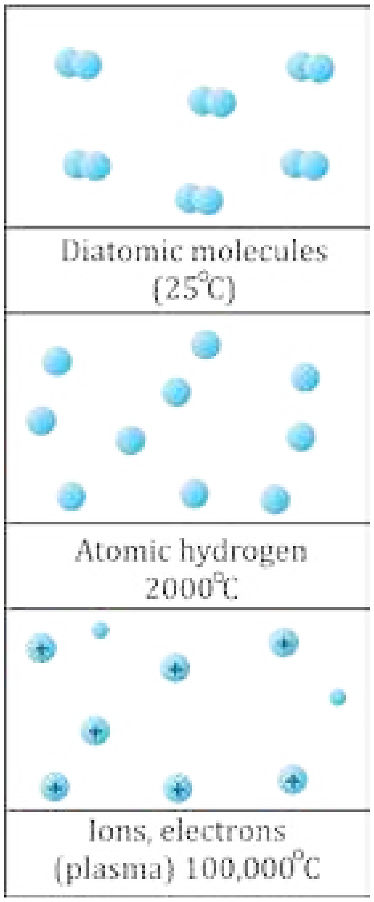
Plasma is often called the “fourth state of matter”, the other three being solid, liquid and gas. Plasma was identified by the English scientist William Crookes in 1879. In addition to being important in many aspects of our daily life, plasmas are estimated to constitute more than 99 percent of the visible universe. Although, naturally occurring plasma is rare on earth, there are many man-made examples.

Inventors have used plasma to conduct electricity in neon signs and fluorescent bulbs. Scientists have constructed special chambers to experiment with plasma in laboratories. It occurs only in lightning discharges and in artificial devices like fluorescent lights, neon signs, etc. It is everywhere in our space environment.

How is Plasma formed ?

When more heat is supplied, the atoms or molecules may be ionized. An electron may gain enough energy to escape its atom. This atom loses one electron and develops a net positive charge. It becomes an ion. In a sufficiently heated gas, ionization happens many times, creating clouds of free electrons and ions. However, all the atoms are not necessarily ionized, and some of them may remain completely intact with no net charge. This ionized gas mixture, consisting of ions, electrons and neutral atoms is called plasma.

It means that a plasma is a distinct state of matter containing a significant number of electrically charged particles a number sufficient to affect its electrical properties and behaviour.



Natural and Artificial Plasma

Artificial plasma can be created by ionization of a gas. as in neon signs. Plasma at low temperatures is hard to maintain because outside a vacuum low temperature plasma reacts rapidly with any molecule it encounters. This aspect makes this material, both very useful and hard to use. Natural plasma exists only at very high temperatures, or low temperature vacuums.

Natural plasma on the other hand do not breakdown or react rapidly, but is extremely hot (over 20,000°C minimum). Their energy is so high that they vaporize any material they touch.

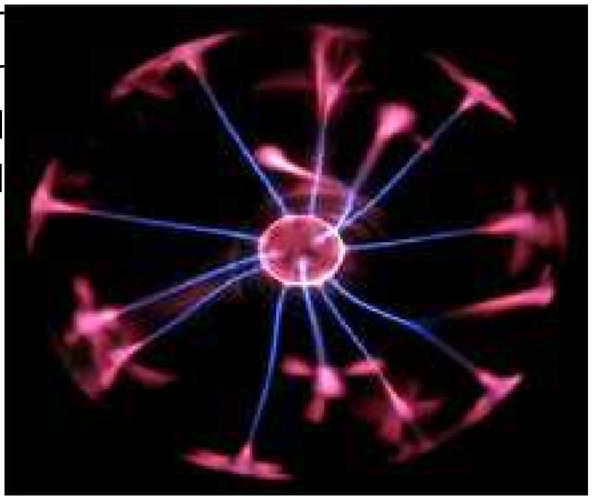
Characteristic of Plasma:

1. A plasma must have sufficient number of charged particles so as a whole, it exhibits a collective response to electric and magnetic fields. The motion of the particles in the plasma generate fields and electric currents from within plasma density. It refers to the density of the charged particles. This complex set of interactions makes plasma a unique, fascinating, and complex state of matter.
2. Although plasma includes electrons and ions and conducts electricity, it is macroscopically neutral. In measurable quantities the number of electrons and ions are equal.

Where is Plasma found ?

Entire universe is almost of plasma. It existed before any other forms of matter came into being. Plasmas are found in everything from the sun to quarks, the smallest particles in the universe.

As stated earlier plasma is the most abundant form of matter in the universe. It is the stuff of stars. A majority of the matter in inner-stellar space is plasma. All the stars that shine are all plasma. The sun is a 1.5 million kilometer ball of plasma, heated by nuclear fusion.



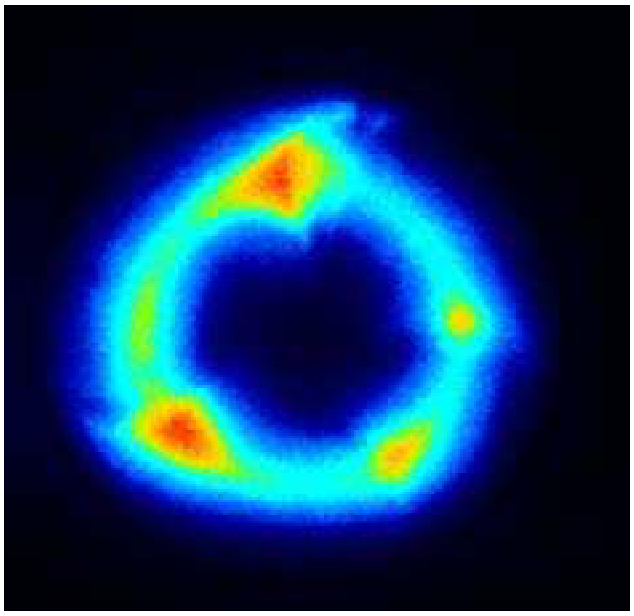
Animation 3.6.:Plasma ball
source & Credit: giphy

One arth it only occurs in a few limited places, like lightning bolts, flames, auroras, and fluorescent lights. When an electric current is passed through neon gas, it produces both plasma and light.

Applications of Plasma:

Plasma has numerous important technological applications. It is present in many devices. It helps us to understand much of the universe around us. Because plasmas' are conductive respond to electric and magnetic fields and can be efficient sources of radiation, so they can be used in innumerable applications where such control is needed or when special sources of energy or radiation are required.

1. A fluorescent light bulb is not like regular light bulbs. Inside the long tube is a gas. When the light is turned on, electricity flows through the tube. This electricity acts as that special energy and charges up the gas. This charging and exciting of the atoms creates a glowing plasma inside the bulb.
2. Neon signs are glass tubes filled with gas. When they are turned on then the electricity flows through the tube. The electricity charges the gas, possibly neon, and creates a plasma inside the tube. The plasma glows with a special colour depending on what kind of gas is inside.
3. They find applications such as plasma processing of semiconductors, sterilization of some medical prodjucts, lamps, lasers, diamond coated films, high power microwave sources and pulsed power switches.
4. They also provide the foundation for important potential applications such as the generation of electrical energy from fusion pollution control and removal of hazardous chemicals.
5. Plasma light up our offices and homes, make our computers and electronic equipment work.
6. They drive lasers and particle accelerators, help to clean up the environment, pasteurize foods and make tools corrosion-resistant.



Animation 3.7.:Application of Plasma
Source & Credit: pag

Future Horizons:

Scientists are working on putting plasma to effective use. Plasma would have to be low energy and should be able to survive without instantly reacting and degenerating. The application of magnetic fields involves the use of plasma. The magnetic fields create low energy plasma which create molecules that are in what scientist call a metastable state. The magnetic fields used to create the low temperature plasma give the plasma molecules, which do not react until they collide with another molecule with just the right energy. This enables these metastable molecules to survive long enough to react with a designated molecule. These metastable particles are selective in their reactivity. It makes them a potentially unique solution to problems like radioactive contamination. Scientist are currently experimenting with mixtures of gases to work as metastable agents on plutonium and uranium, and this is just the beginning.

KEY POINTS

1. The behaviour of a gas is described through four variables i.e., pressure, volume , temperature and its number of moles. The relationships between gas variables are known as the simple gas laws. Boyle's law relates pressure of a gas with its volume, while Charles's law relates gas volume with temperature. Avogadro's law is concerned with volume and amount of a gas. The important concept of absolute zero of temperature originates from the simple gas laws.
2. By combining the above mentioned three laws, a more general equation about the behaviour of gas is obtained i.e., $PV = n RT$. This equation can be solved for any one of the variables when values for others are known. This equation can be modified for the determination of molar masses and the density of the gas.
3. Dalton's law of partial pressures can be used to calculate the partial pressures of gases.
4. The processes of diffusion and effusion are best understood by Graham's law of diffusion.
5. Kinetic molecular theory of gases provides a theoretical basis for various gas laws. With the help of this theory a relationship is established between average molecular kinetic energy and kelvin temperature. The diffusion and effusion of the gases can be related to their molar masses through the kinetic molecular theory of gases.
6. The real gases show ideal behaviour under specific conditions. They become non-ideal at high pressure and low temperature. The non-ideal behaviour results chiefly from intermolecuiar attractions and the finite volume occupied by the gas molecules.
7. Gases can be liquified by applying sufficient pressure but temperature should either be critical one or below it.
8. To calculate the pressure or volume of a real gas under the non-ideal conditions, alternative kinetic equation has been developed. This is known as the van der Waal's equation.
9. The plasma, a forth state of matter, consist of neutral particles, positive ions and negative electrons, 99% of the known universe is in the plasma state.

Excercise

Q 1: Select the correct answer out of the following alternative suggestions.

(i) Pressure remaining constant, at which temperature the volume of a gas will become twice of what it is at 0°C.

a. 546°C b. 200°C c. 546K d. 273K

(ii) Number of molecules in one dm³ of water is close to

a. $\frac{6.02}{22.4} \times 10^{23}$ b. $\frac{12.04}{22.4} \times 10^{23}$ c. $\frac{18}{22.4} \times 10^{23}$ d. $55.6 \times 6.02 \times 10^{23}$

(iii) Which of the following will have the same number of molecules at STP?

a. 280 cm³ of CO_2 and 280 cm³ of N_2O
b. 11.2 dm³ of O_2 and 32 g of O_2
c. 44 g of CO_2 and 11.2 dm³ of CO
d. 28 g of N_2 and 5.6 dm³ of oxygen

(iv) If absolute temperature of a gas is doubled and the pressure is reduced to one half, the volume of the gas will

a. remain unchanged b. increase four times
c. reduce to 1/4 d. be doubled

(v) How should the conditions be changed to prevent the volume of a given gas from expanding when its mass is increased?

a. Temperature is lowered and pressure is increased.
b. Temperature is increased and pressure is lowered.
c. Temperature and pressure both are lowered.
d. Temperature and pressure both are increased.

(vi) The molar volume of CO_2 is maximum at

a. S TP b. 127°C and 1 atm c. 0°C and 2 atm d. 273°C and 2 atm

(vii) The order of the rate of diffusion of gases NH_3, SO_2, Cl_2, an CO_2 is:

a. $NH_3 > SO_2 > Cl_2 > CO_2$ b. $NH_3 > CO_2 > SO_2 > Cl_2$
c. $Cl_2 > SO_2 > CO_2 > NH_3$ d. $NH_3 > CO_2 > Cl_2 > SO_2$

(viii) Equal masses of methane and oxygen are mixed in an empty container at 25°C. The fraction of total pressure exerted by oxygen is

a. 1/3 b. 8/9 c. 1/9 d. 16/17

(ix) Gases deviate form ideal behaviour at high pressure. Which of the following is correct for non-ideality?

a. At high pressure, the gas molecules move in one direction only.
b. At high pressure, the collisions between the gas molecules are increased manifold.
c. At high pressure, the volume of the gas becomes insignificant.
d. At high pressure, the intermolecular attractions become significant.

(x) The deviation of a gas from ideal behaviour is maximum at

a. -10°C and 5.0atm b. -10 °C and 2.0 atm
c. 100 °Cand2.0 atm d. 0 °C and 2.0 atm

(xi) A real gas obeying van derW aals equation will resemble ideal gas if

a. both 'a' and 'b' are large b. both'a'and'b'are small
c. 'a' is small and 'b' is large d. 'a' is large and 'b' is small

Q2: Fill in the blanks

(i). The product PV has the S.I. unit of ____________

(ii).Eight grams each of O_2, and H_2, at 27 °C will have total K.E in the ratio of ____________

(iii).Smell of the cooking gas during leakage from a gas cylinder is due to the property of____________ of ____________ gases.

(iv).Equal ________ of ideal gases at the same temperature and pressure contain____________ number of molecules.

(v).The temperature above which a substance exists only as a gas is called____________.

Q3: Label the follow in g sentences as True or False.

(i). Kinetic energy of molecules of a gas is zero at 0°C.

(ii). A gas in a closed container will exert much higher pressure at the bottom due to gravity than at the top.

(iii). Real gases show ideal gas behaviour at low pressure and high temperature.

(iv). Liquefaction of gases involves decrease in intermolecular spaces.

(v). An ideal gas on expansion will show Joule-Thomson effect.

Q4 . a. What is Boyle's law of gases? Give its experimental verification.

b. What are isotherms? What happens to the positions of isotherms when they are plotted at high temperature for a particular gas.

c. Why do w e get a straight line when pressures exerted on a gas are plotted against inverse of volumes? This straight line changes its position in the graph by varying the temperature. Justify it.

d. How will you explain that the value of the constant k in the equation PV = k depends upon (i) the temperature of a gas (ii) the quantity of a gas

Q5.a. What is the Charles's law? Which scale of temperature is used to verify that V/T = k (pressure and number of moles are constant)?

b. A sample of carbon monoxide gas occupies 150.0 mL at 25.0°C. It is then cooled at constant pressure until it occupies 100.0 mL. What is the new' temperature? (Ans: 198.8K or -74.4 °C)

c. Do you think that the volume of any quantity of a gas becomes zero at - 273.16 °C. Is it not against the law of conservation of mass? How do you deduce the idea of absolute zero from this information?

Q6 . a. What is Kelvin scale of temperature? Plot a graph for one mole of an a real gas to prove that a gas becomes liquid, earlier than -273.16 ’C.

b. Throw some light on the factor 1/273 in Charles's law.

Q7. a. What is the general gas equation? Derive it in various forms.

b. Can we determine the molecular mass of an unknown gas if we know the pressure, temperature and volume along with the mass of that gas.

c. How do you justify from general gas equation that increase in temperature or decrease of pressure decreases the density of the gas?

c. Why do we feel comfortable in expressing the densities of gases in the units of g dm^{-3} rather than g cm^{-3}, a unit which is used to express the densities of liquids and solids.

Q8 . Derive the units for gas constant R in general gas equation:

a. when the pressure is in atmosphere and volume in dm^3.

b. when the pressure is in N m^{-2} and volume in m^3.

c. when energy is expressed in ergs.

Q9. a. What is Avogadro’s law of gases?

b. Do you think that 1 mole of H_2 and 1 mole of NH_3 at 0 °C and 1 atmpressure will have Avogadro’s number of particles?

c. Justify that 1 cm^3 of H_2 and 1 cm^3 of CH_4 at STP will have same number of molecules, when one molecule of CH_4 is 8 times heavier than that of hydrogen.

Q10. a. Dalton's law of partial pressures is only obeyed by those gases which don't have attractive forces among their molecules. Explain it.

b. Derive an equation to find out the partial pressure of a gas knowing the individual moles of component gases and the total pressure of the mixture.

c. Explain that the process of respiration obeys the Dalton's law of partial pressures.

d. How do you differentiate between diffusion and effusion? Explain Graham's law of diffusion.

Q11. a. What is critical temperature of a gas? What is its importance for liquefaction of gases? Discuss Linde's method of liquefaction of gases.

b. What is Joule-Thomson effect? Explain its importance in Linde's method of liquefaction of gases.

Q12. a. What is kinetic molecular theory of gases? Give its postulates.

b. How does kinetic molecular theory of gases explain the following gas laws:

(i) Boyle's law (ii) Charles's law
(iii) Avogadro's law (iv) Graham's law of diffusion

Q13. a. Gases show non-ideal behaviour at low temperature and high pressure. Explain this with the help of a graph.

b. Do you think that some of the postulates of kinetic molecular theory of gases are faulty? Point out these postulates.

c. Hydrogen and helium are ideal at room temperature, but SO_2, and Cl_2 are nonideal. How will you explain this?

Q14. a. Derive van der Waal's equation for real gases.

b. What is the physical significance of van der Waals'constants, 'a' and 'b? Give their units.

Q15 Explain the following facts

a. The plot of PV versus P i s a straight line at constant temperature and with a fixed number of moles of an ideal gas.

b. The straight line in (a) is parallel to pressure-axis and goes away from the pressure axis at higher pressures for many gases.

c. Pressure of NH_3 gas at given conditions (say 20 atm pressure and room temperature) is less as calculated by van der Waals equation than that calculated by general gas equation.

d. Water vapours do not behave ideally at 273K.

e. SO_2 is comparatively non-ideal at 273K but behaves idealy at 327 "C.

Q16 Helium gas in a 100 cm^3 container at a pressure of 500 torr is transferred to a container with a volume of 250 cm^3. What will be the new pressure

a. if no change in temperature occurs (Ans: 2 0 0 torr)

b. if its temperature changes from 20 "C to 15°C? (Ans: 196.56 torr)

Q17

a. What are the densities in kg/dm^3 of the following gases at STP (P = 101325 Nm^{-2}, T = 273 K, molecular masses are in kg mol^{-1} (i) methane, (ii) oxygen, (iii) hydrogen

b. Compare the values of densities in proportion to their mole masses.

c. How do you justify that increase of volume upto 100 dm^3 at 27°C of 2 moles of NH_3 will allow the gas behave ideally, as compared to S.T.P conditions. (Ans: CH_4=0.714kgm, O_2=1.428kgm^{-3}, H_2=0.089kgm^{-3})

Q18 A sample of krypton with a volume of 6.25 dm^3, a pressure of 765 torr and a temperature of 20 °C is expanded to a volume of 9.55 dm^3 and a pressure of 375 torr. What will be its final temperature in °C? (Ans: T = -53.6°c)

Q19 Working at a vacuum line, a chemist isolated a gas in a weighing bulb with a volume of 255 cm^3, at a temperature of 25 °C and under a pressure in the bulb of 10.0 torr. The gas weighed 12.1 mg. What is the molecular mass of this gas?

(Ans: 87.93g mol^{-1})

Q20 What pressure is exerted by a mixture of 2.00g of H_2 and 8.00g of N_2 at 273K in a 10 dm^3 vessel? (Ans: P = 2.88 atm)

Q21. a. The relative densities of two gases A and B are 1:1.5. Find out the volume of B which will diffuse in the same time in which 150 dm^3 of A will diffuse?

(Ans: 122.47dm^3)

b. Hydrogen (H_2) diffuses through a porous plate at a rate of 500 cm^3 per minute at 0 "C. What is the rate of diffusion of oxygen through the same porous plate at0 °C?

(Ans: 125 cm^3)

c. The rate of effusion of an unknown gas A through a pinhole is found to be 0.279 times the rate of effusion of H_2 gas through the same pinhole. Calculate the molecular mass of the unknown gas at STP. (Ans: = 25.7 $gmol^{-1}$)

Q22 Calculate the number of molecules and the number of atoms in the given amounts of each gas

(a) 20 cm^3 of CH_4 at 0 °C and pressure of 700 mm of mercury (Ans: 4.936 $x10^{20,}$ 24.7 x 10^{20}

(b) 1 cm^3 of NH_3 at 100 °C and pressure of 1.5 atm (Ans:$2.94x10^{19}$,1.177 x 10^{20})

Q23 Calculate the masses of 10^{20} molecules of each of H_2, O_2, and CO, at STP. What will happen to the masses of these gases, when the temperature of these gases are increased by 100 °C and the pressure is decreased by 100 torr.

(Ans: 3.3 x 10^{-4}g; 5.31 x 10^{-3}g; 7.30 x 10^{-3}g)

Q24 a. Two moles of NH_3 are enclosed in a 5 dm^3 flask at 27 °C. Calculate the pressure exerted by the gas assuming that

(i) it behaves like an ideal gas

(ii) it behaves like a real gas

a=4.17 atm dm^6 mol^{-2}

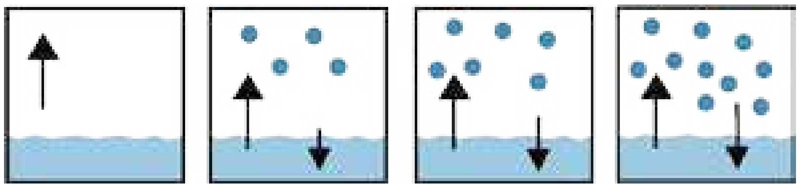
b = 0.0371 dm^3 mol^{-1} (Ans: 9.85 atm)

b. Also calculate the amount of pressure lessened due to forces of attractions at these conditions of volume and temperature. (Ans: 0.51atm)

c. Do you expect the same decrease in the pressure of two moles of NH_3 having a volume of 40 dm^3 and at temperature of 27 °C.

CHAPTER

4



LIQUIDS AND SOLIDS

Animation 4.1: Solid, Liquid, Gas
Source & Credit: everythingscientific

INTRODUCTION

The existence of matter in our surrounding in the form of gases, liquids and solids is due to difference of interacting forces among the constituent particles.

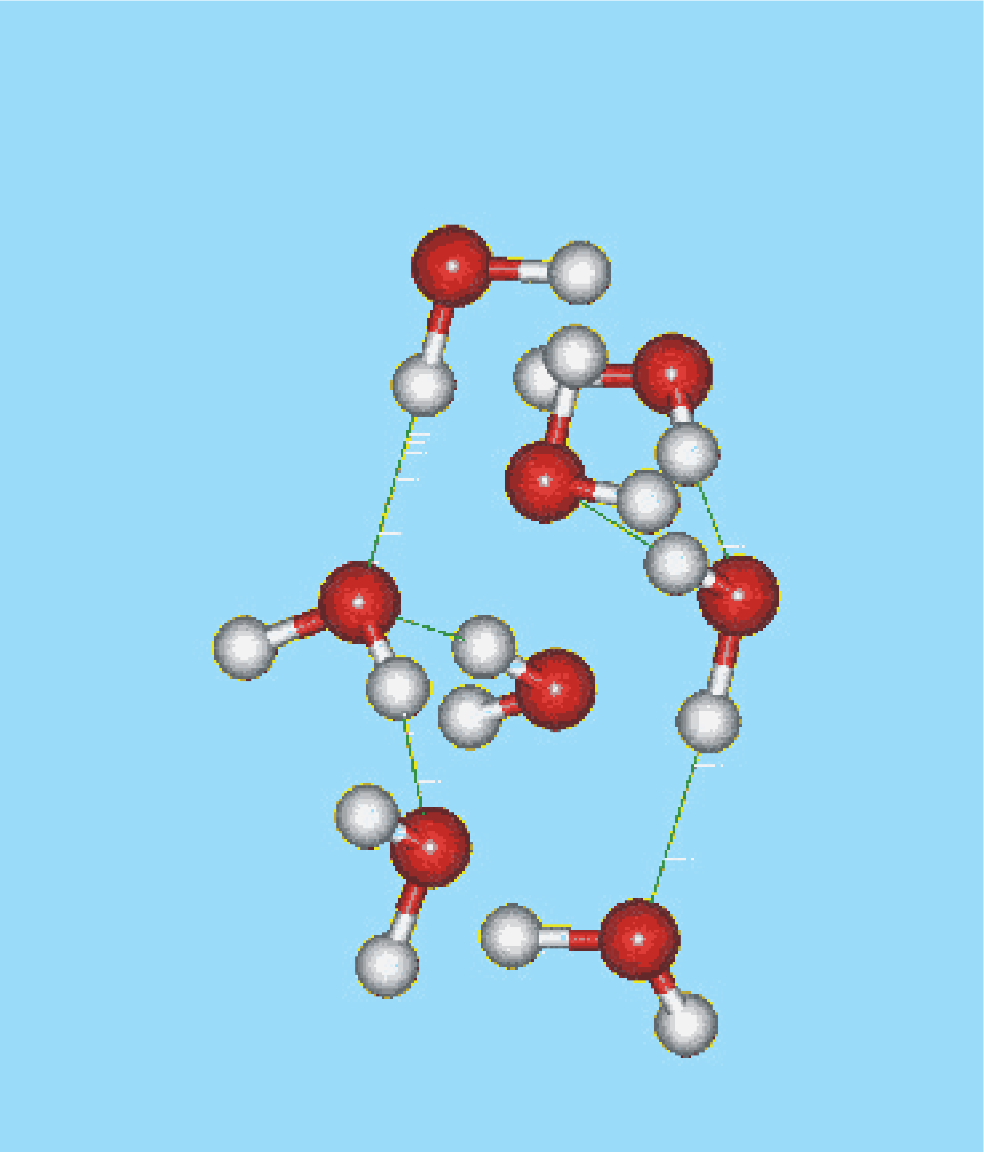
4.1 INTERMOLECULAR FORCES

To understand the properties of liquids and solids, we need to know the kinds of intermolecular forces present in them and their relative strength. It is important to realize that the attraction between the molecules is much weaker than the attraction between atoms within a molecule. In a molecule of HCl, there is a covalent bond between H and Cl which is due to the mutual sharing of electrons. Both atoms satisfy their outermost shells and it is their firm need to remain together, hence this linkage is very strong.

HCl molecules in the neighbourhood attract each other, but the forces of attraction are weak. These forces are believed to exist between all kinds of atoms and molecules when they are sufficiently close to each other. Such intermolecular forces are called van der Waals forces and they have nothing to do with the valence electrons.

These intermolecular forces bring the molecules close together and give particular physical properties to the substances in gaseous, liquid and solid states. Four types of such forces are mentioned here.

1. Dipole-dipole forces
2. Ion-dipole forces
3. Dipole-induced dipole forces
4. Instantaneous dipole-induced dipole forces or London dispersion forces



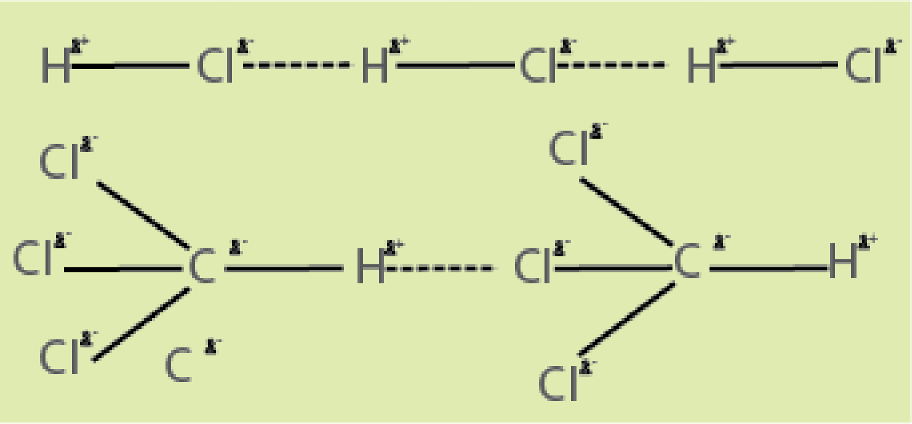
Animation 4.2 : Intermolecular forces
Source & Credit: intermolecularforcess

4.1.1 Dipole-dipole Forces

In case of HCl molecule both atoms differ in electronegativity. Chlorine being more electronegative, develops the partial negative charge and hydrogen develops the partial positive charge. So, whenever the molecules are close to each other, they tend to line up. The positive end of one molecule attracts the negative end of the other molecule and these electrostatic forces of attraction are called dipole-dipole forces. However, thermal energy causes the molecules not to have a perfect alignment.

Anyhow, there is a net attraction between the polar molecules. These forces are called as dipole-dipole forces and they are approximately one percent as effective as a covalent bond. The strength of these forces depends upon the electronegativity difference between the bonded atoms and the distance between the molecules. The distances between molecules in the gaseous phase are greater so these forces are very weak in this phase. In liquids these forces are reasonably strong. The examples of the molecules which show dipole-dipole attractions are numerous. Two of these are given below i.e., for HCl and $CHCl_3$ (chloroform) Fig (4.1).

Greater the strength of these dipole-dipole forces, greater are the values of thermodynamic parameters like melting points, boiling points, heats of vapourization and heats of sublimation.



Show Fig. (4.1) Dipole - dipole forces present in HC1 molecules and chloroform ($CHCl_3$) molecules.

4.1.2 Dipole-induced Dipole Forces

Sometimes, we have a mixture of substances containing polar and non-polar molecules. The positive end of the polar molecule attracts the mobile electrons of the nearby non-polar molecule. In this way polarity is induced in non-polar molecule, and both molecules become dipoles. These forces are called dipole-induced dipole forces or as Debye forces. The following figure makes the idea clear Fig (4.2).

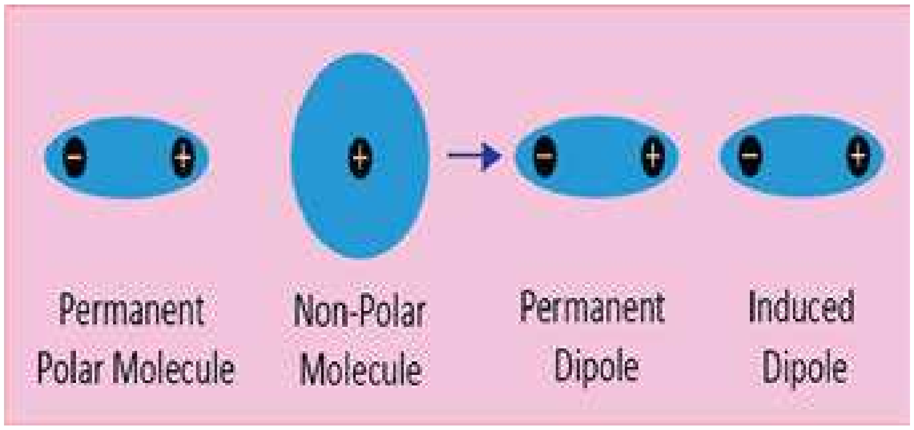


Fig (4.2) Dipole-induced dipole interactions

4.1.3 Instantaneous Dipole-induced Dipole Forces or London Dispersion Forces

Intermolecular forces among the polar molecules, as discussed in section 4.1.1 are very easy to understand. But the forces of attraction present among the non-polar molecules like helium, neon, argon, chlorine and methane need special attention because under normal conditions such molecules don't have dipoles. We know that helium gas can be liquefied under appropriate conditions. In other words forces of attraction operate among the atoms of helium which cause them to cling together in the liquid state.

A German physicist Fritz London in 1930 offered a simple explanation for these weak attractive forces between non-polar molecules.

In helium gas, the electrons of one atom influence the moving electrons of the other atom. Electrons repel each other and they tend to stay as far apart -as possible. When the electrons of one atom come close to the electron of other atom, they are pushed away from each other. In this way,a temporary dipole is created in the atom as shown in the Fig (4.3). The result is that, at any moment, the electron density of the atom is no more symmetrical. It has more negative charge on one side than on the other. At that particular instant, the helium atom becomes a dipole. This is called instantaneous dipole.

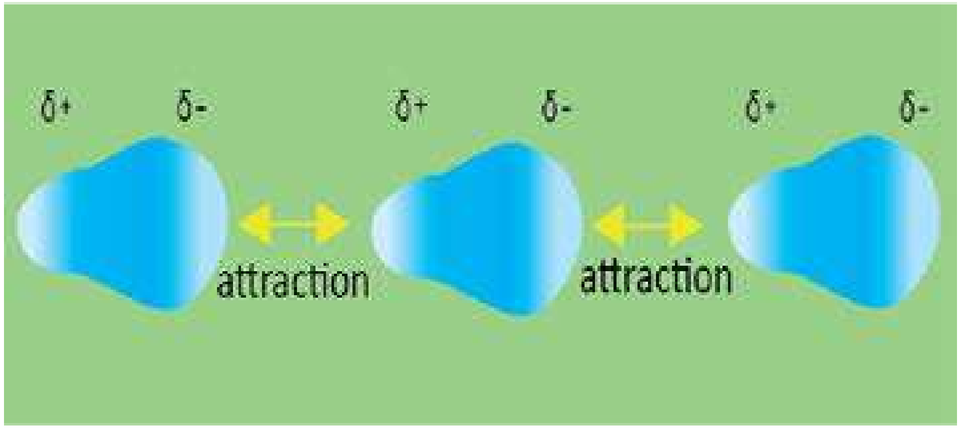
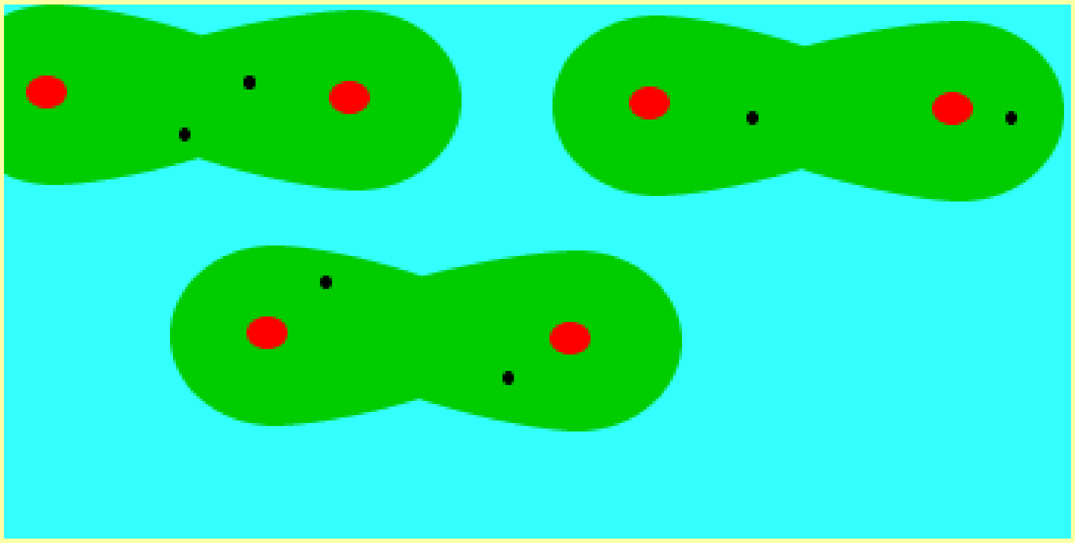


Fig. (4.3) Instantaneous dipole-induced dipole attractions between helium atoms.

This instantaneous dipole then disturbs the electronic cloud of the other nearby atom. So,a dipole is induced in the second atom. This is called induced dipole. The momentary force of attraction created between instantaneous dipole and the induced dipole is called instantaneous dipole-induced dipole interaction or London force.

It is a very short-lived attraction because the electrons keep moving. This movement of electrons cause the dipoles to vanish as quickly as they are formed. Anyhow, a moment later, the dipoles will appear in different orientation and again weak attractions are developed.

London forces are present in all types of molecules whether polar or non-polar, but they are very' significant for non-polar molecules like Cl_2, H_2 and noble gases (helium, neon,etc.)



Animation 4.3 : London Dispersion Forces
Source & Credit: dynamicscience

4.1.4 Factors Affecting the London Forces

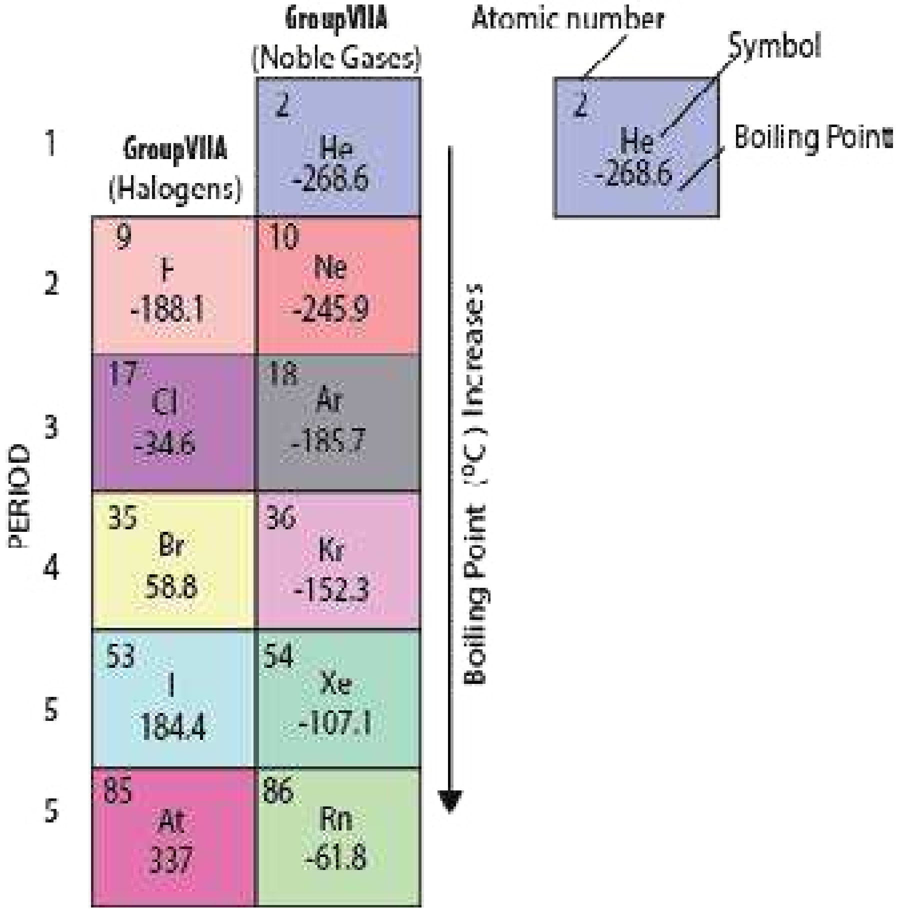
London forces are weaker than dipole- dipole interactions. The strength of these forces depend upor the size of the electronic cloud of the atom or molecules. When the size of the atom or molecule is large then the dispersion becomes easy and these forces become more prominent. The elements of the zero group in the periodic table are all mono-atomic gases. They don't make covalent bonds with other atoms because their outermost shells are complete. Their boiling points increase down the group from helium to radon. Boiling points of noble gases are given in Table (4.1)

The atomic number increases down the group and the outermost electrons move away from the nuclei. The dispersion of the electronic clouds becomes more and more easy. So the polarizability of these atoms go on increasing.

Polarizability is the quantitative measurement of the extent to which the electronic cloud can be polarized or distorted. When we say that a species (atom, molecule or ion) is polarized, it means that temporary poles are created. This is possible if electronic cloud can be disturbed or distorted. This increased distortion of electronic cloud creates stronger London forces and hence the boiling points are increased down the group.

Similarly, the boiling points of halogens in group VII-A also increase from fluorine to iodine Table (4.1). All the halogens are non-polar diatomic molecules, but there is a big difference in their physical states at room temperature. Fluorine is a gas and boils at -188.1 °C, while iodine is a solid at room temperature which boils at +184.4 °C. The polarizability of iodine molecule is much greater than that of fluorine.

Table(4.1) Boiling points of halogens and noble gases



PERIOD	GroupVIIA (Halogens)	GroupVIIA (Noble Gases)
1		2 He -268.6
2	9 F -188.1	10 Ne -245.9
3	17 Cl -34.6	18 Ar -185.7
4	35 Br 58.8	36 Kr -152.3
5	53 I 184.4	54 Xe -107.1
5	85 At 337	86 Rn -61.8

Another important factor that affects the strength of London forces is the number of atoms in a non-polar molecule. Greater the number of atoms in a molecule, greater is its polarizability. Let us discuss the boiling points of saturated hydrocarbons. These hydrocarbons have chain of carbon atoms linked with hydrogen atoms. Compare the length of the chain for C_2H_6 and C_6H_{14}.

They have the boiling points - 88.6 °C and 68.7 C,respectively. This means that the molecule with a large chain length experiences stronger attractive forces. The reason is that longer molecules have more places along its length where they can be attracted to other molecules. It is very interesting to know that with the increasing molecular mass of these hydrocarbons, they change from gaseous to liquid and then finally become solids. The Table (4.2) gives the boiling points and the physical states of some hydrocarbons.

Table (4.2) Boiling points and physical states of some hydrocarbons

Name	B.P ^{0}C (1 atm)	Physical state at S.T.P	Name	B.P ^{0}C (1 atm)	Physical state at S.T.P
Mathane	-164	Gas	Pentane	36.1	Liquid
Ethane	-88.6	Gas	Hexane	68.7	Liquid
Propane	-42.1	Gas	Decane	174.1	Liquid
Butane	0.5	Gas	Isodecane	327	Solid

4.1.5 Hydrogen Bonding

To understand hydrogen bonding, let us consider the molecule of water. Oxygen is more electronegative element as compared to hydrogen, so water is a polar molecule. Hence there will be dipole-dipole interactions between partial positively charged hydrogen atoms and partial negatively charged oxygen atoms. Actually, hydrogen bonding is something more than simple dipole-dipole interaction. Firstly, oxygen atom has two lone pairs. Secondly hydrogen has sufficient partial positive charge. Both the hydrogen atoms of water molecule create strong electrical field due to their small sizes.

The oxygen atom of the other molecule links to form a coordinate covalent bond with hydrogen using one of its lone pairs of electrons. Fig (4.4).

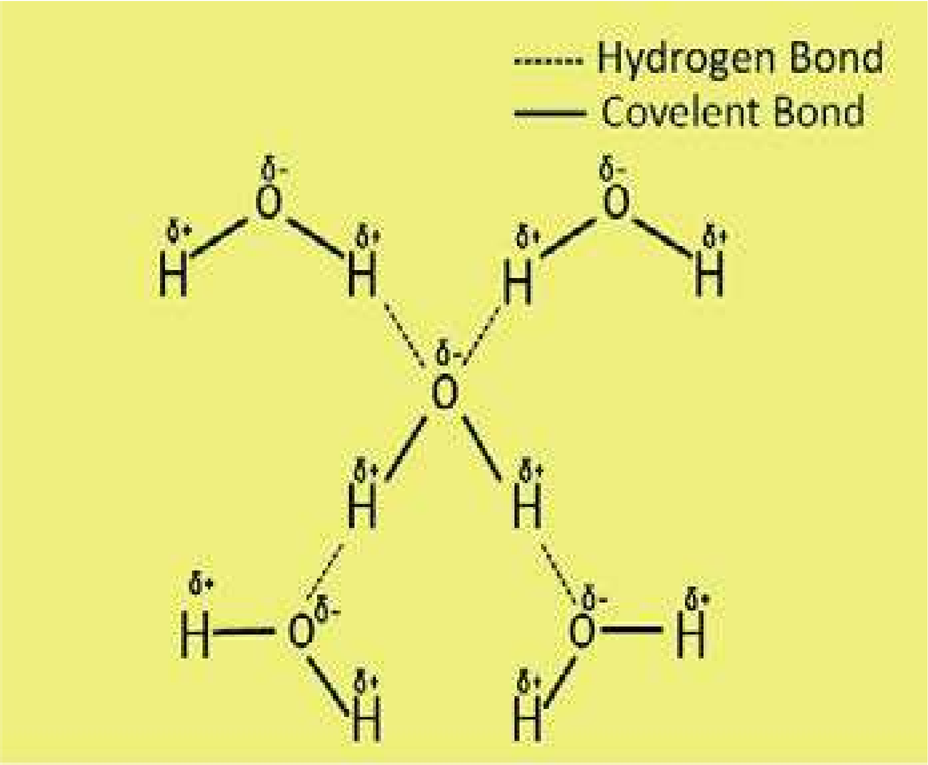
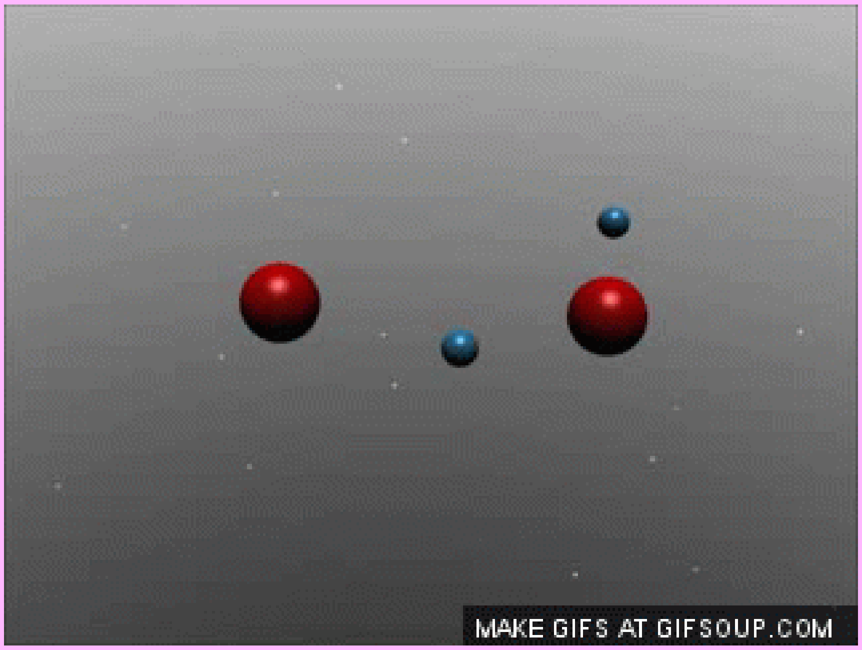


Fig (4.4) Hydrogen bonding in water.

Thus loose bond formed is definitely stronger than simple dipole-dipole interaction. Because of the small size of the hydrogen atom, it can take part in this type of bonding. This bonding acts as a bridge between two electronegative oxygen atoms. Hence hydrogen bonding is the electrostatic force of a atraction between a highly electronegative atom and partial positively charged hydorgen atom.

The electronegative atoms responsible for creating hydrogen bonding are fluorine, oxygen, nitrogen and rarely chlorine. The strength of hydrogen bond is generally twenty times less than that of a covalent bond.



Animation 4.4 : hydrogen bonding
Source & Credit: stream 1

It is not advisable to limit the hydrogen bonding to the above-mentioned electronegative atoms. The three chlorine atoms in chloroform are responsible for H- bonding with other molecules. These atoms deprive the carbon atom of its electrons and the partial positively charged hydrogen can form a strong hydrogen bond with oxygen atom of acetone Fig (4.5).

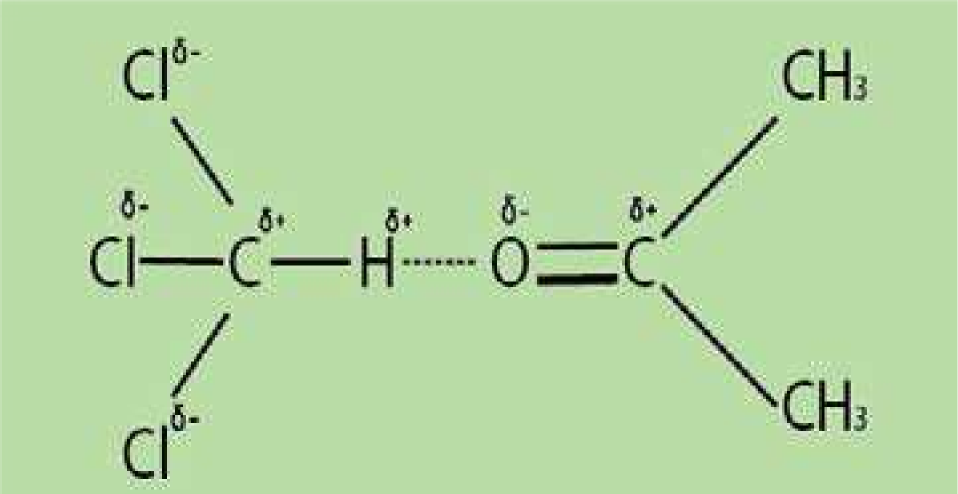


Fig (4.5) Hydrogen bonding between chloroform and acetone

The hydrogen bonding present in the molecules of ammonia and those of hydroflouric acid can be depicted as follows Fig (4.6).The molecules of HF join with each other in a zig- zag manner.

The exceptional, low acidic strength of HF molecule as compared to HCl, HBr and HI is due to this strong hydrogen bonding, because the partial positively charged hydrogen is entrapped between two highly electronegative atoms.

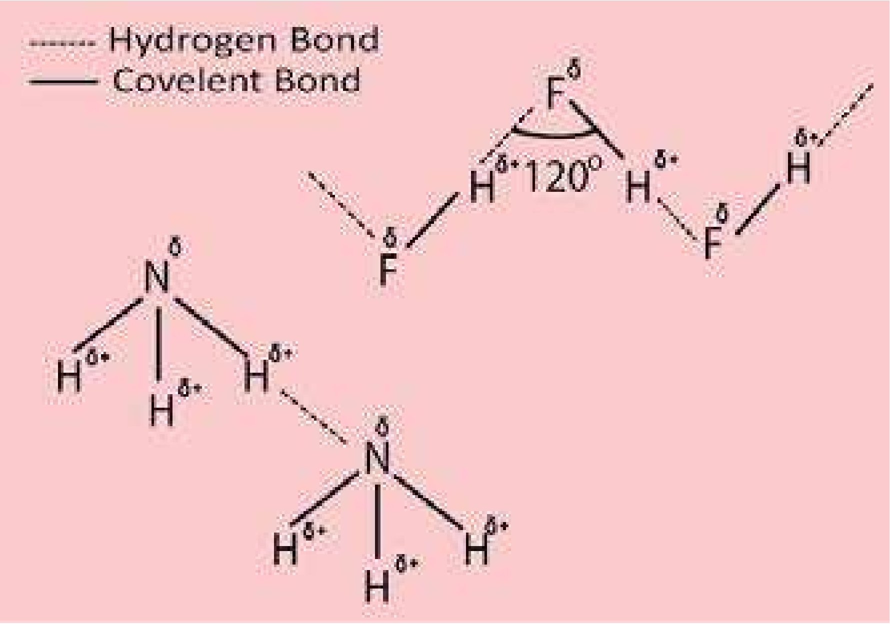
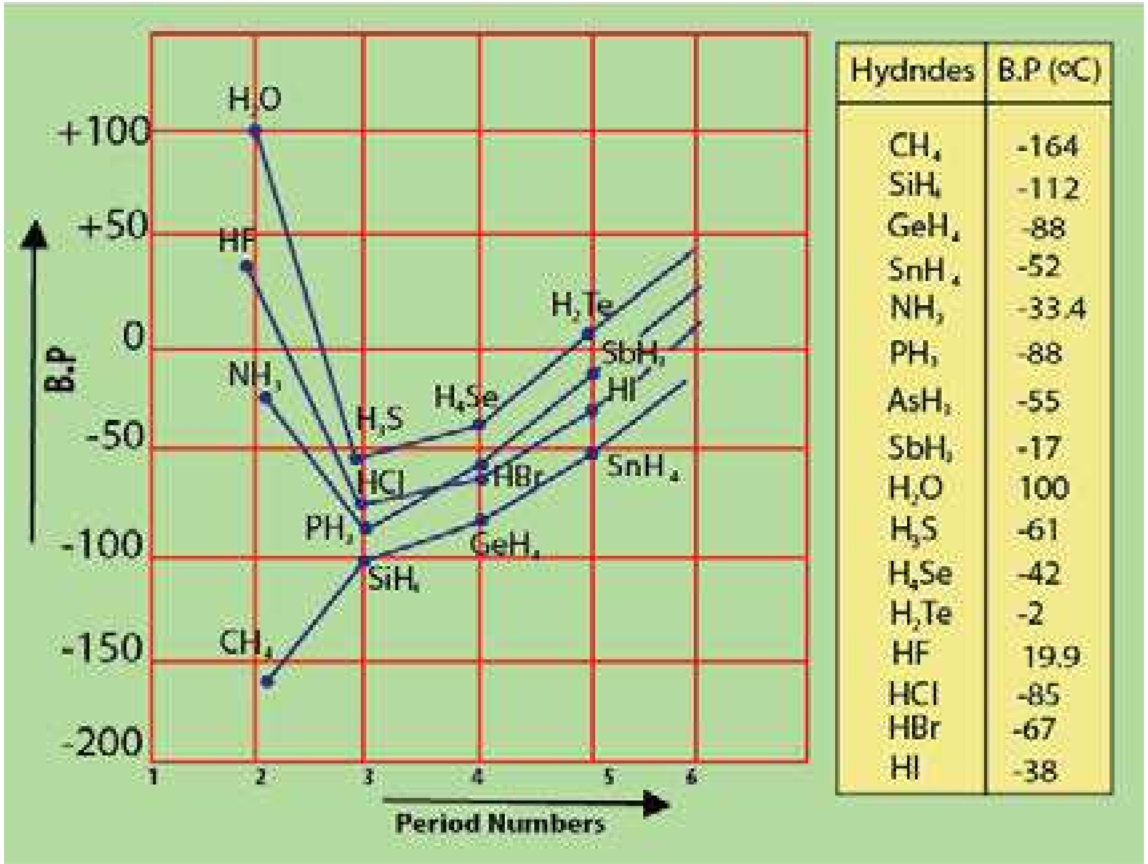


Fig (4.6) Hydrogen bonding in NH_3 and HF molecules.

4.1.6 Properties and Application of Compounds Containing Hydrogen Bonding

1. Thermodynamic Properties of Covalent Hydrides

Our discussion shows that hydrogen bonding exists in compounds having partial positively charged hydrogen and highly electronegative atoms bearing partial negative charge. Obviously such intermolecular attractions will influence the physical properties like melting and boiling points. Let us compare the physical properties of hydrides of group IV-A, V-A, VI-A and VII-A. The graphs are plotted between the period number of the periodic table on x-axis and boiling points in kelvin on y-axis Fig (4.7).



Hydndes	B.P (ºC)
CH_4	-164
SiH_4	-112
GeH_4	-88
SnH_4	-52
NH_3	-33.4
PH_3	-88
AsH_3	-55
SbH_3	-17
H_2O	100
H_2S	-61
H_2Se	-42
H_2Te	-2
HF	19.9
HCl	-85
HBr	-67
HI	-38

Fig (4.7) A Graph between period number and the boiling points of hydrides of IV-A, V-A, VI-A and VII-A group elements.

A look at the boiling points of hydrides of group IV-A convinces us, that they have low boiling points as compared to those of group V-A, VI-A, VII-A. The reason is that these elements are least electronegative. CH_4 has the lowest boiling point because it is a very small molecule and its polarizability is the least.

When we consider the hydrides of group V-A, VI-A, VII-A then NH_3, $H_2$0 and HF show maximum boiling points in the respective series. The reason is, the enhancec electronegative character of N, 0 and F. That is why, water is liquid at room temperature, but H_2S and H_2Se are gases.

It is interesting to know that the boiling point of water seems to be more affected by hydrogen bonding than that of HF Fluorine is more electronegative than oxygen. So, we should expect H-bonding in HF to be stronger than that in water and as a result the boiling point of HF should be higher than that of $H_2$0. However, it is lower and the reason is that the fluorine atom can make only one hydrogen bond with electropositive hydrogen of a neighboring molecule. Water can form two hydrogen bonds per molecule, as it has two hydrogen atoms and two lone pairs on oxygen atom. Ammonia can form only one hydrogen bond per molecule as it has only one lone pair.

The boiling point of HBris slightly higher than that of HCl. It means that chlorine is electronegative enough to form a hydrogen bond. Sometimes it is thought that HCl has a strong dipole-dipole interaction but in reality, it is a border line case. The hydrides of fourth period GeH_4, AsH_3, H_2Se, HBr show greater boiling points than those of third period due to greater size and enhanced poiarizabilities.

2. Solubility of Hydrogen- Bonded Molecules

Water is the best example of H-bonded system. Similarly ethyl alcohol (C_2H_5OH) also has the tendency to form hydrogen bonds. So, ethyl alcohol can dissolve in water because both can form hydrogen bonds with each other. Similarly carboxylic acids are also soluble in water, if their sizes are small. Hydrocarbons are not soluble in water at all, because they are non-polar compounds and there are no chances of hydrogen bonding between water and hydrocarbon molecules.

3. Structure of Ice

The molecules of water have tetrahedral structure. Two lone pairs of electrons on oxygen atom occupy two corners of the tetrahedron. In the liquid state, water molecules are extensively associated with each other and these associations break and are reformed because the molecules of water are mobile. When the temperature of water is decreased and ice is formed then the molecules become more regular and this regularity extends throughout the whole structure. Empty spaces are created in the structure as shown in the following Fig (4.8b). That is why when water freezes it occupies 9% more space and its density decreases. The result is that ice floats on water. The structure of ice is just like that of a diamond because each atom of carbon in diamond is at the center of tetrahedron just like the oxygen of water molecule in ice, Fig (4.8 b).

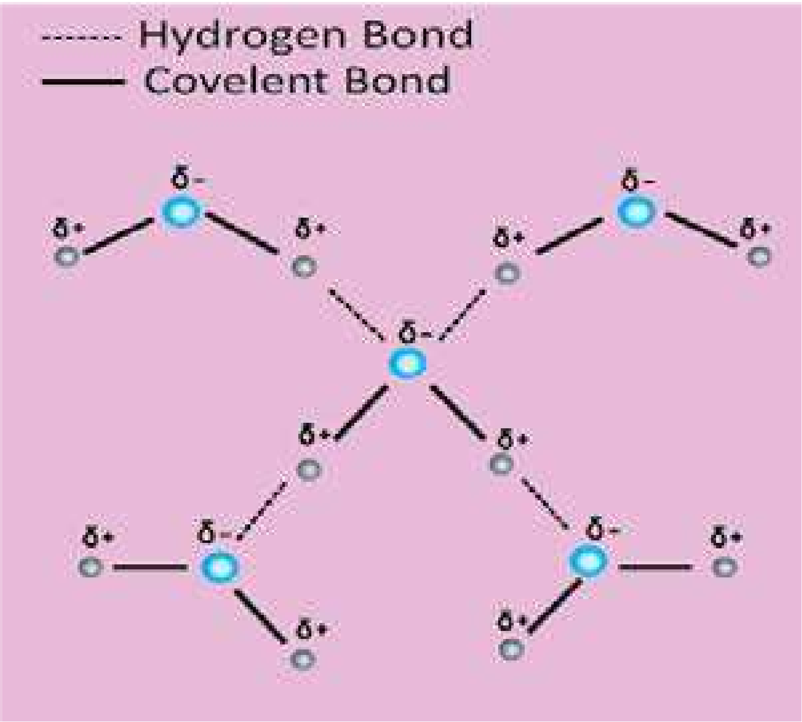


Fig (4.8 a) Structure of liquid water

The lower density of ice than liquid water at 0 °C causes water in ponds and lakes to freeze from surface to the downward direction. Water attains the temperature of 4°C by the fall of temperature in the surrounding. As the outer atmosphere becomes further cold, the water at the surface becomes less dense. This less dense water below 4 °C stays on the top of slightly warm water underneath. A stage reaches when it freezes. This layer of ice insulates the water underneath for further heat loss. Fish and plants survive under this blanket of ice for months.

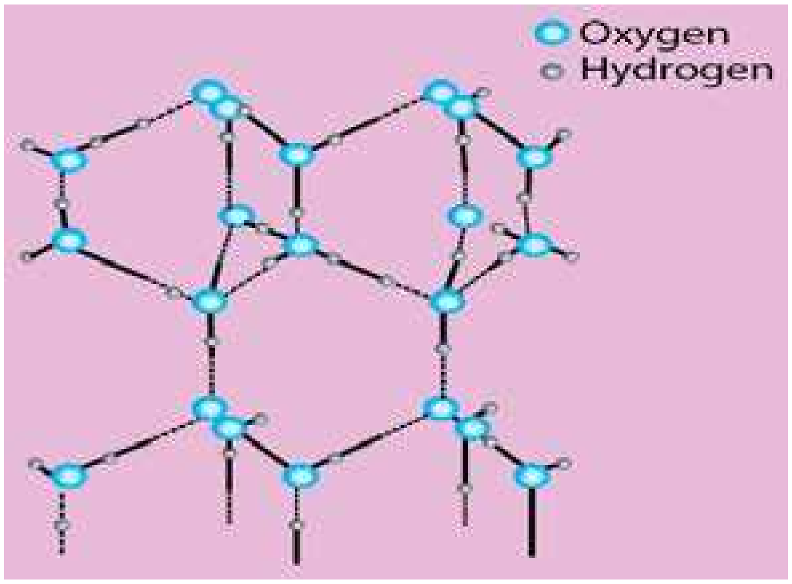


Fig (4.8 b) Structure of ice

Keeping the whole discussion in view we are forced to believe that the pattern of life for the plants and animals would have been totally different in the absence of hydrogen bonding in water.

4. Cleansing Action of Soaps and Detergents

Soaps and detergents perform the cleansing action because the polar part of their molecules are water soluble due to hydrogen-bonding and the non-polar parts remain outside water, because they are alkyl or benzyl portions and are insoluble in water.

5. Hydrogen Bonding in Biological Compounds and Food Materials

Hydrogen bonding exists in the molecules of living system. Proteins are the important part of living organisms. Fibres like those found in the hair, silk and muscles consist of long chains of amino acids. These long chains are coiled about one another into a spiral. This spiral is called a helix. Such a helix may either be right handed or left handed. In the case of right handed helix the groups like >N H and > C = 0 are vertically adjacent to one another and they are linked together by hydrogen bonds. These H-bonds link one spiral to the other. X-ray analysis has shown that on the average there are 27 amino acid units for each turn of the helix, Fig (4.9 a).

Deoxyribonucleic acid (DNA) has two spiral chains. These are coiled about each other on a common axis. In this way, they give a double helix. This is 18-20 Å in diameter. They are linked together by H-bonding between their sub units, Fig (4.9 b).

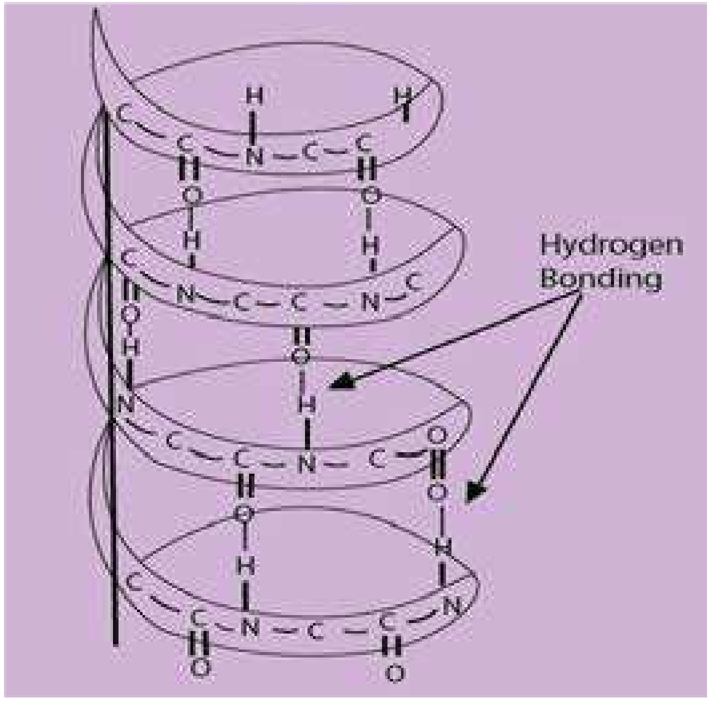


Fig (4.9 a) Hydrogen bonding

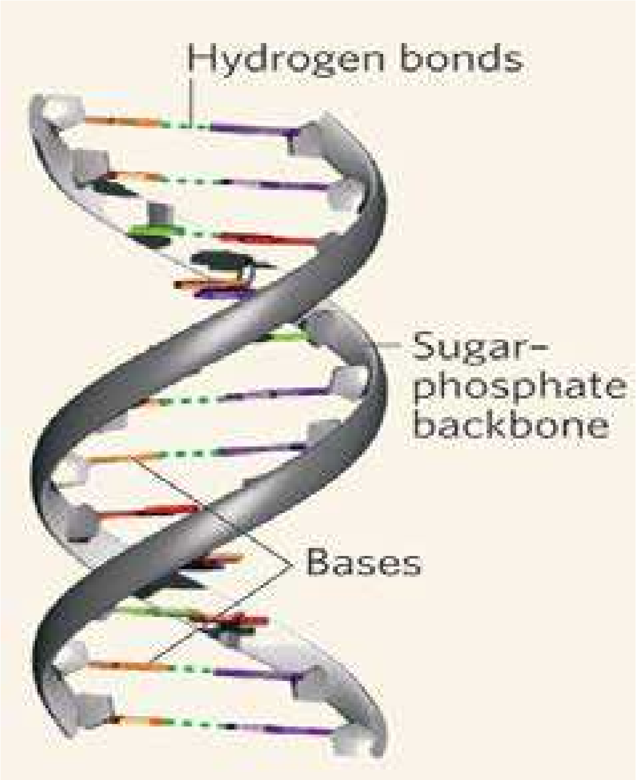


Fig (4.9 b) Hydrogen bonding in DNA double helix

The food materials like carbohydrates include glucose, fructose and sucrose. They all have -OH groups in them which are responsible for hydrogen bonding in them.

6. Hydrogen Bonding in Paints, Dyes and Textile Materials

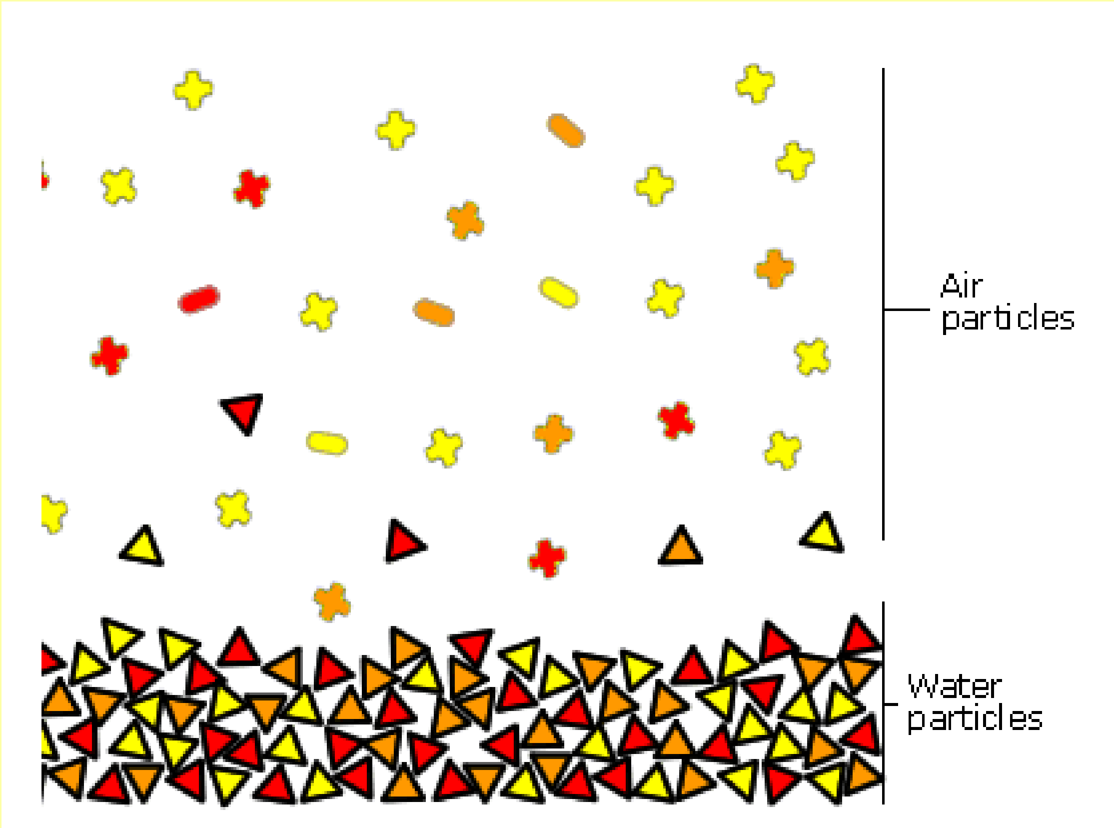
One of the most important properties of paints and dyes is their adhesive action. This property is developed due to hydrogen bonding. Similar type of hydrogen bonding makes glue and honey as sticky substances.

We use cotton, silk or synthetic fibres for clothing. Hydrogen bonding is of vital importance in these thread making materials. This hydrogen bonding is responsible for their rigidity and the tensile strength.

4.2.0 EVAPORATION

In order to understand evaporation, we have to examine the movement of molecules in liquids. The molecules of a liquid are not motionless. The energy of molecules is not equally distributed. The molecules which have low kinetic energy move slowly, while others with high kinetic energy move faster. If one of the high speed molecules reaches the surface, it may escape the attractions of its neighbouring molecules and leaves the bulk of the liquid. **This spontaneous change of a liquid into its vapours is called evaporation and it continues at all temperatures.**

Evaporation causes cooling. The reason is that when high energy molecules leave the liquid and low energy molecules are left behind, the temperature of the liquid falls and heat moves from the surrounding to the liquid and then the temperature of the surrounding also falls.



Animation 4.5 : Evaporation
Source & Credit: stem

There are many factors which control the rate of evaporation of a liquid. Since evaporation occurs from liquid surface, so if surface area is increased then more molecules are able to escape and liquid evaporates more quickly. For liquids having same surface area, the rate of evaporation is controlled by the temperature and the strength of intermolecular forces.

At high temperature, the molecules having greater energy increase and so rate of evaporation increases. Similarly, if intermolecular forces are weak, the rate of evaporation is faster. For example, gasoline, whose molecules experience weaker London forces of attraction, evaporate much faster than water.

4.2.1 Vapour Pressure

When the molecules of a liquid leave the open surface, they are mixed up with air above the liquid. If the vessel is open these molecules go on leaving the surface. But if we close the system the molecules of liquid start gathering above the surface. These molecules not only collide with the walls of the container, but also with the surface of the liquid as well.

There are chances that these molecules are recaptured by the surface of liquid. This process is called condensation. The two-processes i.e., evaporation and condensation continue till a stage reaches when the rate of evaporation becomes equal to the rate of condensation. This is called the state of dynamic equilibrium Fig (4.10). So the vapour pressure of a liquid is a pressure exerted by the vapours of the liquid in equilibrium with the liquid at a given temperature.

$$\text{Liquid} \rightleftharpoons \text{Vapour}$$

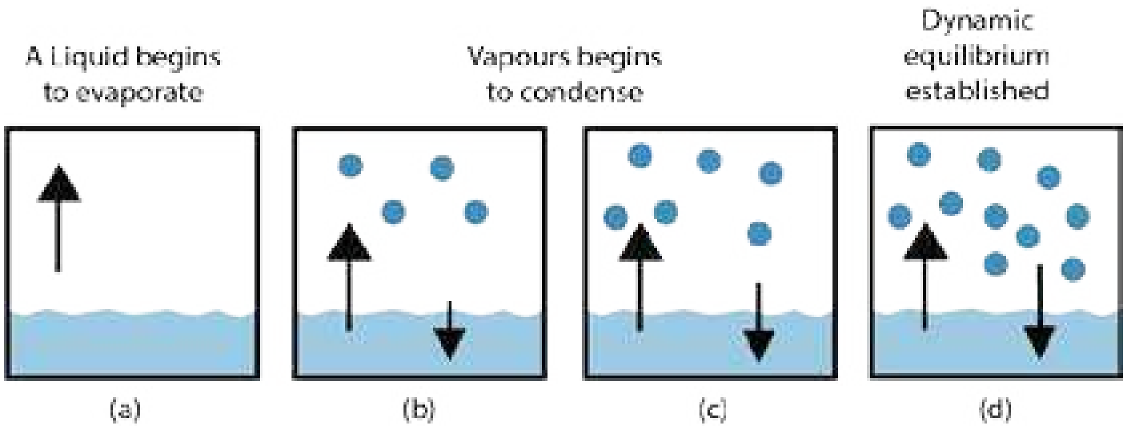


Fig (4.10) Evaporation of a liquid and establishment of dynamic equilibrium between liquid and its vapours.

The number of molecules leaving the surface is just equal to the number of molecules coming back into it at a constant temperature. The molecules which are in the liquid state at any moment may be in vapour state in the next moment.

The magnitude of vapour pressure does not depend upon the amount of liquid in the container or the volume of container. It also does not depend on surface area of a liquid. The larger surface area also presents a larger target for returning the molecules, so the rate of condensation also increases.

Animation 4.6 : Vapour Pressure
Source & Credit: mecaflux

Vapour Pressure Increases with Temperature

The values of vapour pressures of various liquids depend fairly upon the nature of liquids i.e. on the sizes of molecules and intermolecular forces, but the most important parameter which controls the vapour pressure of a liquid is its temperature. At an elevated temperature, the kinetic energy of molecules is enhanced and capability to leave the surface increases.

It causes the increase of vapour pressure. Table(4.3) shows change in vapour pressure of water at different temperatures. The Table (4.3) shows that increases of vapour pressure goes on increasing for the same difference of temperature from 0°C to 100°C for water. There is increase of vapour pressure from 4.579 torr to 9.209 torr for change of temperature from 0°C to 10°C. But the increase is from 527.8 torr to 760 torr when temperature changes from 90°C to 100°C.

The difference in the strength of intermolecular forces in different liquids is directly related to their vapour pressures at a particular temperature. The stronger the intermolecular forces the lower the vapour pressure. The following Table (4.4) shows that at 20 °C isopentane has the highest vapour pressure, while glycerol has the lowest.

Tablc (4.3) Vapour pressures of water (torr) at various temperatures

Temperature (^{0}C)	Vapour Pressure (Torr)
0	4.579
10	9.209
20	17.54
30	31.82
37	47.07
40	55.32
50	92.51
60	149.4
70	233.7
80	355.1
90	527.8
100	760.0

4.2.2 Measuremerr of Vapour Pressure

There are many methods for the measurement of vapour pressure of a liquid. One of the important methods is described in the following paragraph.

Table (4.4) Vapour pressure of some important liquids at 20°C

Name of compound	Vapour pressure at 20 ^{0}C (torr)
Isopentane	580
Ethyl ether	442.2
Chloroform	170
CarbonTetrachloride	87
Ethanol	43.9
Mercury	0.012
Glycerol	0.00016

Manometric Method

Manometric method is comparatively an accurate method. The liquid whose vapour pressure is to be determined is taken in a flask placed in a thermostat, as shown in the Fig(4.11). One end of the tube from the flask is connected to a manometer and the other end is connected to a vacuum pump. The liquid is frozen with the help of a freezing mixture and the space above the liquid is evacuated. In this way, the air is removed from the surface of the liquid alongwith the vapours of that liquid. The frozen liquid is then melted to release any entrapped air. Liquid is again frozen and realeased air To is evacuated. This process is repeated many times till almost all the air is removed.

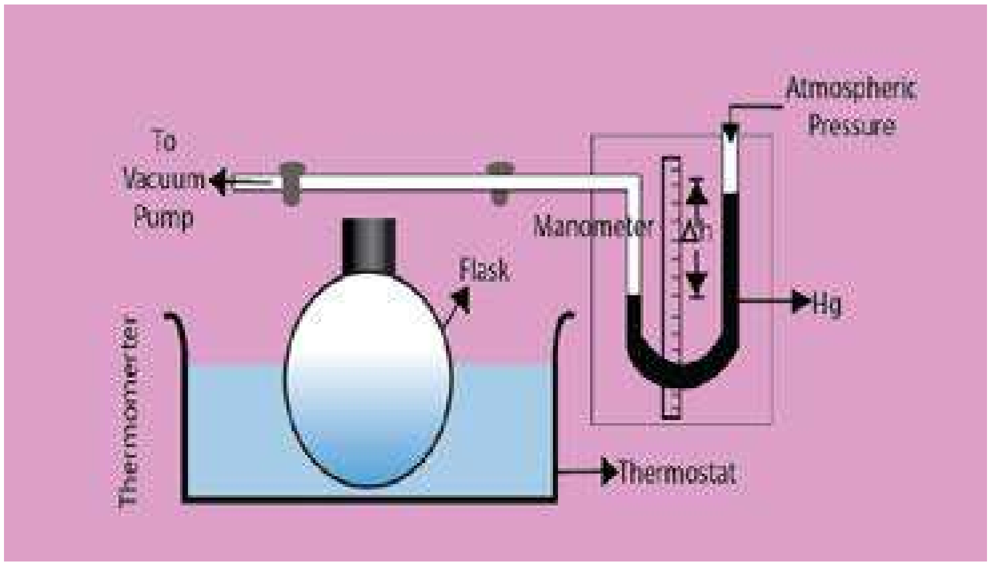


Fig. (4.11) Measurement of vapour pressure of a
in the heights of the columns of-Hg in liquid by manometric method

Now the liquid is warmed in the thermostat to that temperature at which its vapour pressure in the flask is to be determined. Difference in the heights of the columns of-Hg in liquid by manometric method the two limbs of the manometer determines the vapour pressure of the liquid.

The column of mercury in the manometer facing the vapours of the liquid is depressed. The other column, which faces the atmospheric pressure, rises. Actually, the pressure on the surface of the liquid in the flask is equal to the sum of the atmospheric pressure and the vapour pressure of liquid. For this reason, the column of manometer facing the liquid is more depressed than facing the atmosphere, and it is given by the following equation.

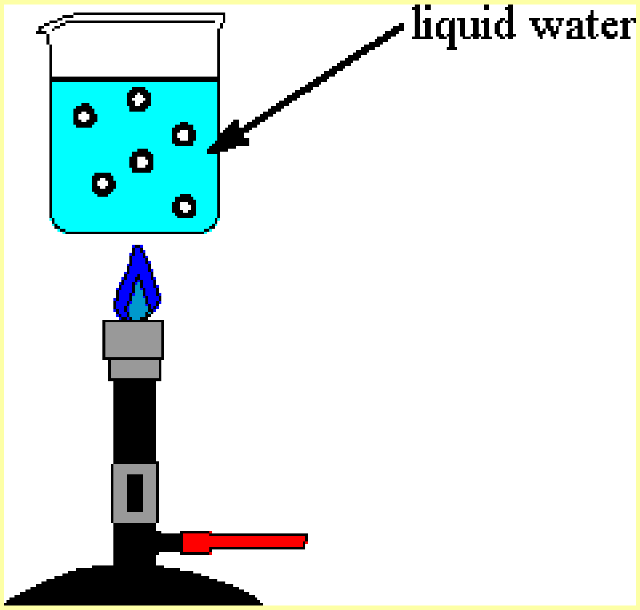
$$P = P_a + \Delta h$$

Where P = Vapour pressure of the liquid at one atm pressure.
P= Atmospheric pressure.
Δh = Difference in the heights of the mercury levels in the two limbs of the manometer, giving us the vapour pressure of liquid.

4.2.3 Boiling Point

When a liquid is heated, the vapour pressure goes on increasing. A stage reaches when the vapour pressure of the liquid becomes equal to the external atmospheric pressure. This temperature is called the boiling point of the liquid. The reason for this is that the bubbles of vapours which are formed in the interior of the liquid have greater internal pressure than atmospheric pressure on the surface of liquid. This thing makes the bubble to come out of the liquid and burst upon the surface. Thus a constant stream of bubbles comes out at the boiling point.

When a liquid is heated, the kinetic energy of its molecules increases and hence the temperature also increases. At the boiling point, the kinetic energy of the molecules becomes maximum and any further heating at this stage will not increase the temperature.



Animation 4.7 : Boiling Point
Source & Credit: chem

This heat will only be utilized to break the intermolecular forces and convert the liquid into its vapours. **The amount of heat required to vapourize one mole of a liquid at its boiling point is called its molar heat of vapourization.** The molar heat of vapourization of water is 40.6 $kjmol^{-1}$. The boiling points of some commonly available liquids at one atmospheric pressure are shown in the Table (4.5).

Table (4.5) Boiling points of some common liquids at 760 torr.

Liquid	B.P (^0C)	Liquids	B.P (^0C)
Acetic Acid	118.50	Carbontetrachloride	76.50
Acetone	56.00	Ethanol	78.26
Aniline	184.4	Naphthalene	218.00
Benzene	80.15	Phenol	181.80
Carbon disulphide	46.30	Water	100.00

The Fig. (4.12) shows the variation of vapour pressure of water, ethyl alcohol, ethylene glycol and diethylether with temperature. It shows that the liquids reach upto their boiling points when their vapour pressures are equal to 760 torr at sea level. The way these curves start at 0 ^0C is interesting. Water takes start at 4.8 torr while diethyl ether at around 200 torr. This is due to difference in the strengths of their intermolecular forces. The curve for water goes alongwith temperature axis to a greater extent at the beginning as compared to ether. It means that water can hardly overcome its intermolecular forces at low temperatures. It is clear from the curves that the vapour pressure increases very rapidly when the liquids are closer to their boiling points.

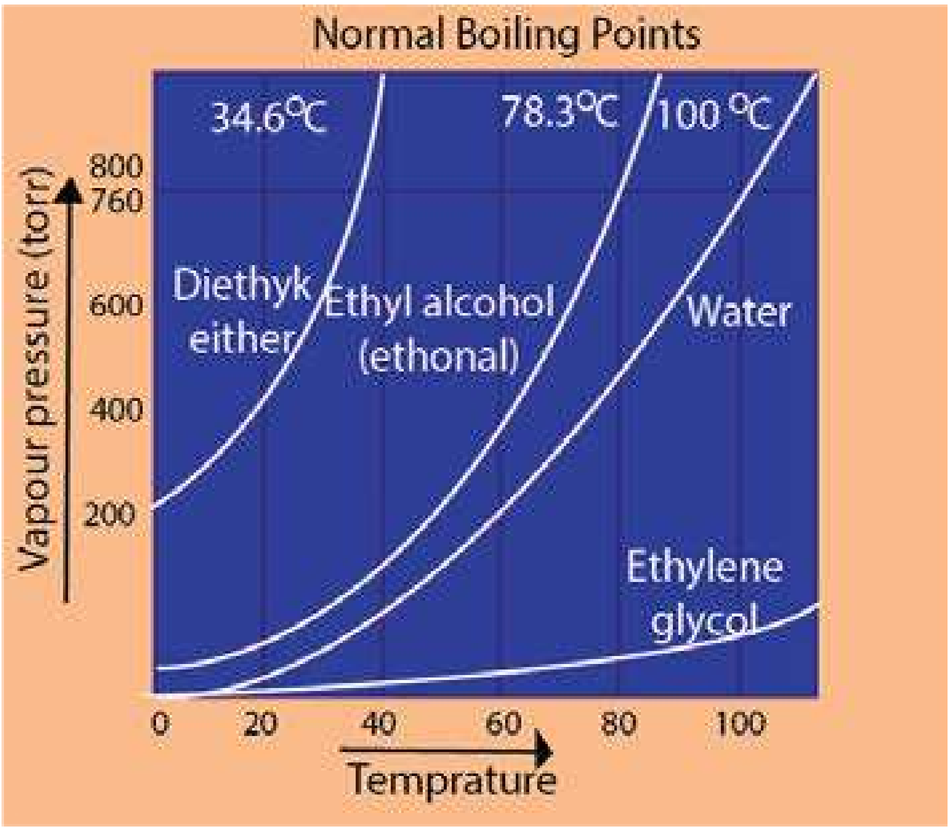


Fig (4.12) Vapour pressures(torr) of four common liquids shown as a function of temperature(°C).

4.2.4 Boiling Point and External Pressure

We have already explained that when vapour pressure of a liquid becomes equal to the external pressure then the liquid boils, so when external pressure is changed, its boiling point will also be changed. A liquid can be made to boil at any temperature by changing the external pressure. When the external pressure is high the liquid requires greater amount of heat to equalize its vapour pressure to external pressure. In this way boiling point is raised. Similarly, at a lower external pressure a liquid absorbs less amount of heat and it boils at a lower temperature.

For example, water shows B.P of 120 °C at 1489 torr pressure and boils at 25 °C at 23.7 torr. Water boils at 98 °C at Murree hills due to external pressure of 700 torr while at the top of Mount Everest water boils at only 69 ^{0}C 323 torr.

We can increase the external pressure artificially on the surface of boiling water by using a pressure cooker. Pressure cooker is a closed container. The vapours of water formed are not allowed to escape. In this way, they develop more pressure in the cooker and the boiling temperature increases. As more heat is absorbed in water, so food is cooked quickly under increased pressure.

Liquids can be made to boil at low temperatures, where they can be distilled easily. This process is called vacuum distillation. Vacuum distillation has many advantages. It decreases the time for the distillation process and is economical because less fuel is required. The decomposition of many compounds can be avoided e.g. glycerin boils at 290 °C at 760 torr pressure but decomposes at this temperature. Hence, glycerin cannot be distilled at 290 °C. Under vacuum, the boiling temperature of glycerin decreases to210 ^{0}C at 50 torr. It is distilled at this temperature without decomposition and hence can be purified easily.

4.2.5 Energetics of Phase Changes

Whenever, matter undergoes a physical change, it is always accompanied by an energy change. This change in energy is the quantitative measurement of the difference in the strength of intermolecular forces.

The change in energy is mostly in the form of heat. **If a physical or a chemical change takes place at a constant pressure, then the heat change during this process is also called enthalpy change.** This is denoted by ΔH. These enthalpy changes are usually expressed per mole of the substances. Three types of enthalpy changes are associated with usual physical changes.

(i) Molar Heat of Fusion (ΔH_f)

It is the amount of heat absorbed by one mole of a solid when it melts into liquid form at its melting point. The pressure, during the change is kept one atmosphere.

(ii) Molar Heat of Vapourization (ΔH_v)

It is the amount of heat absorbed when one mole of a liquid is changed into vapours at its boiling point. The pressure, during the change is kept one atmosphere.

(iii) Molar Heat of Sublimation (ΔH_s)

It is the amount of heat absorbed when one mole of a solid sublimes to give one mole of vapours at a particular temperature and one atmospheric pressure.

All these enthalpy changes are positive, because they are endothermic processes.

4.2.6 Energy Changes and Intermolecular Attractions

When a solid substance melts then atoms, molecules or ions undergo relatively small changes in intermolecular distances and the potential energy also undergoes a small change. But when a liquid evaporates, then larger changes in intermolecular distances and in potential energy takes place. So ΔH of vapourization of a substance is greater than ΔH of fusion. The values of ΔH_s are even larger than ΔH_v because attractive forces in solids are stronger than those in liquids.

The values of ΔH_v and ΔH_s tell us directly the energy needed to separate molecules from each other. So from these values, we can compare the strengths of intermolecular forces in different compounds.

From the following Table (4.6), we are convinced that ΔH_v for H_20, NH_3 and $S0_2$ are reasonably high due to polar nature of molecules. ΔHV for iodine is the highest amongst its family members due to its greater polarizability. Similarly, hexane (C_6H_{14}) has the highest ΔH_v value amongst the hydrocarbons due to larger size of its molecules. Actually, the London dispersion forces in I_2 and C_6H_{14} are sufficiently strong and these are responsible for such a behaviour.

Table (4.6) Heats of Vaporization of some substances

Substance	ΔH$_v$ (kJ/mol)
H_2O	+40.6
NH_3	+21.7
HCl	+15.6
SO_2	+24.3
F_2	+5.9
Cl_2	+10.00
Br_2	+15.00
I_2	+22.00
CH_4	+8.60
C_2H_6	+15.1
C_3H_8	+16.9
C_6H_{14}	30.1

4.2.7 Change of State and Dynamic Equilibrium

Whenever, a change of state occurs the system moves towards the condition of dynamic equilibrium. Dynamic equilibrium is a situation when two opposing changes occur at equal rates. Being a chemist, we should know that the concept of dynamic equilibrium is the fate or the ultimate goal of all the reversible chemical reactions and all the physical changes.

At 0°C, solid water (ice) exists in dynamic equilibrium with liquid water.

$$ice \overset{0^oC}{\rightleftharpoons} water$$

4.3 Liquid Crystals

Whenever we study the properties of crystalline solids, we come to know that the pure solids melt sharply. The temperature remains constant at the melting point until all the solid melts.

In 1888, Frederick Reinitzer, an Austrian botanist discovered a universal property. He was studying an organic compound cholesteryl benzoate. This compound turns milky liquid at 145°C and becomes a clear liquid at 179°C. When the substance is cooled, the reverse process occurs. This turbid liquid phase was called liquid crystal.

Uptil now, it has been reported that, there are many crystalline solids which melt to a turbid liquid phase, before finally melting to a clear liquid. These turbid liquid phases can flow as liquids. They have the properties like liquids as surface tension, viscosity, etc. But it is very interesting to know that the molecules of such turbid liquids possess some degree of order as well. It means that these turbid liquids resemble crystals in certain properties and the most important properties are optical ones. These turbid liquids are hence called liquid crystals. So, **a liquid crystalline state exists between two temperatures i.e. melting temperature and clearing temperature.** A crystalline solid may be isotropic or anisotropic, but liquid crystals are always anistropic.

Crystal□ □ *Liquidcrystal*□ □ *Liquid*

From 1888 to until about 30 years ago, liquid crystals were largely a laboratory curiosity. But now they have found a large number of applications.

Those substances which make the liquid crystals are often composed of long rod like molecules. In the normal liquid phase, these molecules are oriented in random directions. In liquid crystalline phase, they develop some ordering of molecules. Depending upon the nature of ordering, liquid crystals can be divided into nematic, smectic and cholesteric.

The properties of liquid crystals are intermediate between those of crystals and isotropic liquids. They have the fluidity of the liquids and the optical properties of the crystals.

Uses of Liquid Crystals

Due to the remarkable optical and electrical properties, liquid crystals find many practical applications. Many organic compounds and biological tissues behave as liquid crystals. The unique properties of liquid crystals have intrigued the scientists since their discovery, nearly hundred years ago. Some of their important uses are as follows.

(i) Like solid crystals, liquid crystals can diffract light. When one of the wavelengths of white light is reflected, from a liquid crystal it appears coloured. As the temperature changes, the distances between the layers of the molecules of liquid crystals change. Therefore, the colour of the reflected light changes accordingly. Thus liquid crystals can he used as temperature sensors.

(ii) Liquid crystals are used to find the point of potential failure in electrical circuits. Room thermometers also contain liquid crystals with a suitable temperature range. As the temperature changes, figures show up in different colours.

(iii) Liquid crystalline substances are used to locate the veins, arteries, infections and tumors. The reason is that these parts of the body are warmer than the surrounding tissues. Specialists can use the techniques of skin thermography to detect blockages in veins and arteries. When a layer of liquid crystal is painted on the surface of the breast, a tumor shows up as a hot area which is coloured blue. This technique has been successful in the early diagnosis of breast cancer.

(iv) Liquid crystals are used in the display of electrical devices such as digital watches, calculators and laptop computers. These devices operate due to the fact that temperature, pressure and electro-magnetic fields easily affect the weak bonds, which hold molecules together in liquid crystals.

(v) In chromatographic separations, liquid crystals are used as solvents.

(vi) Oscillographic and TV displays also use liquid crystal screens.

SOLIDS

4 .4 INTRODUCTION

Solids are those substances which are rigid, hard, have definite shape and definite volume. The atoms, ions and molecules that make up a solid are closely packed. They are held together by strong cohesive forces. The constituent atoms, ions or molecules of solids cannot move at random. There exists a well ordered arrangement in solids.

4.4.1 Types of Solids

Solids can be classified on the basis of the regular arrangements of constituent atoms, ions or molecules. There are two types of solids in this respect.

(i) Crystalline Solids

Those solids in which atoms, ions or molecules are arranged in a definite three dimensional pattern are called crystalline solids This recurring regular geometrical pattern of structure extends three dimensionally.

(ii) Amorphous Solids

All solids are not crystalline .The word amorphous means shapeless. **Amorphous substances are those whose constituent atoms, ions, or molecules do not possess a regular orderly arrangement.** The best examples are glass, plastics, rubber, glue, etc. These substances have solid state properties and virtually complete maintenance of shape and volume. But they do not have an ordered crystalline state.

Many crystalline solids can be changed into amorphous solids by melting them and then cooling the molten mass rapidly. In this way the constituent particles do not find time to arrange them selves.

A long range regularity does not exist in amorphous solids but they can possess small regions of orderly arrangements. These crystalline parts of otherwise amorphous solids are known as crystallites. Amorphous solids don't have sharp melting points that is why particles of glass soften over a temperature range and can be moulded and blown into various shapes. They do not possess definite heats of fusion.

4.4.2 Properties of Crystalline Solids

1. Geometrical Shape

All the crystalline solids have a definite, distinctive geometrical shape due to definite and orderly arrangement of atoms, ions or molecules in three-dimensional space. For a given crystal, the interfacial angles, at which the surfaces intersect, are always the same no matter in which shape they are grown. The faces and angles remain characteristic even when the material is ground to a fine powder.

2. Melting Points

Crystalline solids have sharp melting points and can be identified from their definite melting points.

3. Cleavage Planes

Whenever the crystalline solids are broken they do so along definite planes. These planes are called the cleavage planes and they are inclined to one another at a particular angle for a given crystalline solid. The value of this angle varies from one solid to another solid.

4. Anisotropy

Some of the crystals show variation in physical properties depending upon the direction. Such properties are called anisotropic properties and the phenomenon is referred to as anisotropy. The physical properties of crystalline solids like refractive index, coefficient of thermal expansion, electrical and thermal conductivities are sometimes anisotropic in nature for some crystals.

The variation in these properties with direction is due to fact that the orderly arrangement of the particles in crystalline solids is different in different directions. For example, electrical conductivity of graphite is greater in one direction than in another. Actually electrons in graphite are mobile for electrical conduction parallel to the layers only. Therefore, its conductivity in this direction is far better than perpendicular to the other direction. Similarly, cleavage itself is an anisotropic behaviour.

5. Symmetry

The repetition of faces, angles or edges when a crystal is rotated by 360° along its axis is called symmetry. This an important property of the crystal and there are various types of symmetry elements found in crystals like, center of symmetry, plane of symmetry and axis of symmetry, etc.

6. Habit of a Crystal

The shape of a crystal in which it usually grows is called habit of a crystal. Crystals are usually obtained by cooling the saturated solution or by slow cooling of the liquid substance. These are formed by growing in various directions. If the conditions for growing a crystal are maintained, then the shape of the crystal always remains the same. If the conditions are changed the shape of the crystal may change. For example, a cubic crystal of NaCl becomes needle like when 10% urea is present in its solution as an impurity.

7. Isomorphism

Isomorphism is the phenomenon in which two different substances exist in the same crystalline form. These different substances are called isomorphs of each other.

A crystalline form is independent of the chemical nature of the atoms and depends only on the number of atoms and their way of combinations.

Mostly the ratio of atoms in various compounds are such that isomophism is possible. Their physical and chemical properties are quite different from each other. Anyway, isomorphic substances crystallize together in all proportions in homogeneous mixtures. Following examples tell us the nature of the compound, their crystalline forms and the ratio of their atoms.

Isomorphs	Crystalline form	Atomic ratio
$NaNO_3$, KNO_3	rhombohedral	1:1:3
K_2SO_4, K_2CrO_4	orthorhombic	2:1:4
$ZnSO_4$, $NiSO_4$	-do-	1:1:4
NaF, MgO	cubic	1:1
Cu, Ag	cubic	1:1
Zn, Cd	hexagonal	1:1

The structures of the negatively charged ions like NO_3^{-1} and CO_3^{2-}, are the same. Similarly shapes of SO_4^{2-} and CrO_4^{2-} are also alike. CO_3^{2-} and NO_3^{1-} are triangular planar units, while SO_4^{2-} and CrO_4^{2-} are both tetrahedral.

8. Polymorphism

Polymorphism is a phenomenon in which a compound exists in more than one crystalline forms. That compound which exists in more than one crystalline forms is tailed a polymorphic, and these forms are called polymorphs, and these forms are called polymorphs of each other.

Polymorphs have same chemical properties, but they differ in the physical properties. The difference in physical properties is due to different structural arrangement of their particles.

The following compounds are important polymorphs.

Substance	crystalline forms
$AgNO_3$	Rhombohedral, Othorhombic
$CaCO_3$	Trigonal and orthorhombic

9. Allotropy

The existence of an element in more than one crystalline forms is known as allotropy and these forms of the element are called allotropes or allotropic forms. Sulphur, phosphorus, carbon and tin are some important examples of elements which show allotropy.

Element	Crystalline forms
Sulphur, S	Rhombic, monoclinic
Carbon, C	cubic (diamond), hexagonal (graphite)
Tin, Sn	grey tin (cubic), white tin (tetragonal)

10. Transition Temperature

It is that temperature at which two crystalline forms of the same substance can co-exist in equilibrium with each other. At this temperature, one crystalline form of a substance changes to another.

Above and below this temperature, only one form exists. A few examples for those substances which show allotropy and possess a transition temperature are given below

(i) Grey Tin (cubic) $\overset{13.2^{o}C}{\rightleftharpoons}$ White tin (Tetragonal)

(ii) Sulphur S_8 (rhombic) $\overset{95.5^{o}C}{\rightleftharpoons}$ Sulphur S_8(monoclinic)

(iii) KNO_3 (orthorhombic) $\overset{128^{o}C}{\rightleftharpoons}$ KNO_3(rhombohedral)

(iv) Na_2S0_4-$10H_20$ (hydrated form) $\overset{32.38^{o}C}{\rightleftharpoons}$ Na_2S0_4(anhydrous from) + 10 H_20

(v) Na_2CO_3- 10 H_20 (higher hydrated form) $\overset{32.38^{o}C}{\rightleftharpoons}$ Na_2CO_3-$7H_20$(lowerhydratedform)+$3H_20$

It has been noticed that the transition temperature of the allotropic forms of an element is always less than its melting point.

4.5 CRYSTAL LATTICE

A crystal is made up of atoms, ions or molecules. In crystalline solids, these atoms, ions or molecules are located at definite positions in space. These positions are represented by points in a crystal. These points are called as lattice points or lattice sites. This arrangement of points in a crystal is called crystal lattice or space lattice.

So a crystal lattice is an array of points representing atoms, ions or molecules of a crystal, arranged at different sites in three dimensional space. Fig. (4.13) shows a crystal lattice with a cubic structure.

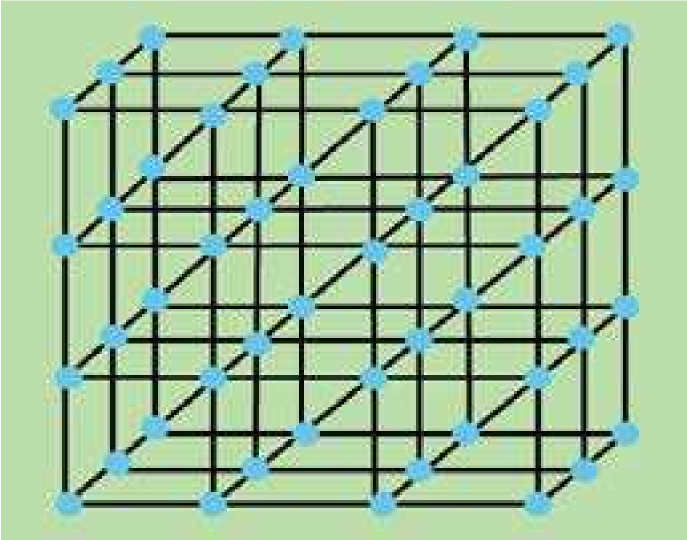


Fig (4.13) Cubic crystal lattice

4.5.1 Unit Cell

When we look at the cubic crystal lattice in Fig (4.14), we see that it is actually composed of many small parts. **The smallest part of the crystal lattice has all the characteristic features of the entire crystal and is called a unit cell.**

It means that a unit cell of a crystal lattice is the smallest block or geometrical figure, from which the entire crystal can be built up by repeating it in three dimensions. It shows the structural properties of a given crystal. The complete information about the crystalline structure is present within a unit cell which repeats itself in three dimensions to form a crystal.

If we know the exact arrangement of atoms in a unit cell, we in fact know their arrangement in the whole crystal.

The quantitative aspects of a crystal lattice are deduced from the size and shape of the unit cell. There are three unit cell lengths a, b, c and three unit cell angles α , β and γ. These six parameters are shown in Fig (4.14)

The angle 'α' is between the lengths 'b' and 'c', the angle 'β' is between the sides 'a' and 'c' and angle' γ' is between sides 'a' and 'b'. The unit cell lengths a, b, c, may be assigned along x, y and z axis, respectivly but angles α , β and γ have to be decided accordingly. The choice of x, y, z may be along any of the three axis. These six parameters of the unit cell are called unit cell dimensions or crystallographic elements.

Keeping in view the structure of the unit cell we can understand the crystal system.

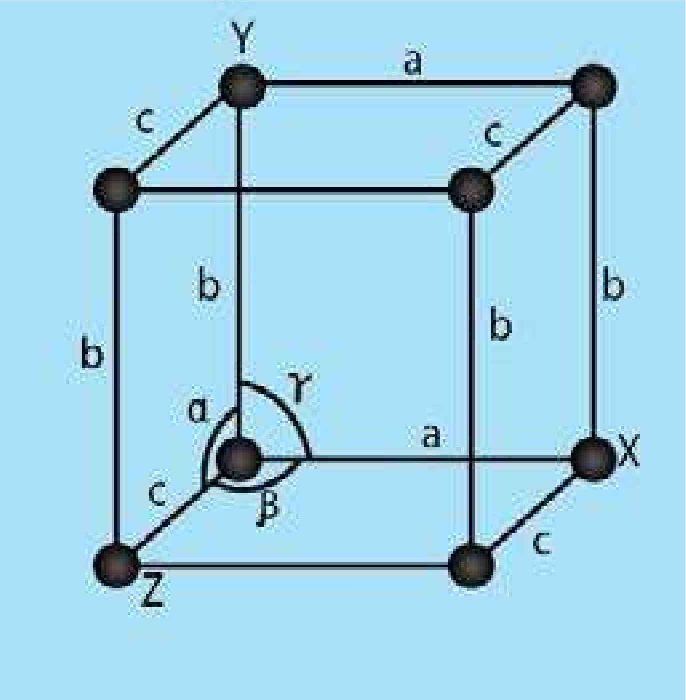
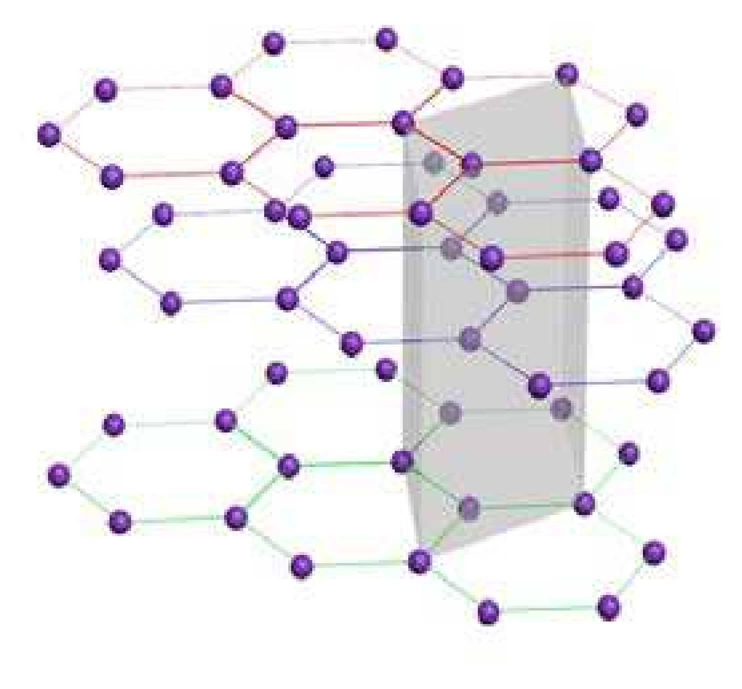


Fig (4.14) Six crystallographic elements specify the size and shape of a unit cell



Animation 4.8: Unit Cell
Source & Credit: Commons

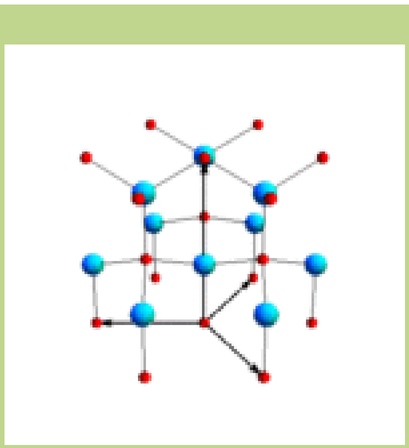
4.6 CRYSTALS AND THEIR CLASSIFICATION

A crystal system may be identified by the dimensions of its unit cell along its three edges or axes, a, b, c and three angles between the axes α , β , γ.

There are seven crystal systems. These seven crystal systems are described as follows Fig (4.15).

1. Cubic system

In this system all the three axes are of equal length and all are at right angles to one another.



Animation 4.9: Classification of Crystals
Source & Credit: wikipedia

2. Tetragonal system

In this system two axes are of equal length and the third axis is either shorter or larger than the other two. All angles are 90°.

3. Orthorhombic Or Rhombic System

All the three axes are of unequal length and all are at right angle to each other.

4. Monoclinic System

All the three axes are of unequal length; two of these axes are at right angle to each other while the third angle is greater then 90°.

5. Hexagonal System

In this system two axes are of equal length and are in one plane making an angle of 120^o with each other. The third axis which is different in length than the other two is at right angle to these two axes.

6. Rhombohedral System Or Trigonal System

All the three axes are of an equal length like cubic system but the three angles are not equal and lie between 90^0 and 120°.

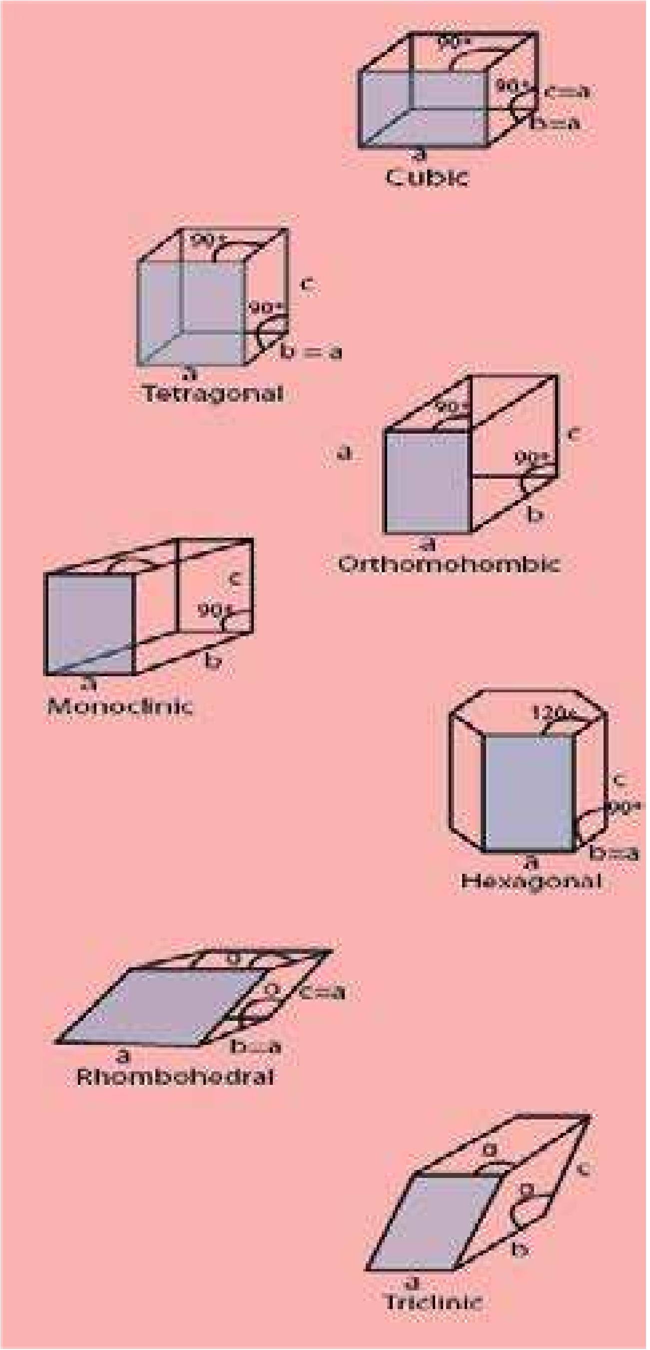


Fig (4.15) Seven crystal systems

7. Triclinic System

All the three axes and the three angles are unequal and none of the angles is 90^0.

Table (4.7) shows the unit cell dimensions of the seven crystal systems alongwith their examples

Table (4.7) Seven Crystal Systems

Sr. No	Crystal system	Axes	Angles	Examples
1.	cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^o$	Fe, Cu, Ag, Au, NaCl, NaBr, Dimond
2.	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^o$	Sn, SnO_2, MnO_2, NH_4Br
3.	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^o$	Idoine, Rhombic, Sulphur, $BaSO_4$, K_2SO_4
4.	Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^o, \beta \neq 90^o$	Sugar, Sulphur, Borax, $NaSO.10H_2O$
5.	Hexagonal	$a = b \neq c$	á=â=90^o , ã=120^0	Graphite, ZnO, CdS, Ice, Zn, Cd
6.	Rhombohedral or Trignol	$a = b = c$	$\alpha = \beta \sphericalangle \gamma \quad 90^o \text{and} \quad 120^o$	Bi, Al_2O_3, $NaNO_3$, KNO_3
7.	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^o$	H_3BO_3, $K_2Cr_2O_7$, $CuSO_4.5H_2O$

4.7 CLASSIFICATION OF SOLIDS

In the preceding section, we noted that the crystals are classified into seven systems depending upon the dimensions of the unit cells. A unit cell contains a definite number of atoms, ions, or molecules. These atoms, ions or molecules are held together by different types of cohesive forces. These forces may be chemical bonds or some type of interactions. There are four types of crystalline solids depending upon the type of bonds present in them.

(i) Ionic solids
(ii) Covalent solids
(iii) Metallic solids
(iv) Molecular solids

4.7.1 Ionic Solids

Crystalline solids in which the particles forming the crystal are positively and negatively charged ions are called ionic solids. These ions are held together by strong electrostatic forces of attraction. These attractive forces are also called ionic bonds. The crystals of NaCl, KBr, etc are ionic solids.

Properties of Ionic Solids

The cations and anions are arranged in a well defined geometrical pattern, so they are crystalline solids at room temperature. Under ordinary conditions of temperature and pressure they never exist in the form of liquids or gases.

Ionic crystals are very stable compounds. Very high energy is required to separate the cations and anions from each other against the forces of attraction. That is why ionic crystals are very hard, have low volatility and high melting and boiling points.

Ionic solids do not exist as individual neutral independent molecules. Their cations and anions attract each other and these forces are non-directional. The close packing of the ions enables them to occupy minimum space. A crystal lattice is developed when the ions arrange themselves systematically in an alternate manner.

The structure of the ionic crystals depends upon the radius ratio of cations and anions. For example.NaCl and CsF have the same geometry because the radius ratio in both the cases is the same.

In the case of ionic crystals we always talk about the formula mass of these substances and not the molecular mass, because they do not exist in the form of molecules.

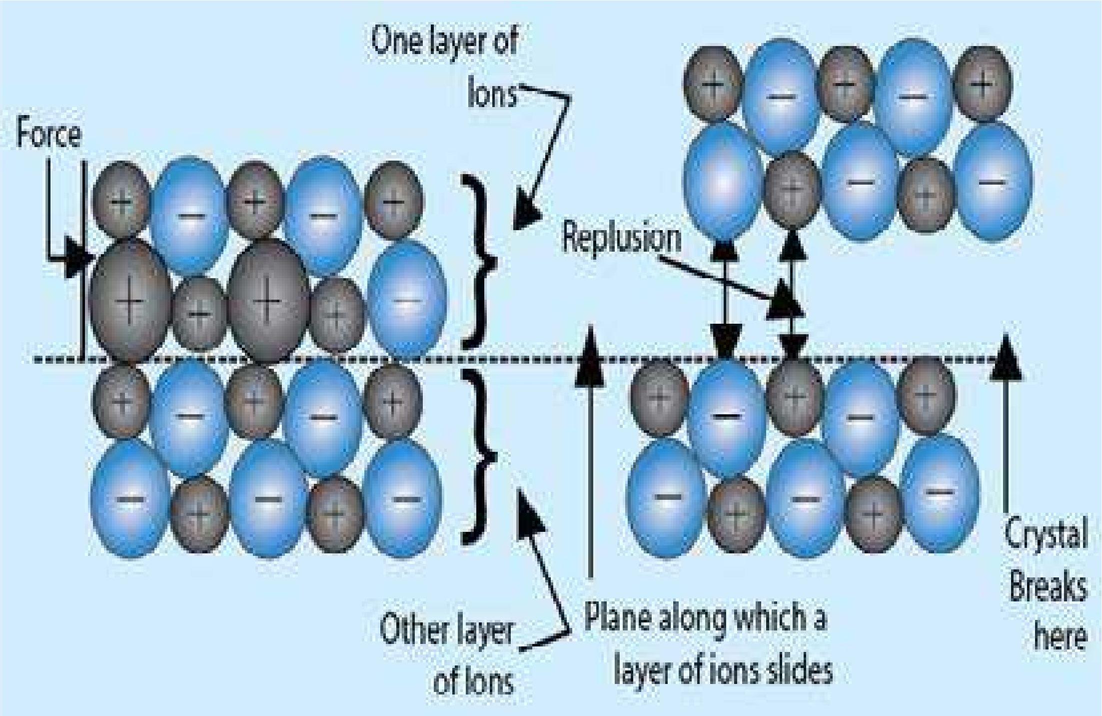
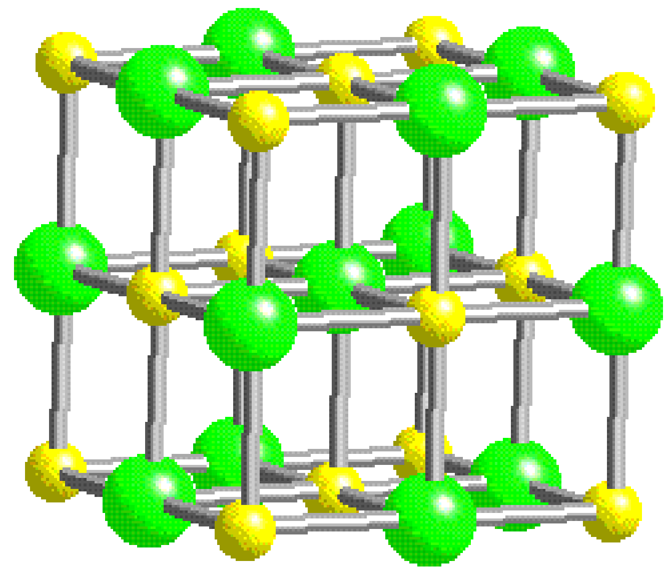


Fig (4.16) Explanation of brittleness of ionic crystals



Animation 4.10: Ionic Solids
Source & Credit: Grandinetti

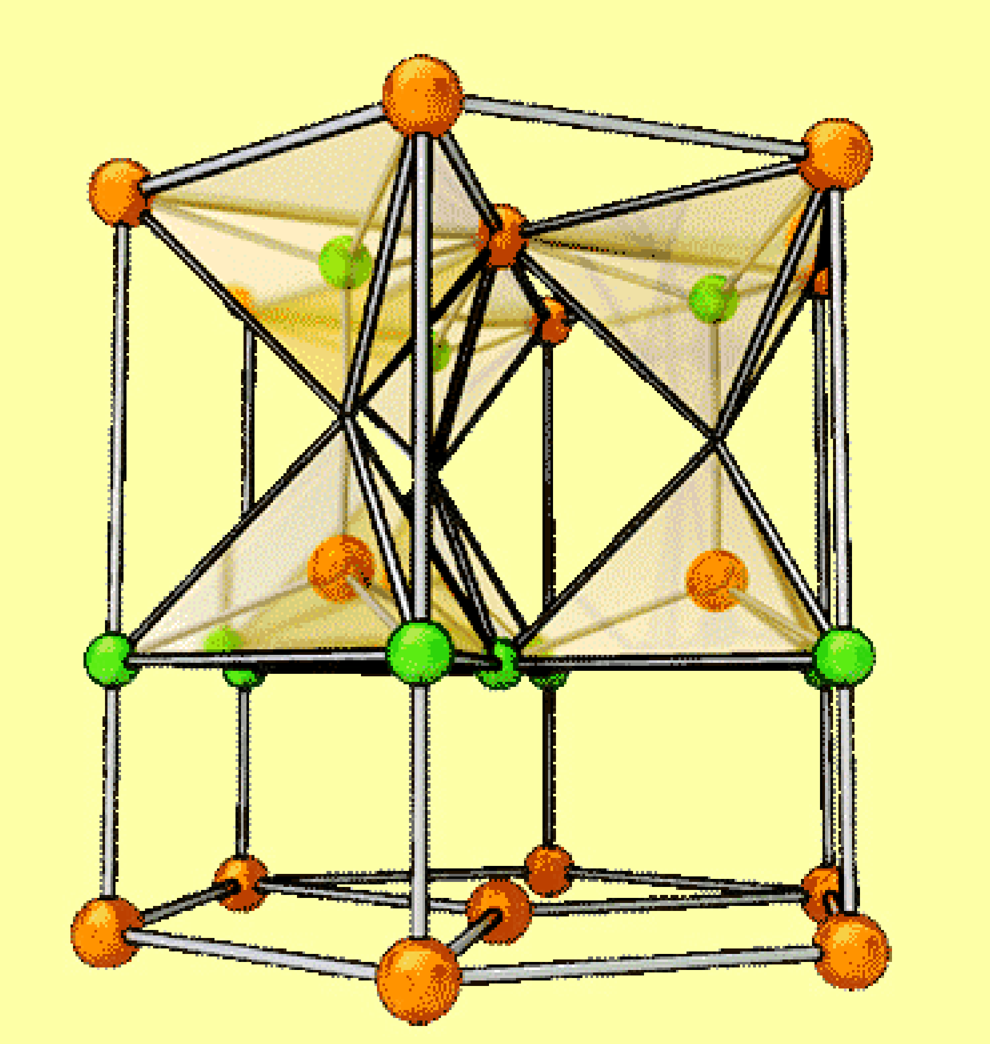
Ionic crystals do not conduct electricity in the solid state, because on account of electrostatic force existing between them the cations and anions remain tightly held together and hence occupy fixed positions. Ionic crystals conduct electricity when they are in solution or in the molten state. In both cases ions become free.

Ionic crystals are highly brittle because ionic solids are composed of parallel layers which contain cations and anions in alternate positions, so that the opposite ions in the various parallel layers lie over each other.

When an external force is applied, one layer of the ions slides a bit over the other layer along a plane. In this way the like ions come in front of each other and hence begin to repel. So, the application of a little external force develops repulsion between two layers causing brittleness Fig (4.16).

Ionic solids are mostly of high density due to close packing of ions. Such compounds having the ionic crystals give ionic reactions in polar solvents and these are very fast reactions.

The properties like isomorphism and polymorphism are also associated with the ionic crystals. In order to understand the structure of ionic crystals, let us explain the structure of sodium chloride crystals.

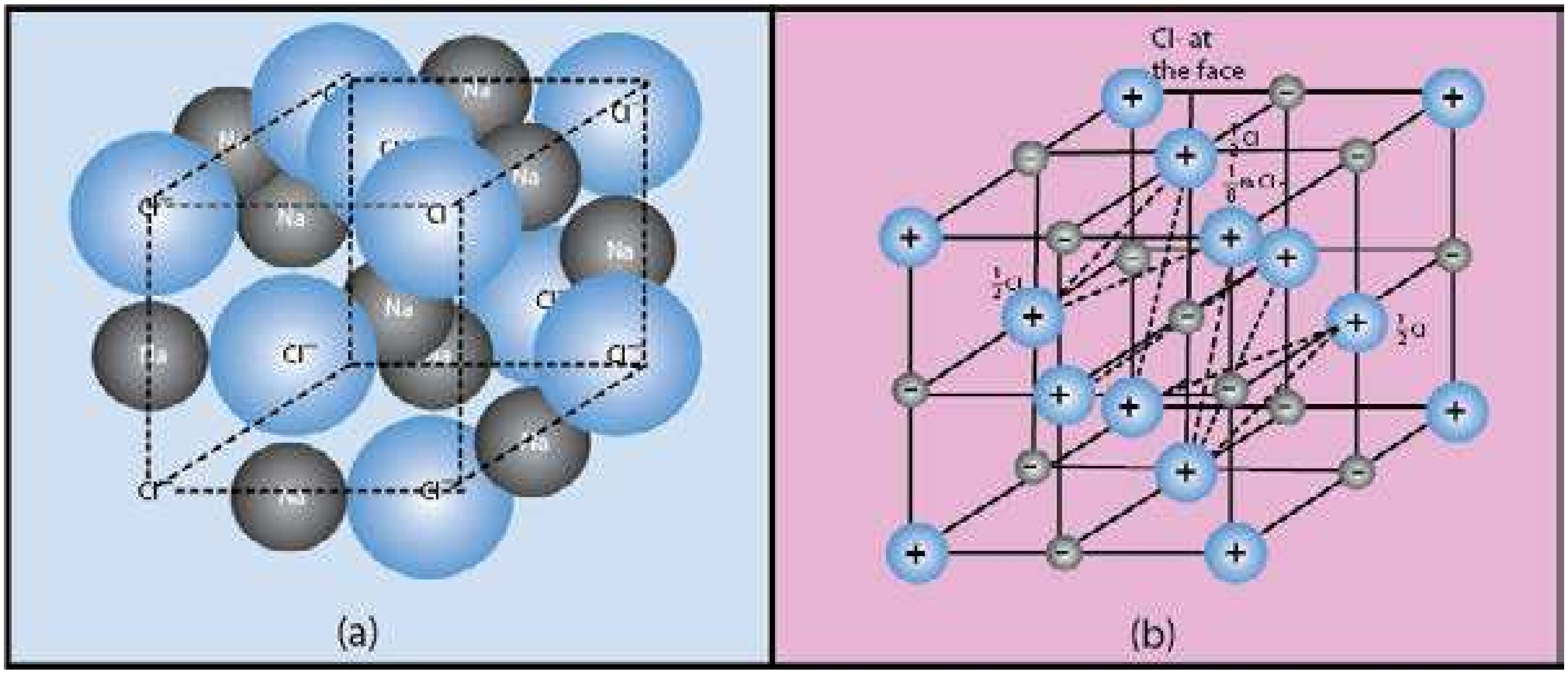


Animation 4.11: classification of solids
Source & Credit: Askiitians

Structure of Sodium Chloride

The structure of ionic crystals depends upon the structure and the size of their ions. Each ion is surrounded by a certain number of ions of opposite charge. In the structure of NaCl each Na^+ ion is surrounded by six chloride ions. Fig (4.17) shows how these ions are arranged in the crystal lattice. It is clear that Na^+ has ten electrons while Cl^- has total 18 electrons. The size of the Cl^- is bigger than that of Na^+

The distance between two nearest ions of the same kind i.e., Cl^- ions is 5.63 $\overset{o}{A}$. So the distance between two adjacent ions of different kind is 5.63/2 = 2.815 $\overset{o}{A}$.



Figs (4.17 a, b) The unit cell of sodium chloride showing that four NaCl formula units are present in a unit cell.

The location of Na^+ and Cl^- is such that each Na^+ is surrounded by six Cl^- placed at the corners of a regular octahedron Fig. (4.17 a). So the coordination number of each Na^+ is six. Similarly, each Cl^- is also surrounded by six Na^+. Na^+ and $C1^-$ are not connected to one another by pairs because all six Cl^- ions are at the same distance away from one Na^+. It has been observed that independent molecules of NaCl do exist in the vapour phase. Anyhow, in solid NaCl there are no independent molecules of NaCl. That is why NaCl is said to have formula unit of NaCl.

While looking at the Fig.(4.17 b), we see that there are eight Cl^- at the comers of the cube, and each is being shared amongst eight cubes. l/8th part of each Cl^- ion is considered for this unit cell. So, one complete Cl^- is contributed by eight corners. Similarly,six chloride ions are present at the face centres and each is being shared between t wo cells. Thus.per unit cell there are 8/8 + 6/2 = 4 Cl^- ions. You can justify the presence of 4 Na^+ , if you take a unit cell having $8Na^+$ at eight corners and $6Na^+$ at faces. So, there are equal number of Na^+ ions, and therefore 4 NaCl units are present per unit cell. Fig (4.17b)

Lattice Energy

Solids are composed of atoms, ions or molecules. However, many solids of daily importance are ionic in nature. As mentioned earlier these ions exist in a three dimensional array which is called as lattice.

When the oppositely charged ions are brought, close to each other energy is released. **So the lattice energy is the energy released when one mole of the ionic crystal is formed from the gaseous ions. It is also defined as the energy required to break one mole of solid into isolated ions in the gas phase.** It is expressed in kj mole^{-1}.

$$Na^{+}(g) + Cl^{-}(g) \rightarrow NaCl(s) \qquad \Delta H = -787\,kJmole^{-1}$$

Tables (4.8) Lattice energies of ionic compounds

Ionic compound	Lattice energy (kJ/mol^{-1})
LiCl	-833
NaF	-895
NaCl	-787
KCl	-690
NaBr	-728
KBr	-665
NaI	-690

Table (4.8) shows the lattice energies of many ionic compounds. It is clear from the table that lattice energy decreases with the increase in the size of the cation keeping the anion same. It also decreases with the increase in the size of anion. The reason in both cases is the same. With the increase in the size of either cation or anion, the packing of oppositely charged ions becomes less and less tight. The calculations related to the measurement of lattice energy will be discussed in chapter seven.

4.7.2. Covalent Solids

Covalent solids are also called atomic solids, because they are composed of neutral atoms of the same or of different elements. These atoms are held together by covalent bonds.

Covalent solids are of two types.

(i) Whenthecovalentbondsjointoformgiantmoleculeslikediamond,siliconcarbideoraluminiumnitride.

(ii) When atoms join to form the covalent bonds and separate layers are produced like that of graphite, cadmium iodide and boron nitride.

Properties of Covalent Crystals

The bonding in covalent crystals extend in three dimensions. They contain a network of atoms. The valencies of atoms are directed in definite directions, so the packing of atoms in these crystals is looser than those of ionic and metallic crystals. Thus covalent crystals have open structure.

These crystals are very hard and considerable amount of energy is required to break them. They have high melting points and their volatility is very low.

Due to the absence of free electrons and ions they are bad conductors of electricity. However, graphite has a layered structure and the electrons are available in between the layers. These electrons are delocalised and conductivity becomes possible. Graphite is not a conductor perpendicular to the layers.

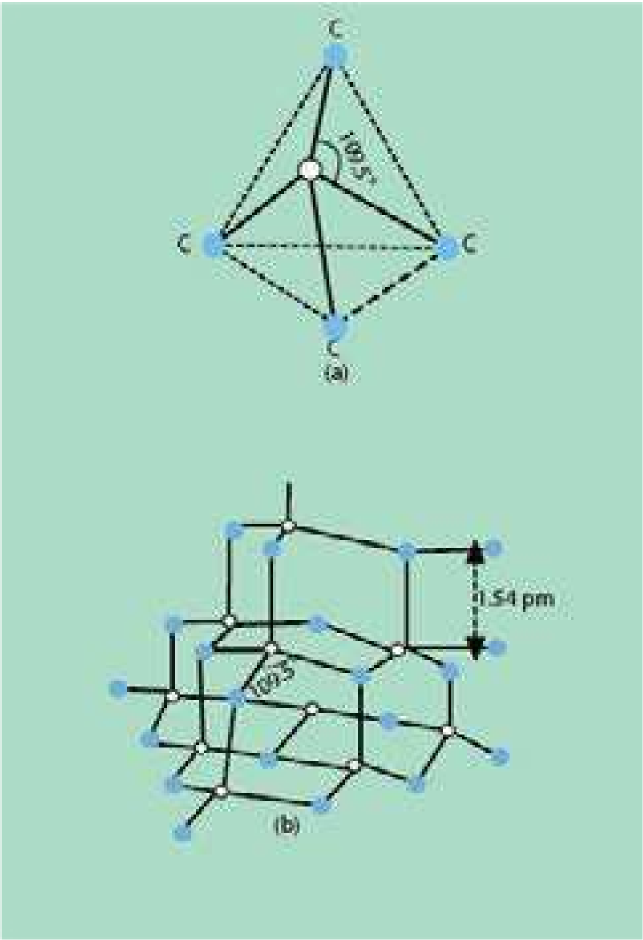
Mostly covalent crystalline solids are insoluble in polar solvents like water but they are readily soluble in non-polar solvents like benzene and carbon tetrachloride. The covalent crystals having giant molecules like diamond and silicon carbide are insoluble in all the solvents. Because of their big size, they do not interact with the solvent molecules. The chemical reactions of such crystalline solids are very slow.

Let us try to understand the structure of diamond, which is a well known covalent solid.

Structure of Diamond

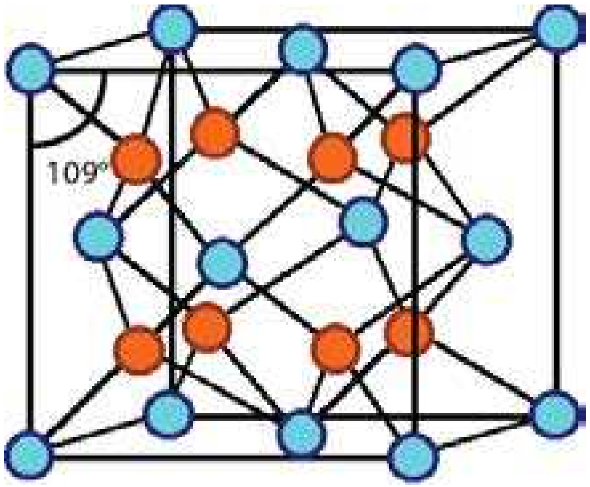
Diamond is one of the allotropic modifications of carbon. It is best understood by taking into consideration the number of electrons in the outermost shell of carbon, which are four. The four atomic orbitals (one 2s and three 2p) undergo sp^3 hybridization to give four sp^3 hybridized orbitals. They are directed in space along the four corners of a tetrahedron Fig. (4.18 a).

This is the unit cell of diamond and a large number of such unit cells undergo sp^3-sp^3 overlapping to form a huge structure. Each carbon atom is linked with four other carbon atoms. The bonds between carbon atoms are covalent which run through the crystal in three-dimensions. All the bond angles are 109.5° and the bond lengths are 154 pm.



The whole lattice is, therefore, continuous and because of the continuity of C-C covalent bonding, the entire diamond crystal behaves as a huge or giant three-dimensional carbon molecule. This is also called a macro-molecule.

Fig.(4.18b), The overall structure of diamond looks face centred-cubic Fig. (4.18 c)



Fig(4.18 c) face-centered cubic structure of diamond

4.7.3. Molecular Solids

Those solid substances in which the particles forming the crystals are polar or non-polar molecules or atoms, of a substance are called molecular solids. For instance, in solidified noble gases, there are non-polar atoms. Two types of of diamond intermolecular forces hold them together.

(i) Dipole-dipole interactions.

(ii) van der Waals forces.

These intermolecular forces are much weaker than the forces of attraction between the cations and the anions in ionic crystals, and between the atoms in the covalent crystals.

Ice and sugar are the best examples of crystals having polar molecules whereas iodine, sulphur, phosphorus and carbon dioxide form the molecular crystals containing nonpolar molecules. Polar molecular solids have usually higher melting and boiling points as compared to non-polar molecular solids.

Properties of the Molecular Solids

X-ray analysis has shown the regular arrangements of atoms in constituent molecules of these solids, and we get the exact positions of all the atoms.

The forces, which hold the molecules together in molecular crystals, are very weak so they are soft and easily compressible.

They are mostly volatile and have low melting and boiling points. They are bad conductors of electricity, have low densities and sometimes transparent to light. Polar molecular crystals are mostly soluble in polar solvents, while non-polar molecular crystals are usually soluble in non-polar solvents.

Iodine is one of the best examples of a molecular solid. Let us discuss the structure of iodine molecule.

Structure of Solid Iodine

In the solid state the molecules of iodihe align in the form of layer lattice. This is shown in Fig (4.19). I -I bond distance is 271.5 pm and it is appreciably longer than in gaseous iodine (266.6 pm). As expected from its structure, iodine is a poor conductor of electricity.

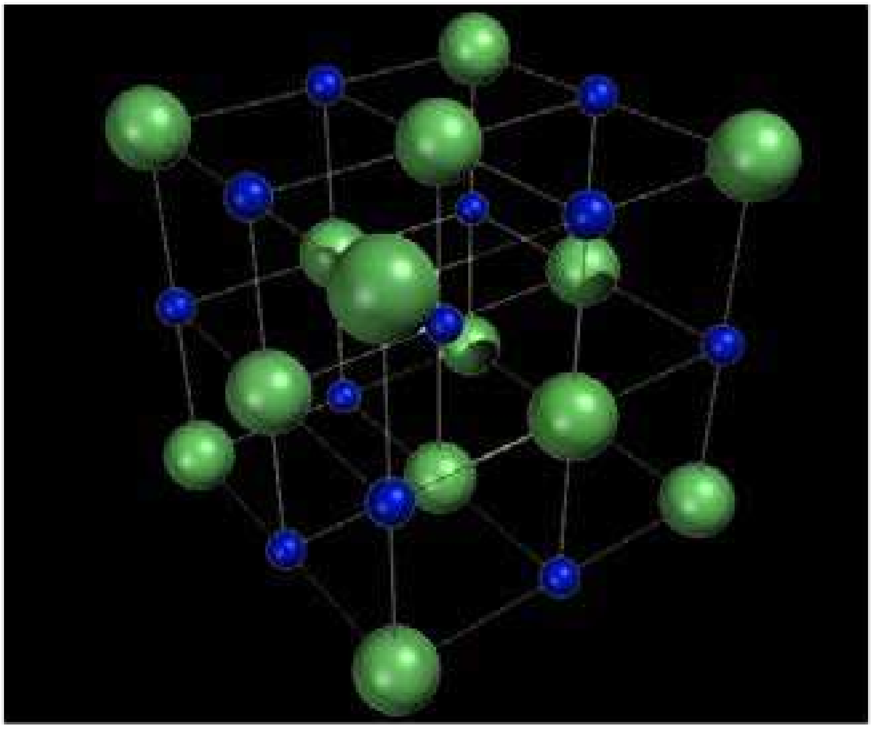


Fig (4.19) Face centered cubic structure of iodine

4.7.4. Metallic Solids

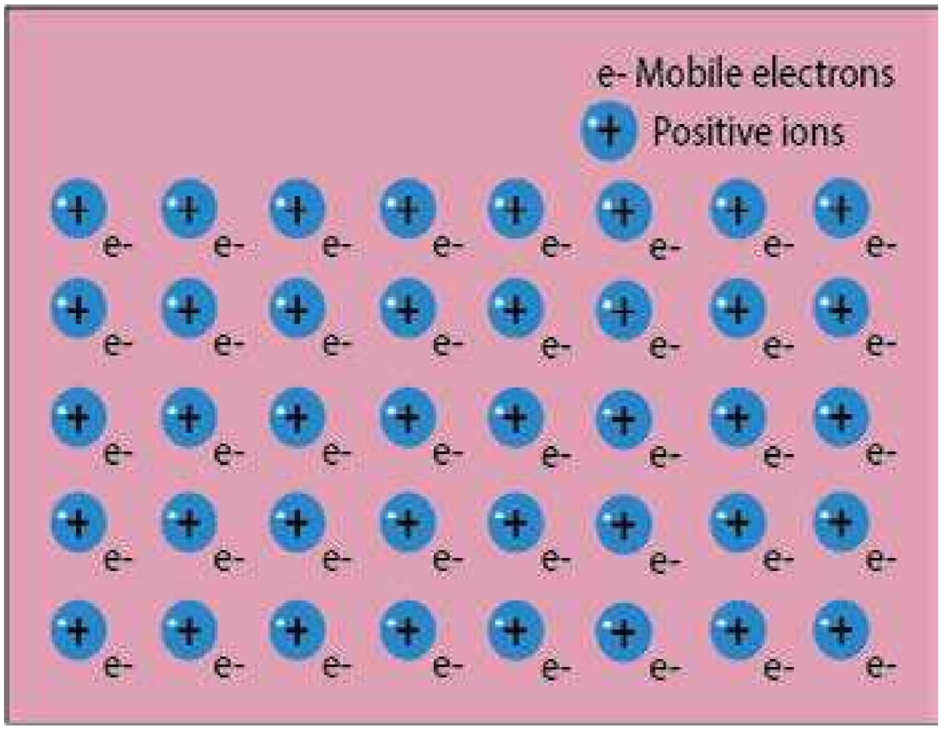


Fig (4.20) Positive ions surrounded by mobile electrons

In order to explain properties of metallic solids various theories have been proposed. A few of them are mentioned here.

The first theory of metallic bonding is called electron pool or electron gas theory. This theory was proposed by Drude and extended by Loren (1923). According to this theory, each atom in a metal crystal loses all of its valence electrons. These valence electrons form a pool or a gas. The positively charged metal ions are believed to be held together by electron pool or gas. These positively charged ions occupy definite positions at measurable distances from each other in the crystal lattice. Valence electrons are not attached to any individual ion or a pair of ions rather belong to the crystal as a whole. These electrons are free to move about from one part of the crystal to the other. The force, which binds a metal cation to a number of electrons within its sphere of- influence, is known as metallic bond. The following Fig. (4.20) gives an idea of electron gas model.

L. Pauling has tried to explain the metallic bond according to valence bond theory. According to this theory, the metallic bond is treated essentially as covalent in character. However, it is assumed that the covalent bonds are not localized but are highly delocalized in metal structure.

Recently, molecular orbital theory was applied to explain the characteristics of metallic solids. According to this theory, it is assumed that the electrons in the completely filled orbitals are essentially localized, while atomic orbitals containing the valence electrons interact or overlap to form a set of delocalized orbitals. These delocalized orbitals are the molecular orbitals which extend over the entire crystal lattice. Such a combination of atomic orbitals produce as a large number of closely spaced states. These states of energy are also known as bands of energy. That is why it is also called a band theory. The energy gap between two bands determines the properties of the metallic solids.

Properties of Metallic crystals

Metals are good conductor of electricity. When electric field is applied between two ends of a metal then the mobile electrons begin to move towards the positive pole and the new electrons from the negative pole take their place Fig. (4.21a) Sometimes, the electrical conductivity of metals decrease with the increase in temperature. The reason is that with the increase in temperature the positive metal ions also begin to oscillate and the motion hinders the free movement of mobile electrons between the positive ions. This hindrance decreases the electrical conductivity.

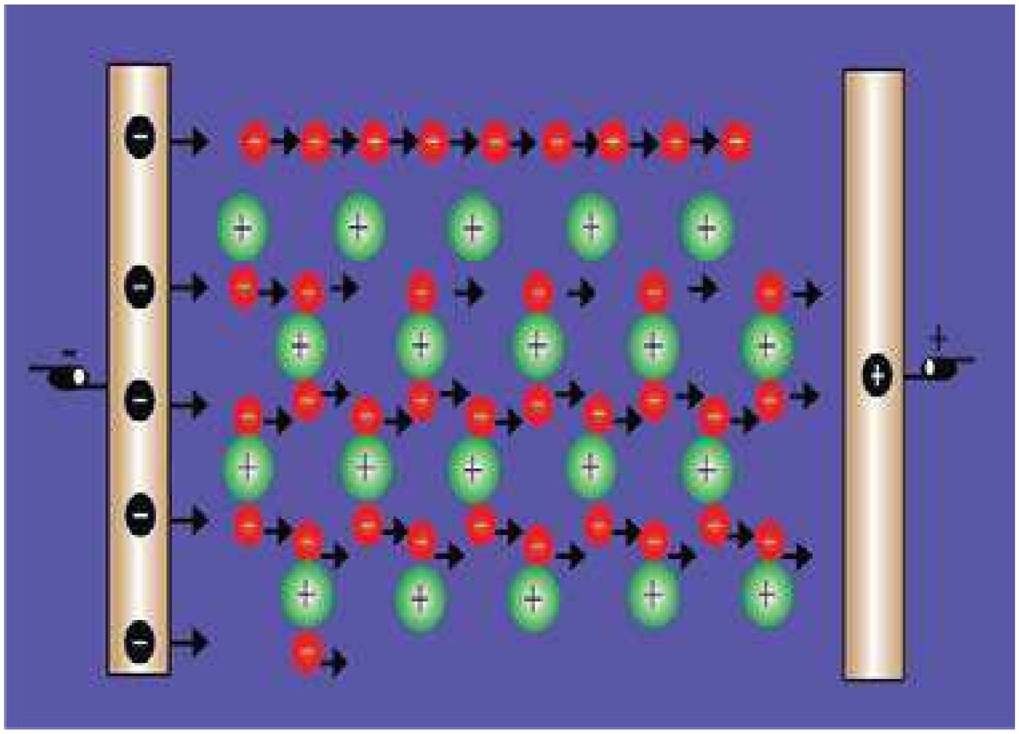
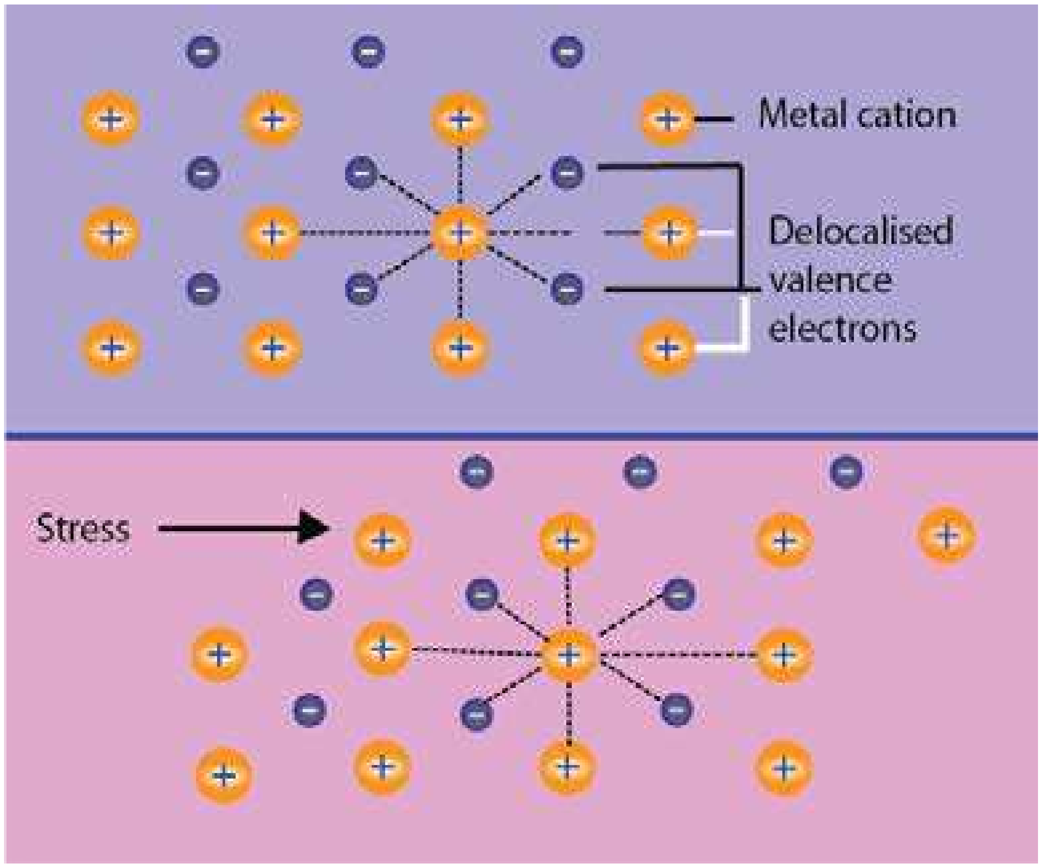


Fig (4.21a) Explanation of electrical conductivity of a metal

The rmal conductivity is another property associated with metallic solids. When a piece of metal is heated at one end, the mobile electrons at this end absorb heat energy and move very rapidly through the metallic lattice towards the cooler end. During the process they collide with adjacent electrons and transfer their heat energy to them.

Whenever the metals are freshly cut, most of them possess metallic luster which means that they have a shining surface. When light falls on the metallic surface, the incident light collides with the mobile electrons and they are excited. These electrons when deexcited give off some energy in the form of light. This light appears to be reflected from the surface of the metal which gives a shining look.

Metals are malleable and ductile whenever stress is applied on them. Their layers slip pass each other. The structure of the metal changes without fracturing as shown in the Fig. (4.21b).



Fig(4.21b) Deformation of metal structures

Structure of Metals

In the previous article of metallic solids, we have learnt that metal atoms are arranged in definite pattern. Free electrons are roaming about in the crystal lattice. So a metal may be regarded as an assembly of the positively charged spheres of identical radii which are packed together to fill the space as completely as possible.

To understand the closed packing of atoms in metal structures, let us suppose that the metal atoms are like hard spherical balls. Take twelve spherical balls and pack in a box as shown in Fig (4.22 a).

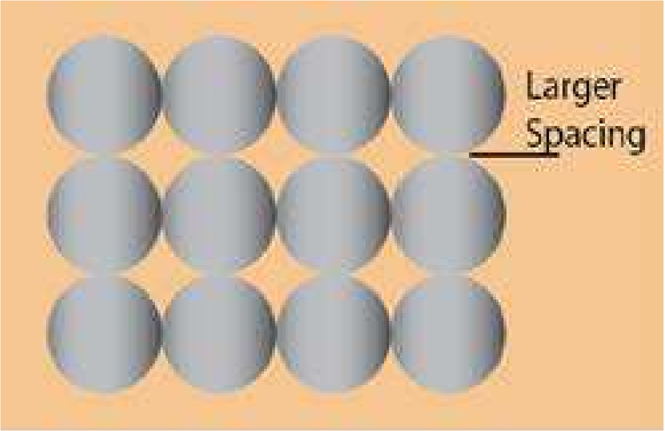


Fig (4.22 a) Packing of twelve sphere in a box (two dimensional view)

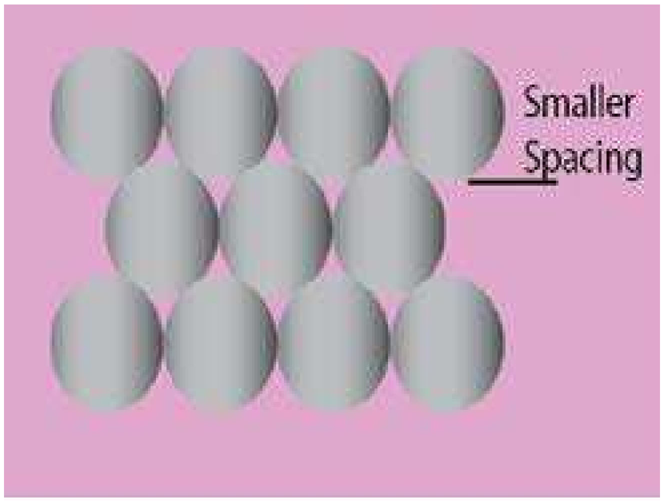


Fig (4.22 b)Packing of eleven spheres in a box
(two dimentional view)

The spaces during the packing are larger. When the box is shaken, the balls will rearrange as shown in Fig (4.22 b). The arrangement of these balls are now stable and more closely packed. It is the natural tendency of the balls to have closely packed arrangement of eleven spheres after shaking.

In order to understand,how various unit cells of the crystal lattice are developed, consider three balls which join together in one plane. The fourth ball is inserted in the space created by the other three as a second layer. In this way tetrahedral structure is obtained Fig (4.22 c). Actually, the fourth ball of the second layer is placed in the depression created by the first three balls. These depressions are also called interstices or crevices or voids.

Consider the Fig (4.22 d) in which eleven balls of Fig. (4.22 b) are present in the first layer (circles with shade). The balls of the second layer (circle without shade) can fit into the depressions or interstices created by the first layer. When the balls of the second layer are arranged, then all the depressions of the first layer are not occupied. There are two types of depressions as ‘a’ and ‘b’. The depressions marked ‘b’ are not occupied by the second layer and one can see the ground from looking at the top through depressions ‘b’. The new depressions marked ‘a’ are created by the second layer. Through the depressions ‘a’, we can not see the ground, but balls of the first layer.
Now arrange the balls of third layer in the depression of second layer. When the balls of the third layer are placed abov the second layer then there are two possibilities. Third layer balls may be accommodated in ‘a’- type or ‘b’-type interstices or depressions.

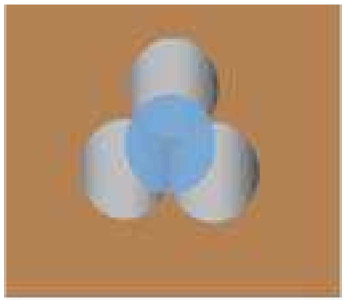


Fig (4.22 c) The formation of a tetrahedral site, due to four balls

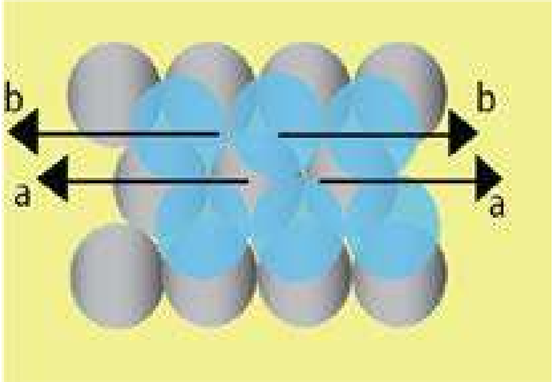


Fig (4.22 d) Close packing of spheres, showing 11 balls in first layer and 6 balls in second layer.

(i) Cubic Close Packing

When the atoms of the third layer fit into the interstices marked b, then the atoms of the third layer will not lie directly above those of the atoms of first layer. This pattern of arrangement is called ABC ABC-------------- or 123 123-----------------. It is named as face centred cubic arrangement Fig. (4.23a). The balls of fourth, seventh and tenth layers will be in front of each other.

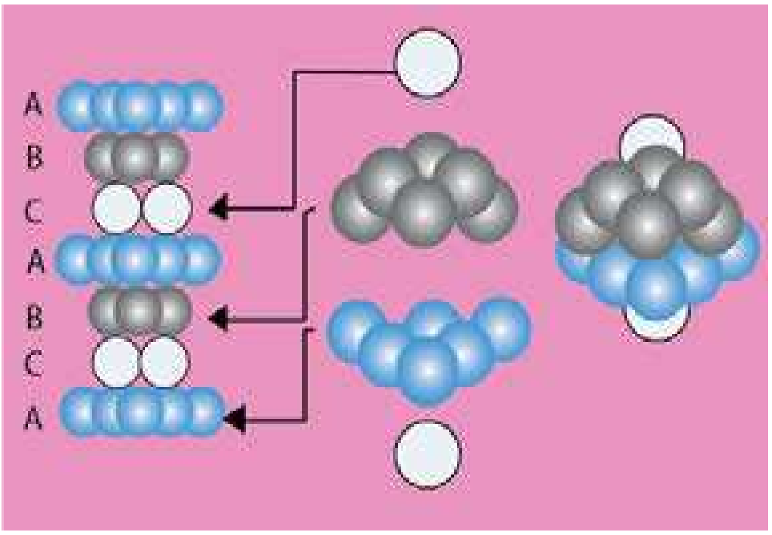


Fig (4.23 a) Cubic close packing or
Face centred cubic arrangement (ABCABC . . .)

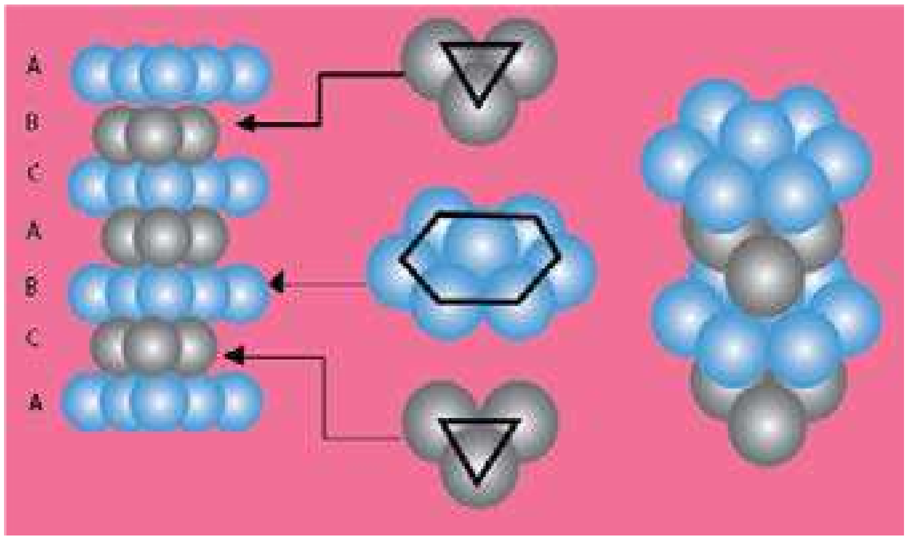


Fig (4.23 b) Hexagonal close packing (ABAB . . .)

(ii) Hexagonal Close Packing

When the atoms of the third layer are arranged in such a way that they occupy the depressions created by the second layer i.e., in the ‘a’ types crevices then these atoms will directly lie above the atoms of first layer. This pattern of arrangement is usually written as ABAB .... or 1212 . This pattern has been named as hexagonal close packing Fig(4.23b). The balls of third, fifth, seventh layers will be in front of each other.

Comparison of Properties of Various Types of Crystals

The following table gives a view to the comparison of properties of four types of crystals.

Table (4.9) Type of Crystalline Solids

Type of Solid	Structural Particles	Intermolecular Forces	Typical Properties	Examples
Metallic	cations plus delicalized electrons	metallic bons	hardness varies from soft to Very hard; melting points varied from low to very high; lustrous; ductile; malleable; very good conductors of heat and electricity	Na; Mg; Al Fe; Zn; Cu; Ag; W
Ionic	cations and anions	electrostatic attractions	hard; moderate to very high melting points: nonconductors of electricity (but good electrical conductors in the molten state)	NaCl;$NaNO_3$, MgO
Molecular	molecules (atoms of noble gases)	Landon and/or dipole-dipole and/or hydrogen bonds	soft; low melting points: nonconductors of heat and electricity; sublime easily in many cases	noble-gas elements; CH_4; CO_2; P_4 S_8; I_2; H_2O
Network covalent	atoms	covalent bonds	very hard; very high melting points: nonconductors of elecrioity	C(diamonds); SiC; SiO_2

4.8 Determination of Avogadro's Number (N_A)

Avagadro number can be calculated in a number of different ways. One of the most accurate methods for determining this number is based on the study of crystalline solids.

In order to calculate this number, we need to know the volume of one gram-mole of a crystalline solid and the distance between its atoms or ions in the crystal lattice.

The volume of one gram-mole of a solid can be calculated from its density while the spacing between its atoms can be measured by X-rays.

The method of determining Avogadro' s number is explained with a help of following solved example which gives a reasonably good value of this number. The crystal of LiF is primitive cubic and can be used to calculate the Avogadro's number.

Example:

The density of LiF is 2.65 g cm^{-3}. It is made up of cubic array of alternate Li^+ and F^- ions and the distance between these ions is 2.01 $\mathring{A}$ (2.01 x 10^{-8} cm). Calculate the Avogadro's number.

Solution:

The formula mass of LiF = 6.939 + 18.9984
= 25.9374 g mol^{-1}
Density of LiF = 2.65 g cm^{-3}

From the density and molar mass, calculate the volume of 1 mole of solid LiF

The volume occupied

by one formula unit of LiF = $\dfrac{25.9374\text{g mol}^{-1}}{2.65\text{g cm}^{-3}}$

= .7889 cm^3 mol^{-1}

From this volume, we can calculate the edge length of the cube. For this, we suppose that 9.788cm^3 of LiF i.e., 1 mole of LiF, is present in the form of a cube. The cube root of this volume will give the length of one edge of cube.

Edge length of the cube $= \sqrt[3]{9.788\text{cm}^3}$

$= 2.139\text{cm}$

The number of ions of both Li^+ and F^- on one edge length can be calculated by dividing the edge length by distance between ions. Hence, the number of ($Li^+$and F^-) ions along one edge length

$$= \frac{2.139\text{cm}}{2.01\times10^{-8}\text{cm ion}^{-1}}$$

$$= 1.064\text{x}10^8$$

When we take the cubes of these ions we get the total number of ions i.e. Li^+ and F^- in the cube.

Total number (Li^+F^-) of ions in the cube $= (1.064\text{x}10^8)^3$

$= 1.204\text{x}10^{24}$

Since the cube of LiF crystal contains one Avogadro's number of Li^+ and one Avogadro's number of F^- , so the Avogadro's number will be

$$\frac{1.204x10^8}{2} \qquad =6.02\text{x}10^{23}$$

KEY POINTS

1. Among three states of matter i.e. gases, liquids and solids, the intermolecular attractive forces in the gases are negligible. In liquids intermolecular forces are strong enough to keep the molecules close together. Anyhow, the molecules in liquids are free to move with respect to one another. In solids the particles occupy specific locations in three dimensional arrangement. Molecules in liquids are free to move with respect to one another. In solids the particles occupy specific locations in three dimensional arrangement.
2. There are four types of intermolecular forces i.e. dipole-dipole forces, London dispersion forces, hydrogen bonding and Ion-dipole forces. The relative strengths of dipole-dipole and dispersion forces depend upon the polarity, polarisability, size and shape of the molecules. Hydrogen bonding occurs in compounds containing 0-H,N - H, H - F bonds.
3. The vapour pressure of a liquid measures the tendency of a liquid to evaporate. It is the pressure exerted by the vapours on the surface of a liquid when the rate of evaporation is equal to the rate of condensation. A liquid boils when its vapour pressure equals the external pressure.
4. Many crystalline solids melt to give a turbid liquid before melting to give a clear liquid. These turbid liquids possess some degree of order and are called liquid crystals. Liquid crystals have the fluidity of liquids and the optical properties of solids.
5. In crystalline solids the particles are arranged in a regular and repeating manner. The essential structural features of a crystalline solid can be represented by its unit cell. The three dimensional array of points representing atoms, ions or molecules is called crystal lattice. The points in the crystal lattice represent positions in the structure where they have identical environments.
6. The simplest unit cell is a cubic unit cell. There are seven crystal systems overall.
7. The properties of solids depend on the arrangement of particles and the attractive forces between them. Ionic solids are hard and brittle and have high melting points. Covalent solids consist of atoms held together by covalent bonds and these bonds extend throughout the solid. They are hard and have high melting points. Metallic solids consist of metal cations immersed in a sea of electrons and give a wide range of properties. Molecular solids consist of atoms or molecules held together by intermolecular forces.
8. The properties of solids depend on the arrangement of particles and the attractive forces between them. Ionic solids are hard and brittle and have high melting points. Covalent solids consist of atoms held together by covalent bonds and these bonds extend throughout the solid. They are hard and have high melting points. Metallic solids consist of metal cations immersed in a sea of electrons and give a wide range of properties. Molecular solids consist of atoms or molecules held together by intermolecular forces.

EXERCISE
(QUESTIONS OF LIQUIDS)

Q1. Choose the best answers from the given choices.

(i) London dispersion forces are the only forces present among the
 (a) molecules of water in liquid state
 (b) atoms of helium in gaseous state at high temperature
 (c) molecules of solid iodine.
 (d) molecules of hydrogen chloride gas.

(ii) Acetone and chloroform are soluble in each other due to
 (a) intermolecular hydrogen bonding (b) ion-dipole interaction
 (c) instantaneous dipole (d) all of the above

(iii) NH, shows a maximum boiling point among the hydrides of Vth group elements due to
 (a) very small size of nitrogen (b) lone pair of electrons present on nitrogen.
 (c) enhanced electronegative character of nitrogen
 (d) pyramidal structure of NH_3

(iv) When water freezes at 0"C, its density decreases due to
 (a) cubic structure of ice (b) empty spaces present in the structure of ice
 (c) change of bond lengths (d) change of bond angles

(v) In order to raise the boiling point of water upto 110°C, the external pressure should be
 (a) between 760 torr and 1200 torr (b) between 200 torr and 760 torr
 (c) 765 torr (d) any value of pressure

Q2. Fill in the blanks with suitable words

(i) The polarizability of noble gases_______down the group and results in the increase in their boiling points.

(ii) _______ is developed in acetone and chloroform when they are mixed together.

(iii) Exceptionally weak_____of HF is due to strong hydrogen bonding present in it.

(iv) The concept of dynamic equilibrium is the ultimate _______of all reversible systems.

(v) ΔH_v of C_6H_{14} should be_____ than that of C_2H_6.

(vi) During the formation of ice from liquid water there is a______ % increase in volume.

(vii) The rate of increase of vapour pressure of water_______at high temperatures.

(viii) A layer of ice on the surface of water____the water underneath for further heat loss.

(ix) Evaporation is a ________process.

(x) Liquid crystals are used in the display of_________ devices.

Q3. Indicate true or false as the case may be

(i) Dipole-dipole forces are weaker than dipole-induced dipole forces.

(ii) The ion dipole interactions are responsible for the dissolution of an ionic substance in water.

(iii) The high polarizability of iodine is responsible for its existence in solid form and its difference from other halogens.

(iv) The strong hydrogen bonding in H_2S makes it different from water.

(v) Hydrocarbons are soluble in water because they are polar compounds.

(vi) The viscosities of liquids partially depend upon the extent of hydrogen bonding.

(vii) The state of equilibrium between liquid state and vapours is dynamic in nature.

(viii) Heat of vapourization of liquids depend upon the intermolecular forces of attraction present between their molecules.

(ix) Ice does not show any vapour pressure on its surface at -1°C.

(x) Boiling point of a liquid is independent of external pressure.

Q4 (a) What type of intermolecular forces will dominate in the following liquids.

(i) Ammonia, NH_3 (ii) Octane, C_8H_{18} (iii) Argon, Ar

(iv) Propanone, CH_3COCH_3 (v) Methanol, CH_3OH

(b) Propanone (CH_3COCH_3), propanol ($CH_3CH_2CH_2OH$) and butane ($CH_3CH_2CH_2CH_3$) have very similar relative molecular masses. List them in the expected order of increasing boiling points. Explain your answer.

Q.5 Explain the following with reasons.

(i) In the hydrogen bonded structure of HF, which is the stronger bond: the shorter covalent bond or the longer hydrogen bond between different molecules.

(ii) In a very cold winter the fish in garden ponds owe their lives to hydrogen bonding?

(iii) Water and ethanol can mix easily and in all proportions.

(iv) The origin of the intermolecular forces in water.

Q6 (a) Briefly consider some of the effects on our lives if water has only a very weak hydrogen bonding present among its molecules.

(b) All gases have a characteristic critical temperature. Above the critical temperature it is impossible to liquefy a gas. The critical temperatures of carbon dioxide and methane are 31.14 °C and -81.9 °C, respectively. Which gas has the stronger intermolecular forces? Briefly explain your choice?

Q7 Three liquids have the properties mentioned against their names

		Water	Propanone	Pentane
(i)	Molecular Formula	H_2O	C_3H_6O	C_5H_{12}
(ii)	Relativemolecularmass(a.m.u.)	18	58	72
(iii)	Enthalpy change of vapourization (kJ mol^{-1})	41.1	31.9	27.7
(iv)	Boiling point (^{0}C)	100	56	36

(a) What type of intermolecular force predominates in each liquid?

(i) water (ii) propanone (iii) pentane

(b) What do you deduce about the relative strength of these forces in the liquids? Justify your conclusions.

(c) If the liquids are shaken together in pairs,

- (i) Which pair would be unlikely to mix?
- (ii) Explain this immiscibility in terms of the forces between the molecules.
- (iii) Choose one of the pairs that mix and say whether the enthalpy change on mixing would be positive or negative.

Q8 Describe the various forces responsible for keeping the particles together in the following elements and compounds and their effects on physical properties making use of the data below.

Substance	Formula	Molar Mass (a.m.u.)	M.P(°C)
Neon	Ne	20	-248
Argon	Ar	40	-189
Water	H_2O	18	0
Sodium fluoride	NaF	42	993
Diamond	C	12	3350

Q9 The boiing points and molar masses of hydrides of some first row elements are tabulated below:

Substance	Boiling Point (K)	Molar Mass (g mol^{-1})
CH_4	109	16
NH_3	240	17
H_2O	373	18

Suggest reasons for the difference in their boiling points in terms of the type of molecules involved and the nature of the forces present between them.

Q10 Explain the term saturated vapour pressure. Arrange in order of increasing vapour pressure: ldm^3 water, 1 dm^3 ethanol, 50 cm^3 water, 50 cm^3 ethanol and 50 cm^3 of ether.

Q11 While a volatile liquid standing in a breaker evaporates, the temperature of the liquid remains the same as that of its surrounding. If the same liquid is allowed to vapourize into atmosphere in an insulated vessel, its temperature falls below that of its surrounding. Explain the difference in behaviour.

Q12 How does hydrogen bonding explain the following indicated properties of the substances?

(i) Structure of DNA (ii) Hydrogen bonding in proteins
(iii) Formation of ice and its lesser density than liquid water
(iv) Solubilities of compounds

Q13 What are liquid crystals? Give their uses in daily life.

Q14 Explain the following with reasons.

(i) Evaporation causes cooling.
(ii) Evaporation takes place at all temperatures.
(iii) Boiling needs a constant supply of heat.
(iv) Earthenware vessels keep water cool.
(v) One feels sense of cooling under the fan after bath.
(vi) Dynamic equilibrium is established during evaporation of a liquid in a closed vessel at constant temperature.
(vii) The boiling point of water is different at Murree hills and at Mount Everest.
(viii) Vacuum distillation can be used to avoid decomposition of a sensitive liquid.
(ix) Heat of sublimation of a substance is greater than its heat of vaporization.
(x) Heat of sublimation of iodine is very high.

(QUESTIONS OF SOLIDS)

Q1. Multiple choice questions.

(i) Ionic solids are characterized by
- (a) low melting points. (b) good conductivity in solid state,
- (c) high vapour pressures. (d) solubility in polar solvents.

(ii) Amorphous solids
- (a) have sharp melting points.
- (b) undergo clean cleavage when cut with knife.
- (c) have perfect arrangement of atoms.
- (d) can possesses small regions of orderly arrangement of atoms.

(iii) The molecules of CO_2 in dry ice form the
- (a) ionic crystals (b) covalent crystals
- (c) molecular crystals (d) any type of crystal

(iv) Which of the following is a pseudo solid?
- (a) CaF_2 (b) Glass (c) NaCl (d) All

(v) Diamond is a bad conductor because
- (a) it has a tight structure (b) it has a high density
- (c) there are no free electron present in the crystal of diamond to conduct electricity
- (d) is transparent to light

Q2. Fill in the blanks
- (i) In a crystal lattice, the number of nearest neighbours to each atom is called the_______.
- (ii) There are__________ Bravis lattices.
- (iii) A pseudo solid is regarded as__________liquid.
- (iv) Glass may begin to crystallize by a process called__________ .
- (v) Crystalline solids which exhibit the same _________ in all directions are called_________.
- (vi) The branch of science which deals with the __________________ of crystals is called crystallography.

Q.3 Indicate True/False as the case mav be
- (i) There are five parameters in unit cell dimensions of a crystal.
- (ii) Ionic crystals are very hard, have low volatility and very low melting and boiling points.

(iii) The value of lattice energy of the ionic substances depends upon the size of ions.
(iv) Molecular orbital theory of solids is also called band theory.
(v) Ionic solid is good conductor of electricity in the molten state.

Q.4 What are solids? Give general properties of solids. How do you differentiate between crystalline solids and amorphous solids?

Q5

(a) Explain the following properties of crystalline solids. Give three examples in each case.

(i) Anisotropy
(ii) Cleavage
(iii) Habit of a crystal
(iv) Isomorphism
(v) Polymorphism
(vi) Transition temperature
(vii) Symmetry
(viii) Growing of a crystal

(b) How polymorphism and allotropy are related to each other? Give examples.

Q6

(a) Define unit cell. What are unit cell dimensions? How the idea of crystal lattice is developed from the concept of unit cell?

(b) Explain seven crystal systems and draw the shapes of their unit cells.

Q7

(a) What are ionic solids? Give their properties. Explain the structure of NaCl. Sketch a model to justify that unit cell of NaCl has four formula units in it.

(b) What are covalent solids? Give their properties. Explain the structure of diamond.

(c) What are molecular crystals? Give their properties. Justify that molecular crystals are softer than ionic crystals.

Q8

(a)Give different theories of a metallic bond. How does electron sea theory justify the electrical conductivity, thermal conductivity and shining surfaces of metals?

(b) Explain with the help of a diagram

(i) Cubic close packing in the structure of metals.
(ii) Hexagonal close packing in the structure of metals.

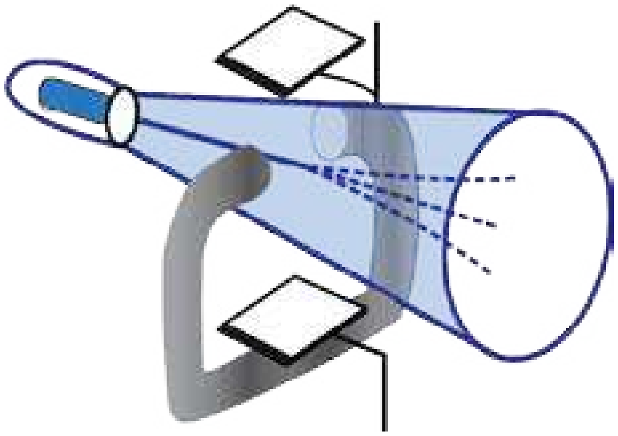
Q9 Crystals of salts fracture easily but metals are deformed under stress without fracturing. Explain the difference.

Q10 What is the coordination number of an ion? What is the coordination number of the cation in (a) NaCl structure and (b) CsCl structure? Explain the reason for this difference?

Q11 Give examples of ionic solids, molecular solids and covalent macromolecular solids. What are the factors which determine whether each of these types of solid will dissolve in water or not?

Q12 Explain the following with reasons:

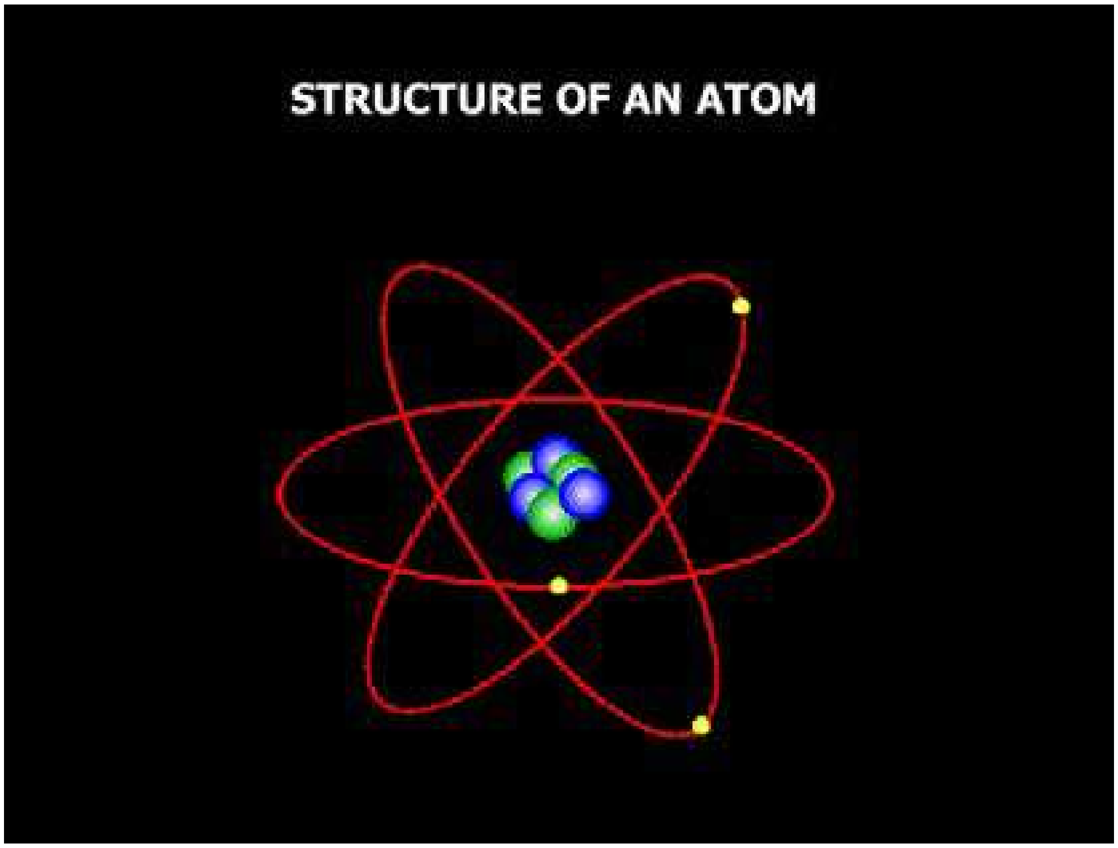
(i) Sodium is softer than copper, but both are very good electrical conductors.
(ii) Diamond is hard and an electrical insulator.
(iii) Sodium chloride and caesium chloride have different structures.
(iv) Iodine dissolves readily in teterachloromethane.
(v) The vapour pressures of solids are far less than those of liquids.
(vi) Amorphous solid like glass is also called super cooled liquid.
(vii) Cleavage of the crystals is itself anisotropic behaviour.
(viii) The crystals showing isomorphism mostly have the same atomic ratios.
(ix) The transition temperature is shown by elements having allotropic forms and by compounds showing polymorphism.
(x) One of the unit cell angles of hexagonal crystal is 120°.
(xi) The electrical conductivity of the metals decrease by increasing temperature.
(xii) In the closest packing of atoms of metals, only 74% space is occupied.
(xiii) Ionic crystals don’t conduct electricity in the solid state.
(xiv) Ionic crystals are highly brittle.
(xv) The number of positive ions surrounding the negative ion in the ionic crystal lattice depends upon the sizes of the two ions.



CHAPTER

5

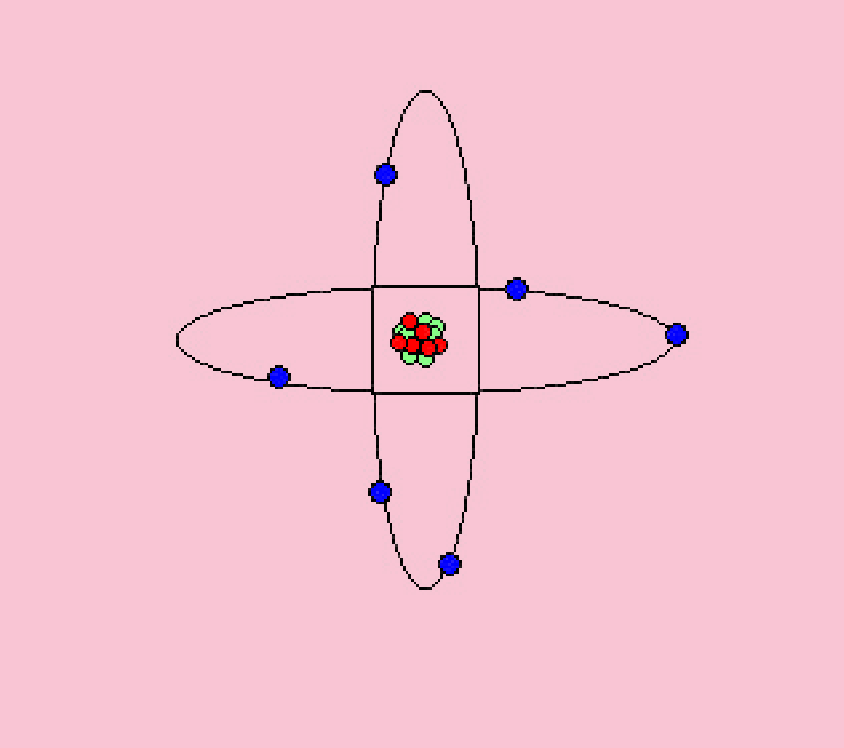
ATOMIC STRUCTURE



Animation 5.1: Atomic Structure
Source & Credit: nuceng

5.1 SUB-ATOMIC PARTICLES OF ATOM

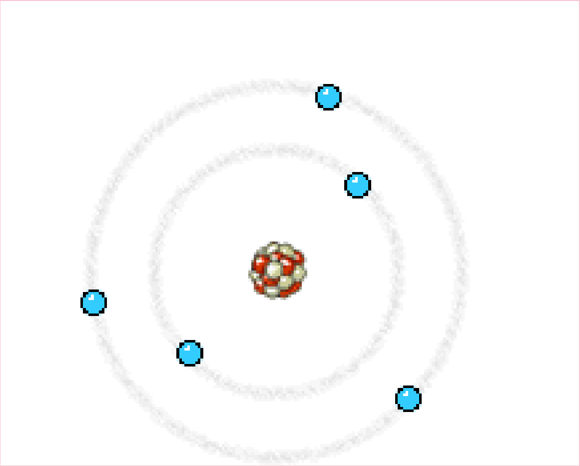
We are familiar with the nature of matter, which is made up of extremely small particles called atoms. According to Dalton's theory, atoms were considered to be ultimate particles which could not be divided any further. Our ideas about structure of atom have undergone radical changes over the years. A number of subatomic particles have been discovered. The experiments which led to the discovery of electron, proton and neutron are described below.



Animation 5.2: Atomic nucleus Model
Source & Credit : myweb.rollins

5.1.1Discovery of Electron (Cathode Rays)

A gas discharge tube is fitted with two metallic electrodes acting as cathode and anode. The tube is filled with a gas, air or vapours of a substance at any desired pressure. The electrodes are connected to a source of high voltage. The exact voltage required depends upon the length of the tube and the pressure inside the tube. The tube is attached to a vacuum pump by means of a small side tube so that the conduction of electricity may be studied at any value of low pressure Fig (5.1).

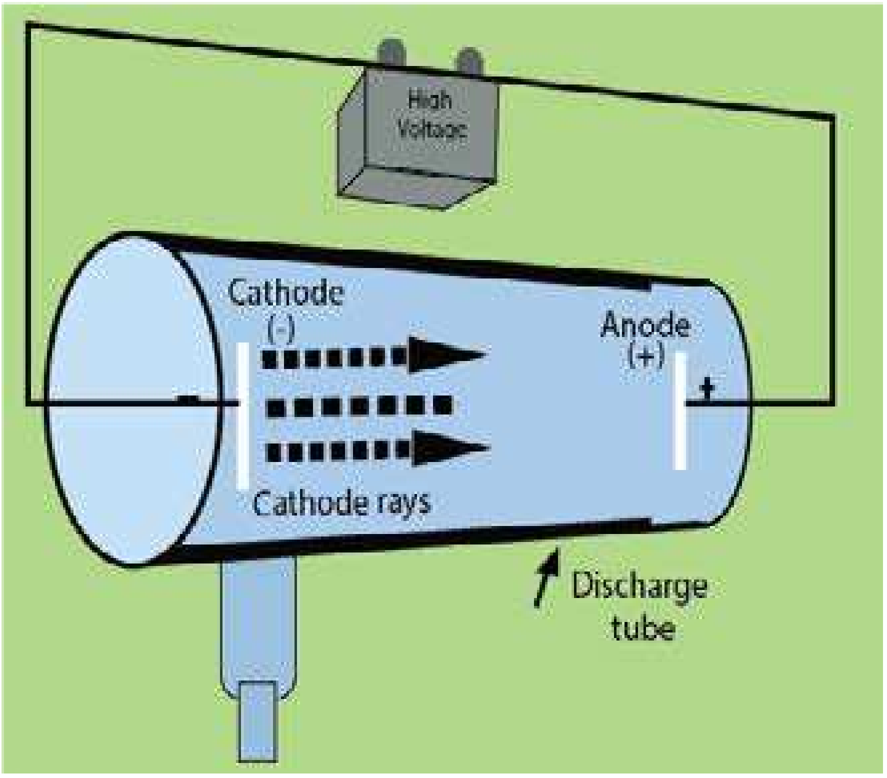


Animation 5.3: Cathode Rays
Source & Credit : wikipedia

It is observed that current does not flow through the gas at ordinary pressure even at high voltage of 5000 volts. When the pressure inside the tube is reduced and a high voltage of 5000-10000 volts is applied, then an electric discharge takes place through the gas producing a uniform glow inside the tube. When the pressure is reduced further to about 0.01 torr, the original glow disappeares. Some rays are produced which create fluorescence on the glass wall opposite to the cathode. These rays are called cathode rays. The colour of the glow or the fluorescence produced on the walls of the glass tube, depends upon the composition of glass.

5.1.2 Properties of Cathode Rays

To study the properties of cathoe rays systematic investigations were made by many scientists. They established the following properties of cathode rays.



Fi g (5.1) Projduct ion of the cath,ode rays

1. Cathode rays are negativelycharged. In 1895, J Perrin showed that when the cathode rays passed between the poles of the magnet, the path of the negatively charged particles was curved downward to point 2 by the magnetic field. Fig (5.2)

In 1897, J. Thomson established their electric charge by the application of electric field, the cathode ray particles were deflected upwards (towards the positive plate) to point 3. Fig. (5.2)

Thomson found that by carefully controlling the charge on the plates when the plates and the magnet were both around the tube, he could make the cathode rays strike the tube at point 1 again Fig.(5.2). In other words, he was able to cancel the effect of the magnetic field by applying an electric field that tended to bend the path of the cathode rays in the opposite direction.

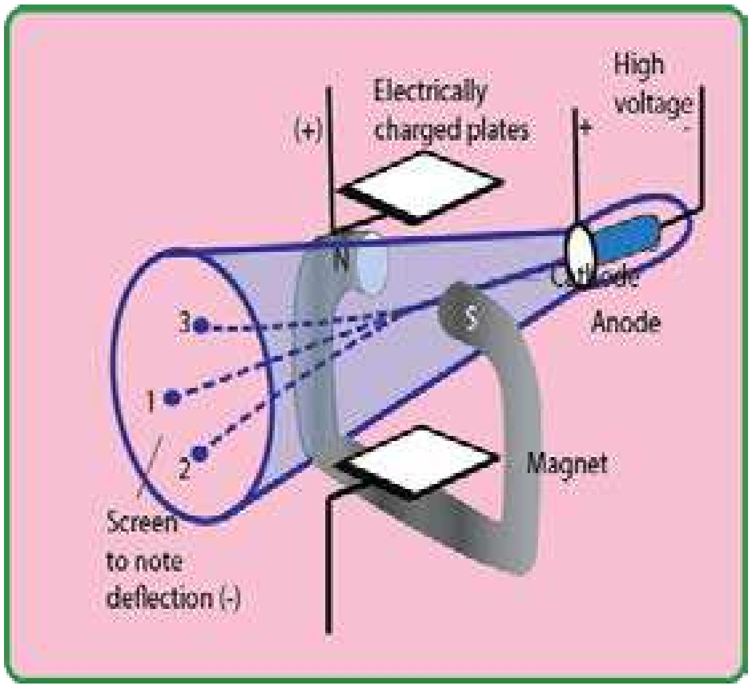


Fig (5.2) Deflection of cathode rays in electric and magnetic fields

2. They produce a greenish fluorescence on striking the walls of the glass tube. These rays also produce fluorescence in rare earths and minerals. When placed in the path of these rays, alumina glows red and tin stone yellow.

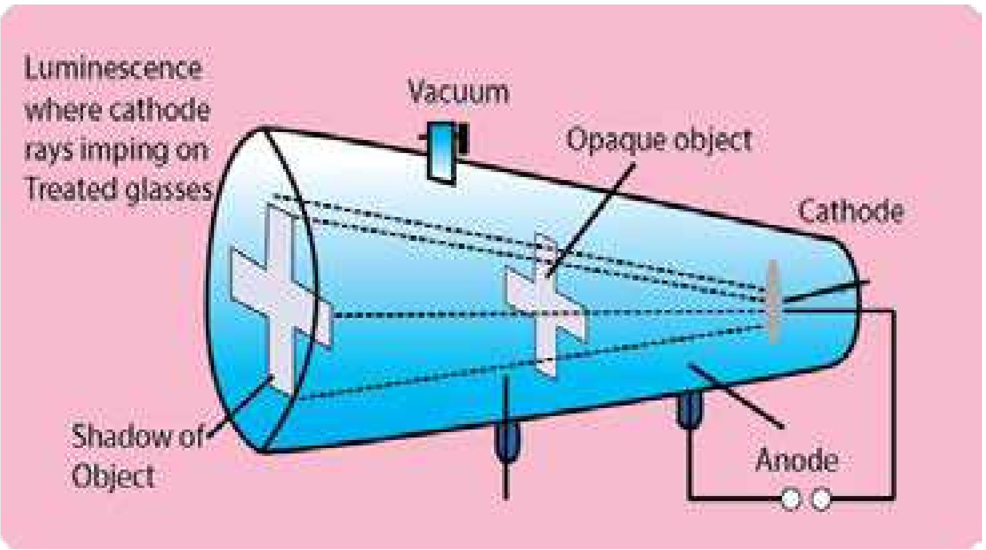
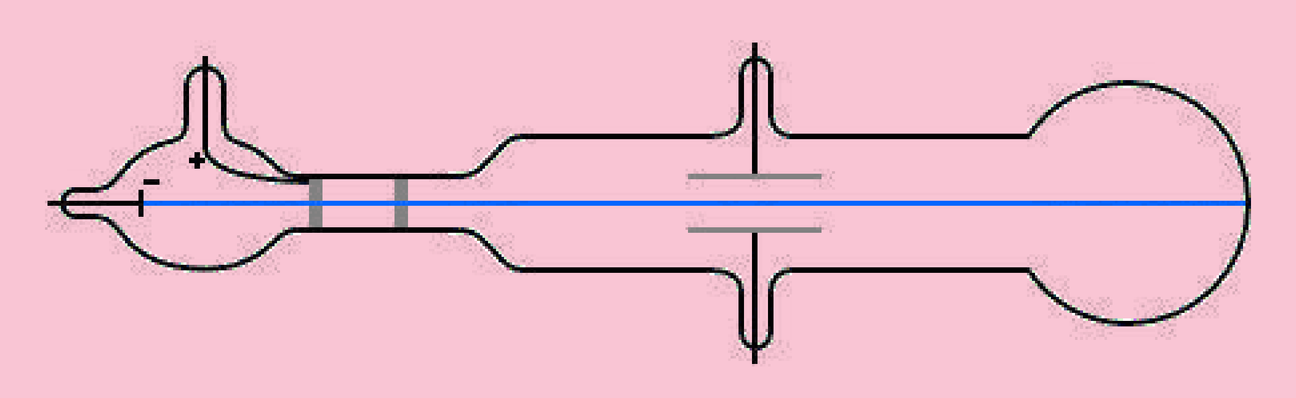


Fig (5.3) Cathode rays cast a shadow of an opaque object



Animation 5.4: X-ray Safety template
Source & Credit : adm.uwaterloo

3. Cathode rays cast a shadow when an opaque object is placed in their path. This proves that they travel q straight line perpendicular to the surface of cathode Fig (5.3).

4. These rays can drive a small paddle wheel placed in their path. This shows that these rays possess momentum. From this observation, it is inferred that cathode rays are not rays but material particles having a definite mass and velocity Fig (5.4).

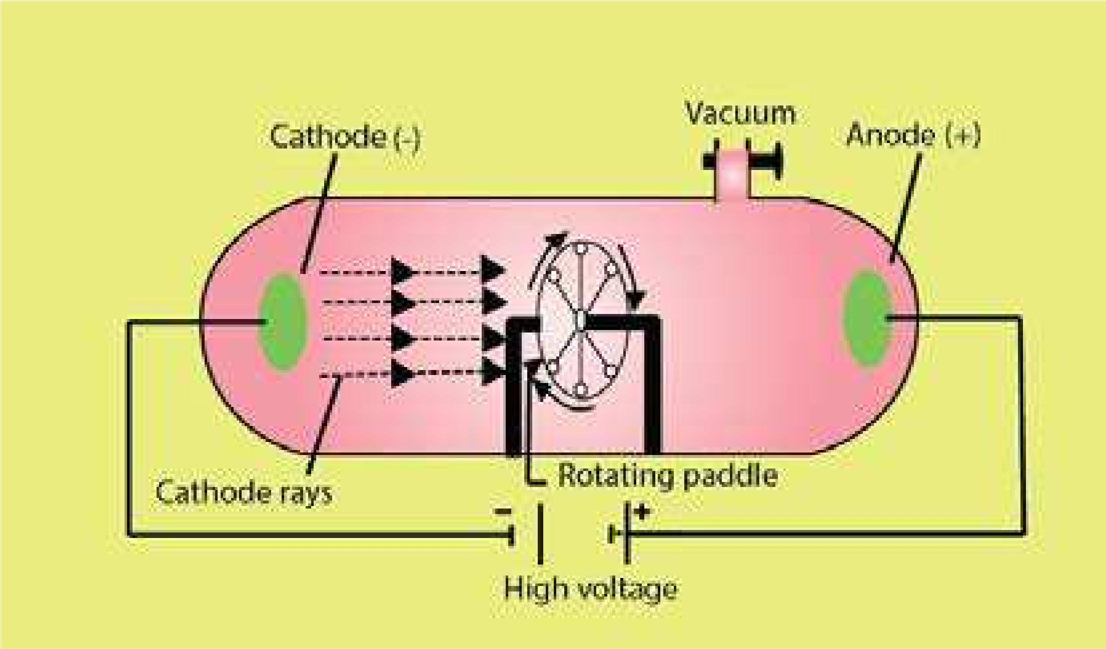


Fig (5.4) cathode rays derive a sman paddle wheel

5. Cathode rays can produce X-rays when they strike an anode particularly with large atomic mass Fig (5.18).

6. Cathode rays can produce heat when they fall on matter e.g. when cathode rays from a concave cathode are focussed on a platinum foil, it begins to glow.

7. Cathode rays can ionize gases.

8. They can cause a chemical change, because they have a reducing effect.

9. Cathode rays can pass through a thin metal foil like aluminum or gold foil.

10. The e/m value of cathode rays shows that they are simply electrons. J.J. Thomson concluded from his experiments that cathode rays consist of streams of negatively charged particles. Stoney named these particles as electrons. Thomson also determined the charge to mass ratio (e/m) of electrons. He found that the e/m value remained the same no matter which gas was used in the discharge tube. He concluded that all atoms contained electrons.

5.1.3 Discovery of Proton (Positive Rays)

In 1886, German physicist, E. Goldstein took a discharge tube provided with a cathode having extremely fine holes in it. When a large potential difference is applied between electrodes, it is observed that while cathode rays are travelling away from cathode, there are other rays produced at the same time. These rays after passing through the perforated cathode produce a glow on the wall opposite to the anode. Since these rays pass through the canals or the holes of cathode, they are called canal rays. These rays are named as positive rays owing to the fact that they carry positive charge Fig (5.5).

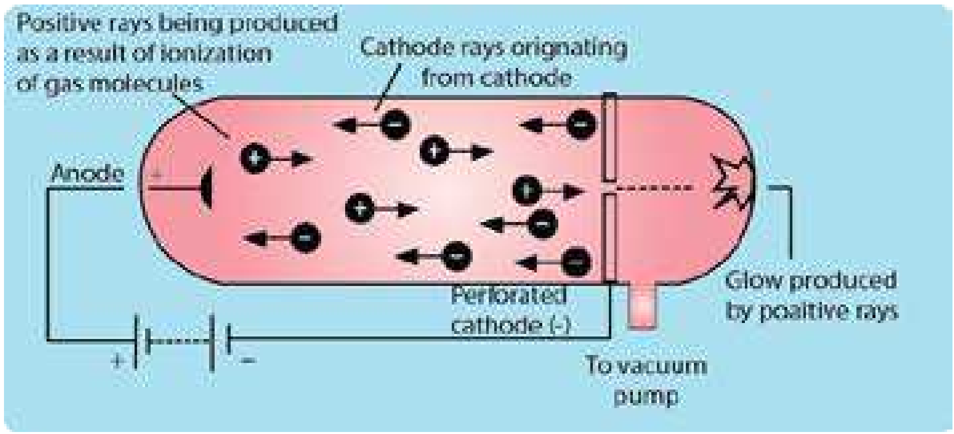
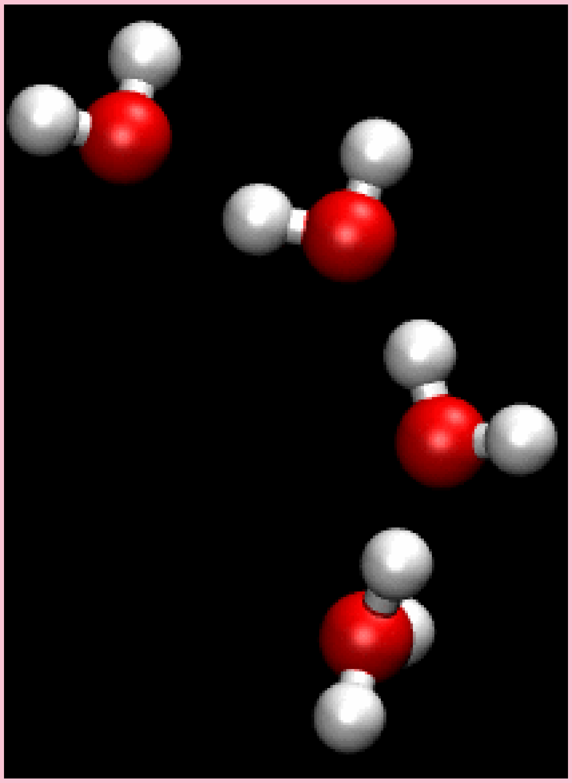


Fig (5.5) Production of positive rays

Reason for the Production of Positive Rays



Animation 5.5: Protons
Source & Credit : wikipedia

These positive rays are produced, when high speed cathode rays (electrons) strike the molecules of a gas enclosed in the discharge tube. They knock out electrons from the gas molecules and positive ions are produced, which start moving towards the cathode Fig (5.5).

$$M + e^- \rightarrow M^+ + 2e^-$$

5.1.4 Properties of Positive Rays

1. They are deflected by an electric as well as a magnetic field showing, that these are positively charged.
2. These rays travel in a straight line in a direction opposite to the cathode rays.
3. They produce flashes on ZnS plate.
4. The e/m value for the positive rays is always smaller than that of electrons and depends upon the nature of the gas used in the discharge tube. Heavier the gas, smaller the e/m value. When hydrogen gas is used in the discharge tube, the e/m value is found to be the maximum in comparison to any other gas because the value of'm' is the lowest for the positive particle obtained from the hydrogen gas. Hence the positive particle obtained from hydrogen gas is the lightest among all the positive particles. This particle is called proton, a name suggested by Rutherford. The mass of a proton is 1836 times more than that of an electron.

5.1.5 Discovery of Neutron

Proton and electron were discovered in 1886 and their properties were completely determined till 1895. It is very strange to know that upto 1932 it was thought that an atom was composed of only electrons and protons. Rutherford predicted in 1920 that some kind of neutral particle having mass equal to that of proton must be present in an atom, because he noticed that atomic masses of atoms could not be explained,if it were supposed that atoms had only electrons and protons. Chadwick discovered neutron in 1932 and was awarded Nobel prize in Physics in 1935.

Experiment

A stream of a-particles produced from a polonium source was directed at beryllium (^9_4Be) target. It was noticed that some penetrating radiation were produced. These radiations were called neutrons because the charge detector showed them to be neutral Fig (5.6). The nuclear reaction is as follows.

$$^4_2He + ^9_4Be \rightarrow ^{12}_6C + ^1_0n$$

(a -particle)

Actually a-particles and the nuclei of Be ate re-arranged and extra neutron is emitted.

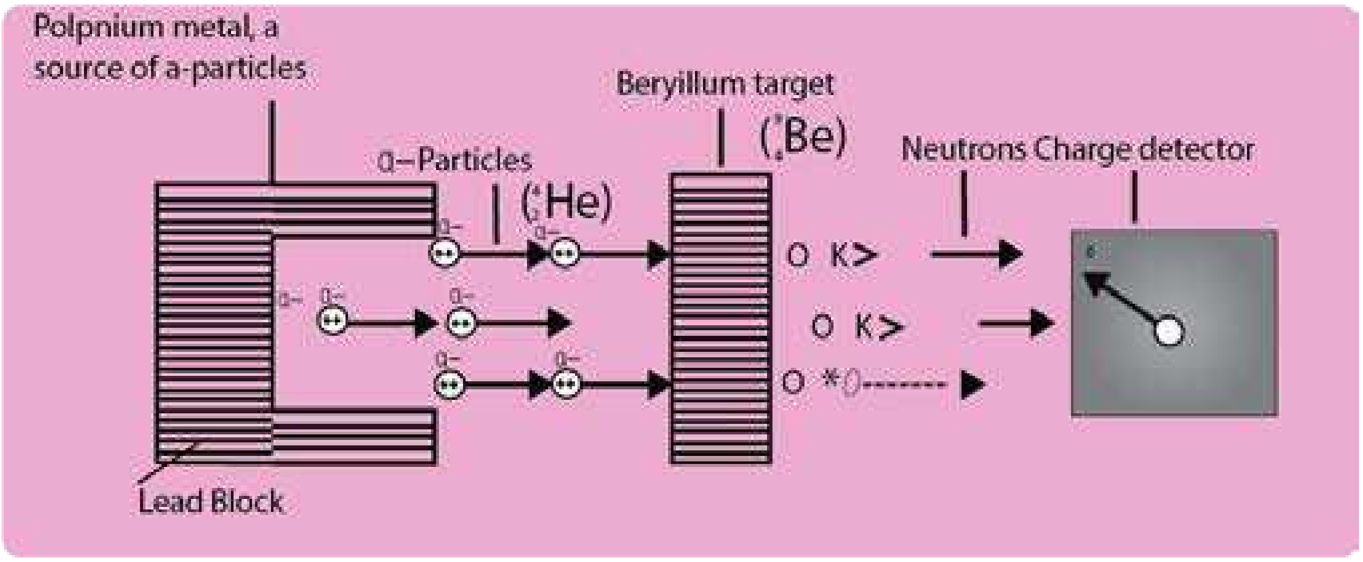
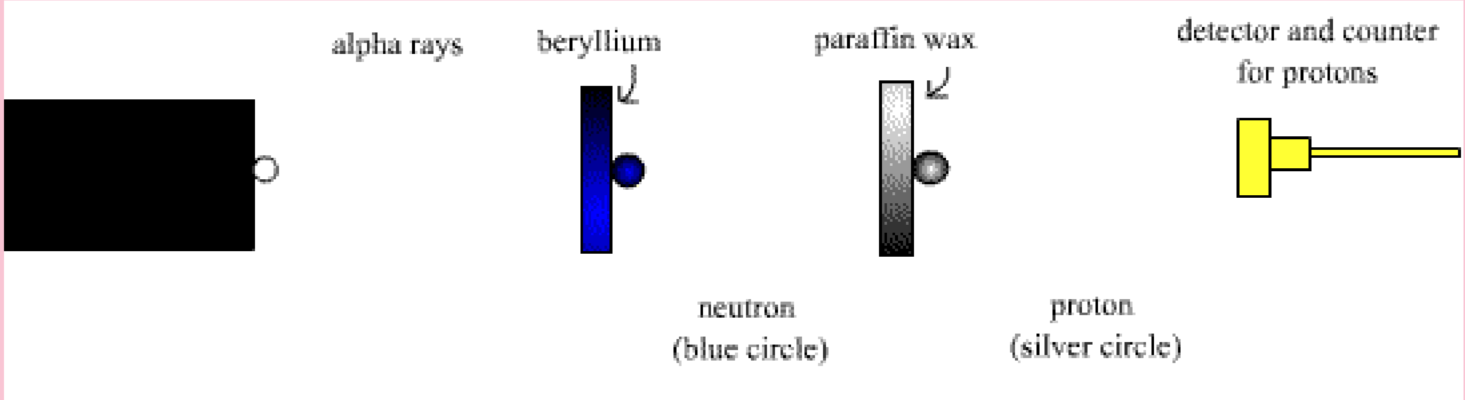


Fig (5.6) Bombardment of Be with α- particles and discovery of neutron



Animation 5.6: chad wicks experiment
Source & Credit : sites.google

5.1.6 Properties of Neutron

1. Free neutron decays into a proton $^{1}_{+}P$ with the emission of an electron $^{0}_{-1}e$ and a neutrino $^{0}_{0}n$.

$$^{1}_{0}n \rightarrow {}^{1}_{+1}P + {}^{0}_{-1}e + {}^{0}_{0}n$$

2. Neutrons cannot ionize gases.
3. Neutrons are highly penetrating particles.
4. They can expel high speed protons from paraffin, water, paper and cellulose.
5. When neutrons travel with an energy 1.2 Mev (Mega electron volt 10^6), they are called fast neutrons but with energy below 1ev are called slow neutrons. Slow neutrons are usually more effective than fast ones for the fission purposes.
6. When neutrons are used as projectiles, they can carry out the nuclear reactions. A fast neutron ejects an a-particle from the nucleus of nitrogen atom and boron is produced, alongwith and a-particles.

$$^{14}_{7}N + {}^{1}_{0}n \rightarrow {}^{11}_{5}B + {}^{4}_{2}He$$

7. When slow moving neutrons hit the Cu metal then γ gamma radiations are emitted. The radioactive $^{66}_{29}Cu$ is converted into $^{66}_{30}Zn$

$$^{65}_{29}Cu + {}^{1}_{0}n \rightarrow {}^{66}_{29}Cu + hv(\gamma - raditions)$$

$$^{66}_{29}Cu \rightarrow {}^{66}_{30}Zn + {}^{0}_{-1}e \text{ (electron)}$$

Actually, neutron is captured by the nucleus of $^{65}_{29}Cu$ and $^{66}_{29}Cu$ is produced. This radio active $^{66}_{29}Cu$ emits an electron (β-particle) and its atomic number increases by one unit. Because of their intense biological effects they are being used in the treatment of cancer.

5.1.7 Measurement of $\frac{e}{m}$ Value of Electron

In 1897, J.J Thomson devised an instrument to measure the e/m value of electron. The apparatus consists of a discharge tube shown in Fig. (5.7).

The cathode rays are allowed to pass through electric and magnetic fields. When both the fields are off then a beam of cathode rays, consisted of electrons, produces bright luminous spot at P_1 on the fluorescent screen.

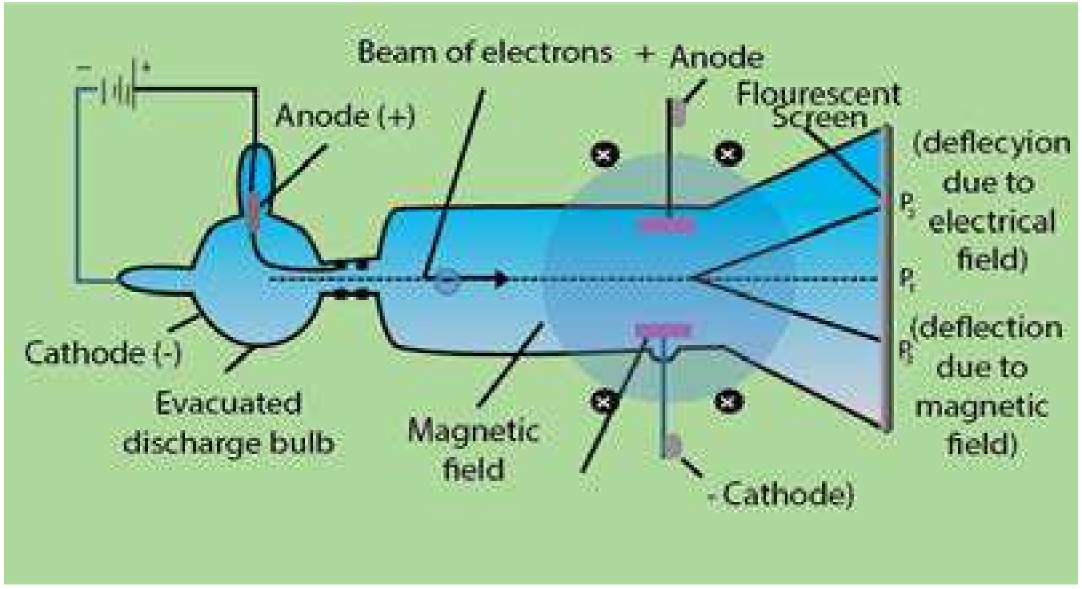


Fig (5.7) Measurement of e/m value of an electron by J.J. Thomson

The north and south poles of magnetic field are perpendicular to the plane of paper in the diagram. The electrical field is in the plane of paper. When only magnetic field is applied, the cathode rays are deflected in a circular path and fall at the point P_3. When only electric field is applied, the cathode rays produce a spot at P_2. Both electric and magnetic fields are then applied simultaneously and their strengths adjusted in such a way that cathode rays again hit the point P_1.

In this way by comparing the strengths of the two fields one can determine the e/m value of ellectrons. It comes out to be 1.7588×10^{11} coulombs kg^{-1}. This means that 1 kg of electrons have 1.7588×10^{11} coulombs of charge.

5.1.8 Measurement of Charge on Electron - Millikan's Oil Drop Method

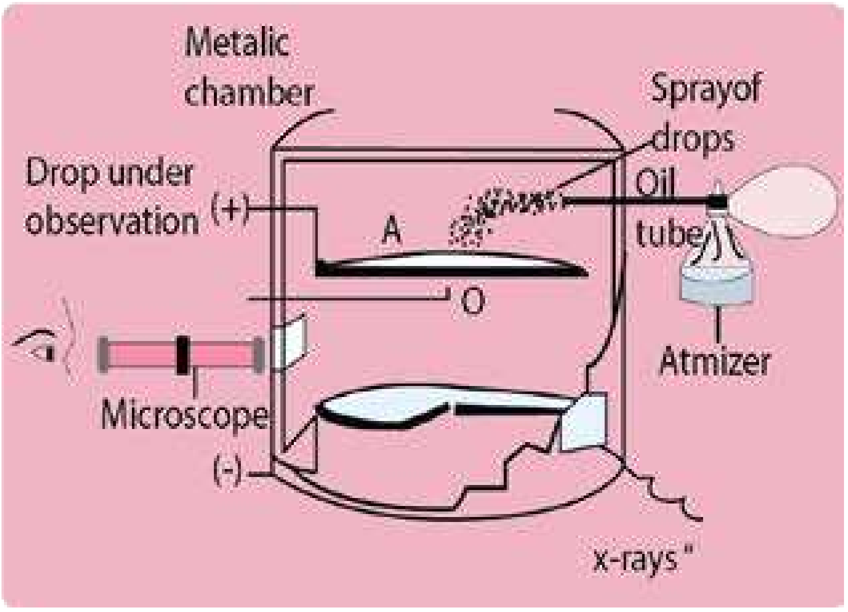


Fig (5.8) Millikan's oil drop method for determination of charge of electron

In 1909, Millikan determined the charge on electron by a simple arrangement. The apparatus consists of a metallic chamber.It has two parts. The chamber is filled with air, the pressure of which can be adjusted by a vacuum pump.

There are two electrodes A and A' These electrodes are used- to generate an electrical field in the space between the electrodes. The upper electrode has a hole in it as shown in Fig (5.8).

A fine spray of oil droplets is created by an atomizer. A few droplets passes through the hole in the top plate and into the region between the charged plates, where one of them is observed though a microscope. This droplet, when illuminated perpendicularly to the direction of view, appears in the microscope as bright speck against a dark background. The droplet falls under the force of gravity without applying the electric field. The velocity of the droplet is determined. The velocity of the droplet (V_1) depends upon its weight, mg.

$$v_1 \alpha \ mg \qquad .... \qquad (1)$$

where 'm' is the mass of the droplet and 'g' is the acceleration due to gravity. After that the air between the electrodes is ionized by X-rays. The droplet under observation takes up an electron and gets charged. Now, connect A and A' to a battery which generates an electric field having a strength, E. The droplet moves upwards against the action of gravity with a velocity (v_2).

$$v_2 \alpha \ Ee - mg \qquad .... \qquad (2)$$

where 'e' is the charge on the electron and Ee is the upward driving force on the droplet due to applied electrical field of strength E.

Dividing equation (1) by (2)

$$\frac{v_1}{v_2} = \frac{mg}{Ee\text{-}mg} \qquad .... \qquad (3)$$

The values of v_1 and v_2 are recorded with the help of microscope. The factors like g and E are also known. Mass of the droplet can be determined by varying the electric field in such a way that the droplet is suspended in the chamber. Hence 'e' can be calculated.

By changing the strength of electrical field, Millikan found that the charge on each droplet was different. The smallest charge which he found was 1.59 x 10^{-19} coulombs, which is very close to the recent value of 1.6022 x 10^{-19} coulombs. This smallest charge on any droplet is the charge of one electron. The other drops having more than one electron on them, have double or triple the amount of this charge. The charge present on an electron is the smallest charge of electricity that has been measured so far.

Mass of Electron

The value of charge on electron is 1.602 x 10^{-19} coulombs, while e/m of electron is 1.7588 x 10^{11} coulombs kg^{-1}. So,

$$\frac{e}{m}=\frac{1.6022\times10^{-19}\text{coulombs}}{\text{Mass of electrons}} = = 1.7588\text{x}10^{11}\text{ coulombs kg}^{-1}$$

$$\text{Mass of electron}=\frac{1.6022\times10^{-19}\text{coulombs}}{1.7588\times10^{11}\text{coulombs kg}^{-1}}$$

Rearranging

$$\text{Mass of electron}= 9.1095\text{x}10^{-31}\text{ kg}$$

Properties of Fundamental Particles

The Table (5.1) shows the properties of three fundamental particles electron, proton and neutron present in an atom.

Table (5.1) Properties of three fundamental particles

Particle	Charge (coul)	Relative charge	Mass (kg)	Mass (amu)
Proton	+1.6022 x 10^{-19}	+1	1.6726 x 10^{-27}	1.0073
Neutron	0	0	1.6750 x 10^{-27}	1.0087
Electron	-1.6022 x 10^{-19}	-1	9.1095 x 10^{-31}	5.4858x10-4

5.2 Rutherford's Model of Atom (Discovery of Nucleus)

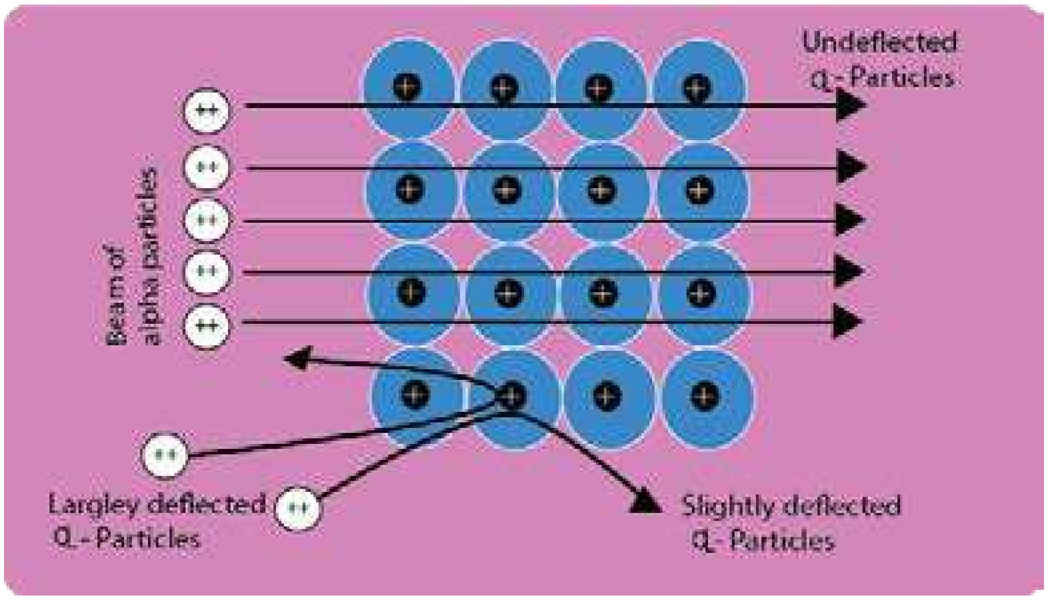


Fig (5.9) Rutherford's experiment for scattering 0f α -partices

In 1911, Lord Rutherford performed a classic experiment. He studied the scattering of high speed α-particles. which were emitted from a radioactive metal (radium or polonium)

A beam of a-partides was directed onto a gold foil of 0.00004 cm thickness as target through a pin-hole in lead plate, Fig (5.9).

A photographic plate or a screen coated with zinc sulphide was used as a detector. Whenever, an a-partide struck the screen, flash of light was produced at that point. It was observed that most of the particles went through the foil undeflected. Some were deflected at fairly large angles and a few were deflected backward. Rutherford proposed that the rebounding particles must have collided with the central heavy portion of the atom which he called as nucleus.

On the basis of these experimental observations, Rutherford proposed the planetary model (similar to the solar system) for an atom in which a tiny nucleus is surrounded by an appropriate number of electrons. Atom as a whole being neutral, therefore, the nucleus must be having the same number of protons as there are number of electrons surrounding it.

In Rutherford's model for the structure of an atom, the outer electrons could not be stationary. If they were, they would gradually be attracted by the nucleus till they ultimately fall into it. Therefore, to have a stable atomic structure, the electrons were supposed to be moving around the nucleus in closed orbits. The nuclear atom of Rutherford was a big step ahead towards understanding the atomic structure, but the behaviour of electrons remained unexplained in the atom.

Rutherford's planet-like picture was Electron defective and unsatisfactory because the moving electron must be accelerated towards the nucleus Fig (5.10).

Therefore, the radius of the orbiting electron should become smaller and smaller and the electron should fall into the nucleus. Thus, an atomic structure as proposed by Rutherford would collapse.

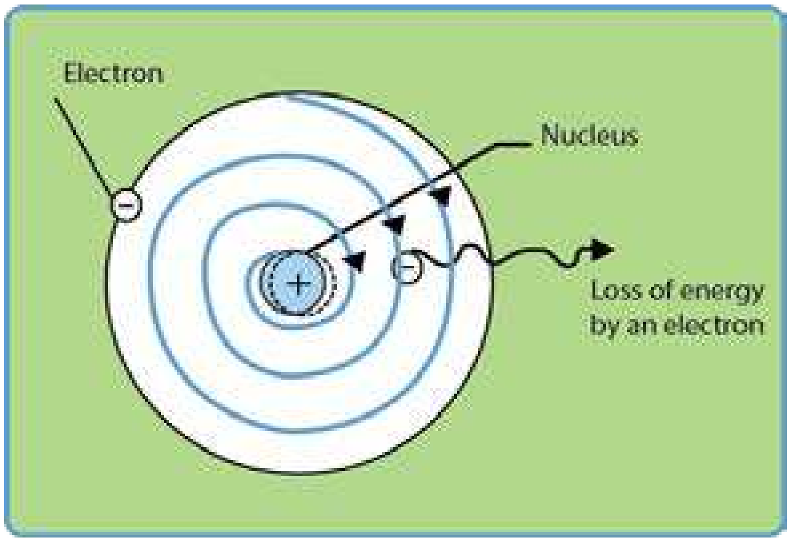


Fig (5.10) Rotation of electron around the nucleus and expected spiral path

5.3 PLANCK'S QUANTUM THEORY

Max Planck proposed the quantum theory in 1900 to explain the emission and absorption of radiation. According to his revolutionary' theory, energy travels in a discontinuous manner and it is composed of large number of tiny discrete units called quanta. The main points of his theory are:

(i) Energy is not emitted or absorbed continuously. Rather, it is emitted or absorbed in a discontinuous manner and in the form of wave packets. Each wave packet or quantum is associated with a definite amount of energy. In case of light, the quantum of energy is often called photon.

(ii) The amount of energy associated with a quantum of radiation is proportional to the frequency (v) of the radiation. Frequency is the number of waves passing through a point per second.

$$E \propto v$$

$$E = hv \qquad \text{.............................} \qquad (4)$$

Where 'h' is a constant known as Planck's constant and its value is 6.626×10^{-34} Js. It is, in fact, the ratio of energy and the frequency of a photon.

(iii) A body can emit or absorb energy only in terms of quanta.

$$E = hv$$

The frequency 'v ' is related to the wavelength of the photon as

$$v=c/\lambda$$

Greater the wavelength, smaller the frequency of photon

So, $E=hc/\lambda$ ....(5)

Wavelength is the distance between the two adjacent crests or troughs and expressed in $\overset{o}{A}$, nm or pm. (1 $\overset{o}{A}$ =10^{-10}'m', lnm = 10^{-9}m, lpm=10^{-12}m)

Greater the wavelength associated with the photon, smaller is its energy. Wave number (v) is the number of waves per unit length, and is reciprocal to wavelength.

$$\bar{v}= 1/\lambda$$

Putting the value of λ in equation (5)

$E = h\,c\,\bar{v}$ ....(6)

So, the energy of a photon is related to frequency, wavelength and wave number. Greater the wave number of photons, greater is the energy associated with them. The relationships of energy, frequency, wavelength, wave number about the photon of light are accepted by scientists and used by Bohr in his atomic model.

5.4 BOHR'S MODEL OF ATOM

Bohr made an extensive use of the quantum theory of Planck and proposed that the electron, in the hydrogen atom, can only exist in certain permitted quantized energy levels. The main postulates of Bohr's theory are:

(i) Electron revolves in one of the circular orbits outside the nucleus. Each orbit has a fixed energy and a quantum number is assigned to it.

(ii) Electron present in a particular orbit neither emits nor absorbs energy while moving in the same fixed orbits. The energy is emitted or absorbed only when an electron jumps from one orbit to another.

(iii) When an electron jumps, the energy change AE is given by the Planck's equation

$$\Delta E = E_2 - E_1 = h\nu \quad .... \quad (7)$$

Where ΔE is the energy difference of any two orbits with energies E_1 and E_2 Energy is absorbed by the electron when it jumps from an inner orbit to an outer orbit and is emitted when the electron jumps from outer to inner orbit. Electron can revolve only in those orbits having a fixed angular momentum (mvr). The angular momentum of an orbit depends upon its quantum number and it is an integral multiple of the factor h/2 π i.e.

$$mvr = \frac{nh}{2\pi} \quad .... \quad (8)$$

Where n = 1,2,3,.............

The permitted values of angular momenta are, therefore, $\frac{h}{2\pi}, \frac{2h}{2\pi}, \frac{3h}{2\pi}$ ....

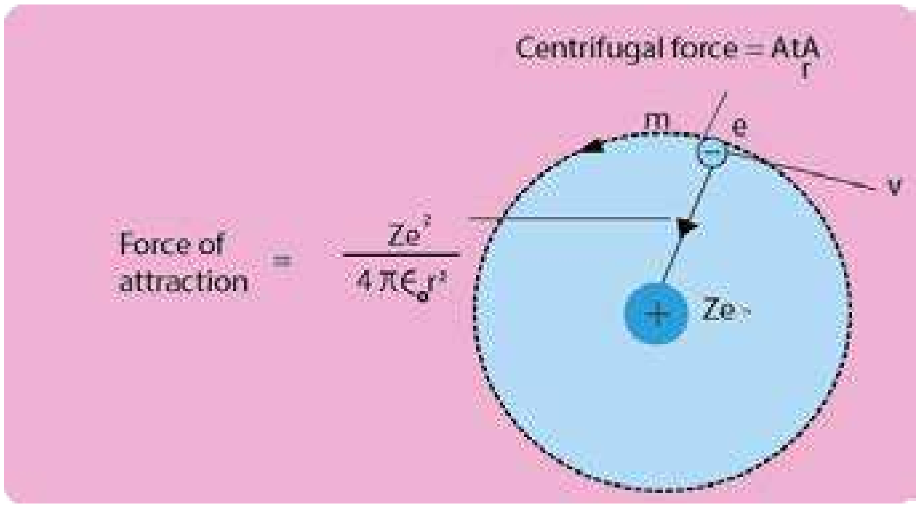
The electron is bound to remain in one of these orbits and not in between them. So, angular momentum is quantized.

Derivation of Radius and Energy of Revolving Electron in nth Orbit.

By applying these ideas, Bohr derived the expression for the radius of the nth orbit in hydrogen atom.

For a general atom, consider an electron of charge 'e' revolving around the nucleus having charge Ze^+. Z being the proton number and e^+ is the charge on the proton Fig (5.11).

Let m be the mass of electron, r the radius of the orbit and v the velocity of the revolving electron. According to Coulombs law, the electrostatic force of attraction between the electron and the nucleus will be given by the f ollowing formula .



Fi'g (5.11) .E, lectr.o n rev. olvingv +m an atom with nuclear charge Ze (If Z=l, then the picture is for H-atom)

$$\frac{Ze^{+}.e^{-}}{4\pi\in_0 r^2}=\frac{Ze^2}{4\pi\in_0 r^2}$$

$\in_0$ is the vacuum permittivity and its value is 8.84 x $10^{-12}C^2J^{-1}m^{-1}$. This force of attraction is balanced by the $\frac{mv^2}{r}$ Therefore, for balanced conditions, we can write

or $$\frac{mv^2}{r}=\frac{Ze^2}{4\pi\in_0 r^2}$$

$$mv^2=\frac{Ze^2}{4\pi\in_0 r} \quad \text{.........................} \quad (9)$$

Rearranging the equation (9)

$$r=\frac{Ze^2}{4\pi\in_0 mv^2} \quad \text{..........................} \quad (10)$$

According to equation (10), the radius of a moving electron is inversely proportional to the square of its velocity. It conveys the idea, that electron should move faster nearer to the nucleus in an orbit of smaller radius. It also tells, that if hydrogen atom has many possible orbits, then the promotion of electron to higher orbits makes it move with less velocity.

The determination of velocity of electron is possible while moving in the orbit. In order to eliminate the factor of velocity from equation (10), we use Bohr's postulate (iv). The angular momentum of the electron is given by.

$$mvr=\frac{nh}{2\pi}$$

Rearranging the equation of angular momentum

$$v=\frac{nh}{2\pi mr}$$

Taking square

$$v^2=\frac{n^2h^2}{4\pi^2m^2r^2} \quad \text{..................} \quad (11)$$

Substituting the value of v^2 from eq. (11) into eq. (10), we get

$$r = \frac{Ze^2 \times 4\pi^2 m^2 r^2}{4\pi\varepsilon_0 m n^2 h^2}$$

Rearranging the above equation, we get

$$r = \frac{\varepsilon_0 n^2 h^2}{\pi m Z e^2} \quad \text{..............................} \quad \mathbf{(12)}$$

For hydrogen atom Z = 1, so the equation for radius of H-atom is

$$r = \frac{\varepsilon_0 n^2 h^2}{\pi m e^2} = (\frac{\varepsilon_0 h^2}{\pi m e^2}) n^2 \quad \text{............................} \quad \mathbf{(13)}$$

According to the equation (13), the radius of hydrogen atom is directly proportional to the square of number of orbit (n). So, higher orbits have more radii and vice versa. The collection of parameters $(\frac{\varepsilon_0 h^2}{\pi m e^2})$ in equation (13) is a constant factor.

When we put the value of $\in_0$, h^2 π, m and e^2 alongwith the units then the calculations show that it is equal to 0.529 x I0^{-10} m or 0.529 Å.(10^{-10} m = I Å)

Hence r=0.529 Å (n^2) .... (14)

By putting the values of na s 1,2.3,4............ the radii of orbits of hydrogen atom are

n=1	r_1=0.529 Å	n=4	r_4=8.4 Å
n=2	r_2=2.11 Å	n=5	r_5=13.22 Å
3 n=	r $_3$=4.75 Å		

The comparison of radii shows that the distance between orbits of H-atom goes on increasing as we move from 1st orbit to higher orbits. The orbits are not equally spaced.

$$r_2 - r_1 < r_3 - r_2 < r_4 - r_3 < \text{.........................}$$

The second orbit is four times away from the nucleus than first orbit, third orbit is nine times away and similarly fourth orbit is sixteen times away.

Energy of Revolving Electron

The total energy of an electron in an orbit is composed of two parts, the kinetic energy which is equal to $\frac{1}{2}mv^2$ and the potential energy. The value of potential energy can be calculated as follows.

The electrostatic force of attraction between the nucleus and the electron is given by $\frac{Ze^2}{4\pi\varepsilon_0 r^2}$. If the electron moves through a small distance dr, then the work done for moving electron is given by

$$\frac{Ze^2}{4\pi\varepsilon_0 r^2}dr \qquad \text{because work=(force x distance)}$$

In order to calculate the potential energy of the electron at a distance r from the nucleus, we calculate the total work done for bringing the electron from infinity to a point at a distance r from the nucleus. This can be obtained by integrating the above expression between the limits of infinity and r.

$$\int_{\infty}^{r}\frac{Ze^2dr}{4\pi\in_0 r^2}=\frac{Ze^2}{4\pi\in_0}\int_{\infty}^{r}\frac{dr}{r^2}=\frac{Ze^2}{4\pi\in_0}\left[\frac{-1}{r}\right]_{\infty}^{r}=\frac{Ze^2}{4\pi\in_0}\left[\frac{-1}{r}\right]=-\frac{Ze^2}{4\pi\in_0 r}$$

The work done is the potential energy of electron, so

$$\text{Work done} = \quad E_{\text{potential}}=-\frac{Ze^2}{4\pi\varepsilon_0 r} \qquad \text{..............................} \qquad (15)$$

The minus sign indicates that the potential energy of electron decreases, when it is brought from infinity to a point at a distance 'r' from the nucleus. At infinity, the electron is not being attracted by any thing and the potential energy of the system is zero. Whereas at a point nearer the nucleus, it will be attracted by the nucleus and the potential energy becomes less than zero. The quantity less than zero is negative. For this reason, the potential energy given by equation (15) is negative.

The total energy (E) of the electron, is the sum of kinetic and potential charges.

So, $E = E_{kinetic} + E_{potential}$

$$= \frac{1}{2}mv^2 - \frac{Ze^2}{4\pi\varepsilon_o r} \qquad \text{..............................} \qquad (16)$$

Now, we want to eliminate the factor of velocity from equation (16). So, from equation (9), substitute the value of mv² in eq. (16)

Since $mv^2 = \frac{Ze^2}{4\pi \in_0 r}$ .... (9)

$$E = \frac{Ze^2}{8\pi \in_0 r} - \frac{Ze^2}{4\pi \in_0 r}$$

Simplifying it, $E = -\frac{Ze^2}{8\pi \in_0 r}$ .... (17)

Now substitute the value of r from eq (12) into eq (17) we get

Since $\frac{\in\ n^2h^2}{mZe}$ .... (12)

$$E_n = \frac{-mZ^2e^4}{8\in_0^2 n^2h^2} \qquad \text{..............................} \qquad (18)$$

Where E_n is the energy of nth orbit.

For hydrogen atom , the number of protons in nucleus is one, so (Z = 1).

$$E_n = -\frac{me^4}{8\in_0^2 h^2}\left[\frac{1}{n^2}\right] \qquad \text{................................} \qquad (19)$$

Eq.(19) gives the energy of electron revolving around the nucleus of hydrogen atom.

The factors outside the brackets in equation (19) are all constants. When the values of these constants are substituted along with their units, then it comes out to be 2.178 x 10 $^{-18}$ J. The equation (19) can be written as,

$$E_n = -2.178\text{x}10^{-18}\left[\frac{1}{n^2}\right]\text{J} \qquad \text{............................} \qquad (20)$$

This equation (20) gives the energy associated with electron in the nth orbit of hydrogen atom. Its negative value shows that electron is bound by the nucleus i.e. electron is under the force of attraction of the nucleus. Actually, the electron has been brought from infinity to distance r from the nucleus.

The value of energy obtained for the electron is in joules/atom. If, this quantity is multiplied by Avogadro's number and divided by 1000, the value of E_n will become

$$E_n = \frac{6.02\times10^{23}\times2.18\times10^{-18}}{1000}\left[\frac{1}{n^2}\right]\text{kJmol}^{-1}$$

$$E_n = -\frac{1313.315}{n^2}\text{kJmol}^{-1} \qquad \text{...................................} \qquad (21)$$

This energy is associated with 1.008g of H-atoms i.e. with Avogadro's number of atoms of hydrogen.

Substituting, the values of n as 1,2,3,4,5, etc. in equation (21), we get the energy associated with an electron revolving in 1st, 2nd, 3rd, 4th and 5th orbits of H-atom.

$$E_1 = -\frac{1313.31}{1^2} = -1313.31\ \text{kJmol}^{-1}$$

$$E_2 = -\frac{1313.31}{2^2} = -328.32\ \text{kJmol}^{-1}$$

$$E_3 = -\frac{1313.31}{3^2} = -145.92\ \text{kJmol}^{-1}$$

$$E \;= -\frac{1313.31}{} = -82.08 \text{ kJmol}^{-1}$$

$$E_5 = -\frac{1313.31}{5^2} = -52.53 \text{ kJmol}^{-1}$$

$$E_\infty = -\frac{1313.31}{\infty^2} = 0 \text{ kJmol}^{-1}$$ (electron is free from the nucleus)

The values of energy differences between adjacent orbits can be calculated as follows

E_2-E_1 = (-328.32)-(-1313.31) = 984.99 kJmol^{-1}

E_3-E_2 = (-145.92)-(-328.32) = 182.40 kJmol^{-1}

E_4-E_3 = (-82.08)-(-145.92) = 63.84 kJmol^{-1}

The differences in the values of energy go on decreasing from lower to higher orbits.

$E_2-E_1 > E_3-E_2 > E_4-E_3 >$.........................

The energy difference between first and infinite levels of energy is calculated as:

E„ - E_1 = 0 - (-1313.31) = 1313.31 kJmol^{-1}

1313.31 kJmol^{-1} is the ionization energy of hydrogen. This value is the same as determined experimentally. These values show that the energy differences between adjacent orbits of Bohr's model of hydrogen atom go on decreasing sharply.

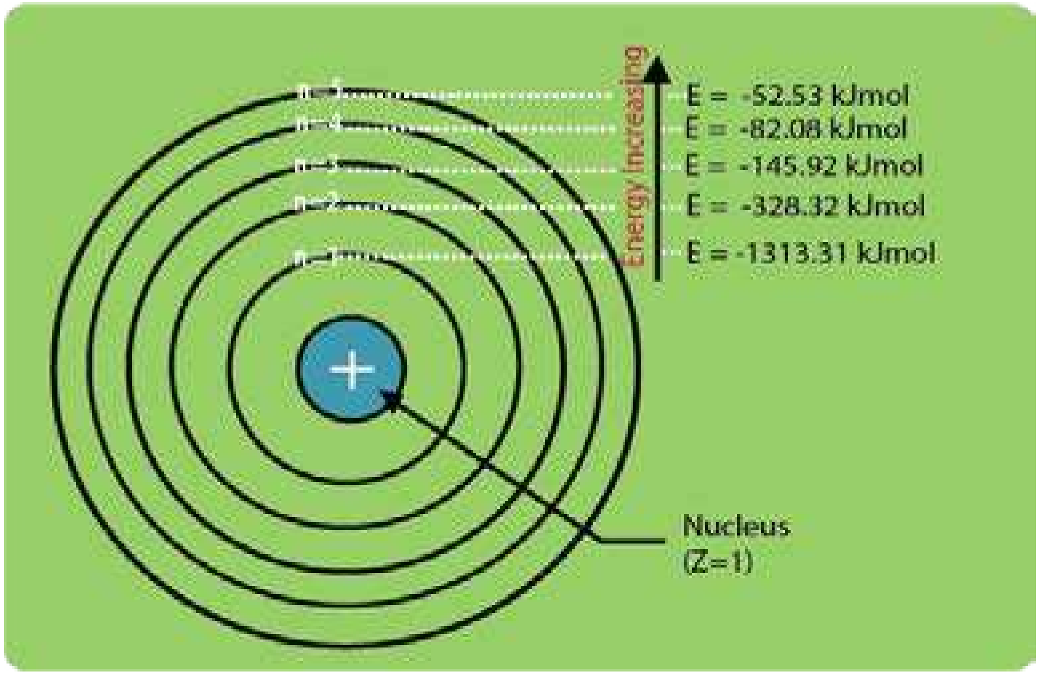


Fig (5.12) Energy values associated with an electron in vanous orbits in hydrogen atom

Keep in mind, that distances between adjacent orbits increase. The Fig (5.12) makes the idea clear.

5.5 SPECTRUM

When a radiation of light is passed through a prism, the radiation undergoes refraction or bending. The extent of bending depends upon the wavelength of the photons. A radiation of longer wavelength is bent to a smaller degree than the radiation of a shorter wavelength. Ordinary, white light consists of radiation of all wavelengths, and so after passing through the prism, white light is splitted up into radiations of different wavelengths.

The colours of visible spectrum are violet, indigo, blue, green, orange, yellow and red and their wavelengths range from 400 nm to 750 nm. In addition to the visible region of the spectrum, there are seven other regions. Ultraviolet, X-rays, y-rays and cosmic rays are towards the lower wavelength end of the spectrum and they possess the photons with greater energies. On the other side of the visible region, there lies infrared, microwave and radio frequency regions. Fig. (5.13) shows the continuity of wavelengths for all types of regions of spectrum. Hence, a visual display or dispersion of the components of white light, when it is passed through a prism is called a spectrum.

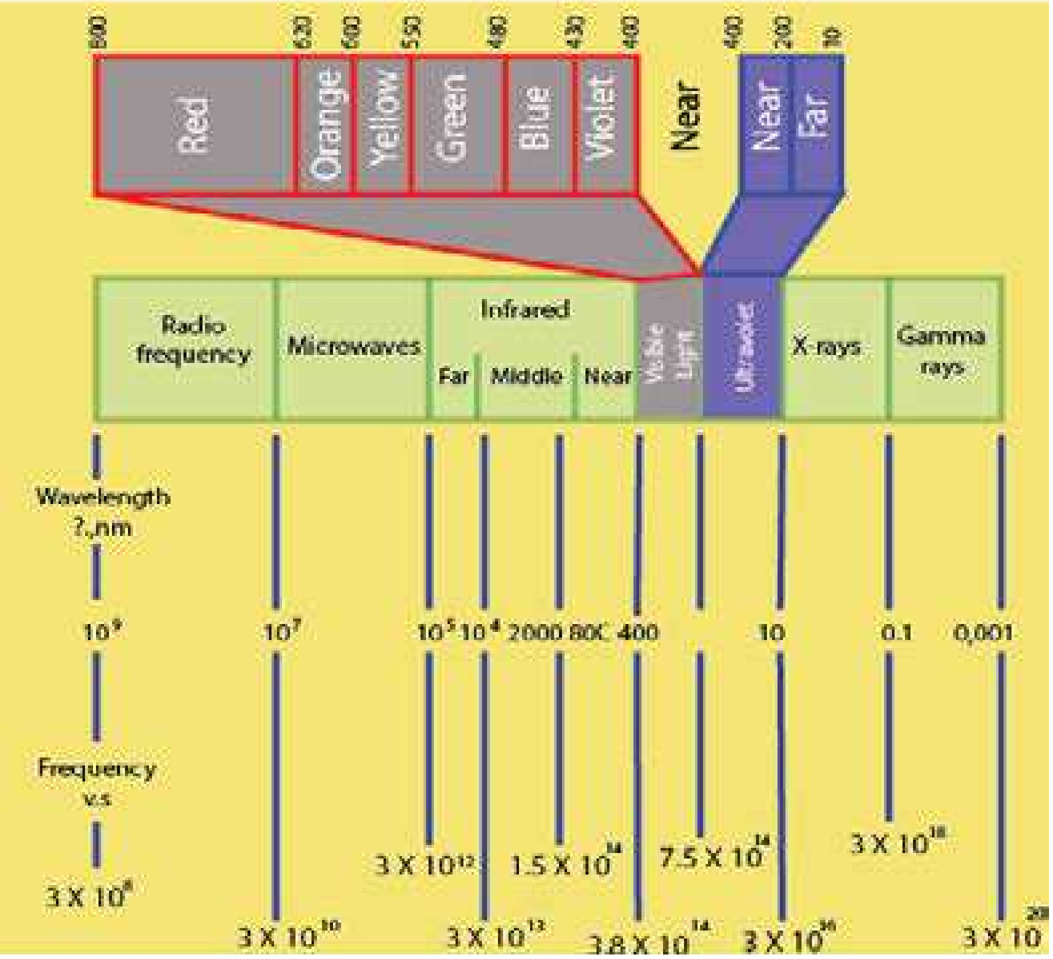


Fig (5.13) The visible and other regions of spectrum

Spectrum is of two types.

(i) Continuous spectrum (ii) Line spectrum

5.5.1 Continuous Spectrum

In this type of spectrum, the boundry line between the colours cannot be marked. The colours diffuse into each other. One colour merges into another without any dark space. The best example of continuous spectrum is rainbow. It is obtained from the light emitted by the sun or incandescent (electric light) solids. It is the characteristic of matter in bulk.

5.5.2 Atomic or Line Spectrum

When an element or its compound is volatilized on a flame and the light emitted is seen through a spectrometer, We see distinct lines separated by dark spaces. This type of spectrum is called line spectrum or atomic spectrum. This is characteristic of an atom. The number of lines and the distance between them depend upon the element volatilized. For example, line spectrum of sodium contains two yellow coloured lines separated by a definite distance. Similarly, the spectrum of hydrogen consists of a number of lines of different colours having different distances from each other. It has also been observed that distances between the lines for the hydrogen spectrum decrease with the decrease in wavelength and the spectrum becomes continuous after a certain value of wavelength Fig (5.14).

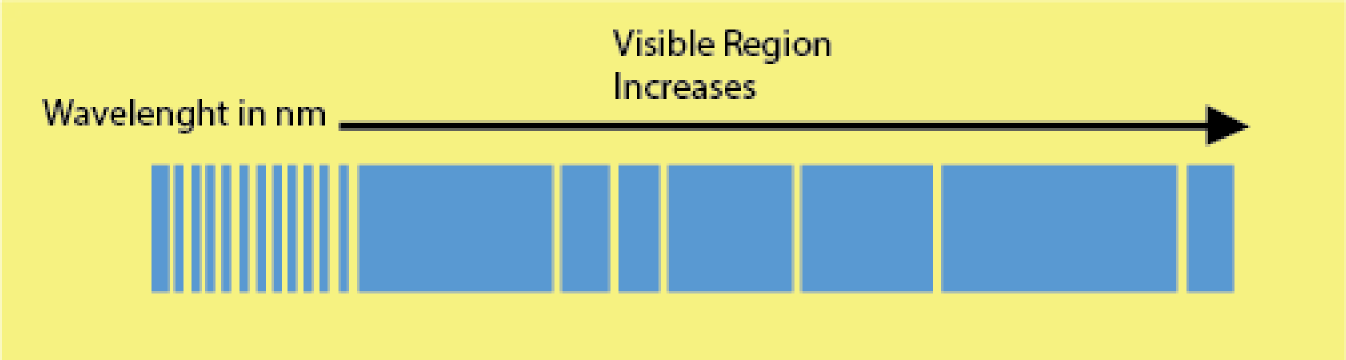


Fig (5.14) Atomic spectrum of hydrogen

Atomic spectrum can also be observed when elements in gaseous state are heated at high temperature or subjected to an electric discharge.

There are two ways in which an atomic spectrum can be viewed.

(i) Atomic emission spectrum
(ii) Atomic absorption spectrum

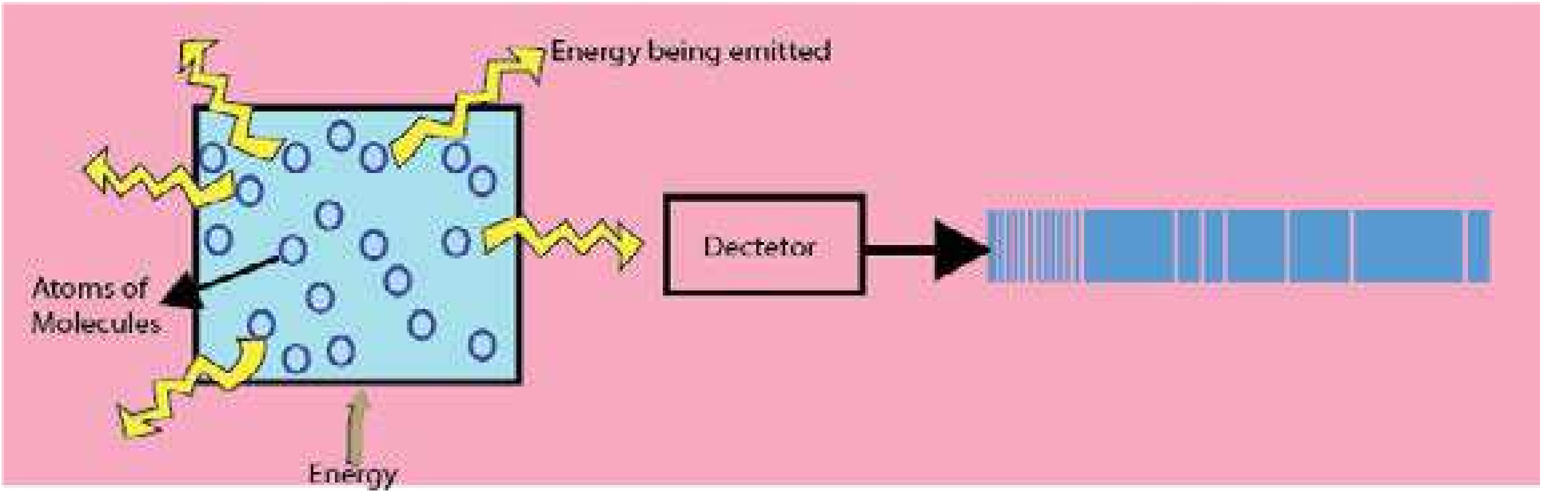


Fig (5.15) Atomic emission spectrum

5.5.3 Atomic Emission Spectrum

When solids are volatilized or elements in their gaseous states are heated to high temperature or subjected to an electrical discharge, radiation of certain wavelengths are emitted. The spectrum of this radiation contained bright lines against a dark background. This is called atomic emission spectrum. Fig (5.15)

5.5.4 Atomic Absorption Spectrum

When a beam of white light is passed through a gaseous sample of an element, the element absorbs certain wavelengths while the rest of wavelengths pass through it. The spectrum of this radiation is called an atomic absorption spectrum. The wavelengths of the radiation that have been absorbed by the element appear as dark lines and the background is bright, Fig (5.16).

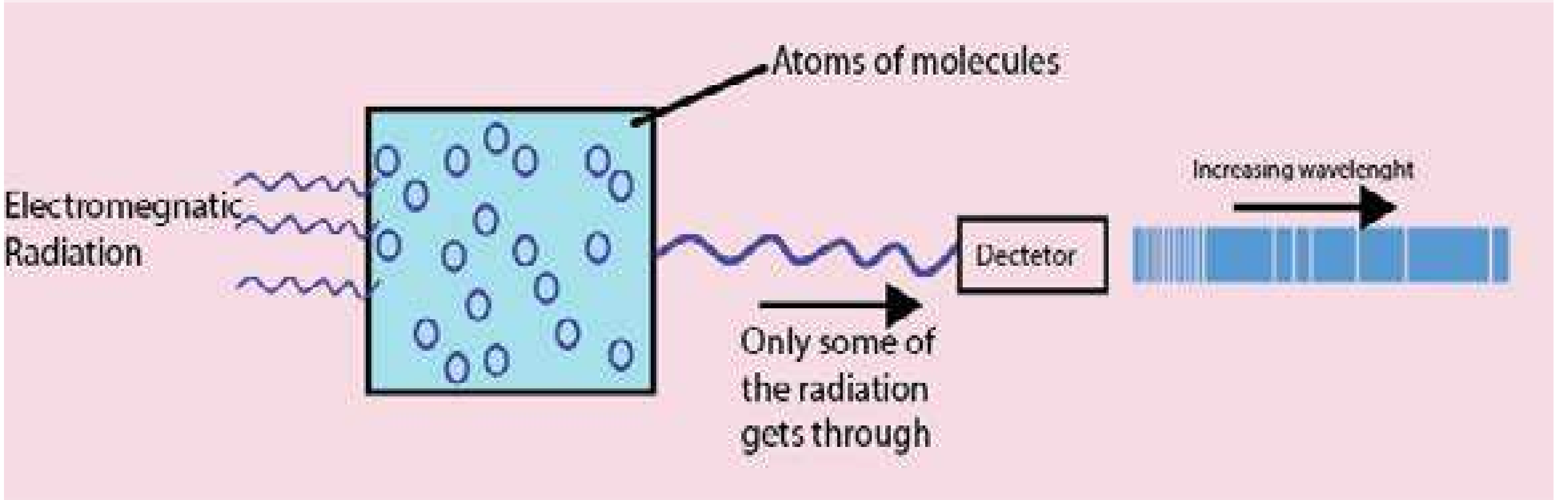


Fig (5.16) Atomic absorption spectrum

It is interesting to note that the positions or the wavelengths of lines appearing in both emission and absorption spectra are exactly the same. In emission spectrum, these lines appear bright because the corresponding wavelengths are being emitted by the element, whereas they appear dark in absorption spectrum because the wavelengths are being absorbed by the element.

5.5.5 Hydrogen Spectrum

Hydrogen-spectrum is an important example of atomic spectrum. Hydrogen is filled in a discharge tube at a very low pressure a bluish light is emitted from the discharge tube. This light when viewed through a spectrometer shows several isolated sharp lines.

These are called spectral lines. The wavelengths of these lines lie in the visible, ultraviolet and infrared regions. These spectral lines can be classified into five groups called spectral series. These series are named after their discoverers as shown below.

(i) Lyman series (U.V region)
(ii) Balmer series (visible region)
(iii) Paschen series (LR region)
(iv) Brackett series (I.R region)
(v) Pfund series (I.R region)

The first four series were discovered before Bohr's atomic model (1913). The wave numbers (m^{-1}) of the series of lines in hydrogen spectrum are given in Table (5.2).

It is seen from the Table (5.2) that as we proceed from Lyman series to Pfund series, the wave numbers (m^{-1}) of spectral lines decrease. The lines of Balmer series have been given specific names as H_{α}, H_{β}........, etc.

Table (5.2)Wave numbers (m^{-1}) of various series of hydrogen spectrum.

Lyman series (U.V. region)	Balmer series (Visible region)	Paschen series (I.R. region)	Brackett series (I.R. region)	Pfund series (I.R. region)
82.20×10^{5}	15.21×10^{5} ($H_{\acute{a}}$line)	5.30×10^{5}	2.46×10^{5}	1.34×10^{5}
97.20×10^{5}	20.60×10^{5} ($H_{\hat{a}}$line)	7.80×10^{5}	3.80×10^{5}	2.14×10^{5}
102.20×10^{5}	23.5×10^{5} ($H_{\tilde{a}}$line)	9.12×10^{5}	4.61×10^{5}	
105.20×10^{5}	24.35×10^{5} ($H_{\ddot{a}}$line)	9.95×10^{5}		
106.20×10^{5}	25.18×10^{5}			
107.20×10^{5}				

5.5.6 Origin of Hydrogen Spectrum on the Basis of Bohr's Model

According to Bohr, electron in hydrogen atom may revolve in any orbit depending upon its energy. When hydrogen gas is heated or subjected to an electric discharge, its electron moves from one of the lower orbit to higher orbit, absorbing particular wavelength of energy. Subsequently, when it comes back, the same energy is released. This energy is observed as radiation of particular wavelengths in the form of bright lines seen in the certain region of the emission spectrum of hydrogen gas.

The spectral lines of Lyman series are produced when the electron jumps from n_2= 2, 3,4,5, to, n, = 1 (Lyman did not know this reason). Similarly, spectral lines of Balmer series discovered in 1887 originated when an electron jumps from n_2 = 3, 4, 5, 6,................ to n_1= 2orbit.

In the same way, Paschen, Brackett and Pfund series of lines are produced as a result of electronic transitions from higher orbits to 3rd, 4th and 5th orbits, respectively Fig (5.17).

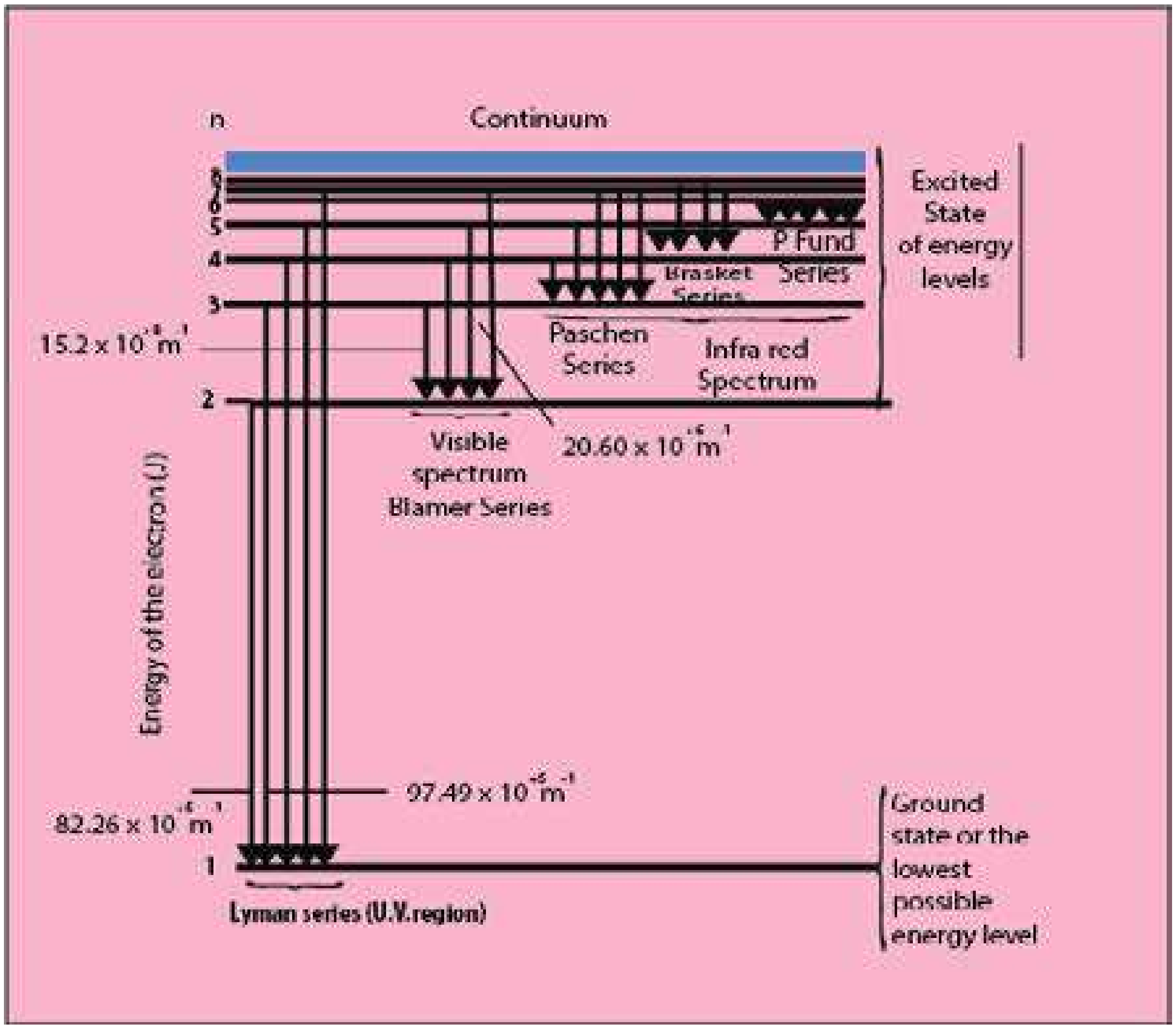


Fig (5.17) Electronic transitions in hydrogen atom and series of spectral lines, justified by Bohr's model atom

Calculations of Wave Numbers of Photons of Various Spectral Series by Bohr's Theory

The wavelength (λ) or wave number ($\overline{v}$) of a spectral line depends on the quantity of energy emitted by the electron. Suppose, an electron jumps from n_2 to n, and emits a photon of light. According to Bohr's equation of energy

$$E_1 = \frac{-Z^2me^4}{8\in_0^2 n^2{}_1 h^2}$$

$$E_2 = \frac{-Z^2me^4}{8\in_0^2 n^2{}_2 h^2}$$

E_1 and E_2 are the energies of electrons in n_1 and n_2 respectively. The energy difference between the two can be calculated as follows: $\Delta E = E_2 - E_1 = \frac{Z^2me^4}{8\in_0^2 h^2}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$Joules .... (22)

For H-atom; Z - 1

and $\frac{me^4}{8\in_0^2 h^2} = 2.18 \text{ x } 10^{-18}\text{J}$ (by putting the values of constants)

$$\text{Ä}E = 2.18\text{x}10^{-18}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]\text{Joules} \quad \text{.....................................} \quad (23)$$

With the help of equation (23), the energy difference between any two orbits of Hatom can be calculated where n_t is the lower level and n_2 is higher level. It is not necessary that n_1 and n_2 are adjacent orbits.

Since $\text{Ä}E = hv$

Therefore $hv = \frac{me^4}{8\in_0^2 h^2}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$

$$v = \frac{me^4}{8\in_0^2 h^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]\text{Hz} \quad \text{...............................} \quad (24)$$

Frequency (v) has the units of the cycles s^{-1} or Hz. (1 Hz = 1 cycle s^{-1})

Equation (24) gives us the frequency of a photon emitted, when electron jumps from higher orbit to lower orbit in H-atom. The frequency values go on decreasing between adjacent levels.

Calculation of Wave Number

Since $v = c\bar{v}$

Putting in equation (24)

Therefore $$c\bar{v} = \frac{Z^2me^4}{8\in_0^2 h^3}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]$$

$$\bar{v} = \frac{Z^2me^4}{8\in_0^2 h^3c}\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]m^{-1} \quad \text{..............................} \quad (25)$$

The value of the factor $\frac{me^4}{8\in_0^2 h^3c}$ in eq. (25) has been calculated to be 1.09678 x 10^7m^{-1}

This is called Rydberg constant. Putting Z = 1 for hydrogen atom, the equation (25)becomes.

$$\bar{v} = 1.09678\times10^7\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]m^{-1} \quad \text{..........................} \quad (26)$$

Equation (26) gives the values of wave number of photons emitted or absorbed when the electron jumps between n_1 and n_2 orbits.

Let us calculate, the wave numbers of lines of various series.

Lyman Series: Fig. (5.17)

Fitrst line n_1 = 1(lower orbit), n_2 = 2 (higher orbit)

$$\bar{v} = 1.09678 \times 10^7 \left[\frac{1}{1^2} - \frac{1}{2^2}\right] = 82.26x10^5 m^{-1}$$

Second line n_1 = 1 n_2 = 3

$$\bar{v} = 1.09678 \times 10^7 \left[\frac{1}{1^2} - \frac{1}{3^2}\right] = 97.49x10^5 m^{-1}$$

Limiting line n_1 = 1 n_2 = ∞

$$\bar{v} = 1.09678 \times 10^7 \left[\frac{1}{1^2} - \frac{1}{\infty^2}\right] = 109.678x10^5 m^{-1}$$

Limiting line is developed, when electron jumps from infinte orbit to, n = 1

The values of all these wave numbers lie in the U.Y region of the spectrum. It means that when electron of H-atom falls from all the possible higher levels to n = 1, then the photons of radiation emitted lie in the range of U.V region.

Balmer Series: Fig (5.17)

Fitrst line n_1 = 2, n_2 = 3

$$\bar{v} = 1.09678 \times 10^7 \left[\frac{1}{2^2} - \frac{1}{3^2}\right] = 15.234x10^5 m^{-1}$$

Second line $n_1 = 2$ $n_2 = 4$

$$\bar{v} = 1.09678 \times 10^7 \left[\frac{1}{2^2} - \frac{1}{4^2}\right] = 20.566\text{x}10^5\text{m}^{-1}$$

Third line $n_1 = 2$ $n_2 = 5$

$$\bar{v} = 1.09678 \times 10^7 \left[\frac{1}{2^2} - \frac{1}{5^2}\right] = 23.00\text{x}10^5\text{m}^{-1}$$

Limiting line $n_1 = 2$ $n_2 = \infty$

$$\bar{v} = 1.09678 \times 10^7 \left[\frac{1}{2^2} - \frac{1}{\infty^2}\right] = 27.421\text{x}10^5\text{m}^{-1}$$

The limiting line of Balmer series lies in U.V region, while other lines fall in visible region. Similarly, we can calculate the wave numbers for all the lines of Paschen, Brackett and Pfund series. These three series of lines lie in the infrared region.

5.5.7 Defects of Bohr's Atomic Model

1. Bohr's theory can successfully explain the origin of the spectrum of H-atom and ions like He^{+1}, Li^{+2} and Be^{+3}, etc. These are all one electron systems. But this theory is not able to explain the origin of the spectrum of multi-electrons or poly-electrons system like He, Li and Be, etc.

2. When the spectrum of hydrogen gas is observed by means of a high resolving power spectrometer, the individual spectral lines are replaced by several very fine lines, i.e. original lines are seen divided into other lines. The H_α- line in the Balmer series is found to consist of five -component lines. This is called fine structure or multiple structure. Actually, the appearance of several lines in a single line suggests that only one quantum number is not sufficient to explain the origin of various spectral lines.

3. Bohr suggested circular orbits of electrons around the nucleus of hydrogen atom, but researches have shown that the motion of electron is not in a single plane, but takes place in three dimensional space. Actually, the atomic model is not flat.

4. When the excited atoms of hydrogen (which give an emission line spectrum) are placed in a magnetic field, its spectral lines are further split up into closely spaced lines. This type of splitting of spectral lines is called Zeeman effect. So, if the source which is producing the Na - spectrum is placed in a weak magnetic field, it causes the splitting of two lines of Na into component lines. Similarly, when the excited hydrogen atoms are placed in an electrical field, then similar splitting of spectral lines takes place which is called “Stark effect”. Bohr’s theory does not explain either Zeeman or Stark effect.

However, in 1915, Sommorfeld suggested the moving electrons might describe in addition to the circular orbits elliptic orbits as well wherein the nucleus lies at one of the focii of the ellipse.

5.6 X-RAYS AND ATOMIC NUMBER

X-rays are produced when rapidly moving electrons collide with heavy metal anode in the discharge tube. Energy is released in the form of electromagnetic waves when the electrons are suddenly stopped. In the discharge tube, the electrons produced by a heated tungsten filament are accelerated by high voltage Fig. (5.18). It gives them sufficient energy to bring about the emission of X-rays on striking the metal target. X-rays are emitted from the target in all directions, but only a small portion of them is used for useful purposes through the windows. The wavelength of X-rays produced depends upon the nature of the target metal. Every metal has its own characteristic X-rays.

The X-rays are passed through a slit in platinum plate and then emerged through aluminum window. This is thrown on a crystal of $K_4[Fe(CN)_6]$, which analyses the X-ray beam. The rays are diffracted from the crystal and are obtained in the form of line spectrum of X-rays. This is allowed to fall on photographic plate. This line spectrum is the characteristic of target material used. This characteristic X-rays spectrum has discrete spectral lines. These are grouped into K-series, L-series and M-series, etc. Each series has various line as K_α, K_β, L_α, L_β, M_α, M_β etc.

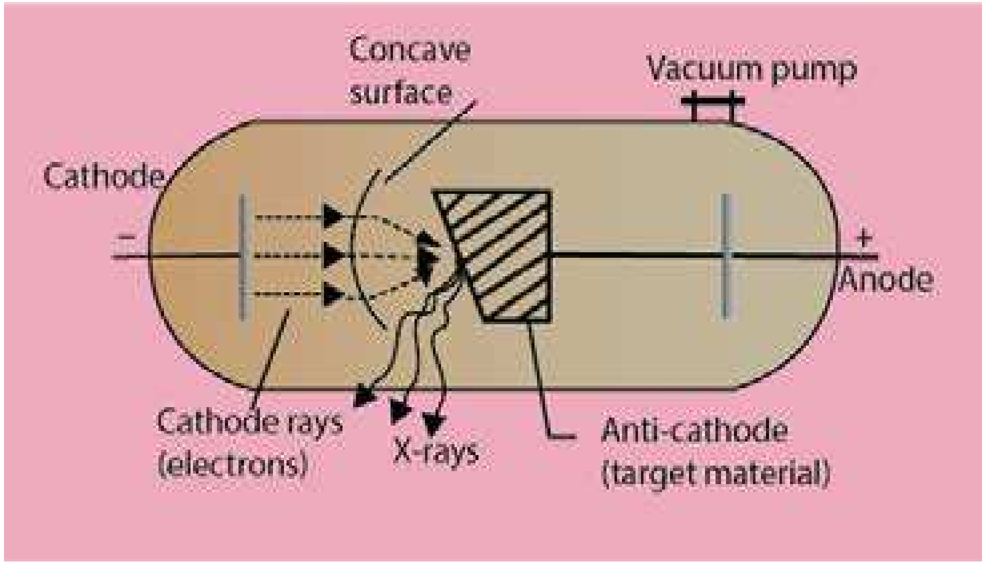


Fig (5.18) Production of X-rays

A systematic and comprehensive study of X-rays was undertaken by Moseley in 1913-1914. His researches covered a range of wavelengths 0.04 - 8 A. He employed thirty eight different elements from aluminium to gold, as target in X-rays tube. Moseley was able to draw the following important conclusions from a detailed analysis of the spectral lines which he obtained.

(i) The spectral lines could be classified into two distinct groups. One of shorter wavelengths are identified by K-series and the other of comparatively longer wavelengths are identified by L-series.

(ii) If the target element is of higher atomic number the wavelength of X-rays becomes shorter.

(iii) A very simple relationship was found between the frequency (v) of a particular line of X-rays and the atomic number Z of the element emitting it.

$$\sqrt{v} = a(Z-b) \qquad \text{..................} \qquad (27)$$

Here 'a' and 'b' are the constants characteristic of the metal under consideration. This linear equation (27) is known as Moseley's Law. 'a" is proportionality constant and 'b' is called screening constant of the metals.

This law states that the frequency of a spectral line in X-ray spectrum varies as the square of atomic number of an element emitting it. This law convinces us that it is the atomic number and not the atomic mass of the element which determines its characteristic properties, both physical and chemical. If value of $\sqrt{v}$ for K-series are plotted against Z, then a straight line is obtained.

Importance of Moseley Law

(i) Moseley arranged K and Ar, Ni and Co in a proper way in Mendeleev's periodic table.
(ii) This law has led to the discovery of many new elements like Tc(43), Pr(59), Rh(45).
(iii) The atomic number of rare earths have been determined by this law.

5.7 WAVE-PARTICLE NATURE OF MATTER (DUAL NATURE OF MATTER)

Planck's quantum theory of radiation tells us that light shows a dual character. It behaves both as a material particle and as a wave. This idea was extended to matter particles in 1924 by Louis de- Broglie. According to de-Broglie, all matter particles in motion have a dual character. It means that electrons, protons, neutrons, atoms and molecules possess the characteristics of both the material particle and a wave.

This is called wave-particle duality in matter. de-Broglie derived a mathematical equation which relates the wavelength (λ) of the electron to the momentum of electron.

$$\lambda=\frac{h}{mv} \quad \text{........................} \qquad (28)$$

Here λ = de-Broglie's wavelength,
m = mass of the particle
v = velocity of electron

According to this equation, the wavelength associated with an electron is inversely proportional to its momentum (mv).

This equation is derived as follows.

According to Planck's equation

$$E = h\nu \qquad \text{........................}$$

According to Einstein's mass energy relationship

$$E = mc^2 \qquad \text{........................} \qquad (29)$$

Where 'm' is the mass of the material particle which has to convert itself into a photon; 'and c' is the velocity of photon. Equating two values of energy;

$$h\nu = mc^2$$

Since

$$\nu = \frac{c}{\lambda}$$

So, $\frac{hc}{\lambda} = mc^2$ or $\lambda = \frac{h}{mc}$ .... (30)

According to equation (30), the wavelength of photon is inversely proportional to the momentum of photon. Considering that nature is symmetrical, we apply this equation (30) to the moving electron of mass'm' and velocity V. This idea gives us the de-Broglie's equation (28)

$$\lambda = \frac{h}{mv} \qquad \text{........................} \qquad (28)$$

According to equation (28), the wavelength of electron is inversely proportional to momentum of electron. Now, consider an electron which is moving with a velocity of 2.188×10^6 ms^{-1} in the first orbit of Bohr's model of hydrogen atom. Then, wavelength associating with it, can be calculated with the help of equation(28)

$h = 6.626 \times 10^{-34}$ Js

$m_e = 9.108 \times 10^{-31}$ kg

$$\lambda = \frac{6.626 \times 10^{-34}\,\text{Js}}{9.108 \times 10^{-31}\,\text{kg} \times 2.188 \times 10^{6}\,\text{ms}^{-1}} \qquad \text{Since } (J = \text{kg m}^2\ \text{s}^{-2})$$

$\lambda = 0.33 \times 10^{-9}$m ($10^{-9}$m=1mm)

$\lambda = 0.33$ nm

This value of wavelength (λ)of electron while moving in the first orbit of H-atom is comparable to the wavelength of X-rays and can be measured.

If we imagine a proton moving in a straight line with the same velocity as mentioned for electron, it's wavelength will be 1836 times smaller than that of electron. Similarly, an α-particle moving with the same velocity should have a wavelength 7344 times smaller as compared to that of ejectron. Now, consider a stone of mass one gram moving with a velocity of 10 ms^{-1}, then its wavelength will be:

$$\lambda = \frac{6.626 \times 10^{-34}\,Js}{10^{-3}\,kg \times 10ms^{-1}}$$

$$= 6.626x10^{-30}\,m$$

This wavelength is so small, that it cannot be measured by any conceivable method. It means that heavy material particles have waves associated with them, but they cannot be captured and we say that the macroscopic bodies don't have the waves.

5.7.1 Experimental Verification of Dual Nature of Matter

In 1927, two American scientists, Davisson and Germer did an experiment to verify the wave nature of moving electron. Electrons were produced from heated tungsten filament and accelerated by applying the potential difference through charged plates. Davisson and Germer proved that the accelerated electrons undergo diffraction, like waves, when they fall on a nickel crystal. In this way, the wave nature of electron got verified. Davisson ahd Germer got the nobel prize for inventing an apparatus to prove the matter waves and de Broglie got the separate nobel prize for giving the equation of matter wave.

5.8 HEISENBERG'S UNCERTAINTY PRINCIPLE

According to Bohr's theory, an electron is a material particle and its position as well as momentum can be determined with great accuracy. But with the advent of the concept of wave nature of electron, it has not been possible for us to measure simultaneously the exact position and velocity of electron. This was suggested by Heisenberg, in 1927.

Suppose, that Δx is the uncertainty in the measurement of the position and Δp is the uncertainty in the measurement of momentum of an electron, then

$$\Delta x \Delta p \geq \frac{h}{4\pi}$$

This relationship is called uncertainty principle. This equation shows that if Δx is small then Δp will be large and vice versa. So, if one quantity is measured accurately then the other becomes less accurate. Hence, certainty in the determination of one quantity introduces uncertainty in the determination of the other quantity.

The uncertainty principle is applicable only for microscopic particles like electrons, protons and neutrons, etc. and has no significance for large particles, i.e. macroscopic particles.

Compton's effect can help us understand the uncertainty principle, Suppose, we wish to determine the position of electron. Visible light cannot help us, because the wavelength of visible light is millions time large as compared to the diameter of electron. For this purpose, we have to use X-rays which have very short wavelength as compared to that of visible light. When this photon of X-rays strikes an electron, the momentum of electron will change. In other words, uncertainty of momentum will appear due to change of velocity of electron. Smaller the wavelength of X-rays, greater will be the energy of the photon. Hence, the collision of X-rays with electron will bring about the greater uncertainty in momentum. So, an effort to determine the exact position of electron has rendered its momentum uncertain. When we use the photons of longer wavelength to avoid the change of momentum, the determination of the position of electron becomes impossible.

Concept of Orbital

Following this principle, the Bohr's picture of an atom does not appear to be satisfactory. In Bohr's atom, the electrons are moving with specific velocities in orbits of specified radii, and according to uncertainty principle, both these quantities cannot be measured experimentally. A theory involving quantities, which cannot be measured does not follow the tradition of scientific work.

In order to solve this difficulty, Schrodinger, Heisenberg and Dirac worked out wave theories of the atom. The best known treatment is that of Schrodinger. He set up a wave equation for hydrogen atom. According to Schrodinger, although the position of an electron cannot be found exactly, the probability of finding an electron at a certain position at any time can be found.

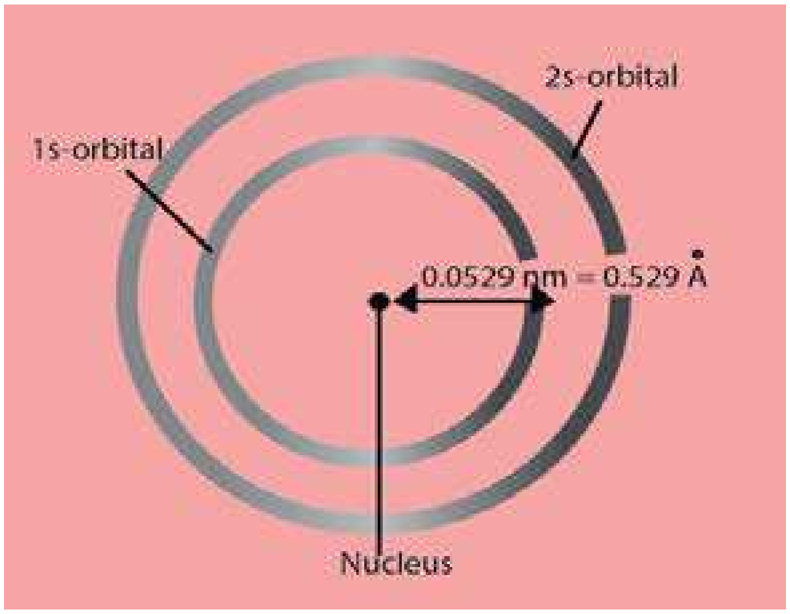


Fig (5.19) Probable electron density diagram for hydrogen atom.

The solution of the wave equation gives probability of finding an electron present in a given small region of space. When the probability of finding the electron at a distance r from the nucleus is calculated for the hydrogen atom in the ground state, Fig (5.19) is obtained.

The maximum probability of finding the electron is at a distance of 0.053 nm. It is the same radius as calculated for the Bohr's first orbit. There is a possibility that the electron is either closer to the nucleus or outside the radius of 0.053 nm, where probability of finding electron decreases sharply.

The volume of space in which there is 95% chance of finding an electron is called atomic orbital. The term orbital should not be confused with the term orbit as used in the Bohr's theory. The orbital can be regarded as a spread of charge surrounding the nucleus. This is often called the "electron cloud".

5.8.1 Quantum Numbers

Schrodinger wave equation, has been solved for hydrogen atom. It may have different solutions. Quantum numbers are the sets of numerical values which give the acceptable solutions to Schrodinger wave equation for hydrogen atom. An electron in an atom is completely described by its four quantum numbers. You know that a complete address of a person comprises his name, city in which he lives, the block, street and the house number. On the similar grounds, quantum numbers serve as identificatio numbers or labels, which completely describe an electron. These quantum numbers specify position of electron in an atom.

There are four quantum numbers which can describe the electron completely.

(1) Principal quantum number (n)
(2) Azimuthal quantum number (ℓ)
(3) Magnetic quantum number (m)
(4) Spin quantum number (s) Let us discuss these quantum numbers one by one.

Principal Quantum Number (n)

The different energy levels in Bohr's atom are represented by 'n'. This is called principal quantum number by Schrodinger. Its values are non-zero, positive integers upto infinity.

$$n = 1, 2, 3, 4, 5, \ldots\ldots\ldots\ldots\ldots\ldots,$$

The value of n represents the shell or energy level in which the electron revolves around the nucleus. Letter notations K, L, M, N, etc are also used to denote the various shells. For example, when n =1, it is called K shell, for n = 2, it is L shell and so on. The values of n also determine the location of electron in an atom, i.e the distance of electron from the nucleus, greater the value of 'n' greater will be the distance of electron from the nucleus. It is a quantitative measure of the size of an electronic shell, 'n' also provides us the energy of electron in a shell. Bohr's results help us to know the relationships of distance and energy of electron.

Azimuthal Quantum Number (ℓ)

It has already been mentioned in the defects of Bohr's model that a spectrometer of high resolving power shows that an individual line in the spectrum is further divided into several very fine lines. This thing can be explained by saying that each shell is divided into subshells. So, only principal quantum number (n) is not sufficient to explain the line spectrum. There is another subsidiary quantum number called azimuthal quantum number and is used to represent the subshells. The values of azimuthal quantum number (ℓ) are

$$\ell = 0, 1, 2, 3, \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (n-1)$$

Its value depends upon n. These values represent different subshells, which are designated by small letters, s, p, d, f. They stand for sharp, principal, diffused and fundamental, respectively. These are the spectral terms used to describe the series of lines observed in the atomic spectrum. The values of azimuthal quantum number always start from zero.

A subshell may have different shapes depending upon the value of ('ℓ'). It may be spherical, dumb-bell, or some other complicated shapes. The value of 'ℓ' is related to the shape of the subshell as follows:

$\ell = 0$	s-subshell	spherical
$\ell = 1$	p-subshell	dumb-bell
$\ell = 2$	d-subshell	(complicated shape)

The relationship between principal and azimuthal quantum numbers is as follows.

n = 1	K-shell	{$\ell = 0$	{s-subshell	should be called as	1s
n = 2	L-shell	$\ell = 0$	s-subshell		2s
		$\ell = 1$	p-subshell		2p
n = 3	M-shell	$\ell = 0$	s-subshell		3s
		$\ell = 1$	p-subshell		3p
		$\ell = 2$	d-subshell		3d
n = 4	N-shell	$\ell = 0$	s-subshell		4s
		$\ell = 1$	p-subshell		4p
		$\ell = 2$	d-subshell		4d
		$\ell = 3$	f-subshell		4f

In 1s, 2s, ..., etc, the digit represents the value of principal quantum number.'ℓ' values also enable us to calculate the total number of electrons in a given subshell. The formula for calculating electrons is $2(2\ell + 1)$.

when	$\ell = 0$	s-subshell	total electrons = 2
	$\ell = 1$	p-subshell	total electrons = 6
	$\ell = 2$	d-subshell	total electrons = 10
	$\ell = 3$	f-subshell	total electrons = 14

Magnetic Quantum Number (m)

In the defects of Bohr's model, it has been mentioned that strong magnetic field splits the spectral lines further. In order to explain this splitting, a third quantum number called the magnetic quantum number (m) has been proposed.

Its values are

$$m = 0, \pm 1, \pm 2, \pm 3, \ldots\ldots\ldots\ldots$$

The value of'm' depends upon values of 'ℓ'

when	$\ell = 0$	s-subshell	m=0
	$\ell = 1$	p-subshell	m=0, ±1(p-subshell has three degenerate orbitals)
	$\ell = 2$	d-subshell	m=0,±1, ±2(d-subshell has five degenerate orbitals)
	$\ell = 3$	f-subshell	m=0,±1, ±2, ±3(f-subshell has seven degenerate orbitals)

This above description shows that for a given value of 'ℓ' the total values of'm' are (2ℓ +1).

Actually, the value of m gives us the information of degeneracy of orbitals in space. It tells us the number of different ways in which a given s, p, d or f-subshell can be arranged along x, y and z-axes in the presence of a magnetic field. Thus, different values of'm' for a given value of 'ℓ', represent the total number of different space orientations for a subshell.

In case of s-subshell ℓ = 0, so, m = 0. It implies that s-subshell of any energy level has only one space orientation and can be arranged in space only in one way along x, y and z-axes. So s-subshell is not sub-divided into any other orbital. The shape of's' orbital is such that the probability of finding the electron in all the directions from the nucleus is the same. It is a spherical and symmetrical orbital. Fig (5.20).

For p-subshell, ℓ = 1 and m = 0, ±1. These values of'm' imply that p-subshell of any energy level has three space orientations and can be arranged in space along x, y, and z axes Fig. (5.21). These three orbitals are perpendicular to each other and named as p_x, p_y, and p_z. They have egg shaped lobes which touch each other at the origin. They are disposed symmetrically along one of the three axes called orbital axis. In the absence of the magnetic field, all the three p-orbitals have the same energy and are called degenerate orbitals. Since, they are three in number, so these orbitals are said to be 3-fold degenerate or triply degenerate.

For d-subshell ℓ = 2 m = 0, ±1, ±2. It implies that it has five space orientations and are designated as d_{xy} (m = -2), d_{yz} (m = -1), d_{zx}(m = +1), $d_{x^2-y^2}$(m = +2) and d_{z^2}(m - 0) Fig. (5.22).

All these five d-orbitals are not identical in shape. In the absence of a magnetic field, all five d-orbitals have the same energy and they are said to be five fold degenerate orbitals.

For f-subshell, ℓ = 3 and m = 0, ±1, ±2, ±3. They have complicated shapes.

The whole discussion shows that magnetic quantum number determines the orientation of orbitals, so it is also called orbital orientation quantum number.

Spin Quantum Number (s)

Alkali metals have one electron in their outermost shell. We can record their emission spectra, when the outermost electron jumps from an excited state to a ground state. When the spectra are observed by means of high resolving power spectrometer, each line in the spectrum is found to consist of pair of lines, this is called doublet line structure. We should keep it in mind, that doublet line structure is different from the fine spectrum of hydrogen (as we have discussed in azimuthal quantum number).

It should be made clear that lines of doublet line structure are widely separated from each other, while those of fine structure are closely spaced together.

In 1925, Goudsmit and Uhlenbech suggested that an electron while moving in an orbital around the nucleus also rotates or spins about its own axis either in a clockwise or anti-clockwise direction. This is also called self-rotation. This spinning electron is associated with a magnetic field and hence a magnetic moment. Hence, opposite magnetic fields are generated by the clockwise and anti-clockwise spins of electrons. This spin motion is responsible for doublet line structure in the spectrum.

The four quantum numbers of all the electrons in the first four shells are summarized in Table (5.3). Notice, that each electron has its own set of quantum numbers and this set is different for each electron.

Table (5.3) Quantum Numbers of Elections

Principal Quantum Number ‘n’	Azimuthal Quantum number ‘ ℓ ’	Magnetic Quantum number ‘m’	Spin Quantum number ‘s’	Number of electrons accommodated
1 K	0 s	0	+½,-½	2
2 L	0 s 1 p	0 +1, 0, −1	+½,-½ +½,-½	2 6 } 8
3 M	0 s 1 p 2 d	0 +1, 0, −1 +2, +1, 0, −1, −2	+½,-½ +½,-½ +½,-½	2 6 } 18 10
4 N	0 s 1 p 2 d 3 f	0 +1, 0, −1 +2, +1, 0, −1, −2 +3, +2, +1, 0, −1, −2, −3	+½,-½ +½,-½ +½,-½ +½,-½	2 6 } 32 10 14

5.8.2 Shapes of Orbitals

In section 5.8.1, we were introduced to the four types of orbitals depending upon the values of azimuthal quantum number. These orbitals are s, p, d and f having azimuthal quantum number values as ℓ = 0,1, 2,3, respectively. Let us, discuss the shapes of these, orbitals.

Shapes of s-Orbitals

s-orbital has a spherical shape and is usually represented by a circle, which in turn, represents a cut of sphere, Fig. (5.20). With the increase of value of principal quantum number (n), the size of s-orbital increases. 2s-orbital is larger in size than ls-orbital. 2s-orbital is also further away form the nucleus Fig. (5.20). The probability for finding the electron is zero between two orbitals. This place is called nodal plane or nodal surface.

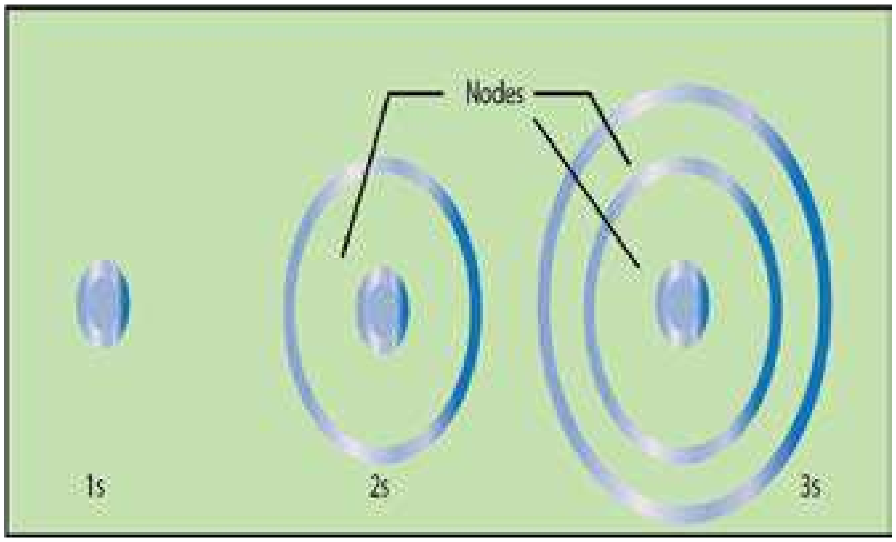


Fig (5.20) Shapes of s-orbitals with increasing principal quantum number

Shapes of p-Orbitals

There are three values of magnetic quantum numbef for p-subshell. So, p-subshell has three orientations in space i.e. along x, y and z-axes. All the three p-orbitals namely, p_x, p_y and p_z have dumb-bell shapes, Fig. (5.21). So, p-orbitals have directional character which determines the geometry of molecules. All the p-orbitals of all the energy levels have similar shapes, but with the increase of principal quantum number of the shell their sizes are increased.

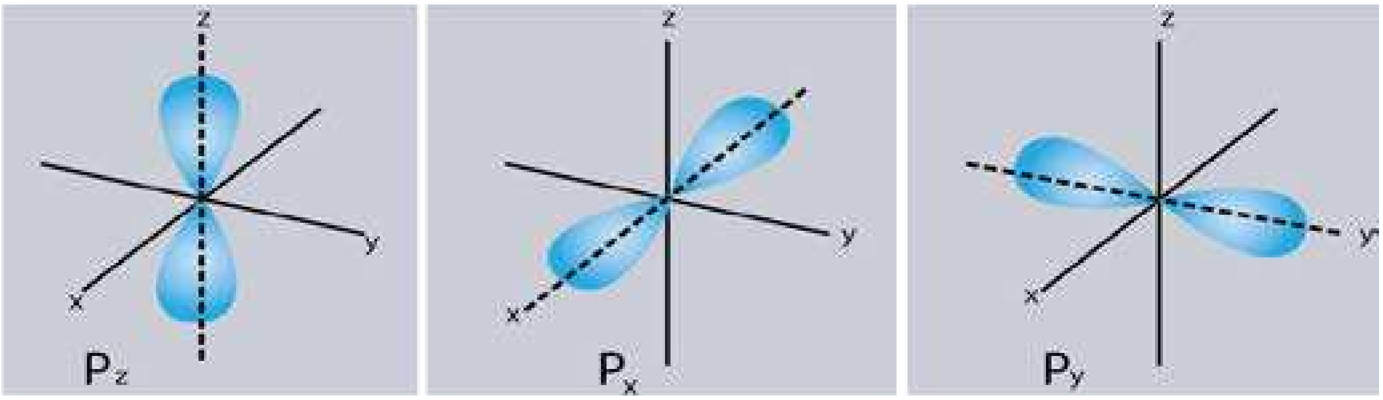
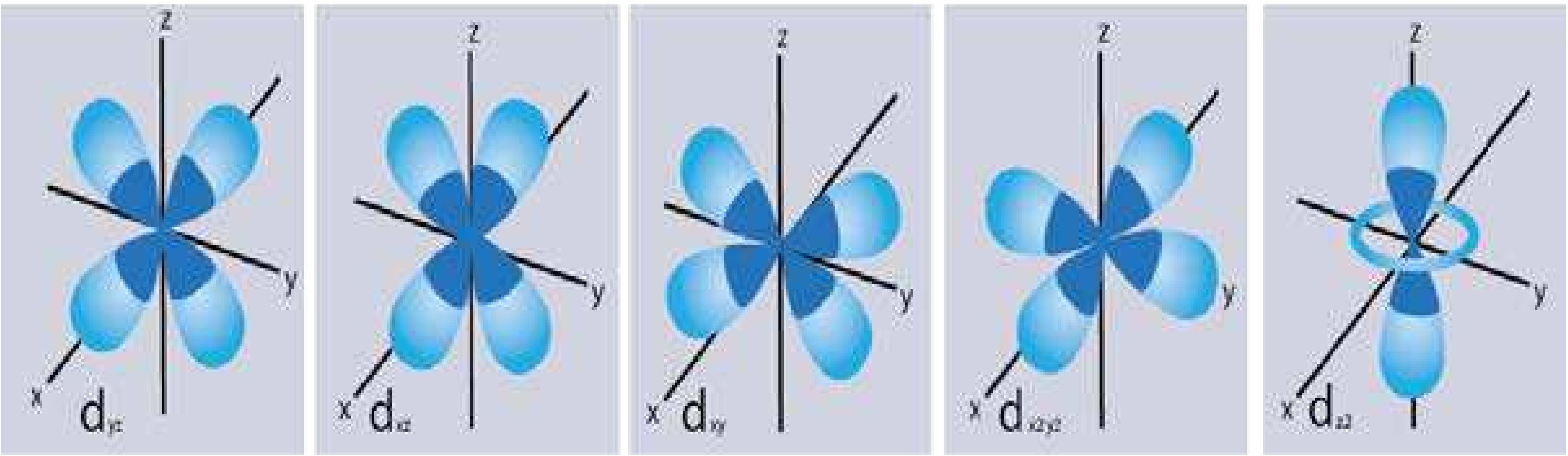


Fig (5.20) Shapes of p-orbitals

Shapes of d-Orbitals

For d subshell there are five values of magnetic quantum number. So, there are five space orientations along x, yand z-axes. Fig (5.22). They are designated as d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$, d_{z^2} .The lobes of first three d-orbitals lie between the axis. The other lie on the axis.

They are not identical in shape. Four d-orbitals out of these five contain four lobes each, while the fifth orbital $d_z{}^2$ consists of only two lobes, Fig (5.22). In the absence of magnetic field, all the five d-orbitals are degenerate. The shape of f-orbital is very complicated.



Fig(5.22)Shapesofd-orbitals

5.9 ELECTRONIC DISTRIBUTION

In order to understand the distribution of electrons in an atom, we should know the following facts.

1. An orbital like s, p_x, p_y, p_z and d_{xy}, etc. can have at the most two electrons.
2. The maximum number of electrons that can be accommodated in a shell is given by $2n^2$ formula where n is principal quantum number and it cannot have zero value.

Moreover, following rules have been adopted to distribute the electrons in subshells or orbitals.

1. Aufbau principle
2. Pauii's exclusion principle
3. Hand's rule

But, before we use these rules, the subshells should be arranged according to $(n + \ell)$ rule, Table(5.4). This rule says that subshells are arranged in the increasing order of $(n + \ell)$ values and if any two subshells have the same $(n + \ell)$ values, then that subshell is placed first whose n value is smaller.

The arrangement of subshells in ascending order of their energy may be as follows: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s and so no.

Aufbau Principle

The electrons should be filled in energy subshells in order of increasing energy values. The electrons are first placed in Is, 2s, 2p and soon.

Pauli's Exclusion Principle

This principle can be stated as follows:

It is impossible for two electrons residing in the same orbital of a poly-electron atom to have the same values of four quantum numbers, or Two electrons in the same orbital should have opposite spins (↓↑).

Table (5.4) Arrangement of orbitals according to (n+1) rule

	n	ℓ	n + ℓ
1s	1	0	1 + 0 = 1
2s	2	0	2 + 0 = 2
2p	2	1	2 + 1 = 3
3s	3	0	3 + 0 = 3
3p	3	1	3 + 1 = 4
3d	3	2	3 + 2 = 5
4s	4	0	4 + 0 = 4
4p	4	1	4 + 1 = 5
4d	4	2	4 + 2 = 6
4f	4	3	4 + 3 = 7
5s	5	0	5 + 0 = 5
5p	5	1	5 + 1 = 6
5d	5	2	5 + 2 = 7
5f	5	3	5 + 3 = 8
6s	6	0	6 + 0 = 6
6p	6	1	6 + 1 = 7
6d	6	2	6 + 2 = 8
6f	6	3	6 + 3 = 9
7s	7	0	7 + 0 = 7

Hund's Rules

If, degenerate orbitals are available and more than one electrons are to be placed in them, they should be placed in separate orbitals with the same spin rather than putting them in the same orbital with opposite spins.

According to the rule, the two electrons in 2p subshell of carbon will be distributed as follows.

$${}_6C = \overset{\boxed{\downarrow\uparrow}}{1s}\ \overset{\boxed{\downarrow\uparrow}}{2s}\ \overset{\boxed{\uparrow}}{2p_x}\ \overset{\boxed{\downarrow}}{2p_y}\ \overset{o}{2p_z}$$

The three orbitals of 2p subshell are degenerate.

5.9.1 Electronic Configuration of Elements

Keeping in view the rules mentioned above, the electronic configurations of first thirty six elements are given in Table (5.5).

Table (5.5) Electron configurations of elements

Element	Atomic number	Electron Configuration Notation
Hydrogen	1	$\overset{\uparrow}{1s}$
Helium	2	$1s^2$
Lithium	3	$1s^2\overset{\uparrow}{2s}$
Beryllium	4	$1s^22s^2$

Table (5.5) continued

Element	Atomic number	Electron Configuration Notation
Boron	5	$1s^2 2s^2 2\overset{\uparrow}{p}_x\, 2\overset{0}{p}_y\, 2\overset{0}{p}_z$
Carbon	6	$1s^2 2s^2 2\overset{\uparrow}{p}_x\, 2\overset{\uparrow}{p}_y\, 2\overset{0}{p}_z$
Nitrogen	7	$1s^2 2s^2 2\overset{\uparrow}{p}_x\, 2\overset{\uparrow}{p}_y\, 2\overset{\uparrow}{p}_z$
Oxygen	8	$1s^2 2s^2 2p^2_x\, 2\overset{\uparrow}{p}_y\, 2\overset{\uparrow}{p}_z$
Fluorine	9	$1s^2 2s^2 2p^2_x\, 2p^2_y\, 2\overset{\uparrow}{p}_z$
Neon	10	$1s^2 2s^2 2p^2_x\, 2p^2_y\, 2p^2_z$
Sodium	11	$[Ne]\, 3\overset{\uparrow}{s}$
Magnesium	12	$[Ne]\, 3\,\overset{\uparrow\downarrow}{s}$
Aluminum	13	$[Ne]\, 3s^2\, 3\overset{\uparrow}{p}_x\, 3\overset{0}{p}_y\, 3\overset{0}{p}_z$
Silicon	14	$[Ne]\, 3s^2\, 3\overset{\uparrow}{p}_x\, 3\overset{\uparrow}{p}_y\, 3\overset{0}{p}_z$
Phosphorus	15	$[Ne]\, 3s^2\, 3\overset{\uparrow}{p}_x\, 3\overset{\uparrow}{p}_y\, 3\overset{\uparrow}{p}_z$
Sulphur	16	$[Ne]\, 3s^2\, 3p^2_x\, 3\overset{\uparrow}{p}_y\, 3\overset{\uparrow}{p}_z$
Chlorine	17	$[Ne]\, 3s^2\, 3p^2_x\, 3p^2_y\, 3\overset{\uparrow}{p}_z$
Argon	18	$[Ne]\, 3s^2\, 3p^2_x\, 3p^2_y\, 3p^2_z$
Potassium	19	$[Ar]\, 4\overset{\uparrow}{s}$
Calcium	20	$[Ar]\, 4s^2$

(continued on next page)

Element	Atomic number	Electron Configuration Notation
Scandium	21	$[Ar]\ 4s^2\,\overset{\uparrow}{3d}_{xy}\,\overset{0}{3d}_{yz}\,\overset{0}{3d}_{xz}\,\overset{0}{3d}_{x^2-y^2}\,\overset{0}{3d}_{z^2}$
Titanium	22	$[Ar]\ 4s^2\,\overset{\uparrow}{3d}_{xy}\,\overset{\uparrow}{3d}_{yz}\,\overset{0}{3d}_{xz}\,\overset{0}{3d}_{x^2-y^2}\,\overset{0}{3d}_{z^2}$
Vanadium	23	$[Ar]\ 4s^2\,\overset{\uparrow}{3d}_{xy}\,\overset{\uparrow}{3d}_{yz}\,\overset{\uparrow}{3d}_{xz}\,\overset{0}{3d}_{x^2-y^2}\,\overset{0}{3d}_{z^2}$
Chromium	24	$[Ar]\ 4\overset{\uparrow}{s}\,\overset{\uparrow}{3d}_{xy}\,\overset{\uparrow}{3d}_{yz}\,\overset{\uparrow}{3d}_{xz}\,\overset{\uparrow}{3d}_{x^2-y^2}\,\overset{\uparrow}{3d}_{z^2}$
Manganese	25	$[Ar]\ 4s^2\,3d^2{}_{xy}\,\overset{\uparrow}{3d}_{yz}\,\overset{\uparrow}{3d}_{xz}\,\overset{\uparrow}{3d}_{x^2-y^2}\,\overset{\uparrow}{3d}_{z^2}$
Iron	26	$[Ar]\ 4s^2\,3d^2{}_{xy}\,3d^2{}_{yz}\,\overset{\uparrow}{3d}_{xz}\,\overset{\uparrow}{3d}_{x^2-y^2}\,\overset{\uparrow}{3d}_{z^2}$
Cobalt	27	$[Ar]\ 4s^2\,3d_{xy}\,3d_{yz}\,3d_{xz}\,\overset{\uparrow}{3d}_{x^2-y^2}\,\overset{\uparrow}{3d}_{z^2}$
Nickel	28	$[Ar]\ 4s^2\,3d_{xy}\,3d_{yz}\,3d_{xz}\,3d_{x^2-y^2}\,\overset{\uparrow}{3d}_{z^2}$
Copper	29	$[Ar]\ 4\overset{\uparrow}{s}\,3d^2{}_{xy}\,3d^2{}_{yz}\,3d^2{}_{xz}\,3d^2{}_{x^2-y^2}\,3d^2{}_{z^2}$
Zinc	30	$[Ar]\ 4s^2\,3d^2{}_{xy}\,3d^2{}_{yz}\,3d^2{}_{xz}\,3d^2{}_{x^2-y^2}\,3d^2{}_{z^2}$
Gallium	31	$[Ne]\ 4s^2\,3d^{10}\,\overset{\uparrow}{4p}_x\,\overset{0}{4p}_y\,\overset{0}{4p}_z$
Germanium	32	$[Ne]\ 4s^2\,3d^{10}\,\overset{\uparrow}{4p}_x\,\overset{\uparrow}{4p}_y\,\overset{0}{4p}_z$
Arsenic	33	$[Ne]\ 4s^2\,3d^{10}\,\overset{\uparrow}{4p}_x\,\overset{\uparrow}{4p}_y\,\overset{\uparrow}{4p}_z$
Selenium	34	$[Ne]\ 4s^2\,3d^{10}\,4p^2{}_x\,\overset{\uparrow}{4p}_y\,\overset{\uparrow}{4p}_z$
Bromine	35	$[Ne]\ 4s^2\,3d^{10}\,4p^2{}_x\,4p^2{}_y\,\overset{\uparrow}{4p}_z$
Krypton	36	$[Ne]\ 4s^2\,3d^{10}\,4p^2{}_x\,4p^2{}_y\,4p^2{}_z$

KEY POINTS

1. Matter is made up of extremely small particles called atoms.
2. Cathode rays and positive rays were discovered during discharge tube experiments. The properties of cathode rays showed them to be negatively charged particles called electrons, whereas, the positive rays were found to contain positively charged particles called protons.
3. Neutron was discovered through artificial radioactivity.
4. Electrons, protons and neutrons are regarded as the fundamental particles of an atom.
5. Rutherford discovered the nucleus and successfully explained the presence of moving electrons around the nucleus.
6. In 1905, Planck put forward his famous Planck's quantum theory.
7. Neil Bohr explained the structure of hydrogen atom by using Planck's quantum theory. He also calculated the radius and energy of electron in the nth shell of hydrogen atom.
8. Bohr's atomic model successfully explained the origin of line spectrum and the lines present in the spectrum of hydrogen atom in the visible and invisible regions.
9. X-rays are produced when rapidly moving electrons collide with heavy metal anode in the discharge tube.
10. Moseley discovered a simple relationship between the frequency of X-rays and the atomic number of the target element.
11. de-Broglie discovered wave particle duality of material particles. According to him, all material particles in motion have a dual character. Davisson and Germer experimentally verified the wave concept of an electron.
12. Heisenberg pointed out that it is not possible for us, to measure the exact position and the exact momentum of electron simultaneously.
13. After the failure of Bohr's atomic model, Schrodinger developed the wave mechanical model of hydrogen atom. According to him, although the position of an electron cannot be found exactly, the probability of finding an electron at a certain position at any time can be calculated.
14. An electron in an atom is completely described by its four quantum numbers. Three out of these four quantum numbers, have been derived from Schrodinger wave equation, when it is solved for hydrogen atom.

EXERCISE

Q1. Select the most suitable answer for the given one.

(i) The nature of the positive rays depend on

(a) the nature of the electrode (b) the nature of the discharge tube
(c) the nature of the residual gas (d) all of the above

(ii) The velocity of photon is

(a) independent of its wavelength (b) depends on its wavelength
(c) equal to square of its amplitude (d) depends on its source

(iii) The wave number of the light emitted by a certain source is 2 x 10^{6} m^{-1}. The wavelength of this light will be

(a) 500 nm (b) 500 m (c) 200nm (d) 5xl0^{7}m

(iv) Rutherford's model of atom failed because

(a) the atom did not have a nucleus and electrons
(b) it did not account for the attraction between protons and neutrons
(c) it did not account for the stability of the atom
(d) there is actually no space between the nucleus and the electrons

(v) Bohr model of atom is contradicted by

(a) Planck's quantum theory (b) dual nature of matter
(c) Heisenberg's uncertainty principle (d) all of the above

(vi) Splitting of spectral lines when atoms are subjected to strong electric field is called,

(a) Zeeman effect (b) Stark effect
(c) Photoelectric effect (d) Compton effect

(vii) In the ground state of an atom, the electron is present

(a) in the nucleus (b) in the second shell
(c) nearest to the nucleus (d) farthest from the nucleus

(viii) Quantum number values for 2p orbitals are

(a) $n = 2, \ell = 1$ (b) $n = 1, \ell = 2$
(c) $n = 1, \ell = 0$ (d) $n = 2, \ell = 0$

(ix) Orbitals having same energy are called

(a) hybrid orbitals (b) valence orbitals
(c) degenerate orbitals (d) d-orbitals

(x) When 6d orbital is complete, the entering electron goes into

(a) 7f (b) 7s (c) 7p (d) 7d

Q2. Fill in the blanks with suitable words.

(i) β-particles are nothing but __________ moving with a very high speed.
(ii) The charge on one mole of electrons is__________coulombs.
(iii) The mass of hydrogen atom is____________ grams.
(iv) The mass of one mole of electrons is______________ .
(v) Energy is __________ when electron jumps from higher to a lower orbit.
(vi) The ionization energy of hydrogen atom can be calculated from_____model of atom.
(vii) For d-subshell, the azimuthal quantum number has value of __________.
(viii) The number of electrons in a given subshell is given by formula_________ .
(ix) The electronic configuration of H^+ is__________ .

Q3. Indicate true or false as the case may be.

(i) A neutron is slightly lighter particle than a proton.
(ii) A photon is the massless bundle of energy but has momentum.
(iii) The unit of Rydberg constant is the reciprocal of unit of length.
(iv) The actual isotopic mass is a whole number.
(v) Heisenberg's uncertainty principle is applicable to macroscopic bodies.
(vi) The nodal plane in an orbital is the plane of zero electron density.
(vii) The number of orbitals present in a sublevel is given by the formula $(2\ell + 1)$.
(viii) The magnetic quantum number was introduced to explain Zeeman and Stark effect.
(ix) Spin quantum number tells us the direction of spin of electron around the nucleus.

Q 4: Keeping in mind the discharge tube experiment, answer the following questions.

(a) Why is it necessary to decrease the pressure in the discharge tube to get the cathode rays?

(b) Whichever gas is used in the discharge tube, the nature of the cathode rays remains the same. Why?

(c) Why e/m value of the cathode rays is just equal to that of electron?

(d) How the bending of the cathode rays in the electric and magnetic fields shows that they are negatively charged?

(e) Why the positive rays are also called canal rays?

(f) The e/m value of positive rays for different gases are different but those for cathode rays the e/m values are the same. Justify it.

(g) The e/m value for positive rays obtained from hydrogen gas is 1836 times less than that of cathode rays. Justify it.

Q5 (a) Explain Millikan's oil drop experiment to determine the charge of an electron.

(b) What is J.J Thomson's experiment for determining e/m value of electron?

(c) Evaluate mass of electron from the above two experiments.

Q6 (a) Discuss Chadwick's experiment for the discovery of neutron. Compare the properties of electron, proton and neutron.

(b) Rutherford's atomic model is based on the scattering of α-particles from a thin gold foil. Discuss it and explain the conclusions.

Q7. (a) Give the postulates of Bohr's atomic model. Which postulate tells us that orbits are stationary and energy is quantized?

(b) Derive the equation for the radius of nth orbit of hydrogen atom using Bohr's model.

(c) How does the above equation tell you that

(i) radius is directly proportional to the square of the number of orbit.

(ii) radius is inversely proportional to the number of protons in the nucleus.

(d) How do you come to know that the velocities of electrons in higher orbits, are less than those in lower orbits of hydrogen atom?

(e) Justify that the distance gaps between different orbits go on increasing from the lower to the higher orbits.

Q8 Derive the formula for calculating the energy of an electron in nth orbit using Bohr's model. Keeping in view this formula explain the following:

(a) The potential energy of the bounded electron is negative.

(b) Total energy of the bounded electron is also negative.

(c) Energy of an electron is inversely proportional to n^2, but energy of higher orbits are always greater than those of the lower orbits.

(d) The energy difference between adjacent levels goes on decreasing sharply.

Q9. (a) Derive the following equations for hydrogen atom, which are related to the

(i) energy difference between two levels, n_1 and n_2.

(ii) frequency of photon emitted when an electron jumps from n_2 to n_1.

(iii) wave number of the photon when the electron jumps from n_2 to n_1.

(b) Justify that Bohr's equation for the wave number can explain the spectral lines of Lyman, Balmer and Paschen series.

Q10. (a) What is spectrum. Differentiate between continuous spectrum and line spectrum.

(b) Compare line emission and line absorption spectra.

(c) What is the origin of line spectrum?

Q11. (a) Hydrogen atom and He^+ are mono-electronic system, but the size of He^+ is much smaller than H^+, why?

(b) Do you think that the size of Li^{+2} is even smaller than He^+? Justify with calculations.

Q12. (a) What are X-rays? What is their origin? How was the idea of atomic number derived from the discovery of X-rays?

(b) How does the Bohr's model justify the Moseley's equation?

Q13. Point out the defects of Bohr's model. How these defects are partially covered by dual nature of electron and Heisenberg's uncertainty principle?

Q14. (a) Briefly discuss the wave mechanical model of atom. How has it given the idea of orbital. Compare orbit and orbital.

(b) What are quantum numbers? Discuss their significance.

(c) When azimuthal quantum number has a value 3, then there are seven values of magnetic quantum number. Give reasons.

Q15. (a) Discuss rules for the distribution of electrons in energy subshells and in orbitals.

(b) What is $(n + \ell)$ rule. Arrange the orbitals according to this rule. Do you think that this rule is applicable to degenerate orbitals?

(c) Distribute electrons in orbitals of $_{57}La$, $_{29}Cu$, $_{79}Au$, $_{24}Cr$, $_{53}1$, $_{86}Rn$.

Q16 Draw the shapes of s, p and d-orbitals. Justify these by keeping in view the azimuthal and magnetic quantum numbers.

Q17 A photon of light with energy 10^{-19} J is emitted by a source of light.

(a) Convert this energy into the wavelength, frequency and wave number of the photon in terms of meters, hertz and m^{-1}, respectively.

(Ans:1.51xl0^{14}s^{-1}; 1.98x10^{-6}m; 5xl0^{5}m^{-1})

(b) Convert this energy of the photon into ergs and calculate the wavelength in cm, frequency in Hz and wave number in cm^{-1}.

[h = 6.626x 10^{-34} Js or 6.625x 10^{-27} ergs, c = 3x10^{8} ms^{-1} or 3x 10^{+10} cms^{-1}]

(Ans:1.51xl0^{14}s^{-1}; 1.98xl0^{-4}cm; 5xl0^{3}cm^{-1})

Q18 The formula for calculating the energy of an electron in hydrogen atom given by Bohr's model

$$E_n = \frac{-m^2e^4}{8\varepsilon_0^2h^2n^2}$$

Calculate the energy of the electron in first orbit of hydrogen atom. The values of various parameters are same as provided in Q19.

(Ans:-2.18xlO^{-18}J)

Q 19 Bohr's equation for the radius of nth orbit of electron in hydrogen atom is

$$r_n = \frac{\epsilon_0 h^2n^2}{\pi e^2 m}$$

(a) When the electron moves from n = 1 to n = 2, how much does the radius of the orbit increases.

(Ans: 1.587 $\mathring{A}$)

(b) What is the distance travelled by the electron when it goes from n=2 to n=3 and n=9 ton=10?

$[\varepsilon_0 = 8.85 \times 10^{-12}\ c^2 J^{-1} m^{-1}$, $h = 6.624 \times 10^{-34}$ js, $\pi = 3.14$, $m = 9.108 \times 10^{-31}$ kg, $e = 1.602 \times 10^{-19} c]$ while doing calculations take care of units of energy parameter.

$[J = kgm^2 s^{-2}, c = kg^{1/2} m^{3/2} s^{-1}]$

(Ans: 2.65 $\mathring{A}$; 10.05 $\mathring{A}$)

Q 20 Answer the following questions, by performing the calculations.

(a) Calculate the energy of first five orbits of hydrogen atom and determine the energy differences between them.

(b) Justify that energy difference between second and third orbits is approximately five times smaller than that between first and second orbits.

(c) Calculate the energy of electron in He+ in first five orbits and justify that the energy differences are different from those of hydrogen atom.

(d) Do you think that groups of the spectral lines of He^+ are at different places than those for hydrogen atom? Give reasons.

Q 21 Calculate the value of principal quantum number if an electron in hydrogen atom revolves in an orbit of energy- 0.242 xlO^{-18} J.

(Ans:n=3)

Q 22 Bohr's formula for the energy levels of hydrogen atom for any system say H, He^+, Li^{2+} ,etc. is

$$E_n = \frac{-Z^2 e^4 m}{8\varepsilon_0{}^2 h_2 n^2}$$

or

$$E_n = -K\left[\frac{Z^2}{n^2}\right]$$

For hydrogen:Z = 1 and for He^+, Z = 2.

(a) Draw an energy level diagram for hydrogen atom and He^+ .

(b) Thinking that $K = 2.18 \times 10^{-18}$J, calculate the energy needed to remove the electron from hydrogen atom and from He^+.

(Ans: 2.18×10^{-18}J; 8.72×10^{-18}J)

(c) How do you justify that the energies calculated in (b) are the ionization energies of H and He^+?

(d) Use Avogadro's number to convert ionization energy values in $kJmol^{-1}$ for H and He^+.

(Ans: $1313.3kJmol^{-1}$; $5249.4kJmol^{-1}$)

(e) The experimental values of ionization energy of H and He^+ are 1331 $kJmol^{-1}$ and 5250 $kJmol^{-1}$, respectively. How do you compare your values with experimental values?

(Ans: $5249kJ\ mol^{-1}$)

Q 23 Calculate the wave number of the photon when the electron jumps from

(i) n = 5 to n = 2. (Ans:$2.3\text{x}10^6m^{-1}$)

(ii) n = 5 to n = 1 (Ans: $1.05 \text{ x } 10^7 m^{-1}$)

In which series of spectral lines and spectral regions these photons will appear.

(Ans: (i) Balmer Series (ii) Lyman Series)

Q 24 A photon of a wave number 102.70 x 10 m is emitted when electron jumps from higher to n = 1.

(a) Determine the number of that orbit from where the electron falls.

(Ans: n=4)

(b) Indicate the name of the series to which this photon belongs.

(Ans: Lyman series)

(c) If the electron will fall from higher orbit to n = 2, then calculate the wave number of the photon emitted. Why this energy difference is so small as compared to that in part (a)?

(Ans: $20.5 \text{ x } 10^5m^{-1}$)

Q 25. (a) What is de-Broglie's wavelength of an electron in meters travelling at half a speed of light?

[$m = 9.109 \text{ x } 10^{-31}$ kg , $c = 3 \text{ x } 10^8\ ms^{-1}$]

(Ans: λ=0.048 $\overset{o}{A}$)

(b) Convert the mass of electron into grams and velocity of light into cms^{-1} and then calculate the wavelength of an electron in cm. (Ans:$0.048\text{x}10^{-8}$ cm)

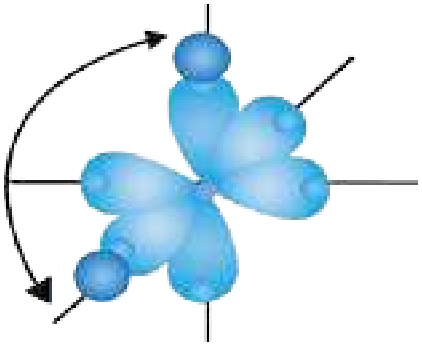
(c) Convert the wavelength of electron from meters to

(i) nm (ii) $\overset{o}{A}$ (iii) pm.

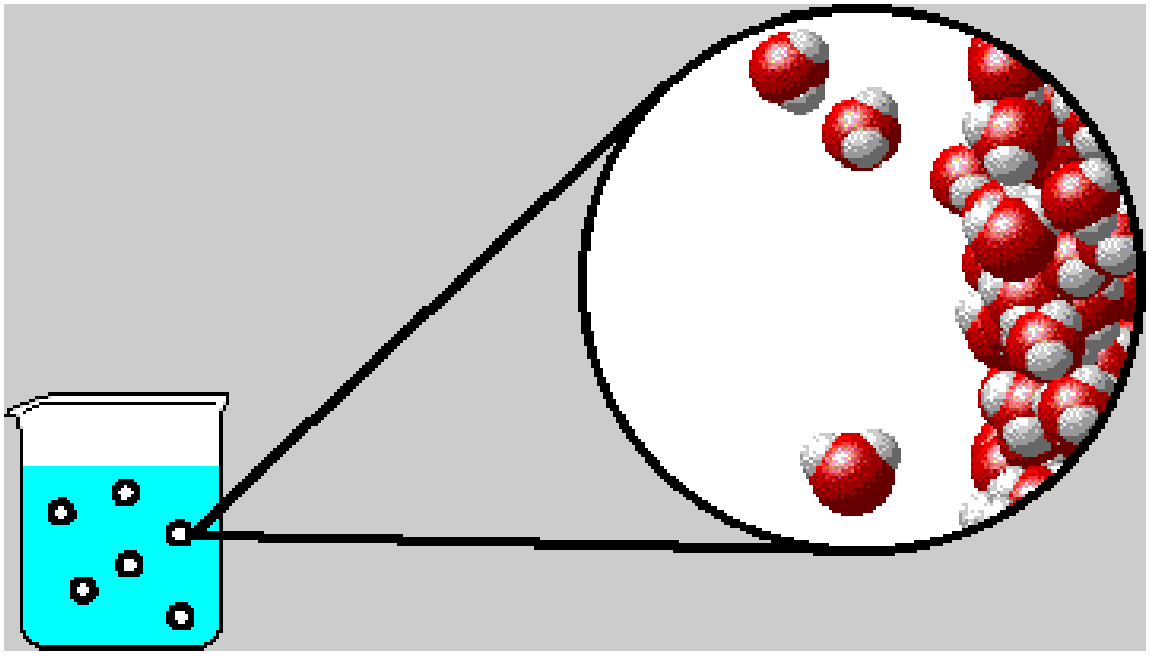
(Ans: 0.0048nm; 0.048; 4.85 $\overset{o}{A}$ pm)

CHAPTER

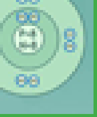
6



CHEMICAL BONDING



Animation 6.1: Chemical Bonding
Source & Credit: chemistry.elmhurst



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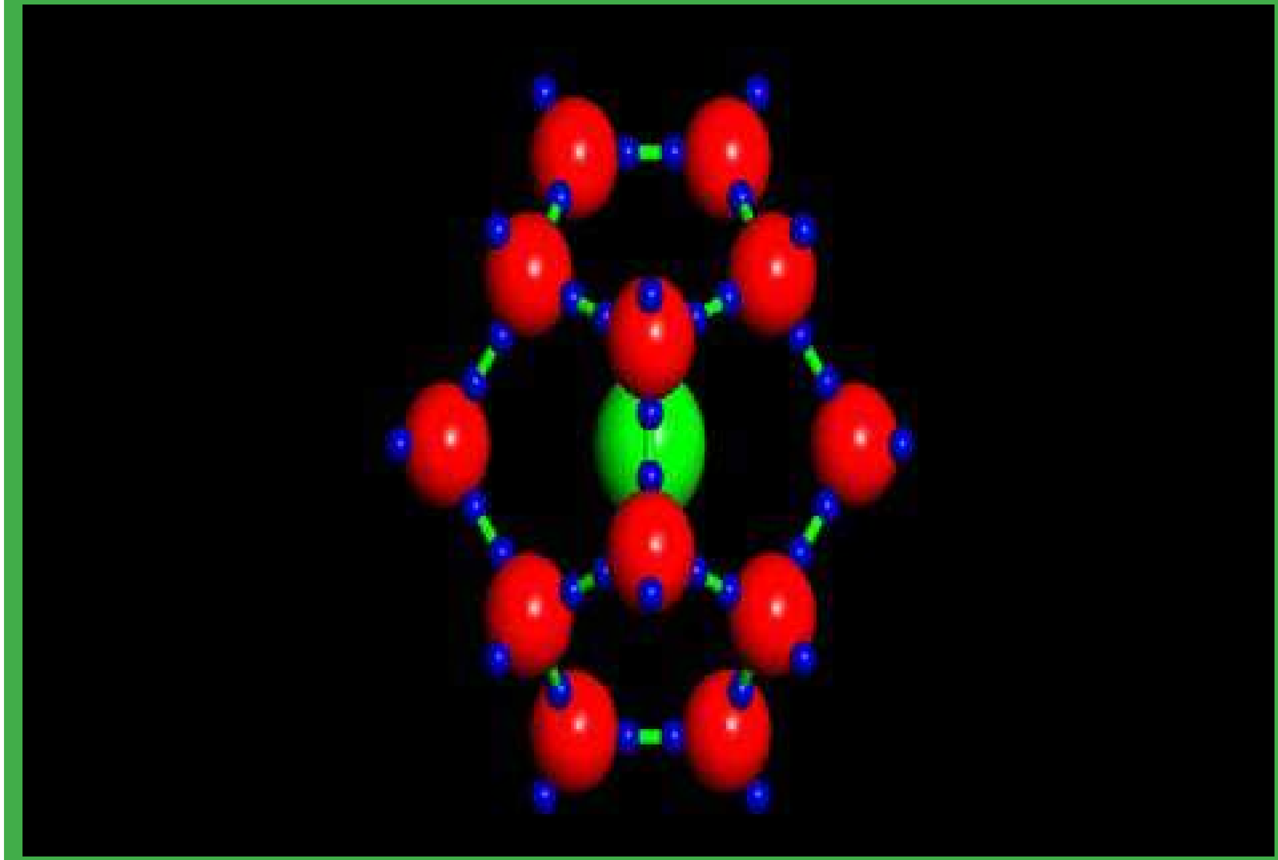
6.1.0 INTRODUCTION

A chemical bond is the force, which holds together two or more atoms or ions to form a large variety of compounds. The forces which are responsible for such bonding and the shapes of the molecules formed are as a result of chemical combination.

The theory of chemical bonding has been a major problem of modern chemistry. In this chapter, we shall look into the nature of the chemical bonds formed between the atoms.



Animation 6.2: Chemical Bond
Source & Credit : geo.arizona

6.1.1 Cause of Chemical Combination

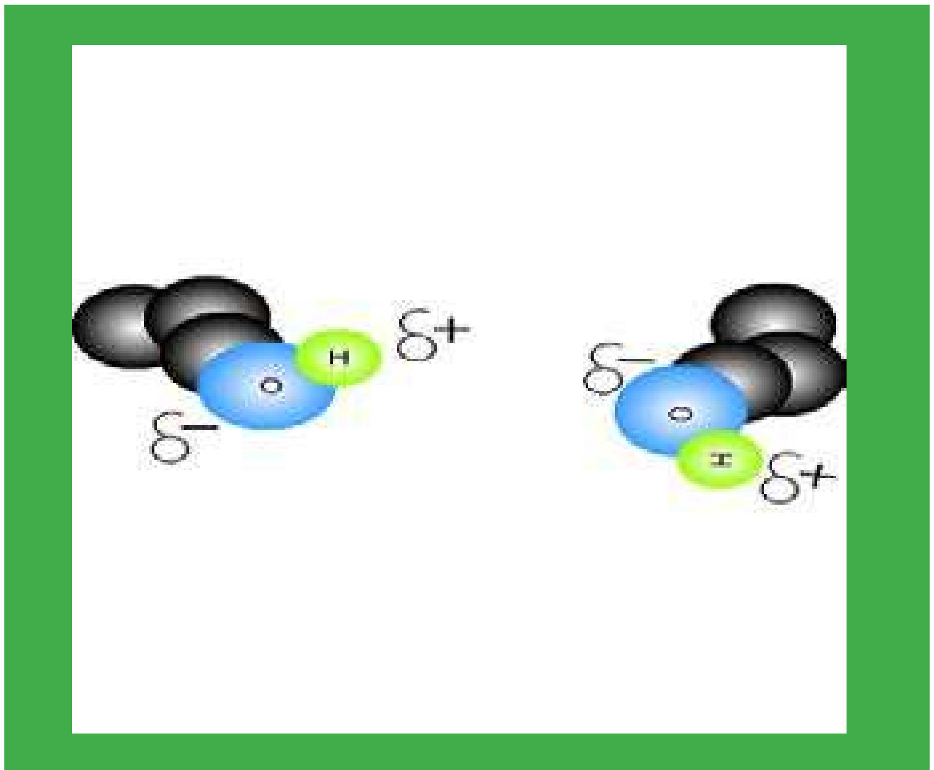
It has been observed that the chemical reactivities of elements, depend upon their characteristic electronic configurations. The noble gases with electronic configuration of valence shell Is^2 (He) or $ns^2\ np^6$ (Ne, Ar, Kr, Xe, etc.) show little tendency to react chemically. There are just only a few stable compounds, formed by these elements like XeF_2, XeF_4, $XeOF_2$, XeO_3, etc. A noble gas does not react with another noble gas. Thus, these gases are the most stable of all the elements. Let us, see why noble gases are most stable. This can be explained on the basis of their special electronic configuration. Their outermost s and p orbitals are completely filled.

$$_{2}He = \underset{\text{Is}}{\boxed{\uparrow\downarrow}} \qquad _{10}Ne = \underset{\text{Is}}{\boxed{\uparrow\downarrow}}\ \underset{2s}{\boxed{\uparrow\downarrow}}\ \underset{2p_x}{\boxed{\uparrow\downarrow}}\ \underset{2p_y}{\boxed{\uparrow\downarrow}}\ \underset{2p_y}{\boxed{\uparrow\downarrow}}\ \underset{2p_z}{\boxed{\uparrow\downarrow}}$$

All other elements, combine with one another, due to an inherent tendency to stabilize themselves. They get their stabilization by losing, gaining or sharing electrons to attain the nearest noble gas configuration. The tendency of atoms to attain a maximum of eight electrons in the valence shell is known as the 'octet rule'. A few examples are given in Table (6.1).

In certain cases, both tendencies i.e. to lose or gain electrons have been observed. But the system will go by the conditions in which the chemical combination takes place. For example, in the chemical combination between sodium and hydrogen to form NaH, hydrogen atom gains an electron. In the formation of HF the hydrogen atom donates the major share of its electron to fluorine atom.

Any how, the 'octet' rule could not be made universal as the formation of compounds PF_5, SF_6, BCl_3 are not according to this rule.



Animation 6.3: bonding
Source & Credit : dynamicscience

Table (6.1) Change in the electronic configurations of some elements after losing or gaining electrons

Element	Tendency	Electronic configuration		Nearest
		Befor electron loss or gain	After electron loss or gain	nobel gas
$_{3}$Li	Electron loss	$1s^2\ 2s^1$	$1s^2$	He (2)
$_{12}$Mg	Electron loss	$1s^2\ 2s^2\ 2p^6\ 3s^2$	$1s^2\ 2s^2\ 2p^6$	Ne (10)
$_{9}$F	Electron gain	$1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^1$	$1s^2\ 2s^2\ 2p^6$	Ne (10)
$_{16}$S	Electron gain	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^2\ 3p_y^1\ 3p_z^1$	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$	Ar (18)

6.1.2 ENERGETICS OF BOND FORMATION

According to the modern theory of chemical bonding, atoms form bonds as it leads to a decrease in energy. For example, when two hydrogen atoms approach each other, forces of attraction and repulsion operate simultaneously.

The attractive forces tend to bring the two atoms close to each other and the potential energy of the system is decreased. On the other hand, the repulsive forces tend to push the atoms apart and potential energy of the system is increased. It has been found that the magnitude of potential energy for attractive forces is more than for repulsive forces. Therefore, potential energy decreases as the two hydrogen atoms approach each other Fig(6.1).

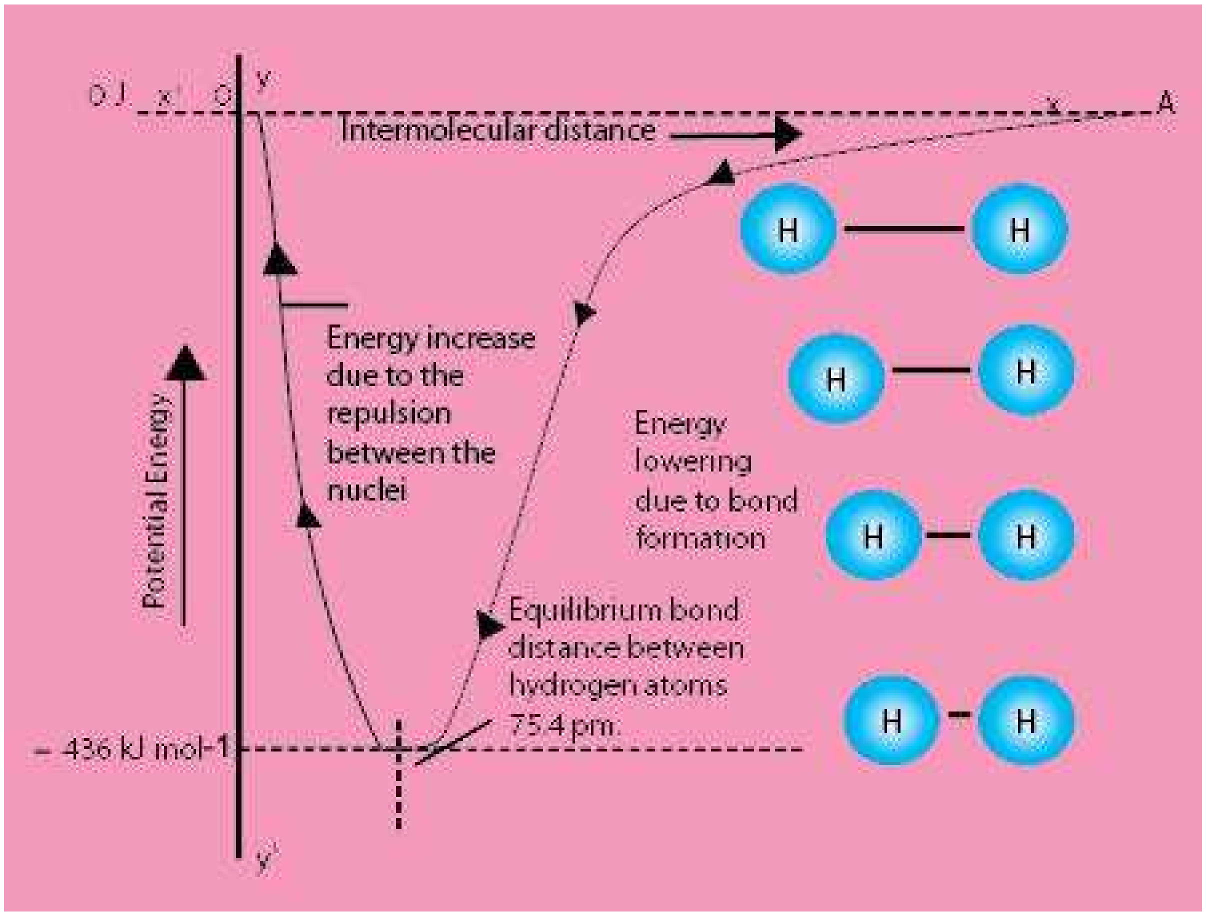
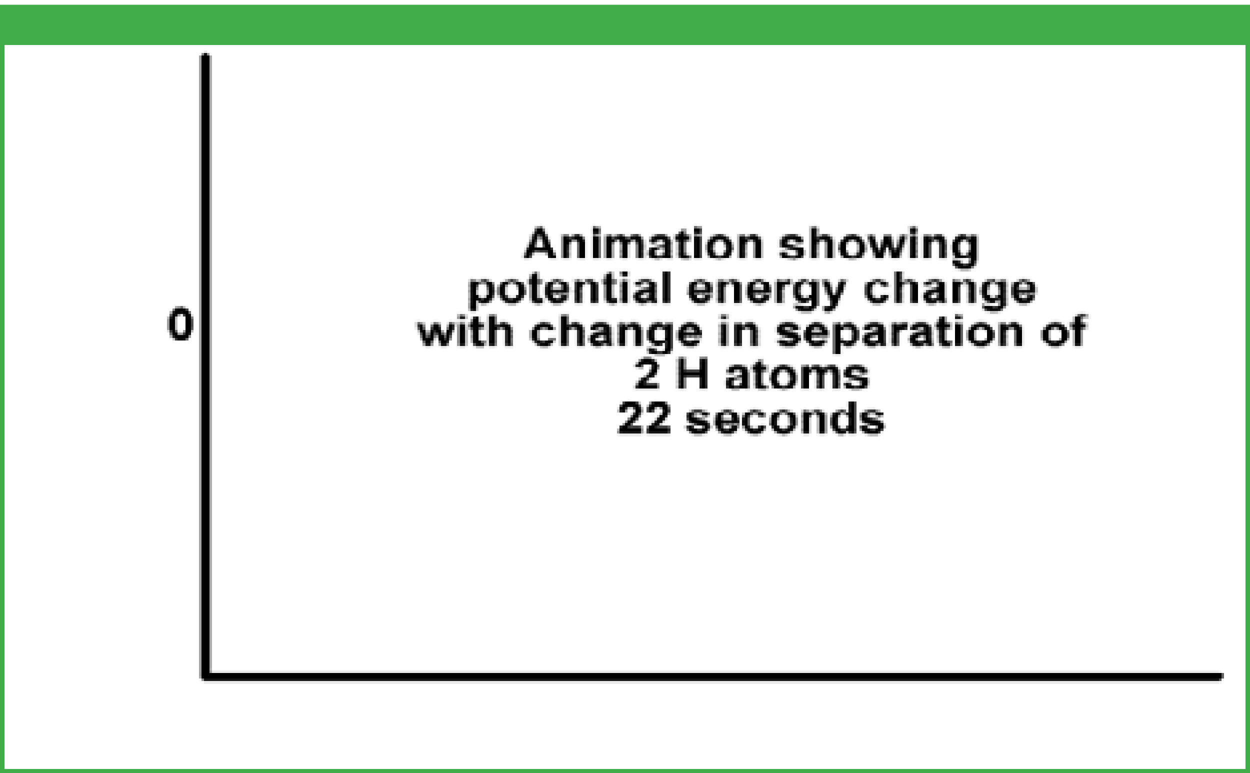


Fig: (6.1) Potential energy curve for the formation of H_2 molecule.

Eventually, a state corresponding to the distance of 75.4pm is reached, where the attractive forces dominate the repulsive forces. Here,the potential energy of the system is minimum and the hydrogen atoms are said to be bonded to form a stable molecule. So,this distance of 75.4 pm is called bond distance or bond length or compromise distance of two hydrogen atoms. When the atoms approach the distance of minimum energy, then the system of two hydrogen atoms is stabilized to maximum extent. The amount of energy evolved is 436.45k.Jmol^{-1} and is called bond formation energy. In order to break the bond, the same amount of energy has to be provided.



Animation 6.4: ENERGETICS OF BOND FORMATION
Source & Credit : 800mainstreet

For the case, where repulsive forces are dominant than the attractive forces, the energy of the system increases and it leads to instability. Consequently, a bond is not formed. In order to understand bonding, the relative sizes of atoms should be known.

6.2. ATOMIC SIZES

ATOMIC RADII, IONIC RADII AND COVALENT RADII.

The size of an atom is very important because many physical and chemical properties are related to it. Atoms are assumed to be spherical. That is why, we report the various types of radii to guess their sizes For this reason, the sizes of atoms are expressed in terms of atomic radii, ionic radii and covalent radii, etc,. depending upon the type of the compound used for its measurement.

The atomic radius means the average distance between the nucleus of the atom and its outermost electronic shell.

The radius of an atom cannot be determined precisely due to the following reasons.

(i) There is no sharp boundary of an atom. The probability of finding an electron never becomes exactly zero even at large distances from the nucleus.

(ii) The electronic probability distribution is affected by neighbouring atoms. For this reason,the size of an atom may change from one compound to another.

Atomic radii can be determined, by measuring the distances between the centres of adjacent atoms with the help of X-rays or by spectroscopic measurements. Atomic radii of elements of the periodic table in pm are shown in Table (6.2).

Animation 6.5: ATOMIC SIZES
Source & Credit : sustainable-nano

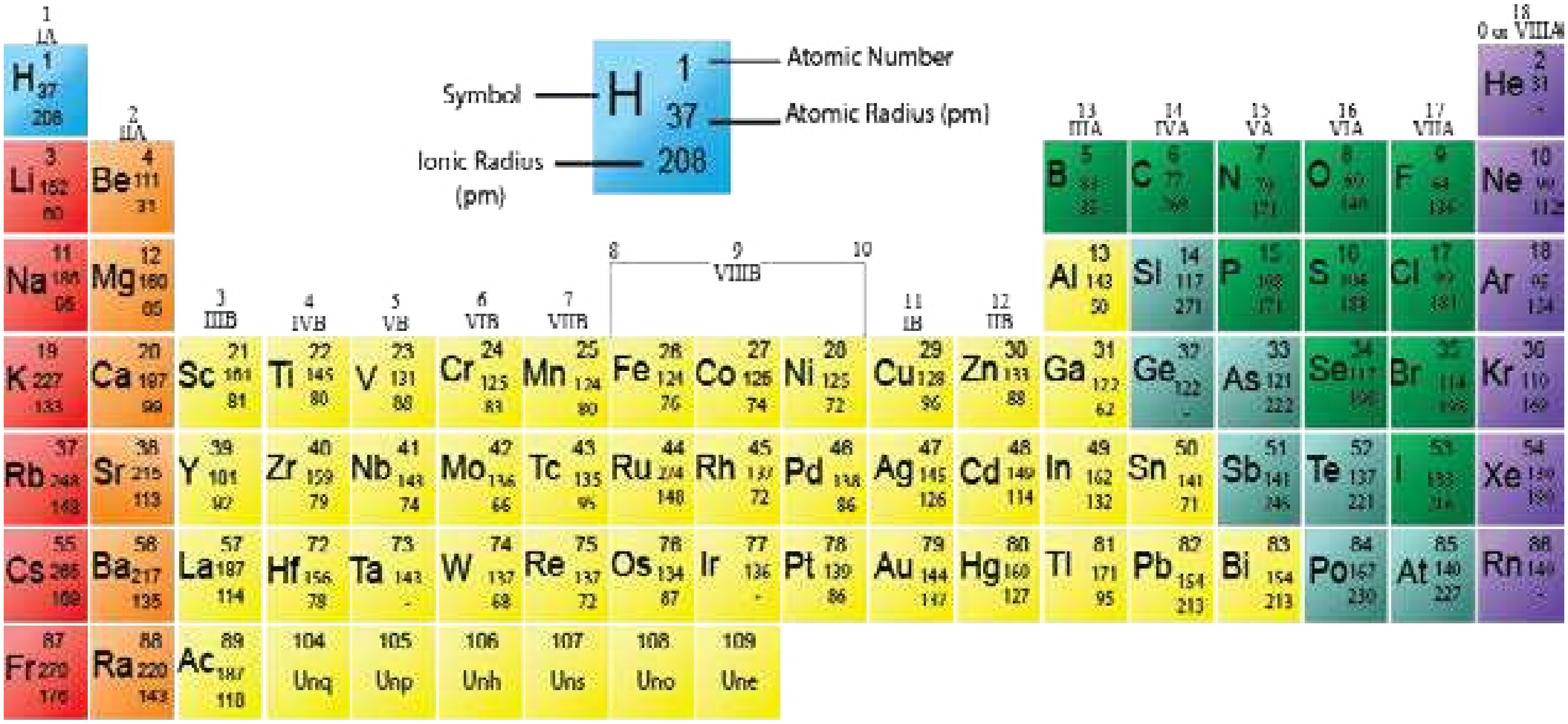
Variation of Atomic Radii in the Periodic Table

In general, the atomic radii decrease from left to the right in a period and increase from top to bottom in a group of the periodic table. The decreasing trend in a period is due to the increase in the nuclear charge. As the nuclear charge increases, the pull on the electrons is increased and size of an atom decreases. Moreover, the shielding effect remains the same from left to right in a period.

Animation 6.6: Periodic trends
Source & Credit : kaiserscience.wordpress

The increase in atomic radii in a group is due to increase in the number of shells and the screening effect. The decrease of atomic radii is very prominent in second period, but less in higher periods. Moreover, the decrease is small, when we travel from left to right in transition elements Sc(21) -Zn(30), Y(39) -Cd(48) due to the intervening electrons. The screening effect is also called shielding effect. This is responsible for the decrease in force of attraction of the nucleus for the electrons present in the valence shell.

Table (6.2) Radii of atoms and ions in the periodic table.



1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 0 or VIIIA
H 1 37 208																	He 2 31 -
Li 3 152 60	Be 4 111 31											B 5 88 20	C 6 77 260	N 7 70 171	O 8 66 140	F 9 64 136	Ne 10 69 112
Na 11 186 95	Mg 12 160 65											Al 13 143 50	Si 14 117 271	P 15 108 171	S 16 104 188	Cl 17 99 181	Ar 18 95 154
K 19 227 133	Ca 20 197 99	Sc 21 161 81	Ti 22 145 80	V 23 131 88	Cr 24 125 83	Mn 25 124 80	Fe 26 124 76	Co 27 126 74	Ni 28 125 72	Cu 29 128 96	Zn 30 133 88	Ga 31 122 62	Ge 32 122 -	As 33 121 222	Se 34 117 198	Br 35 114 195	Kr 36 110 169
Rb 37 248 148	Sr 38 215 113	Y 39 101 93	Zr 40 159 79	Nb 41 143 74	Mo 42 136 66	Tc 43 135 95	Ru 44 134 148	Rh 45 137 72	Pd 46 138 86	Ag 47 145 126	Cd 48 149 114	In 49 162 132	Sn 50 141 71	Sb 51 141 245	Te 52 137 221	I 53 133 216	Xe 54 130 190
Cs 55 265 169	Ba 56 217 135	La 57 187 114	Hf 72 156 78	Ta 73 143 -	W 74 137 68	Re 75 137 72	Os 76 134 87	Ir 77 136 -	Pt 78 139 86	Au 79 144 137	Hg 80 160 127	Tl 81 171 95	Pb 82 154 213	Bi 83 154 213	Po 84 167 230	At 85 140 227	Rn 86 140 -
Fr 87 270 176	Ra 88 220 143	Ac 89 187 118	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Une									

6.2.1 Ionic Radii and Covalent Radii

Ionic Radic

The ionic radius of an ion is the radius of the ion while considering it to be spherical in shape. The ionic radii of some ions in pm are given in Table (6.2). The ionic radius of a cation is smaller than the atomic radius of the element from which it is derived. The ionic radius of an anion is greater than the atomic radius of the corresponding atom. The radius of Na atom, for example, reduces from 186 pm to 95 pm after conversion into Na^+ ion. The ionic radius of Cl^- ion increases from 99 pm to 181 pm. The cationic radius decreases with the increase in the effective nuclear charge on the ion. The decrease in radius is larger for divalent ions (Mg^{2+}) and still larger for trivalent ions (Al^{3+}). This is due to the reason that with the successive loss of electrons, the nuclear charge attracts the remaining electrons with a greater force.

The increase in the size of the anion is due to the increase in the electron-elenctron repulsion because of the increase in the valence shell electrons. Greater the amount of negative charge on an atom, greater the size of ion.

The variation of ionic radii in groups and periods have the same trend as for atomic radii. But keep in mind that ionic radius for metals is for positive ions and for elements of group number VA to VIIA are for negative ions.

Let us consider, the positive and negative ions, which are held together by electrostatic forces of attraction in a crystal lattice. Fig. (6.2), r_+ and r_- are the values of radii of cation and anion, respectively.

The interionic distance 'R' in a crystal lattice is equal to the sum of the cationic radius r_+ and the anionic radius r.

$$R = r_+ + r_-$$

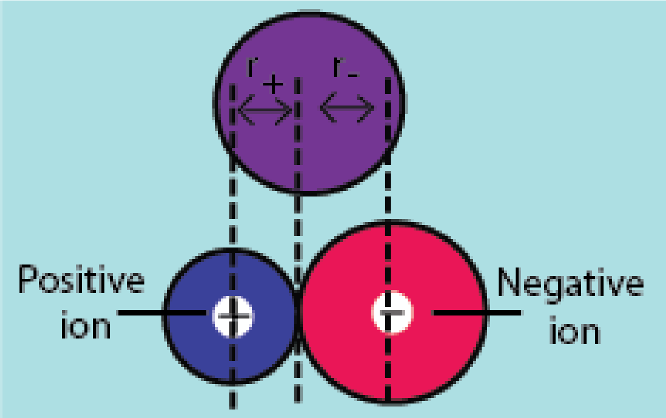
Pauling was able to determine the distance between K^+ and Cl^- ions in potassium chloride crystal and found that it was equal to the sum of the radii of the two ions.

$$R = 133pm + 181\ pm = 314\ pm$$

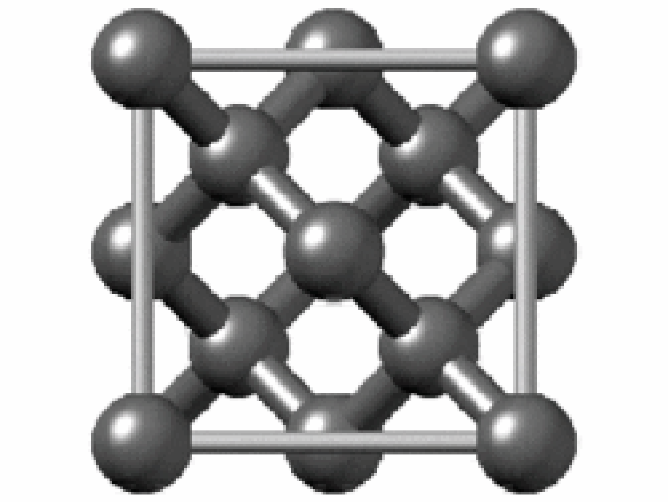
Thus, the ionic radius appeared to be an additive property. Pauling extended this concept to other K^+ salts and calculated the radii of other ions from the relationship:

$$r_- = R - r_+$$

Similarly, the ionic radii of different cations can also be determined.



F. ig (6.2) The relationaship of interionic distance R and ionic. radii (r_+ and r_-)



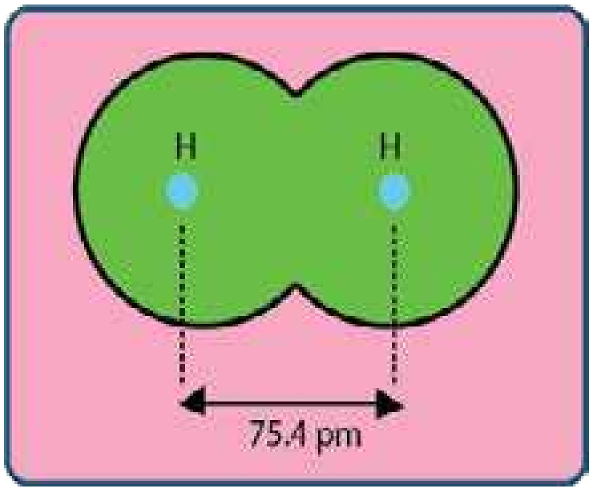
Animation 6.7: Ionic Radii and Covalent Radii Ionic Radii
Source & Credit : chemwiki.ucdavis

Covalent Radii

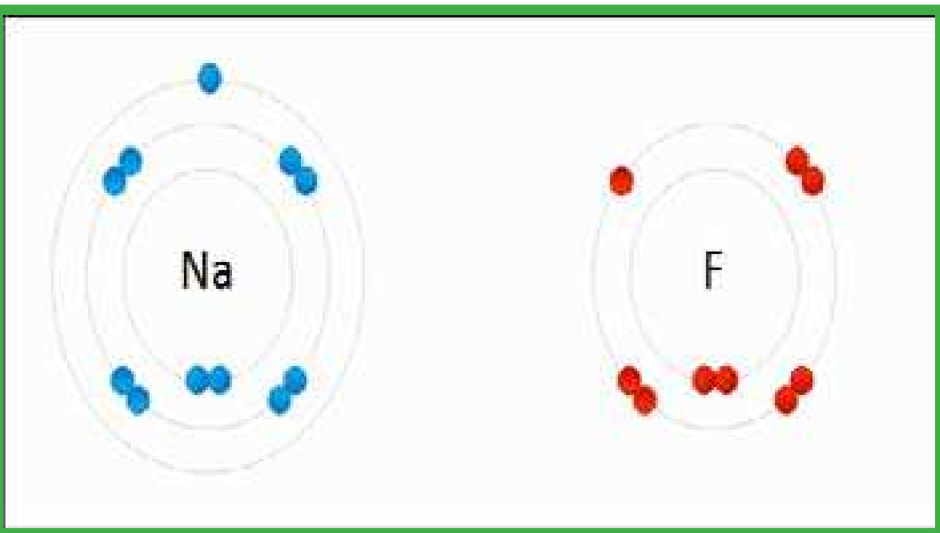
The covalent radius of an element is defined as half of the single bond length between two similar atoms covalently bonded in a molecule.

The covalent radius of hydrogen, for example, is 37.7 pm. It is half of the single bond length (75.4 pm) between the two H atoms in H-H molecule, as shown in Fig (6.3).

The covalent radius of an atom can be used to determine the covalent radius of another atom. For example, the experimentally determined bond length of C-Cl in CH_3Cl is 176.7 pm. The covalent radius of Cl-atom being known as 99.4 pm, that of C-atom can be calculated by subtracting this value from C-Cl bond length. So, the covalent radius of C-atom = 176.7- 99.4 = 77.3 pm.



Fig(6.3)Covalent radius of H atom,(75.4/2=37.7pm)



Animation 6.8: Covalent Radii
Source & Credit : boundless

The variation of covalent radii in groups and periods is almost the same as of atomic radii. Since energy changes are involved in the bond formation, so thermodynamic properties of elements need to be discussed before understanding the chemical bond.

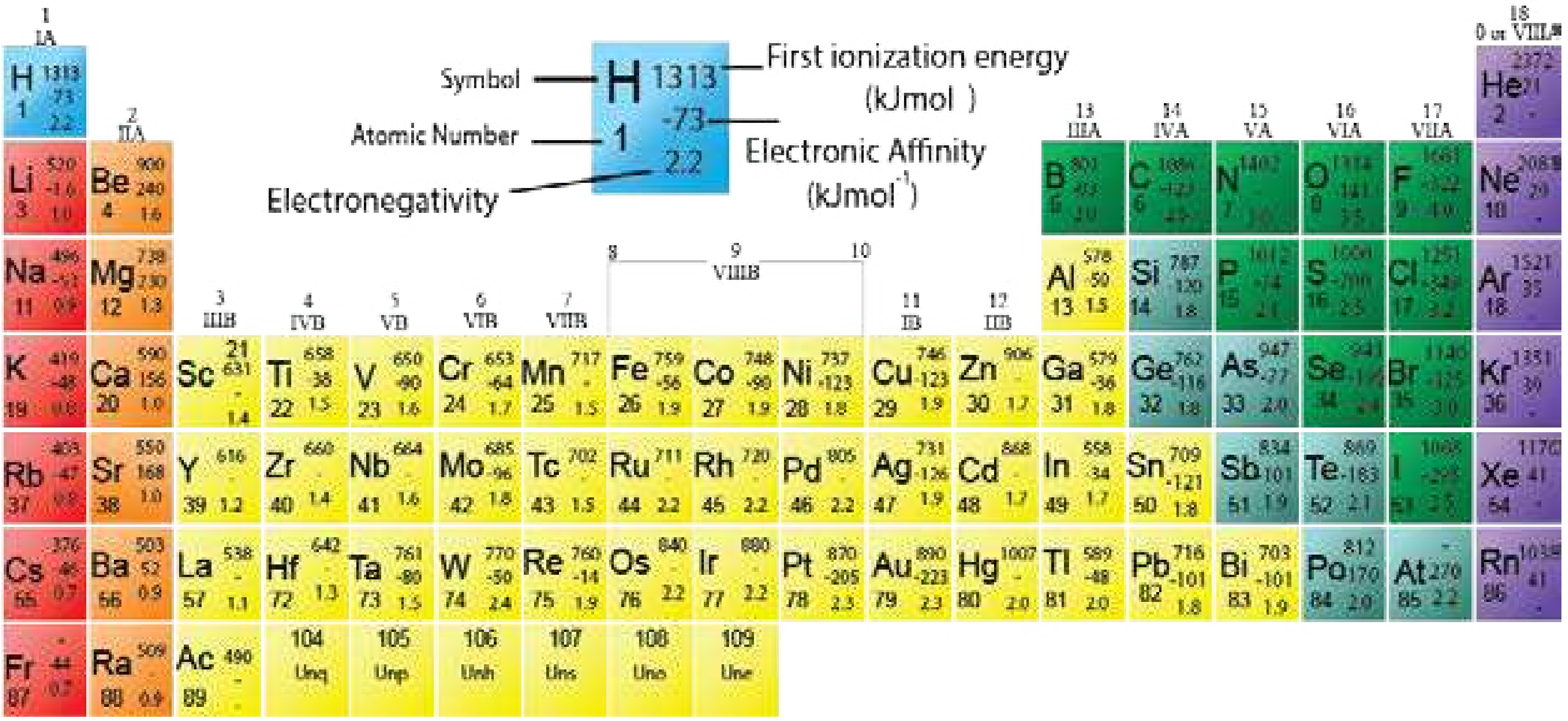
6.3 IONIZATION ENERGY, ELECTRON AFFINITY AND ELECTRONEGATIVITY

6.3.1 Ionization Energy

The ionization energy of an element is the minimum energy required to remove an electron from its gaseous atom to form an ion. The process is called ionization, e.g.

$$Mg \rightarrow Mg^{+} + e^{-} \qquad \Delta H = 738 kJmol^{-1}$$

Table (6.3) First ionization energies, electron affinities and electronegativities values of elements



Symbol

Atomic Number

Electronegativity

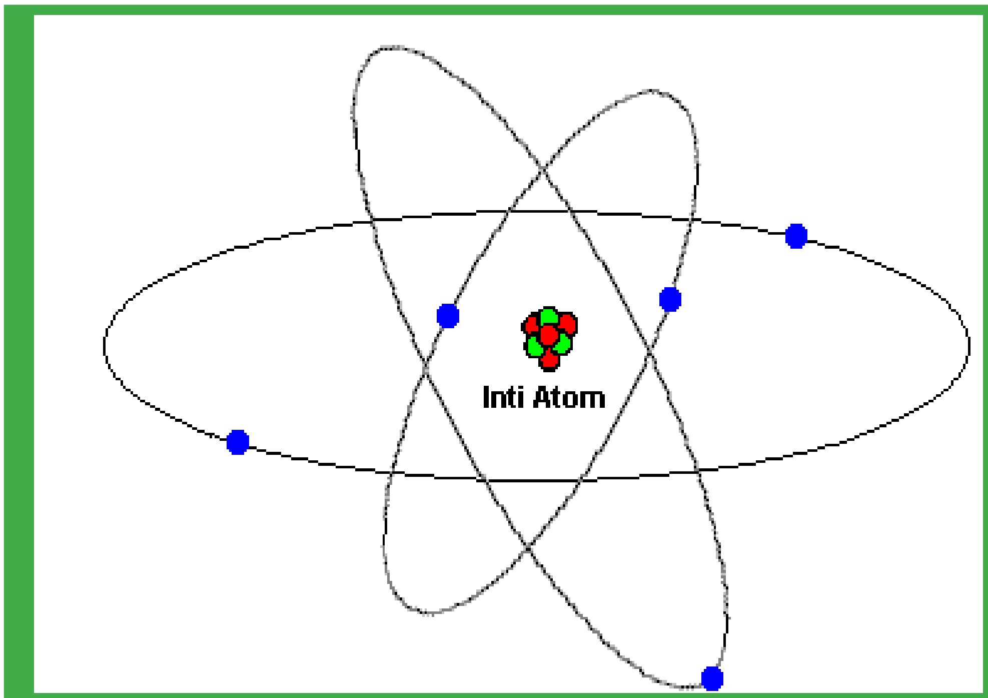
H 1313 -73 1 2.2

First ionization energy (kJmol)

Electronic Affinity (kJmol⁻¹)

1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 0 or VIIIA
H 1 1313 73 2.2																	He 2 2372 21 -
Li 3 520 -60 1.0	Be 4 900 240 1.6											B 5 801 -83 2.0	C 6 1086 -122 2.5	N 7 1402 - 3.0	O 8 1314 141 3.5	F 9 1681 -322 4.0	Ne 10 2081 29 -
Na 11 496 -53 0.9	Mg 12 738 230 1.3											Al 13 578 -50 1.5	Si 14 787 120 1.8	P 15 1012 -74 2.1	S 16 1000 -200 2.5	Cl 17 1251 -348 3.0	Ar 18 1521 35 -
K 19 419 -48 0.8	Ca 20 590 156 1.0	Sc 21 631 - 1.4	Ti 22 658 -38 1.5	V 23 650 -90 1.6	Cr 24 653 -64 1.7	Mn 25 717 - 1.5	Fe 26 759 -56 1.9	Co 27 748 -90 1.9	Ni 28 737 -123 1.8	Cu 29 746 -123 1.9	Zn 30 906 - 1.7	Ga 31 579 -36 1.8	Ge 32 762 -116 1.8	As 33 947 -77 2.0	Se 34 941 -195 2.4	Br 35 1140 -325 3.0	Kr 36 1351 39 -
Rb 37 403 -47 0.8	Sr 38 550 168 1.0	Y 39 616 - 1.2	Zr 40 660 - 1.4	Nb 41 664 - 1.6	Mo 42 685 -96 1.8	Tc 43 702 - 1.5	Ru 44 711 - 2.2	Rh 45 720 - 2.2	Pd 46 805 - 2.2	Ag 47 731 -126 1.9	Cd 48 868 - 1.7	In 49 558 34 1.7	Sn 50 709 -121 1.8	Sb 51 834 101 1.9	Te 52 869 -183 2.1	I 53 1008 -295 2.5	Xe 54 1170 41 -
Cs 55 376 -46 0.7	Ba 56 503 52 0.9	La 57 538 - 1.1	Hf 72 642 - 1.3	Ta 73 761 -80 1.5	W 74 770 -50 2.4	Re 75 760 -14 1.9	Os 76 840 - 2.2	Ir 77 880 - 2.2	Pt 78 870 -205 2.3	Au 79 890 -223 2.3	Hg 80 1007 - 2.0	Tl 81 589 -48 2.0	Pb 82 716 -101 1.8	Bi 83 703 -101 1.9	Po 84 812 170 2.0	At 85 - 270 2.2	Rn 86 1037 41 -
Fr 87 - 44 0.7	Ra 88 509 - 0.9	Ac 89 490 - -	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Une									

In the gaseous phase, the atoms and ions are isolated and are free from all external influences. Thus, the ionization energy is the qualitative measure of the stability of an isolated atom. The first ionization energies of elements are given in Table (6.3).

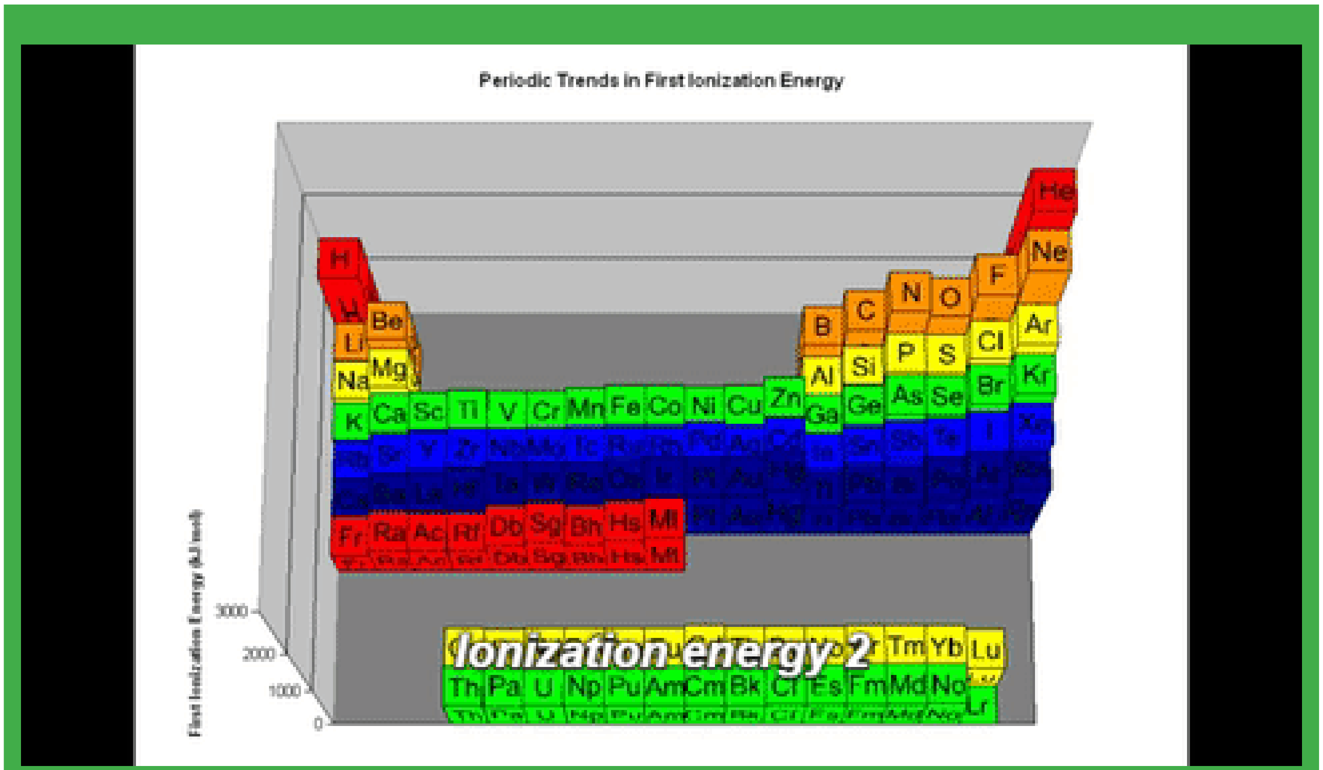


Animation 6.9: Ionization Energy
Source & Credit : kaiserscience.wordpress

Factors Influencing the Ionization Energies

It is observed that the ionization energies of atoms depend upon the following factors.

(i) Atomic radius of atom
(ii) Nuclear charge or proton number of the atom
(iii) Shielding effect of inner electrons
(iv) Nature of orbital



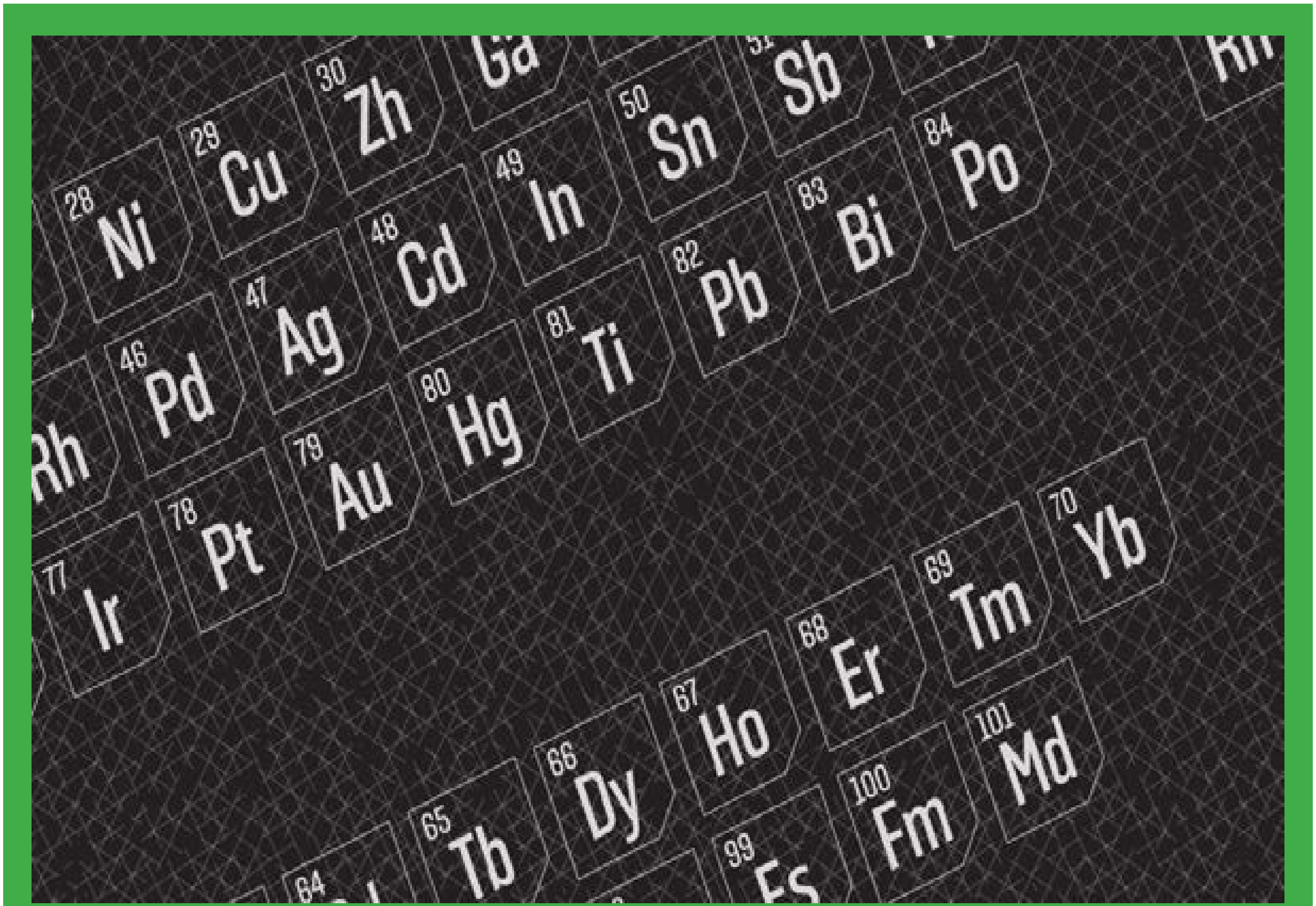
Animation 6.10: Factors Influencing the Ionization Energies
Source & Credit : kaiserscience.wordpress

Variation of Ionization Energy in the Periodic Table

In the periodic table, the ionization energies increase from left to right in a period with the increase in the proton number, until a maximum value is reached at the end of the period. This may be explained in terms of the periodicity of the electronic configuration of elements. Each period begins with an element which has one electron in its valence shell and ends with the completion of an electronic shell. The increase in the atomic number is associated with the increase in nuclear charge which leads to a stronger force of attraction between the nucleus and the increasing number of electrons. The stronger force of attraction, ultimately results in difficult removal of electrons.

In groups, the ionization energy decrease in spite of the increase in proton number or nuclear charge. This is due to successive addition of electronic shells as a result of which the valence electrons are placed at a larger distance from the nucleus. As the force of attraction between the nucleus and the outer electron decreases with the increase in distance, the electron can be removed more easily or with less energy. Moreover, the force of attraction also decreases due to increasing shielding effect of the intervening electrons.

The ionization energies of group III-A and VI-A show abnormal trend. This can be understood from the distribution of the electrons.



Animation 6.11: Variation of Atomic Radii in the Periodic Table
Source & Credit : dynamicscience

Higher Ionization Energies

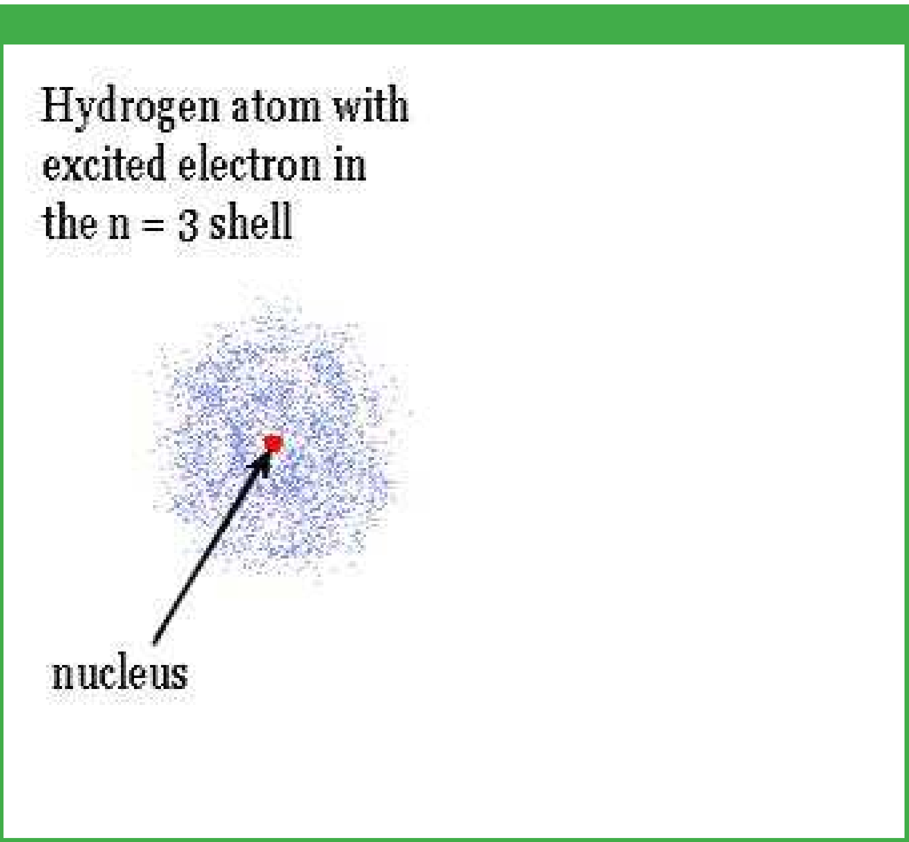
So far, we have explained the first ionization energy. The energy required to remove an electron after the removal of first electron is called second ionization energy.

$$Mg \rightarrow Mg^{++} + e^{-} \qquad \Delta H = 1450 kJmol^{-1}$$

Similarly, the energy required to remove third electron after the removal of second one is called the third ionization energy, and it is 7730kJ for Mg. It means that the ionization energy values undergo an increase with the increase in the number of electrons to be removed. This is due to the reason that second electron is removed from a positively charged ion rather than a neutral atom. The dominant positive charge holds the electrons more tightly and thus further removal of electrons becomes more difficult.

Ionization energy is an index to the metallic character. The elements having low ionization energies are metals and those having high ionization energies are non-metals. Those with intermediate values are mostly metalloids.

The gaps in the first, second, third and higher ionization energies help us to guess the valency of an element. If, there is sufficient gap between first ionization energy and second one, then the element shows valency of one.

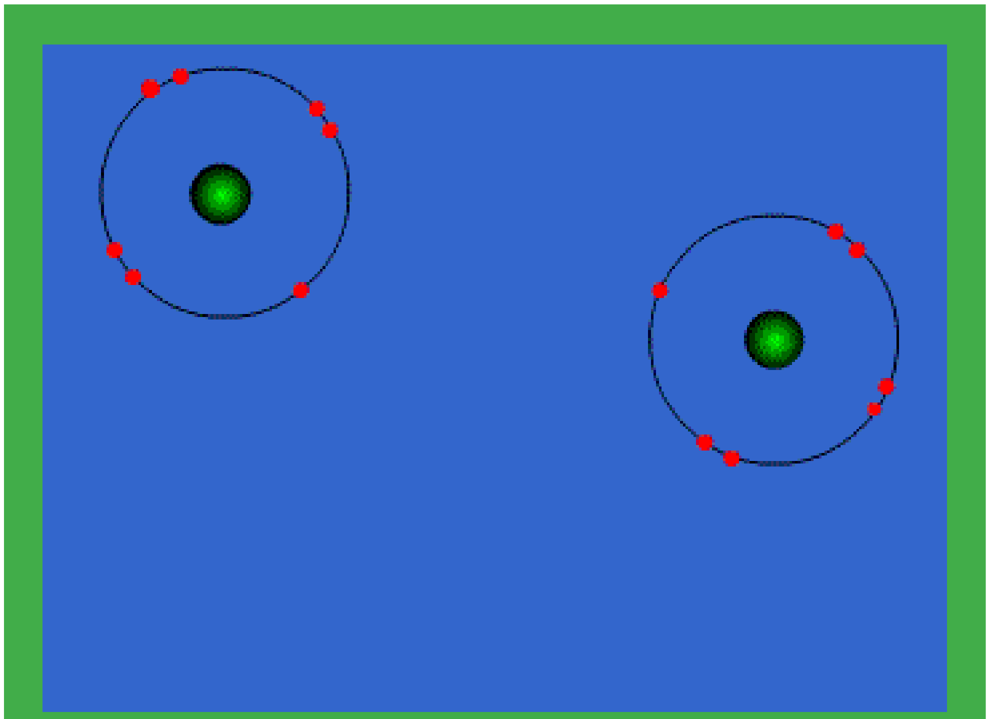


Animation 6.12: Higher Ionization Energies
Source & Credit : 800mainstreet

6.3.2 Electron Affinity

The electron affinity of an atom is the energy released when an electron adds to an empty or partially filled orbital of an isolated gaseous atom in its valence energy level to form an anion having a unit negative charge, e.g.

$$Cl(g) + e^- \rightarrow Cl^-(g) \qquad \Delta H = -349 kJmol^{-1}$$

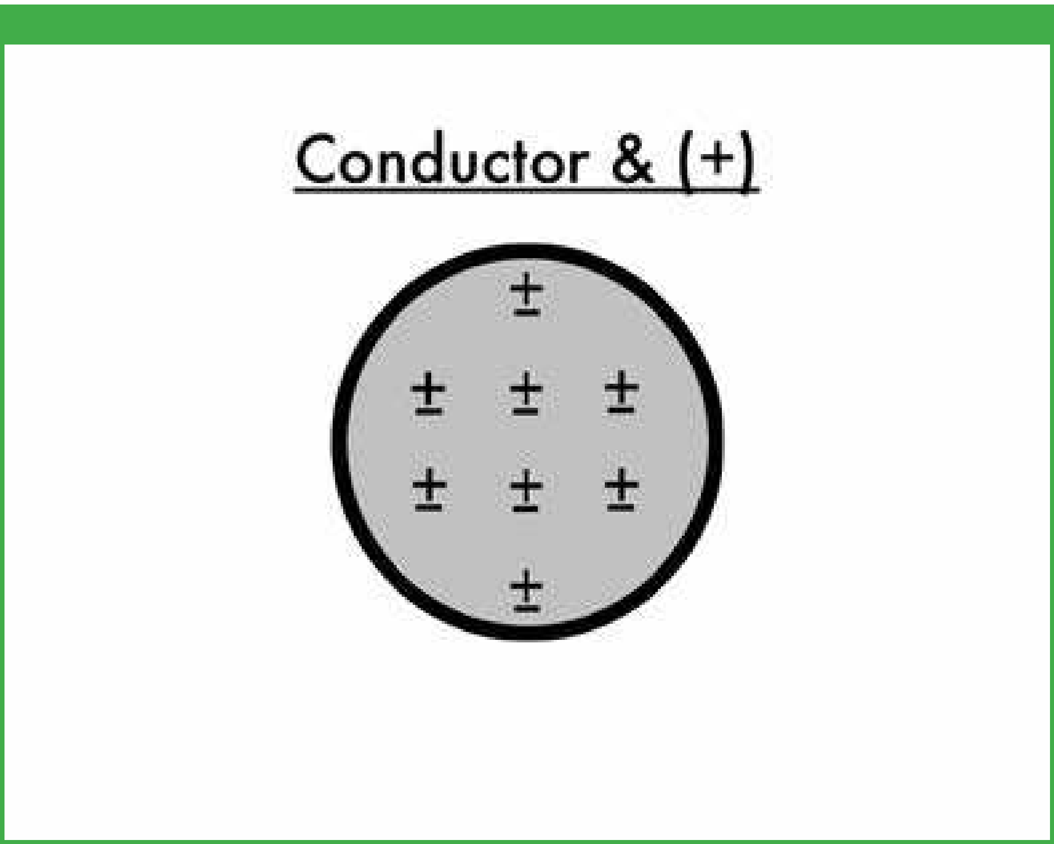


Animation 6.13: Electron Affinity
Source & Credit : hcchrisp.blogspot

Since, energy is released, so electron affinity is given the negative sign. Electron affinity is the measure of the attraction of the nucleus of an atom for the extra electron. The electron affinities of elements of the periodic table are given in Table (6.3).

Factors Influencing the Electron Affinity

The electron affinities, like ionization energies, are influenced by the factors such as atomic radius, the nuclear charge and the shielding effect of inner electrons.



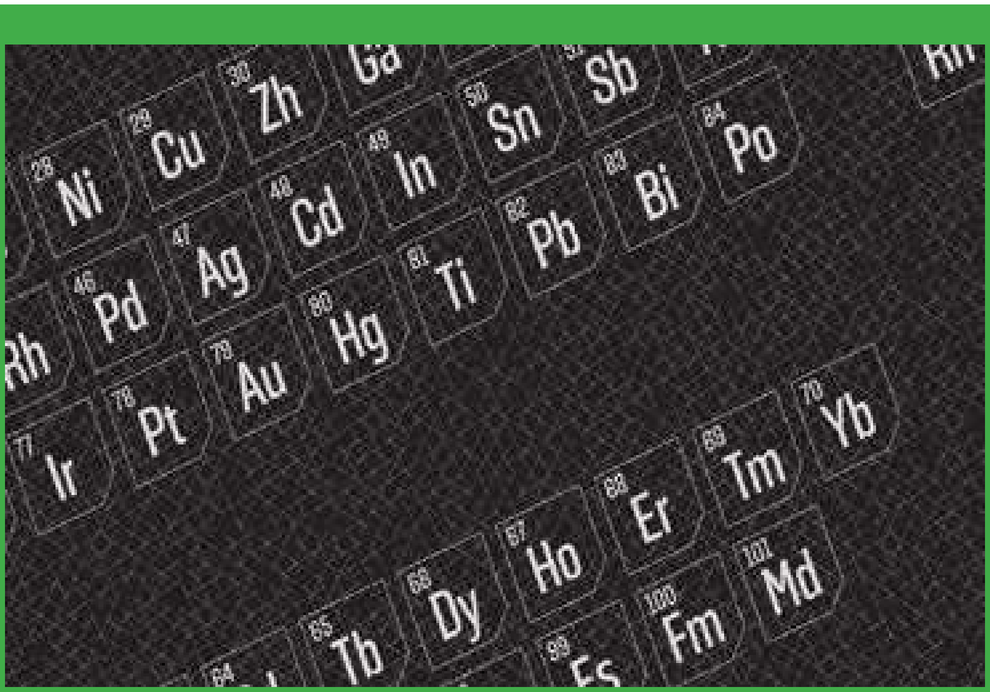
Animation 6.14: Factors Influencing the Electron Affinity
Source & Credit : northhillsprep

As the force of attraction between the valence electrons and the nucleus decrease with the increase in the atomic radius, the electron affinities usually decrease.

Variation in the Periodic Table

In a period, the atomic radius decreases due to increase in the nuclear charge. Thus, the electron affinities of elements increase from left to right in the periodic table. That is why, the alkali metals have the lowest and the halogens have the highest electron affinities. In groups, on the other hand, the atomic radii increase with the increase in the proton number due to successive increase of electronic shells.

This also exerts a shielding effect on the force of attraction between the nucleus and the valence electrons. Thus, the electron affinities usually decrease from top to bottom.



Animation 6.15: Variation in the Periodic Table
Source & Credit : vocativ

There are, of course, exceptions to this generalization e.g. fluorine has electron affinity less than that of chlorine, Table (6.3). Actually, fluorine has very small size and seven electrons in 2s and 2p subshells have thick electronic cloud. This thick cloud repels the incoming electron.

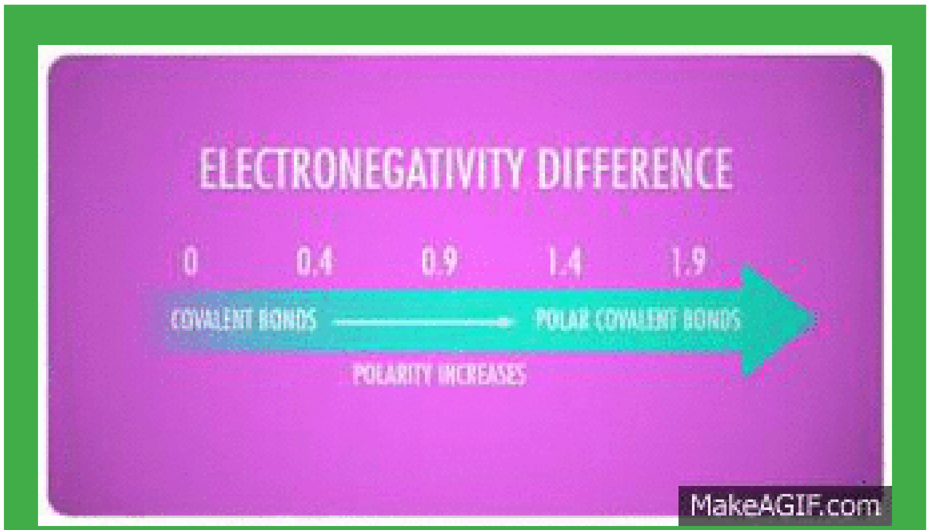
The elements of group IIA, VA and VIII show abnormally low values in every period of the periodic table. This can be understood from their electronic configurations.

6.3.3 Electronegativity

For a homonuclear diatomic molecule e.g. H_2, the bonding pair of electrons is equally shared between the atoms. On the other hand, in a bond between dissimilar atoms such as in HF the electron density of the bonding electrons lies more towards the fluorine atom than towards the hydrogen atom. The tendency of an atom to attract a shared electron pair towards itself is called its electronegativity.

It is related to the ionization energy and the electron affinity of the element. Thus, fluorine atom is more electronegative than hydrogen atom. Pauling calculated the electronegativity values of elements from the difference between the expected bond energies for their normal covalent bond and the experimentally determined values.

He devised an electronegativity scale on which fluorine is given an arbitrary standard value 4.0. It is the most electronegative element. The electronegativity values of other elements are compared with fluorine, and are given in Table (6.3). Electronegativity has no units.



Animation 6.16: Electronegativity
Source & Credit : makeagif

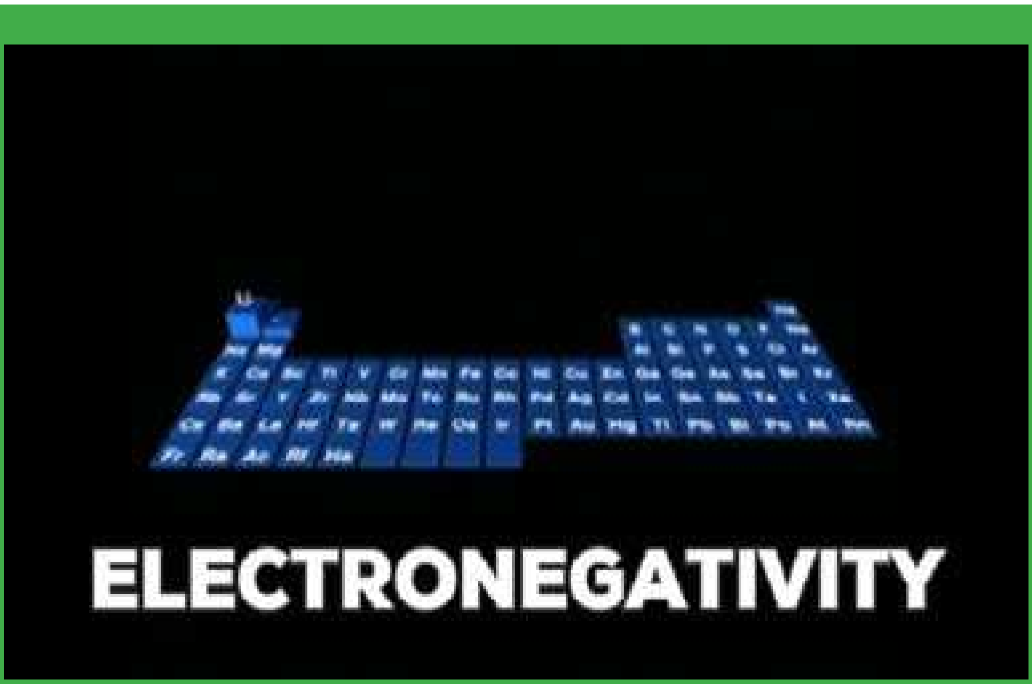
Variation of Electronegativities in Periodic Table

A comparison of electronegativities shows that the values increase in a period with the decrease in atomic size. These values decrease in a group as the size of the atoms increase. The electronegativity differences of the elements can be related to the properties of bonds such as dipole moments and bond energies.

The difference in the electronegativity values of the bonded atoms is an index to the polar nature of the covalent bond. When the difference is zero, the bond between the two atoms is non-polar. Thus, all the bonds which are formed between similar atoms are nonpolar in character, while those formed between different elements are mostly polar. Elements of widely different electronegativities form ionic bonds.

A difference of 1.7 units shows roughly equal contributions of ionic and covalent bonds. Some examples of polar and non-polar bonds are discussed under covalent bond in section 6.4.1.

Having understood the periodic properties of elements, let us discuss types of bonds.



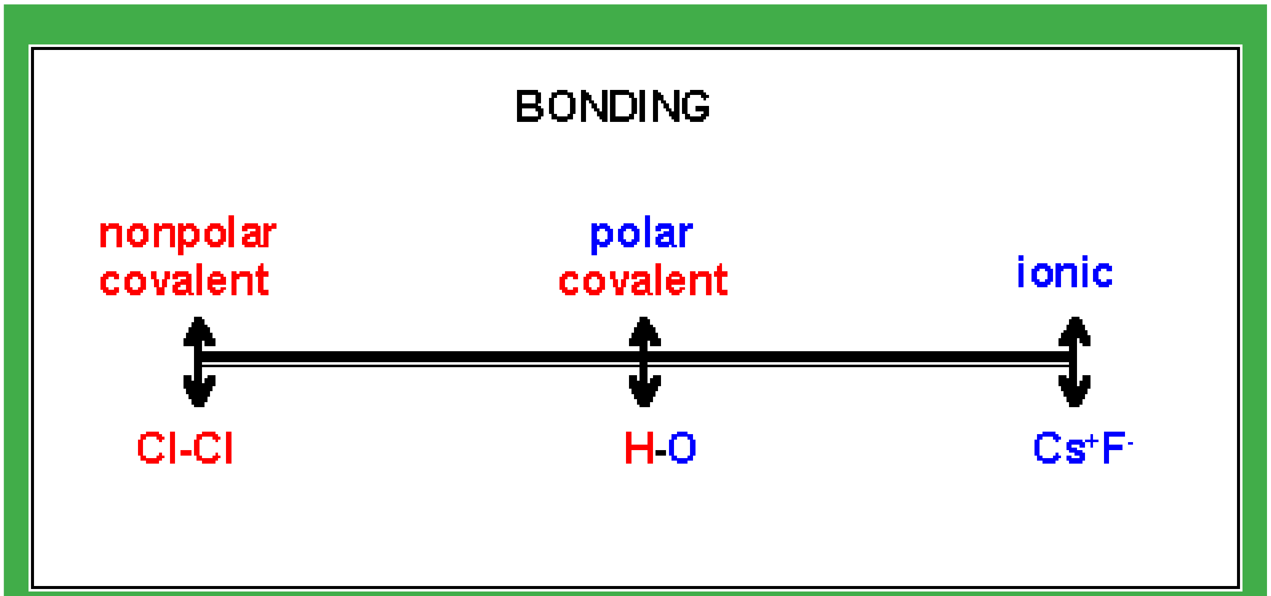
Animation 6.17: Variation of Electronegativities in Periodic Table
Source & Credit : kaiserscience.wordpress

6.4 TYPES OF BONDS

Chemical bonds can be classified as :

(i) Ionic bond
(ii) Covalent bond
(iii) Coordinate covalent bond

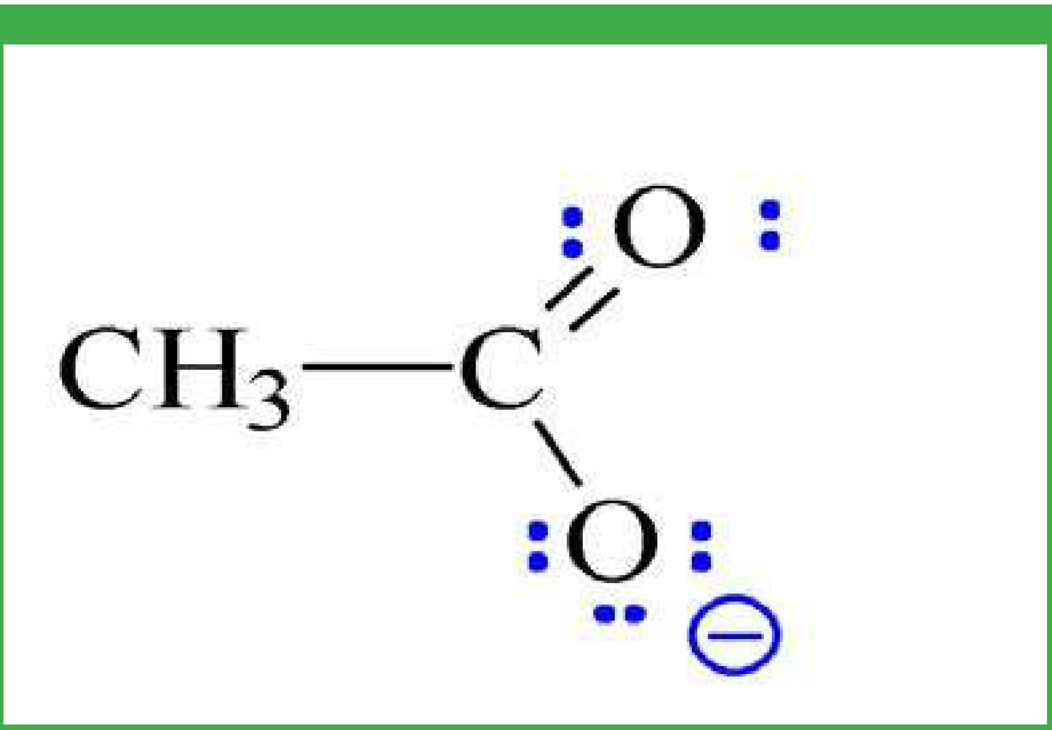
We shall explain these bonds with the help of different theories of chemical bonding. First of all let us discuss the Lewis concept of bond formation.



Animation 6.18: TYPES OF BONDS
Source & Credit : employees.csbsju

6.4.1 LEWIS CONCEPT

With the help of this concept, we can understand the tendencies of elements to have relation with each other.



Animation 6.19: LEWIS CONCEPT
Source & Credit : nku

(i) Ionic Bond

According to the Lewis theory, ionic bond is formed by the complete transfer of electron or electrons from an atom with low ionization energy to another atom with high electron affinity. In energy terms, the electropositive elements are at a higher energy state than the electronegative elements. The energy difference will be responsible for the transfer of electrons from a higher energy state to a lower energy state.

Let us consider, the example of the formation of potassium chloride. The electronic configuration of potassium is $Is^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$. It may be represented as K (2,8,8,1). It tends to lose the outermost electron and to form K^+ ion. The energy needed to detach an electron from potassium atom is equal to its first ionization energy. So

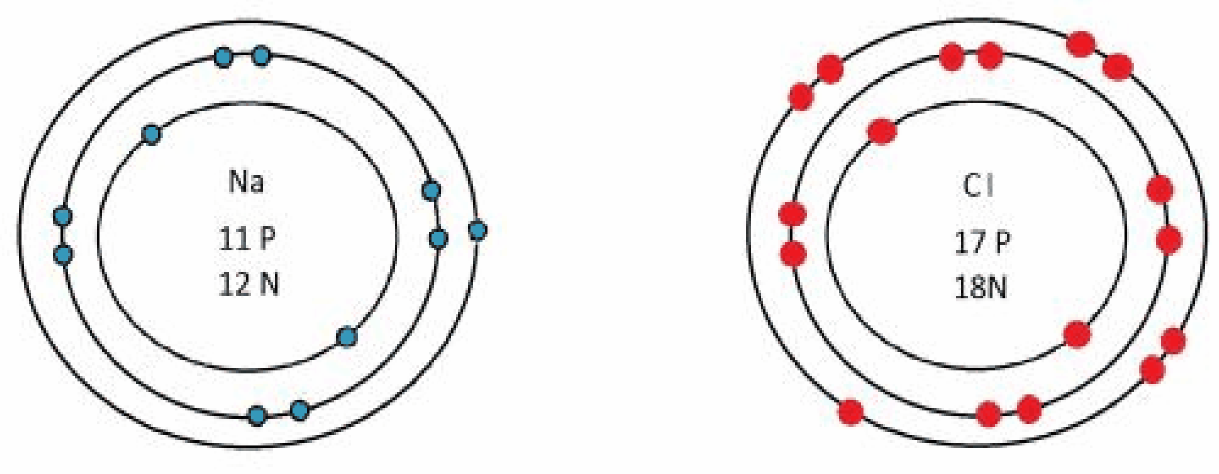
$$K(2,8,8,1) \rightarrow K^{+}(2,8,8) + e^{-} \qquad \Delta H = 419.0 kJmol^{-1}$$

The oppositely charged K^+ and Cl^- ions are held together by strong electrostatic force of attraction. K^+ and Cl^- ions arrange themselves to form a crystal lattice where proportionate number of cations and anions are packed together. The energy released during the formation of crystal lattice is 690 $kJmol^{-1}$. It is called lattice energy of KCl.

After the loss of an electron, potassium attains the nearest inert gas configuration of Ar (2,8,8). Chlorine atom has the electronic configuration $Is^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$ or Cl (2,8,7). It tends to gain electron lost from potassium atom to attain the nearest inert gas configuration of Ar (2,8,8) releasing 348.6 $kJmol^{-1}$ energy. This energy corresponds to the electron affinity of chlorine.

$$:\underset{..}{\ddot{C}}l\cdot + e^{-} \rightarrow :\underset{..}{\ddot{C}}l^{-} : \qquad \Delta H = -349 kJmol^{-1}$$

Similarly, the elements of I-A Li, Na, K, Rb, Cs are good losers of electron. The elements of VII-A, F, Cl, Br, I are good gainers. So, ionic bonds are there in these atoms. A similar type of bond is expected between elements of group II-A and VI-A.



Animation 6.20: Ionic Bond
Source & Credit : gcsechemistryhelp.tumblr

In most of the cases the formation of dipositive, tripositive and dinegative ions takes place as follows:

$$\mathbf{Ca\ (2,8,8,2) \longrightarrow Ca^{2+}\ (2,8,8) + 2e^-}$$
$$\mathbf{Al\ (2,8,3) \longrightarrow Al^{3+}\ (2,8) + 3e^-}$$
$$\mathbf{O\ (2,6) + 2e^- \longrightarrow O^{2-}\ (2,8)}$$
$$\mathbf{S\ (2,8,6) + 2e^- \longrightarrow S^{2-}\ (2,8,8)}$$

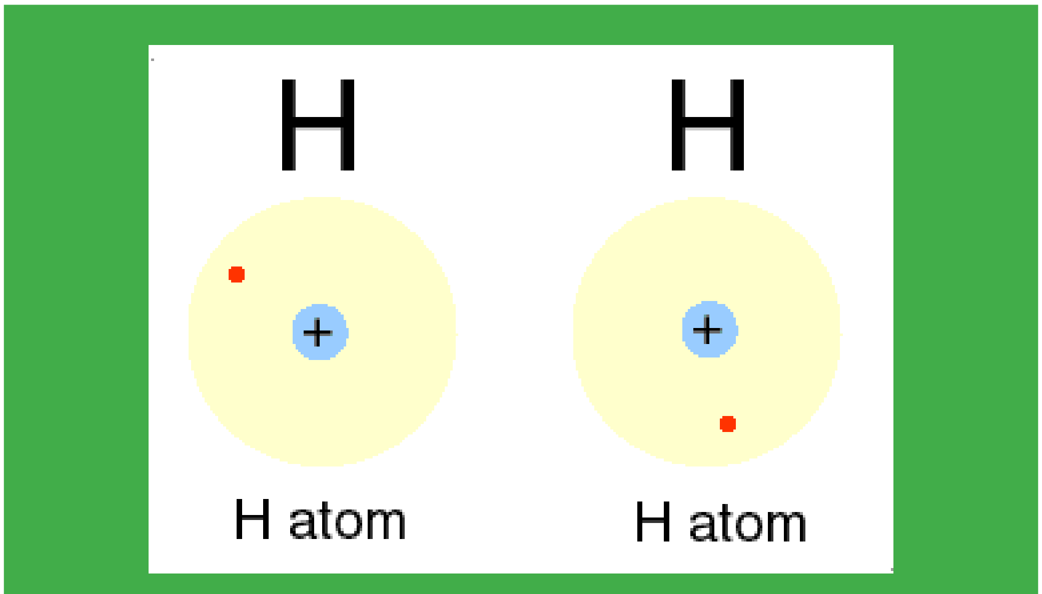
Calcium oxide contains ions in the ratio of Ca^{2+} : O^{2-} and its formula is CaO, while in aluminium oxide, Al^{3+} and O^{2-} ions are present in the ratio 2 :3. Its formula is Al_2O_3. Similarly, CaS and Al_2S_3, are also ionic compounds to some extent.

The compounds formed by the cations and anions are called ionic or electrovalent compounds. There exists a strong electrostatic force of attraction between cations and anions in these compounds.

Criteria of electronegativity also helps us to understand the nature of bond. So, in order to decide the % of ionic nature in a compound, it is better to note the difference of electronegativity between the bonded atoms. If the difference is 1.7 or more than that, then the bond is said to be ionic. Keeping this aspect in view, NaCl has 72% ionic character. CsF has 92% ionic character and calculations tell us that there is no bond with 100% ionic character.

(ii) Covalent Bond (electron pair bond)

According to Lewis and Kossel, a covalent bond is formed by the mutual sharing of electrons between two atoms. While sharing, each atom completes its valence shell and attains the nearest inert gas configuration. A covalent bond may be non-polar or polar in character.



Animation 6.21: Covalent Bond (electron pair bond)
Source & Credit : edcoogle

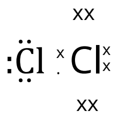
Non-Polar Covalent Bonds

In such bonds, the bonding electron pairs are equally shared. For example, in H_2 or Cl_2 molecules, the two electrons forming the covalent bond are equally shared by the two identical atoms having same electronegativities.

Hydrogen

H : H or H - H

Chlorine

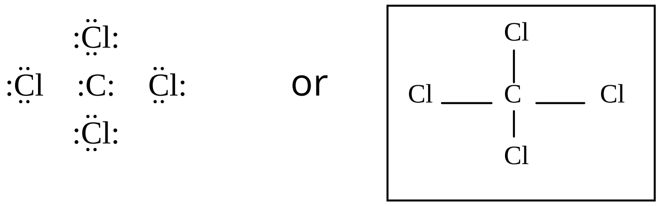


$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}\,\overset{\times}{\underset{\cdot}{}}\,\overset{\times\times}{\underset{\times\times}{Cl}}{}^{\times}_{\times}$ or Cl----Cl

Due to an even distribution of charge, the bonded atoms remain electrically neutral.The other such molecules are F_2, Br_2 and I_2.Similarly, CCl_4 is a non-polar compound. This is due to cancellation of all the dipoles of this molecules due to its symmetry. Actually, all the C-Cl bonds are polar, but molecule is non-polar overall.

Animation 6.22: Non-Polar Covalent Bonds
Source & Credit : bsc2.ehb-schweiz2

Tetrachloromethane



The molecules like CH_4, SiH_4, and $SiCl_4$ also follow the same attitude of non-polarity due to symmetry of structure.

Polar Covalent Bonds

When two different atoms are joined by a covalent bond, the electron pair is not equally shared between the bonded atoms. The bonding pair of electrons will be displaced towards the more electronegative atom

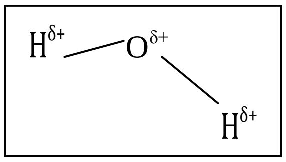
This would make one end of the molecule partially positive and the other partially negative as shown by the following examples.

Hydrogen fluoride

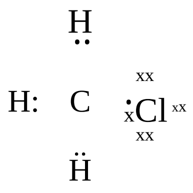
$H\times\ddot{\underset{\cdot\cdot}{F}}:$ or $H^{\delta+}\,x\;F^{\delta-}$

Water

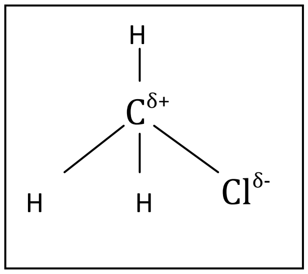
$H\dot{\times}\ddot{\underset{\cdot\cdot}{O}}\dot{\times}H$



Methyl chloride

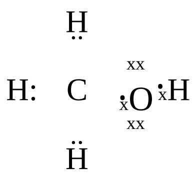


or



Methanol is an other best example of a polar covalent molecule, because it contains a polar bond.

Methanol



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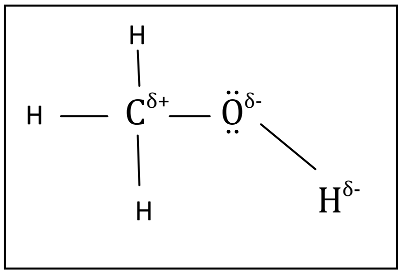


An atom can share more than one electrons to form what is called a double or triple bond. The examples are O_2, N_2, CO_2, CS_2, etc.

N_2 is an inert gas having a strong triple bond.

Nitrogen

$:N:::N:$ or $:N\equiv N:$

The molecule: of 0_2 makes a double bond.

Oxygen

Ö̤::Ö̤ or Ö̤=Ö̤

Here, carbon dioxide is a non-polar covalent compound, although it is formed from heteroatoms. The linear structure balances the polar character on both sides of the carbon atom.

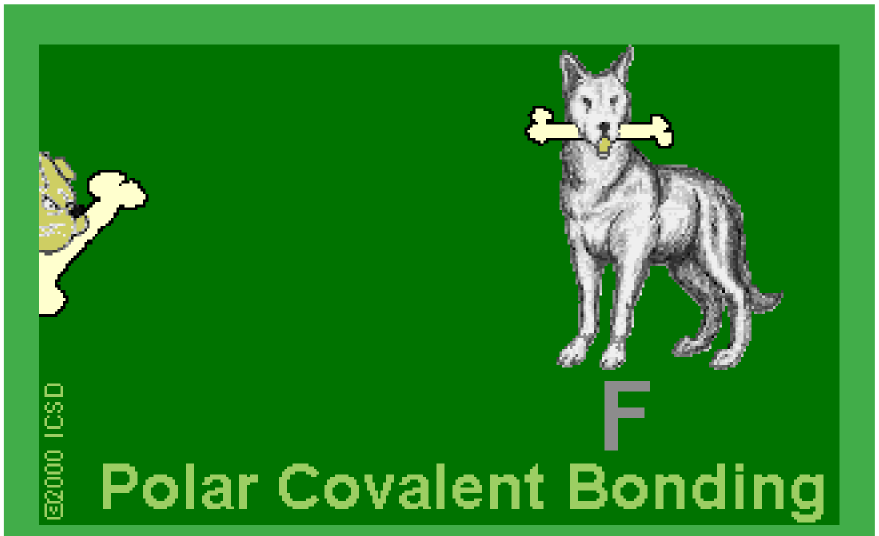
Carbon dioxide

:Ö::C::Ö: or Ö̤=C=Ö̤

Here, each bond represents a pair of electrons. Thus, in the formation of a double bond (=), two shared pairs and in that of a triple bond (≡), three shared pairs of electrons are involved.

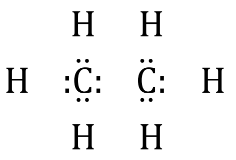
Some of the non-metallic atoms, particularly carbon atoms mutually share their electrons with each other. This leads to the formation of extended chains which is the basis of the formation of large sized molecules called macromolecules. Diamond, graphite and SiC are the best examples of such molecules.

Carbon can make single, double and triple covalent bonds in alkanes, alkenes and alkynes.



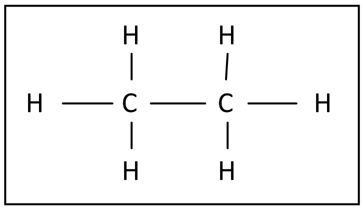
Animation 6.23: Polar Covalent Bonds
Source & Credit : bsc2.ehb-schweiz2

Ethan



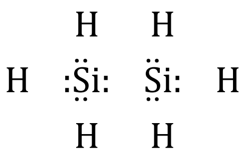
$$\begin{array}{cccc} & H & H & \\ H & :\ddot{\underset{..}{C}}: & \ddot{\underset{..}{C}}: & H \\ & H & H & \end{array}$$

or



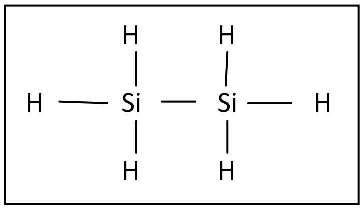
Silicon also gives similar type of hydrides, called silanes. The formula of disilane is like that of ethane.

Disilane



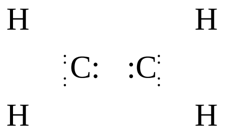
$$\begin{array}{cccc} & H & H & \\ H & :\ddot{\underset{..}{Si}}: & \ddot{\underset{..}{Si}}: & H \\ & H & H & \end{array}$$

or



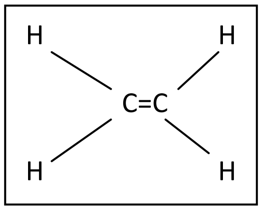
The compounds of carbon and hydrogen showing double and triple bonds are called alkenes and alkynes. Let us, take the examples of ethene and ethyne.

Ethan



$$\begin{array}{cccc} H & & & H \\ & \vdots C: & :C\vdots & \\ H & & & H \end{array}$$

or



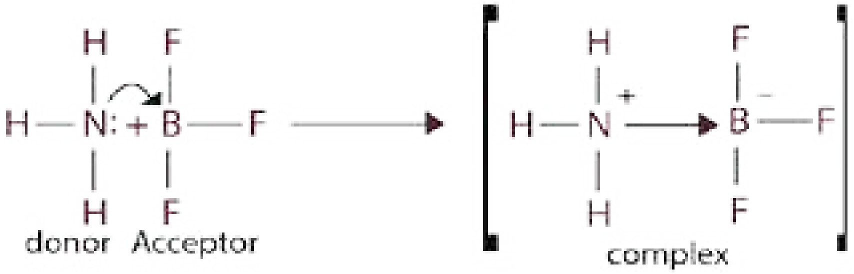
Ethan

$H:C:::C:H$ or $H\text{-}C\equiv C\text{-}H$

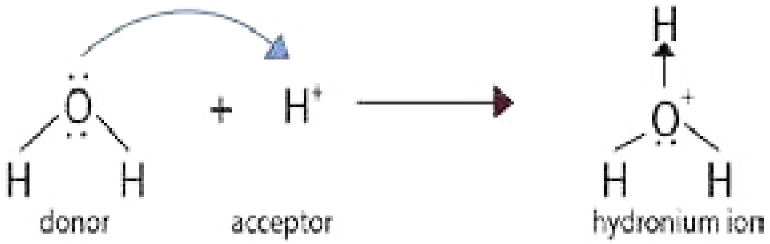
(iii) Coordinate Covalent Bond

A coordinate covalent bond is formed between two atoms when the shared pair of electrons is donated by one of the bonded atoms. Let us consider, the example of bond formation between NH_3 and BF_3. NH, has three covalent bonds and there is a lone pair of electrons on nitrogen atom. On the other hand, boron atom in BF_3 is deficient in electrons. Actually, the octet of B is not complete in BF_3. Therefore, nitrogen can donate the pair of electrons to the acceptor BF_3 and this results in the formation of a coordinate covalent bond.

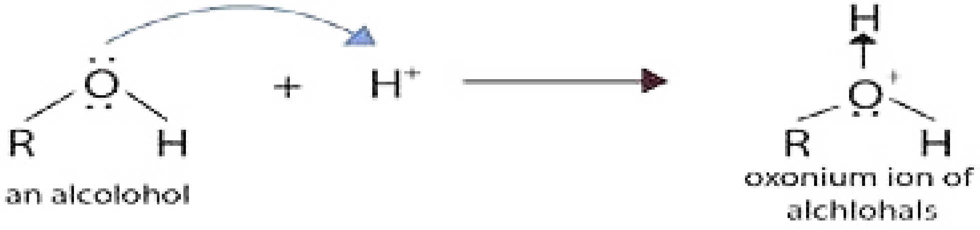
The complex so produced is overall neutral, and charges are indicated on N and B atoms. In some of the compounds, after the formation of a coordinate covalent bond, the distinction between covalent bond and coordinate bond vanishes.

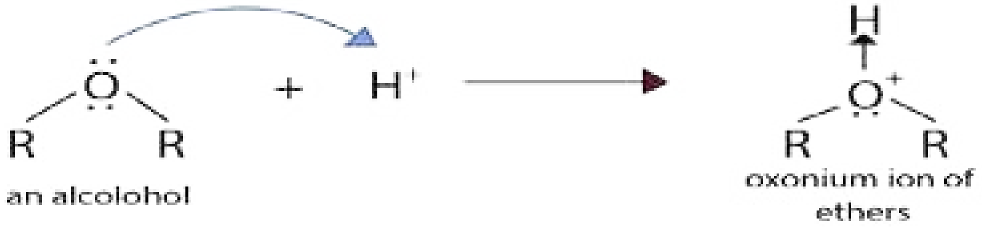


Water donates its electron pair to H^+ ion to give H_30^+ ion. All the three bonds between oxygen and hydrogen have equal status. Every bond is 33% coordinate covalent and 66% covalent.

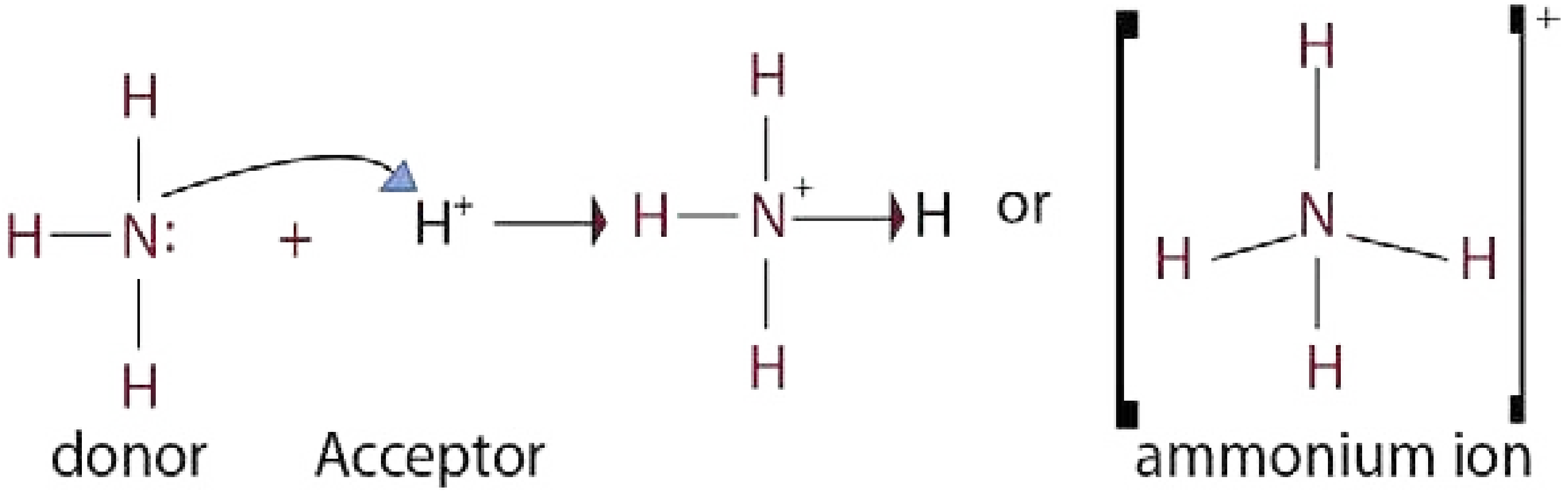


Similarly, all the alcohols and ethers offer their lone pairs to H^+, just like water to give coordinate covalent bonds. The ions so produced are called oxonium ions.





Ammonia donates its electron pair to H^+ ion to give NH_4^+ ion. All the four bonds behave alike, in NH_4^+ion.



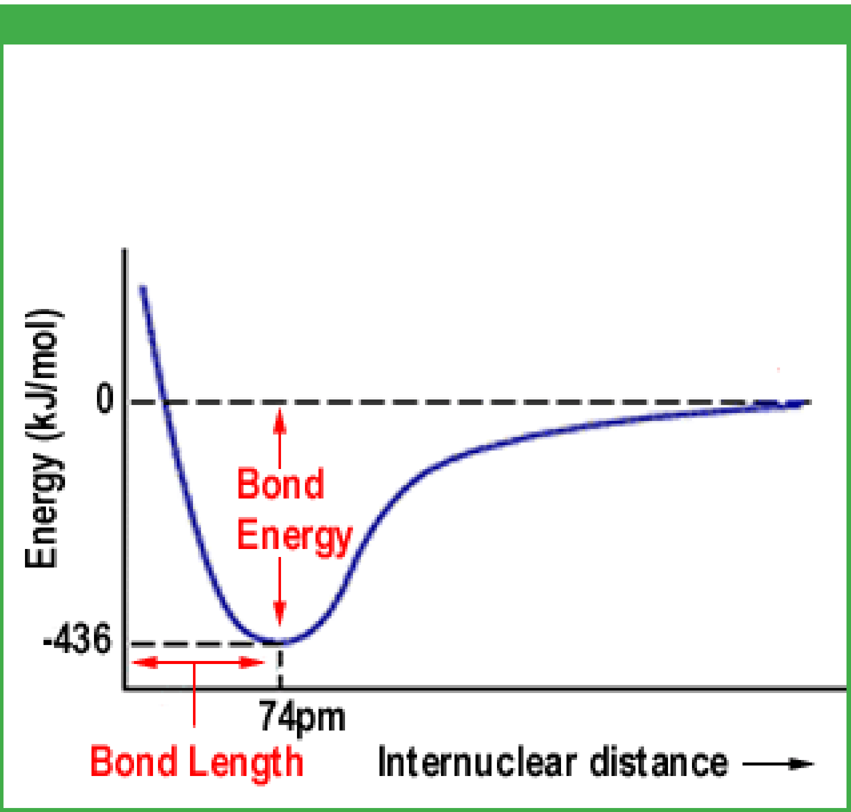
All the primary, secondary and tertiary amines like ammonia make such bonds with H^+. PH_3 combines with H^+ to give PH_4^+ ion called phosphonium ion. Coordinate covalent bonds are present in HNO_3. Many oxyacids of halogens, like ($HClO_2$, $HClO_3$, $HClO_4$) have coordinate covalent bonds between chlorine and oxygen.

6.4.2 MODERN THEORIES OF COVALENT BOND

Limitations of Lewis Model

Classical Lewis model does explain, that how atoms are bonded to one another. It also tells, how the electron pairs are shared between the bonded atoms. But a logical question arises:
Are these explanations just enough to justify the diversified world of molecules and how do the electrons avoid each other inspite of their repulsions?

The answer simply lies in the fact, that the Lewis model seems to be an over simplification. Shapes of molecules are very important because many physical and chemical properties depend upon three dimensional arrangement of their atoms.



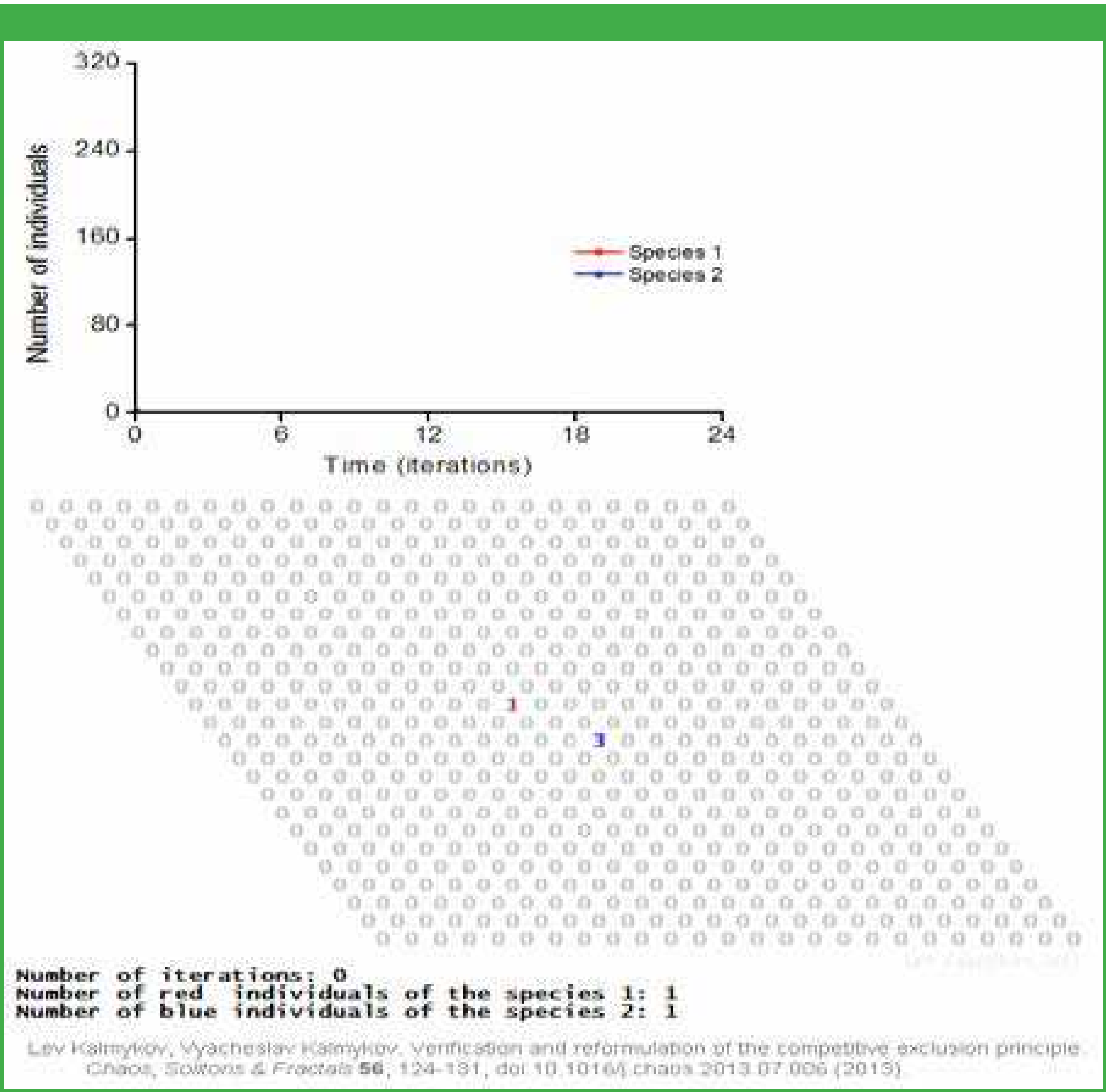
Animation 6.24: MODERN THEORIES OF COVALENT BOND
Source & Credit : chem.umass

A true model should be able to justify molecular shapes and geometries of molecules, bond polarities, bond distances and various energy transitions as evident by spectroscopic techniques. This model should also make clear the unique behaviouria! features of molecules during chemical reactions.

Following are the modern theories, which explain satisfactorily the above requirements for covalent bond formation, based on wave-mechanical structure of atoms:

1. Valence shell electron pair repulsion theory (VSEPR Theory)
2. Valence bond theory (VBT)
3. Molecular orbital theory (MOT)

In addition to above, crystal field theory and ligand field theory explain the formation of coordination complex compounds formed by transition metals.



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Number of iterations: 0
Number of red  individuals of the species 1: 1
Number of blue individuals of the species 2: 1
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Lev Kalmykov, Vyacheslav Kalmykov. Verification and reformulation of the competitive exclusion principle. Chaos, Solitons & Fractals **56**, 124-131, doi:10.1016/j.chaos.2013.07.006 (2013)

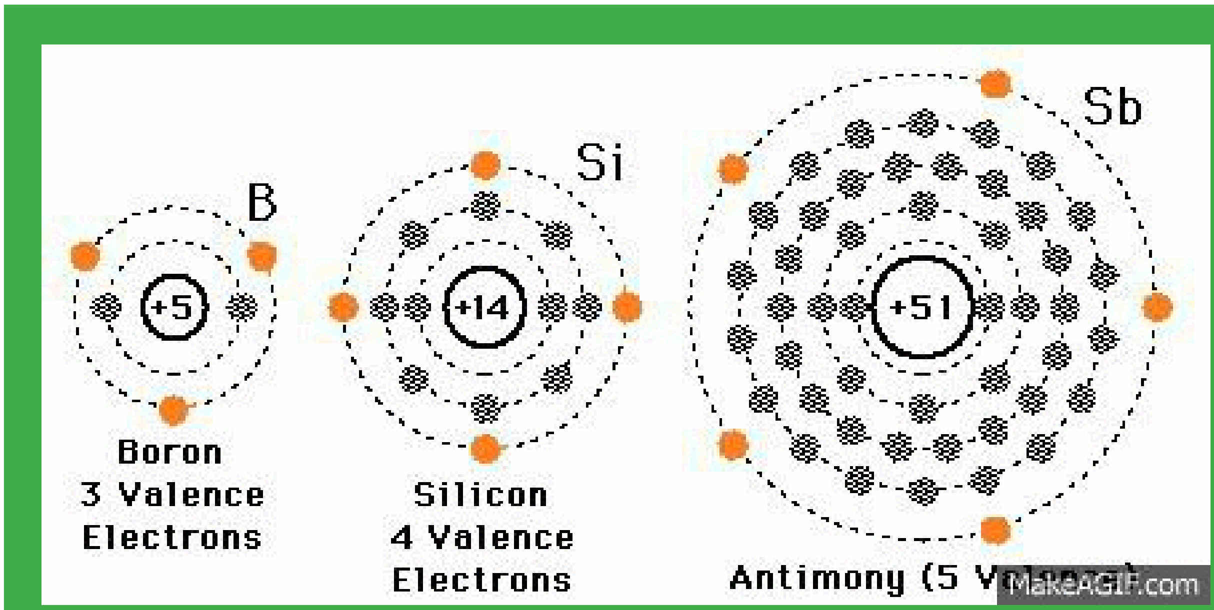
Animation 6.25: Limitations of Lewis Model
Source & Credit : en.wikipedia

6.4.3 VALENCE SHELL ELECTRON PAIR REPULSION THEORY

Sidgwick and Powell (1940) pointed out that the shapes of molecules could be interpreted in terms of electron pairs in the outer orbit of the central atom. Recently, Nylholm and Gillespie developed VSEPR theory, which explains the shapes of molecules for non- transition elements.

Basic Assumption

The valence electron pairs (lone pairs and the bond pairs) are arranged around the central atom to remain at a maximum distance apart to keep repulsions at a minimum.



Animation 6.26: VALENCE SHELL ELECTRON PAIR REPULSION THEORY
Source & Credit : barmaton.info

Postulates of VSEPR Theory

(i) Both the lone pairs as well as the bond pairs participate in determining the geometry of the molecules.

(ii) The electron pairs are arranged around the central polyvalent atom so as to remain at a maximum distance apart to avoid repulsions.

(iii) The electron pairs of lone pairs occupy more space than the bond pairs.

A bonding electron pair is attracted by both nuclei of atoms while non- bonding by only one nucleus. Because a lone pair experiences less nuclear attraction, its electronic charge is spread out more in space than that for bonding pair. As a result, the non- bonding electron pairs exert greater repulsive forces on bonding electron pairs and thus tend to compress the bond pairs.

The magnitude of repulsions between the electron pairs in a given molecule decreases in the following order:

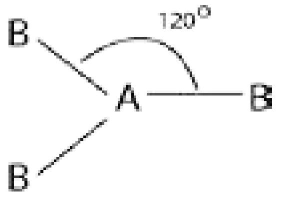
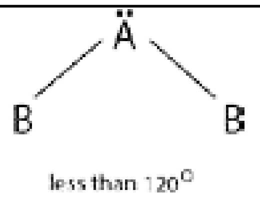
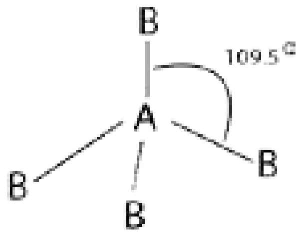
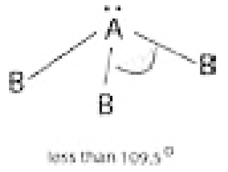
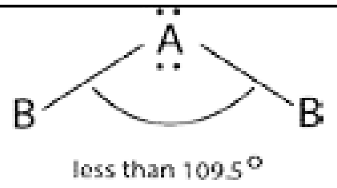
Lone pair- lone pair > lone pair -bond pair > bond pair - bond pair

These repulsions are called van der Waals repulsions

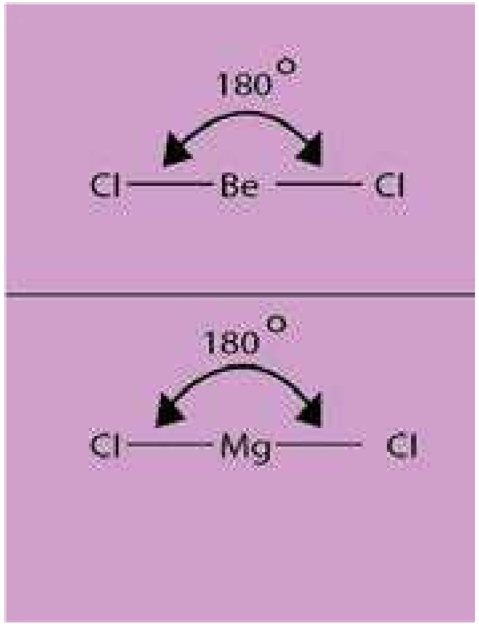
(iv) The two electron pairs of a double bond and three electron pairs of a triple bond, contain a higher electronic charge density. Therefore, they occupy more space than one electron pair of a single bond, but behave like a single electron pair in determining the geometry of the molecule. This is because, they tend to occupy the same region between the two nuclei like a single bond.

In order to illustrate this theory, let us consider, that the central atom is 'A' and this atom is polyvalent. More than one 'B' type atoms are linked with 'A' to give AB_2, AB_3, AB_4, etc. type molecules. It depends upon the valency of A, that how many B are attached with that. Following Table (6.4) gives the shapes of different types of molecules.

Table (6.4) Shapes of molecules according to VSPER Theory

Type	Electron Pairs			Arrangement of pairs	Molecular geometry	Shape	Example
	Total	Bonding	Lone				
AB_2	2	2	0	Linear	Linear	B-A-B	$BeCl_2$ $HgCl_2$
AB_3	3	3	0	Trigonal planar	Trignol planar		BH_3, BF_3 $AlCl_3$
		2	1		Bent (or angular)		$SnCl_2$, SO_2
AB_4	4	4	0	Tetrahedral	Tetrahedral		CH_4, $SiCl_4$, CCl_4, BF_4, NH_4^+, SO_4^{2-}
		3	1		Trignol pyramidal		NH_3, NF_3, PH_3
		2	2		Bent (or angular)		H_2O, H_2S

1 Molecules Containing Two Electron Pairs (AB_2 type)



In such, molecules two electrons, pairs around the central atom are arranged at farther distance apart at an angle of 180°, in order to minimize repulsions between them. Thus, they form a linear geometry.

Beryllium chloride is a typical linear molecule, which contains two electrons pairs. $MgCl_2$, $CaCl_2$, $SrCl_2$. $CdCL_2$ and $HgCl_2$ are also linear molecules. The central atoms have two electrons in outer most orbitals.

2. Molecules Containing Three Electron Pairs – (AB_3 type:)

(a) AB_3 Type with no Lone Pairs

In such molecules, central atom contains three bonding electron pairs, which are arranged at maximum distance apart at a mutual angle of 120°, giving a triangular planar geometry. The boron atom in BH_3 is surrounded by three charge clouds, which remain farthest apart in one plane, each pointing towards the corners of an equilateral triangle. Thus, BH_3, molecules has a trigonal planar geometry, with each H- B-H bond angles of 120°.

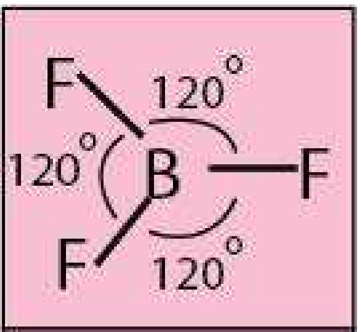
We expect similar geometries in hydrides of group III-A (AlH_3, GaH_3, InH_3 and TlH_3)and their halides (BF_3, $AlCl_3$,etc.)

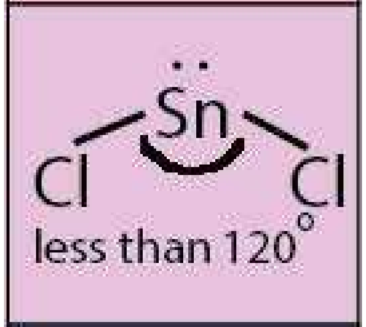
(b) AB_3-Type with One Lone Pair and Two Bond Pairs

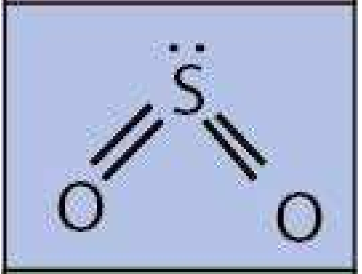
In $SnCl_2$, one of the corner of the triangle is occupied by a lone pair, giving rise to a distorted triangular structure in vapour phase.

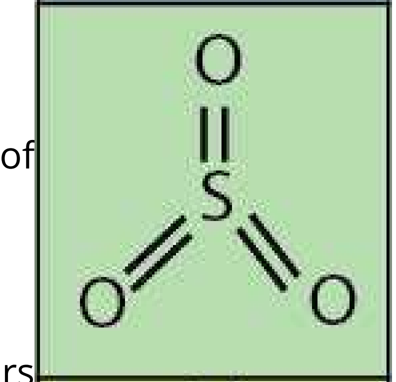
(c) AB_3-Type with Multiple Bonds

In SO_2, one corner of triangle is occupied by a lone pair and two corners each by S=O double bond, while in SO_3 all three regions, each are occupied by S = O bonds. This structure of SO_3 is perfectly triangular.









(iii) Molecules Containing Four Electron Pairs (AB_4- Type:)

(a) AB_4 Type with no Lone Pairs

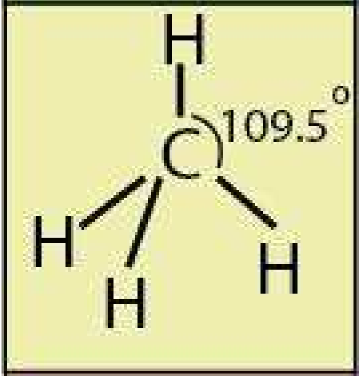
The charge clouds due to four electron pairs avoid their electrostatic repulsions by drifting apart, so as to maintain a mutual bond angle of 109.5 °. Such geometry enables to a form a shape of regular tetrahedron.

Examples:

Each of the four valence electrons of carbon pair up with sole electron of hydrogen in methane.

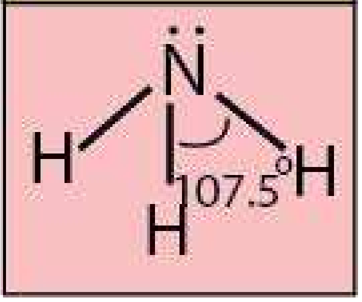
$$_6C = 1s^2, 2s^1, 2px^1, 2py^1, 2py^1$$

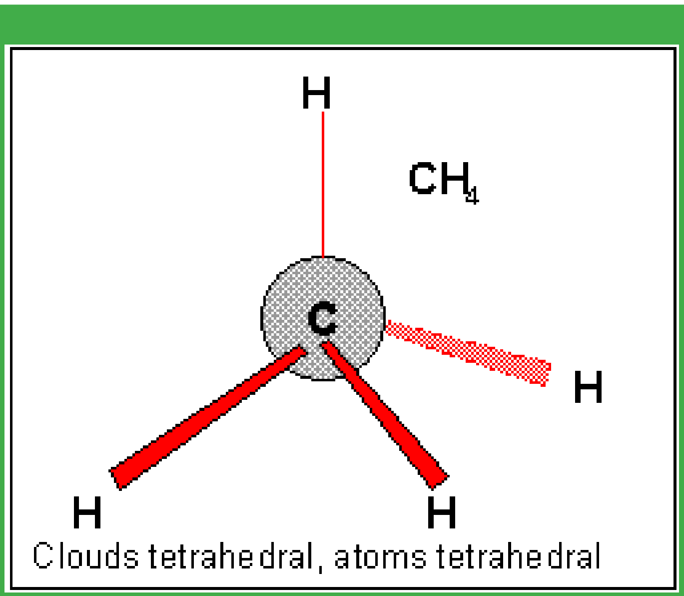
The four electron pairs are directed from the center towards the corners of a regular tetrahedron, with each apex representing a hydrogen nucleus. The arrangement permits a non-planar arrangement of electron pairs. Each H-C-H bond is perfectly 109.5 °. On the same grounds, SiH_4, GeH_4, CCl_4 form similar geometries. This structure has four corners, four faces, six edges and six bond angles.



(b) AB_4 - Type with One Lone Pair and Three Bond Pairs

In such cases, the charge cloud of lone pair electrons (nonbonding electrons) spreads out more than that of bonding electrons.





Animation 6.27: Molecules Containing Two Electron Pairs (AB2 type)
Source & Credit : employees.csbsju

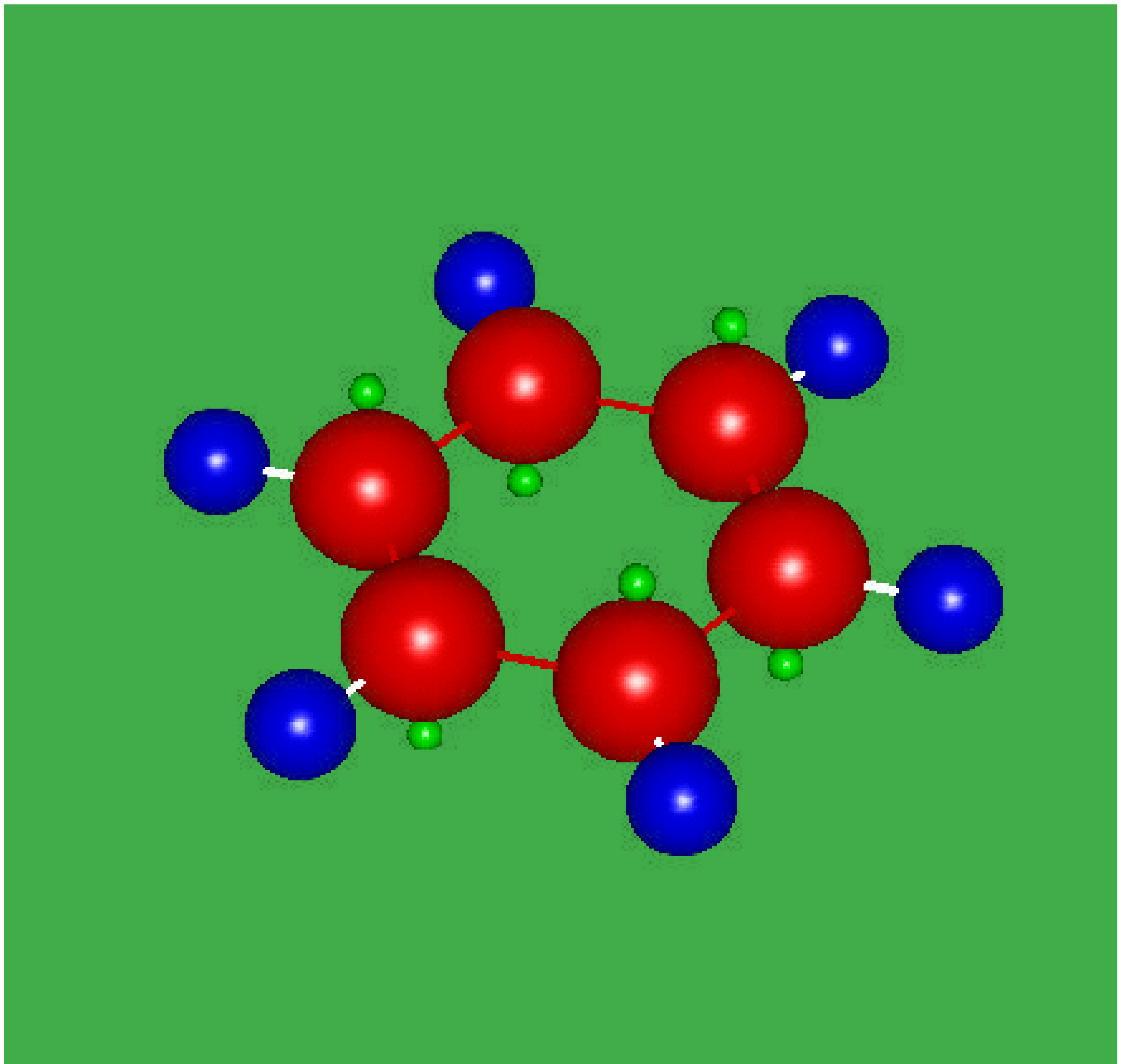
As a result, some what large lone pair charge cloud tend to compress the bond angles in rest of the molecules.

Ammonia, $\ddot{N}H_3$ is a typical example.

$_7N = 1s^2, 2s^2, 2p_x^{\ 1}, 2p_y^{\ 1}, 2p_z^{\ 1}$

The non-bonding electron in 2s orbital takes up more space and exerts a strong repulsive force on the bonding electron pairs. Consequently, to avoid a larger repulsion, the bonding electron pairs move closer that reduces the ideal bond angle from 109.5^0 to 107.5°. This effect compels ammonia to assume a triangular pyramidal geometry instead of tetrahedral, as in methane.

Similar, affects are evident in the geometries of molecules like $\ddot{P}H_3, \ddot{A}sH_3, \ddot{S}bH_3$ and $\ddot{B}iH_3$. Substitution of hydrogen with electronegative atoms like F or Cl further reduces the bond angle. In NF_3, the strong polarity of N-F bond pulls the lone pair of N atom closer to its nucleus, which in turn exerts a stronger repulsion over bonding electrons. Thus, the angle further shrinks to 102°. Moreover, the bond pairs N-F bonds are more close to F atoms than N atoms. The increased distances in these bond pairs makes their repulsions less operative.



Animation 6.28: Molecules Containing Three Electron Pairs — (AB;i type:)
Source & Credit : nano-ou

(c) AB_4-Type with Two lone Pairs and Two Bond Pairs:

Presence of two lone pairs, introduces three types of repulsion i.e. lone pair-lone pair, lone pair-bond pair and bond pair-bond pair repulsion. For example: water (H_2O), a triatomic molecule is expected to be an AB_2 type linear molecule like $BeCl_2$ and CO_2. But, experimental evidences confirm a bent or angular geometry. VSEPR theory, successfully justifies the experimental results by arguing the participation of lone pairs, in addition to bond pairs in determining overall geometry of water molecule.

$$_8O = 1s^2, 2s^2, 2p^2_x, 2p^1_y, 2p^1_z$$

Two of the corners of a tetrahedron are occupied by each of the two lone pairs and remaining by bond pairs. But owing to spatial arrangement of lone pairs and their repulsive action among themselves and on bond pairs, the bond angle is further reduced to 104.5°. H_2S, H_2Se, H_2Te form similar geometries.

6.4.4 Valence Bond Theory (VBT)

VSERP theory predicts and explains the shapes of molecules but does not give reasons for the formation of bonds. VBT is concerned with both the formation of bonds and the shapes of molecules. This method of describing a covalent bond considers the molecule as a combination of atoms. According to the quantum mechanical approach, a covalent bond is formed when half-filled orbitals in the outer or valence shells of two atoms overlap, so that a pair of electrons, one electron from each atom, occupies the overlapped orbital, As a result of this overlap, the electrons with opposite spins become paired to stabilized themselves.

Larger the overlap, the stronger is the bond. The essential condition for chemical bonding, is that the orbitals of atoms participating in bond formation must overlap and the direction of the bond is determined by the direction of the two overlapping orbitals.

The formation of few molecules as a result of s and s orbital overlap, s and p orbital overlap and p and p orbital overlap are discussed below.

The formation of a hydrogen molecules according to VB theory is shown in Fig. (6.4). As the two atoms approach each other, their 1s orbitals overlap, thereby giving the H-H bond.

Fig. (6.4) s and s orbital overlap in H_2

The electron density becomes concentrated between the two nuclei. The bond is called a sigma (σ) bond and it is defined as follows:

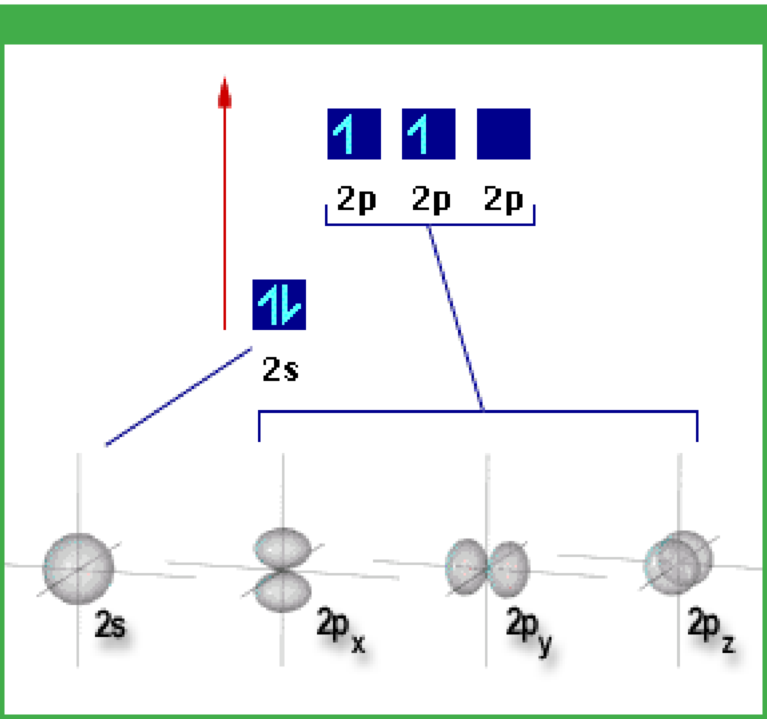
A single bond is formed when two partially filled atomic orbitals overlap in such a way that the probability of finding the electron is maximum around the line joining the two nuclei.

Let’s look at a molecule hydrogen fluoride, HF. The H-F bond is fomed by the pairing of electrons - one from hydrogen and one from fluorine. According to VB theory, we must have two half-filled orbitals - one from each atom that can be joined by overlap.

$$_1H = \overset{\boxed{\uparrow}}{1s}$$

$$_9F = \overset{\boxed{\uparrow\downarrow}}{2s}\,\overset{\boxed{\uparrow\downarrow}}{2p_x}\,\overset{\boxed{\uparrow\downarrow}}{2p_y}\,\overset{\boxed{\uparrow}}{2p_z}$$

The overlap of orbitals provides a means for sharing electrons, thereby allowing each atom to complete its valence shell. The fluorine atom completes its 2p subshell by acquiring a share of an electron from hydrogen as shown below.



Animation 6.29: Valence Bond Theory (VBT)
Source & Credit : chem.umass

$$_9F = \overset{\boxed{\uparrow\downarrow}}{2s}\,\overset{\boxed{\uparrow\downarrow}}{2p_x}\,\overset{\boxed{\uparrow\downarrow}}{2p_y}\,\overset{\boxed{\uparrow\downarrow}}{2p_z}$$

The requirements for bond formation are met by overlapping the half-filled Is orbital of hydrogen with the half-filled 2p orbital of fluorine. There are then two orbitals plus two electrons whose spins can adjust so they are paired. The formation of the bond is illustrated in Fig.(6.5)

The bond in the fluorine molecule, F_2 is formed by the overlap of half-filled $2p_z$ orbital on each fluorine atom,Fig (6.6).

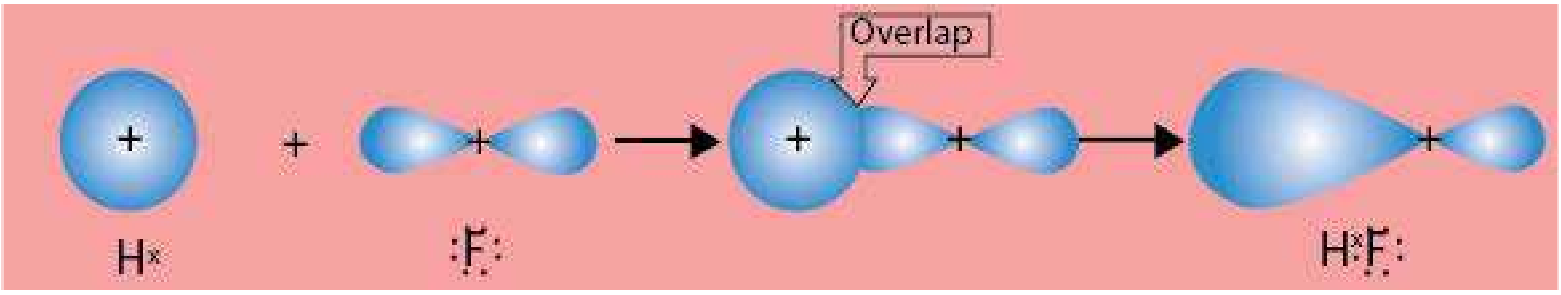


Fig. (6.5) The formation of the hydrogen fluoride molecules.

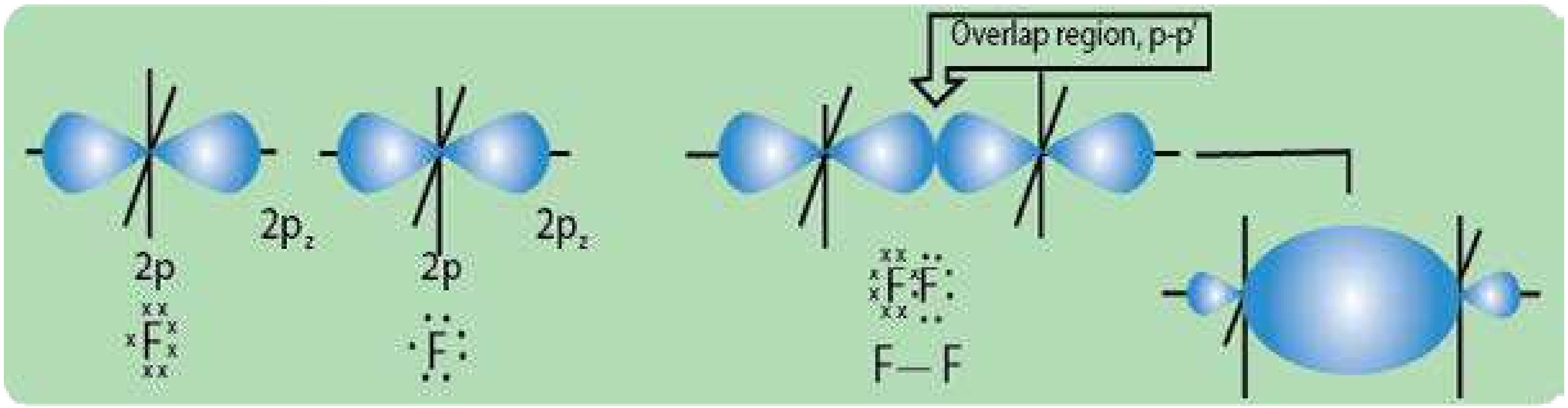


Fig.(6.6) The formation of the fluorine molecule.

Covalent bonds can also form by side-to-side overlap of p orbitals, as shown in Fig.(6.7). The result is a pi (π) bond, in which the greatest electron density lies above and below the internuclear axis.

Consider, the bonding between nitrogen atoms having the electronic configuration $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$. The three unpaired electrons on each atom are located in perpendicular p orbitals, which are oriented so that if one end-to-end p orbital overlap occurs (resulting in a sigma bond), the other two p orbital cannot overlap in the same fashion. Rather, they are aligned parallel to the corresponding orbital in the other atom Fig(6.8).

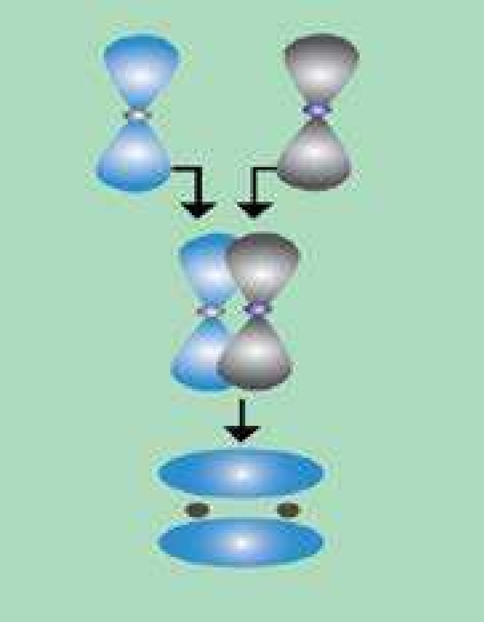


Fig. (6.7) The sideway overlap of two atomic p orbitals to give a n bond.

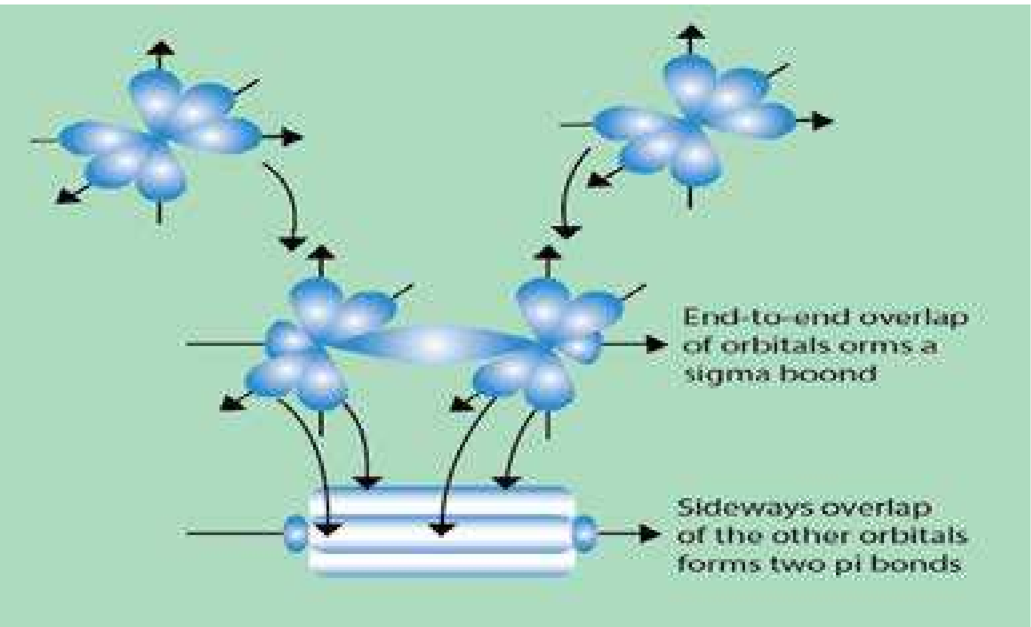


Fig.(6.8) The two nitrogen atoms showing one sigma bond and two n bonds

Now, let us look at the molecule of H_2S. This is a non-linear molecule, and the bond angle between the two H-S bonds is about 92°.

Each two 3p orbitals of sulphur containing one electron can overlap with the 1s orbitals of hydrogen atoms.

$$S = \overset{\boxed{\upharpoonleft\downharpoonright}}{3s}\ \overset{\boxed{\upharpoonleft\downharpoonright}}{3p_x}\ \overset{\boxed{\upharpoonleft\downharpoonright}}{3p_y}\ \overset{\boxed{\upharpoonleft\downharpoonright}}{3p_z}$$

Thus, the VBT requires the idea of overlap to explain the geometry of the hydrogen sulphide molecule, Fig. (6.9).

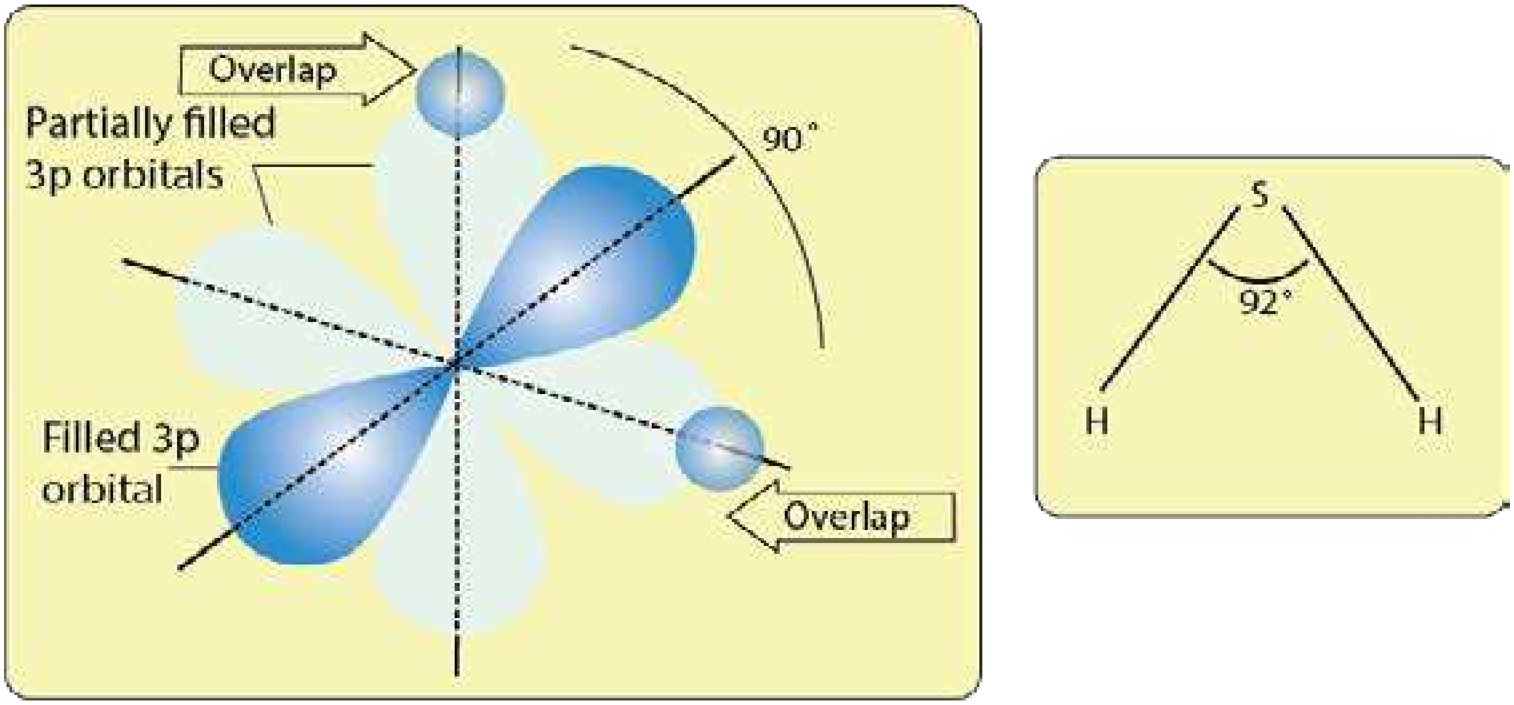


Fig.(6.9)BondinginH$_2$Sshowingoverlapoforbitals

6.4.5 Atomic Orbital Hybridization and Shapes of Molecules

So far we have regarded overlap taking place between unmodified atomic orbitals. Formation of some molecules present problems.

We face the problem of explaining equivalent tetra-valency of carbon and the bond angles in H_2O and NH_3 molecules. In order to explain the formation of bonds and shapes or geometry of molecules, the idea of hybridization has been introduced.

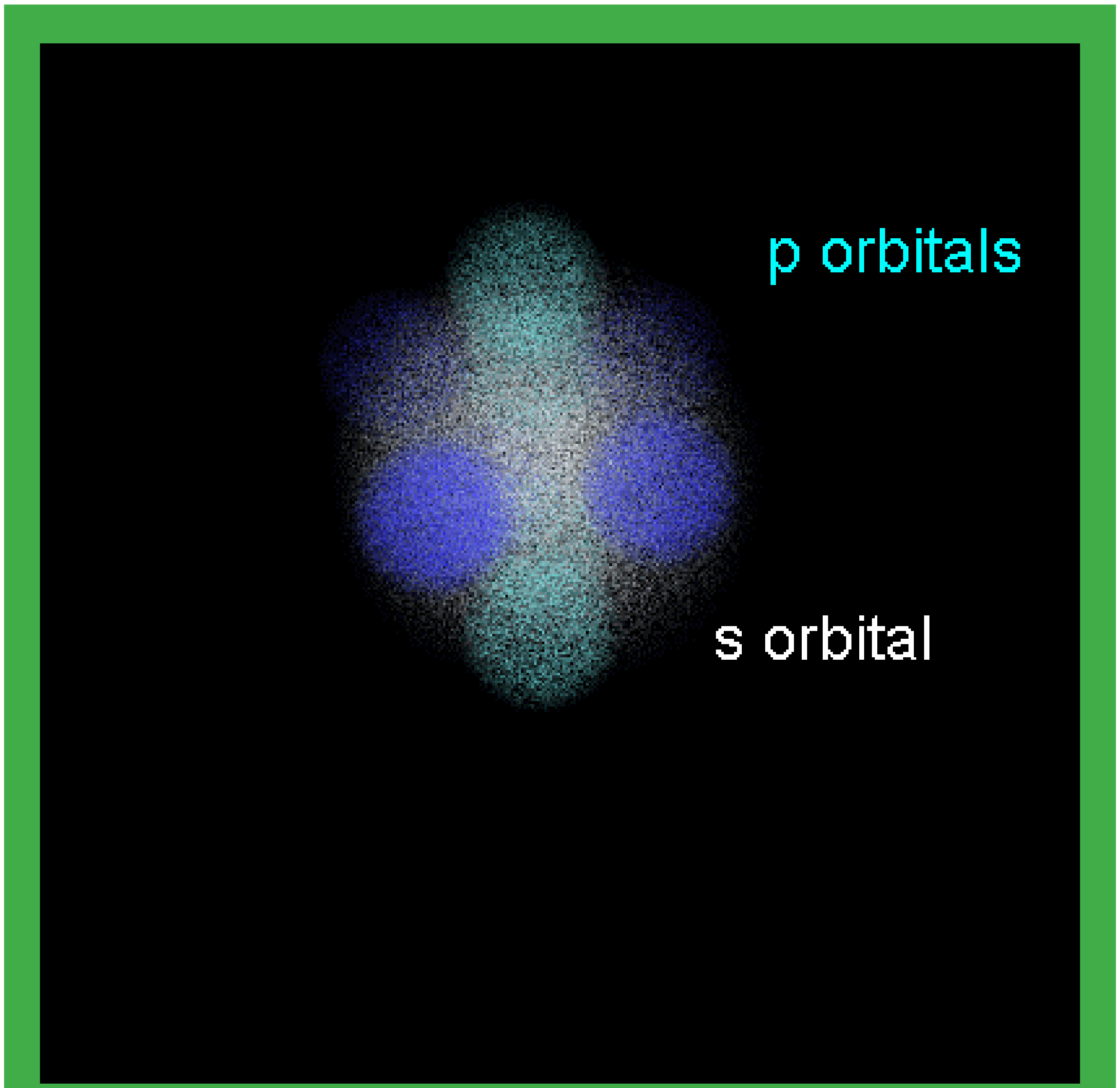
According to this, atomic orbitals differing slightly in energy intermix to form new orbitals, which are called hybrid atomic orbitals. They differ from the parent atomic orbitals in shape and possess specific geometry.
The atomic orbital hybridization gives a satisfactory explanation for the valency of the elements. In some cases, the electrons belonging to the ground state are promoted to the excited state as a result of which there is an increase in the number of unpaired electrons.

These excited orbitals undergo hybridization simultaneously, because promotion of electrons and hybridization is a simultaneous process. The energy required for the excitation is compensated by the energy released during hybridization and the process of bond formation with other atoms. Hybridization leads to entirely new shape and orientation of the valence orbitals of an atom. It holds significant importance in determining the shape and geometry of molecules.

Depending upon the number and nature of the orbitals participating in hybridization, different types of hybridization take place. For example, s and p orbitals of simple atoms are hybridized to give sp^3, sp^2 and sp hybridized orbitals.

(i) sp^3 Hybridization

In sp^3 hybridization, one s and three p atomic orbitals intermix to form four equivalent orbitals called sp^3 hybrid atomic orbitals. Let us discuss the structures of CH_4 ,NH_3 and H_2O by understanding the sp^3 hybridization of carbon, nitrogen and oxygen-atoms.



Animation 6.30: Atomic Orbital Hybridization and Shapes of Molecules
Source & Credit : web.clark

Bonding and Structure of Methane, Ammonia and Water

The electronic distribution of carbon atom should be kept in mind to understand intermixing of orbitals.Electronic configuration of $_6C$, its electronic excitation and hybrization is giyen as follows.

C_6=(ground state) $= \overset{\uparrow\downarrow}{1s}\ \overset{\uparrow\downarrow}{2s}\ \overset{\uparrow}{2p_x}\ \overset{\uparrow}{2p_y}\ \overset{0}{2p_z}$

C_6=(excited state) $= \overset{\uparrow\downarrow}{1s}\ \overset{\uparrow}{2s}\ \ \overset{\uparrow}{2p_x}\ \overset{\uparrow}{2p_y}\ \overset{\uparrow}{2p_z}$

C_6=(hybridized state) $= \overset{\uparrow\downarrow}{1s}\ \overset{\uparrow}{sp^3}\ \overset{\uparrow}{sp^3}\ \overset{\uparrow}{sp^3}\ \overset{\uparrow}{sp^3}$

The energies of hybrid orbitals are lower than unhybridized orbitals. Following diagram Fig. (6.10) shows, how outermost four atomic orbitals of carbon mix up to give four hybrid orbitals of equal energy and shape. hen 90°.

The four new hybrid orbitals of equal energy have a tetrahedral geometry with carbon at the centre. The four equivalent hybrid orbitals are directed towards the four corners of a regular tetrahedron. Each sp^3 hybrid orbital consists of two lobes, one larger and the other smaller. For the sake of simplicity, the small lobe is usually not shown while representing sp^3 hybrid orbitals.

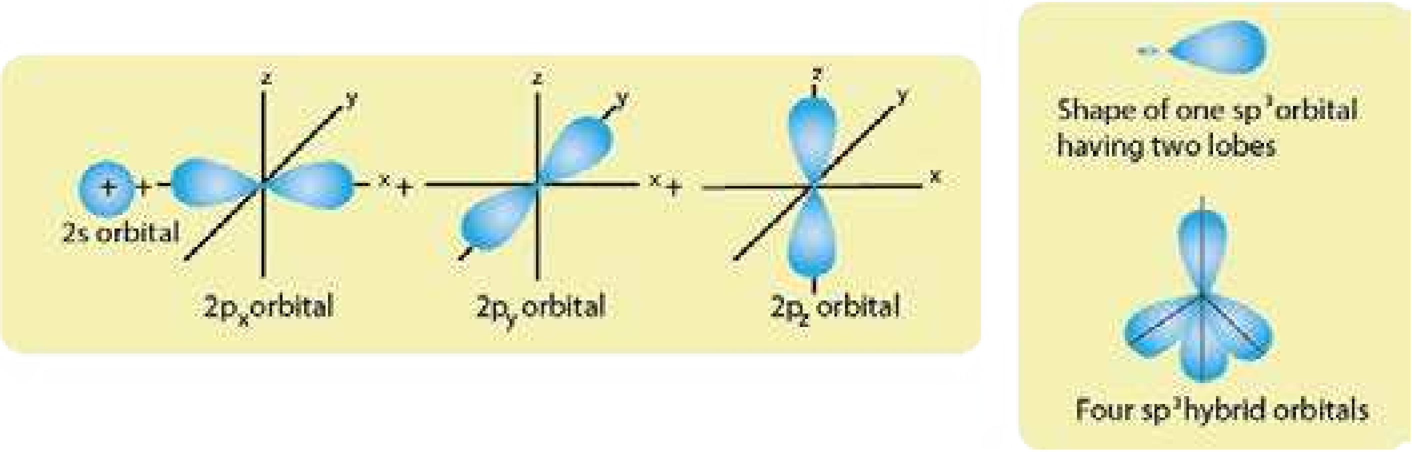
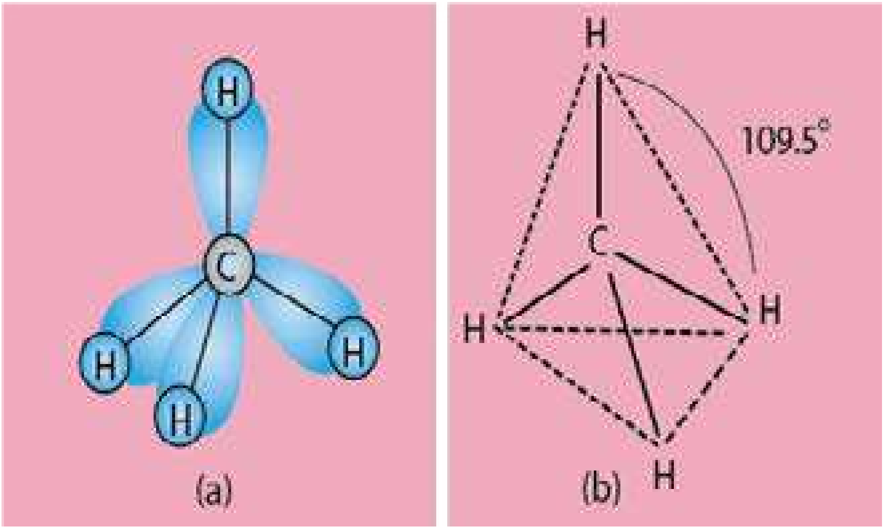


Fig (6.10) sp^3 hybridization of carbon atom to give four sp^3-hybrid orbitals

The hybrid orbitals are oriented in space in such a manner that the angle between them is 109.5° as shown in Fig(6.11a,b). Methane molecule is formed by the overlap of sp^3 hybrid orbitals of carbon with 1s orbitals of four hydrogen atoms separately to form four sigma bonds. The molecule, thus formed, possesses a tetrahedral geometry. The four C-H bonds which result from sp^3 -s overlaps are directed towards the corners of a regular tetrahedron. There are six bond angles each 109.5°. The tetrahedral structure of CH_4 has four faces, four corners and six edges.



Fig(6.11) Four sp^3-s overlaps in tetrahedral structure of CH_4 molecule.

(b) Ammonia

To understand the sp^3 hybridization of nitrogen-atom in NH^3, we should know electronic configuration of $_7N$.

$_7N$ (ground state) $= \overset{\boxed{\uparrow\downarrow}}{1s}\ \overset{\boxed{\uparrow\downarrow}}{2s}\ \overset{\boxed{\uparrow}}{2p_x}\ \overset{\boxed{\uparrow}}{2p_y}\ \overset{\boxed{\uparrow}}{2p_z}$

$_7N$ (hybridized state) $= \overset{\boxed{\uparrow\downarrow}}{1s}\ \overset{\boxed{\uparrow\downarrow}}{sp^3}\ \overset{\boxed{\uparrow}}{sp^3}\ \overset{\boxed{\uparrow}}{sp^3}\ \overset{\boxed{\uparrow}}{sp^3}$

One s and three p orbitals of nitrogen atom hybridize to form four sp^3 hybrid atomic orbitals. They are directed towards the four corners of a tetrahedron. One of the hybrid orbitals is completely filled with electrons and the remaining three orbitals are half filled. The nitrogen atom undergoes three sp^3-s overlaps with three s-orbitals of hydrogen atoms. The three hydrogen atoms are located at three corners whereas the lone pair of electrons is at the fourth corner of the tetrahedron. The result is a pyramidal molecule in which the three hydrogen atoms form the base and the lone pair of electrons the apex Fig(6.12).

The experimentally determined angle in ammonia is 107.5°. The deviation from the tetrahedral angle (109.5°) is explained on the basis of repulsion between the lone pair and the bond pairs of electrons. The lone pair is closer to the nucleus of nitrogen, then the bond pair and bond angles are decreased.

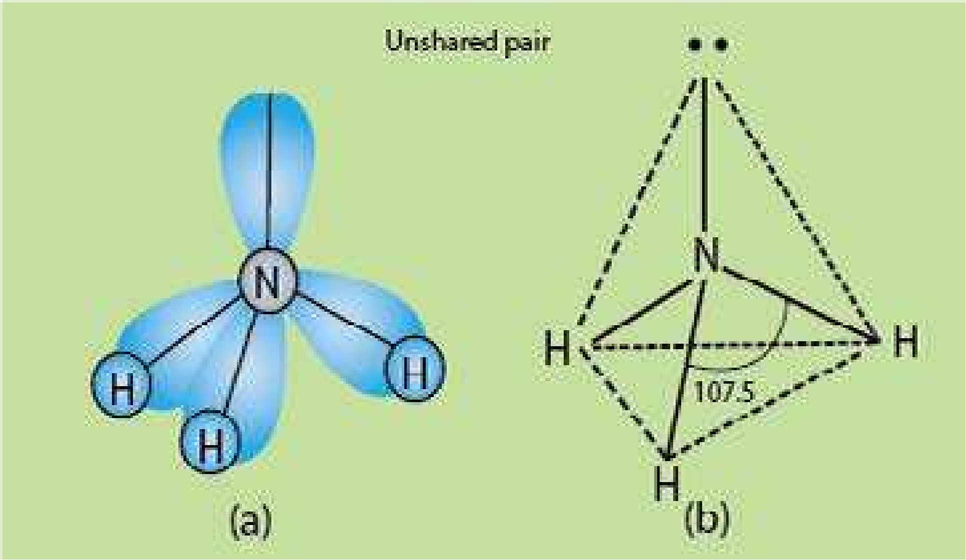


Fig (6.12) Three sp^3- s overlaps in NH_3 molecule to form a pyramidal structure.

(c) Water, H_20

To know the structure of water write down the electronic configuration of $_8O$:

$_8O$ (ground state) $=\overset{\boxed{\uparrow\downarrow}}{1s}\ \overset{\boxed{\uparrow\downarrow}}{2s}\ \overset{\boxed{\uparrow\downarrow}}{2p_x}\ \overset{\boxed{\uparrow}}{2p_y}\ \overset{\boxed{\uparrow}}{2p_z}$

$_8O$ (hybridized state) $=\overset{\boxed{\uparrow\downarrow}}{1s}\quad \overset{\boxed{\uparrow\downarrow}}{sp^3}\ \overset{\boxed{\uparrow\downarrow}}{sp^3}\ \overset{\boxed{\uparrow}}{sp^3}\ \overset{\boxed{\uparrow}}{sp^3}$

Here, 2s and three 2p orbitals of oxygen hybridize to form four sp^3 hybrid orbitals which will have a tetrahedral arrangement. Two hybrid orbitals are completely filled by the two available lone pairs of electrons. The remaining two half filled hybrid orbitals undergo sp^3-s overlaps with H atoms to form two sigma bonds. The two H atoms occupy two corners of the tetrahedron and the remaining two are occupied by two lone pairs of electrons, Fig(6.13).

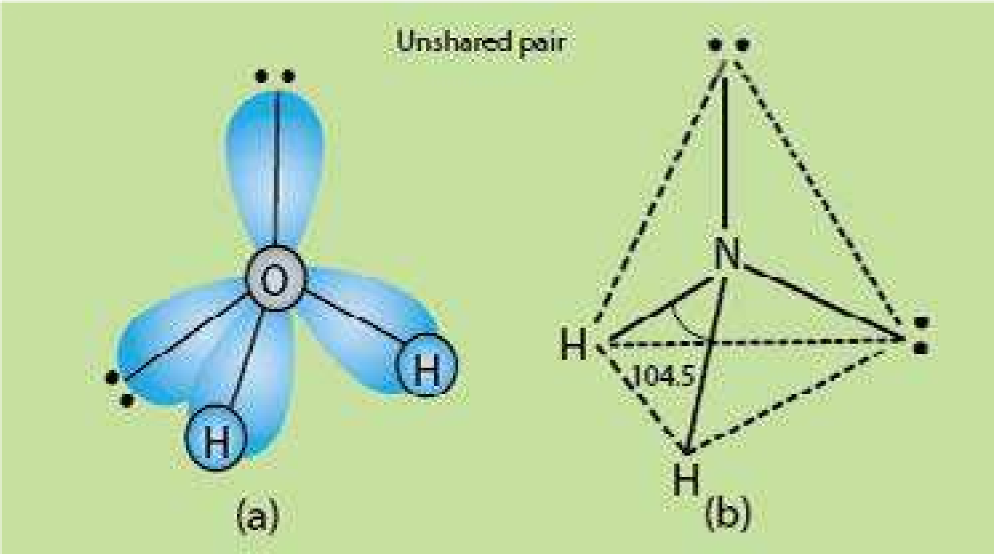


Fig (6.13) sp^3-s overlaps in H_20 to form an angular structure

The bond angle in water is 104.5°. The deviation from the tetrahedral angle (109.5°) is explained on the basis of repulsion between the two lone pairs of electrons, with bond pairs. The lone pairs are closer to the nucleus of oxygen. They repel bond pairs and the bond angle decreases from 109.5° to 104.5°. So, the molecule of water has bent or angular structure.

(ii) sp^2- Hybridization

In sp^2 hybridization, one 's' and two 'p' atomic orbitals of an atom intermix three orbitals called sp^2 hybrid orbitals.

Bonding and Structure of Boron Trifluoride and Ethene

(a) Boron Trifluoride (BF_3)

The three half filled sp^2 hybrid orbitals are planar and are oriented at an angle of 120°, Fig(6.14). The sp^2 hybridization explains the geometry of planar molecules such as BF_3. Electronic configuration of $_5B$ is,

$_5B$ (ground state) $= 1\overset{\uparrow\downarrow}{s}\,2\overset{\uparrow\downarrow}{s}\quad 2\overset{\uparrow}{p}_x\,2\overset{0}{p}_x\,2\overset{0}{p}_z$

$_5B$ (excited state) $= 1\overset{\uparrow\downarrow}{s}\,2\overset{\uparrow}{s}\,2\overset{\uparrow}{p}_x\,2\overset{\uparrow}{p}_y\,2\overset{0}{p}_z$

$_5B$ (hybridized state) $= 1\overset{\uparrow\downarrow}{s}\quad \overset{\boxed{\uparrow}}{sp^2}\,\overset{\boxed{\uparrow}}{sp^2}\,\overset{\boxed{\uparrow}}{sp^2}$

In sp^2 hybridization, one s and two p atomic orbitals of an atom intermix to form three orbital called sp^2 hybrid orbitals.

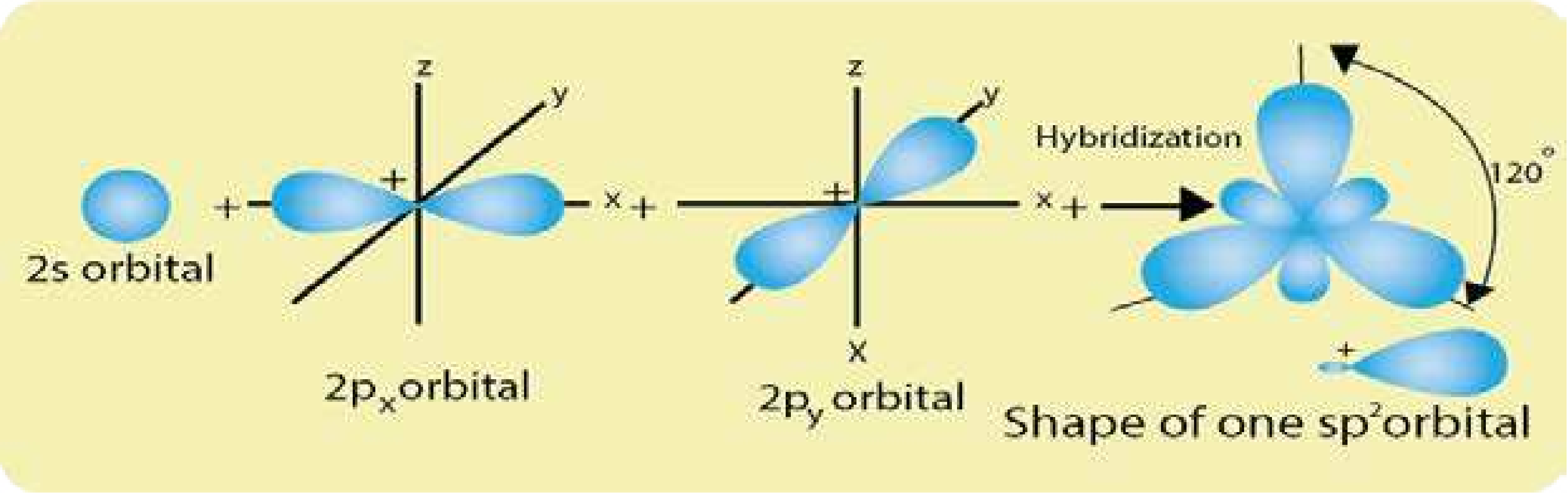


Fig (6.14) Three sp^2 hybridized orbitals in one plane and at 120° to each other.

One of the p orbitals of fluorine is half filled i.e. $2p_z$. This p-orbital of F is in the form of a lobe. BF_3 is formed by the overlap of three half filled sp^2 hybrid orbitals of boron with lobe shaped p-orbitals of three fluorine atoms Fig.(6.15). The structure is triangular planer.

(b) Ethene (CH_2=CH_2)

Electronic configuration of $_6C$ is

$_6C$ (ground state) $= \overset{\boxed{\uparrow\downarrow}}{1s}\ \overset{\boxed{\uparrow\downarrow}}{2s}\ \overset{\boxed{\uparrow}}{2p_x}\ \overset{\boxed{\uparrow}}{2p_y}\ \overset{0}{2p_z}$

$_6C$ (excited state) $= \overset{\boxed{\uparrow\downarrow}}{1s}\ \overset{\boxed{\uparrow}}{2s}\ \overset{\boxed{\uparrow}}{2p_x}\ \overset{\boxed{\uparrow}}{2p_y}\ \overset{\boxed{\uparrow}}{2p_z}$

$_6C$ (hybridized state) $= \overset{\boxed{\uparrow\downarrow}}{1s}\quad \overset{\boxed{\uparrow}}{sp^2}\ \overset{\boxed{\uparrow}}{sp^2}\ \overset{\boxed{\uparrow}}{sp^2}\quad \overset{\boxed{\uparrow}}{2p_z}$

In the formation of ethene molecule, each carbon atom undergoes sp^2 hybridization to form three hybrid orbitals which are co-planar and are oriented at an angle of 120°. Each atom is left with one half filled p-orbital perpendicular to the planar sp^2 hybrid orbitals.

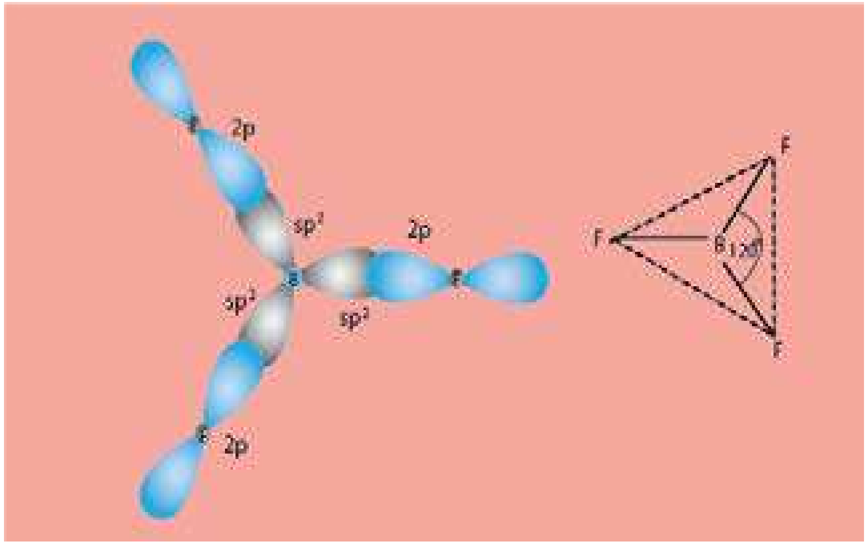


Fig. (6.15) sp^2-p overlaps in BF_3 to form triangular planar structure.

One of the p-orbitals does not take part in hybridization. Each carbon atom undergoes sp^2-s overlaps with two hydrogen atoms and sp^2-sp^2 overlap between themselves to form sigma bonds. These overlaps lead to the shapes shown in Fig.(6.16a). The partially filled p-orbitals undergo sidwrays overlap to form a π–bond.

So, a π-bond is formed by the sideways overlap of two half filled co-planar p-orbitals in such a way that the probability of finding the electron is maximum perpendicular to the line joining the two nuclei. It should be made clear that a π-bond is formed between two atoms only when they are already bonded with a sigma bond.

The two clouds of the π-bond are perpendicular to the plane in which five π-bonds are lying. Just like σ-bond, π -bond can be represented by a line as in Fig (6.16 b). The final shape of C_2H_4 is shown in Fig. (6.16 c).

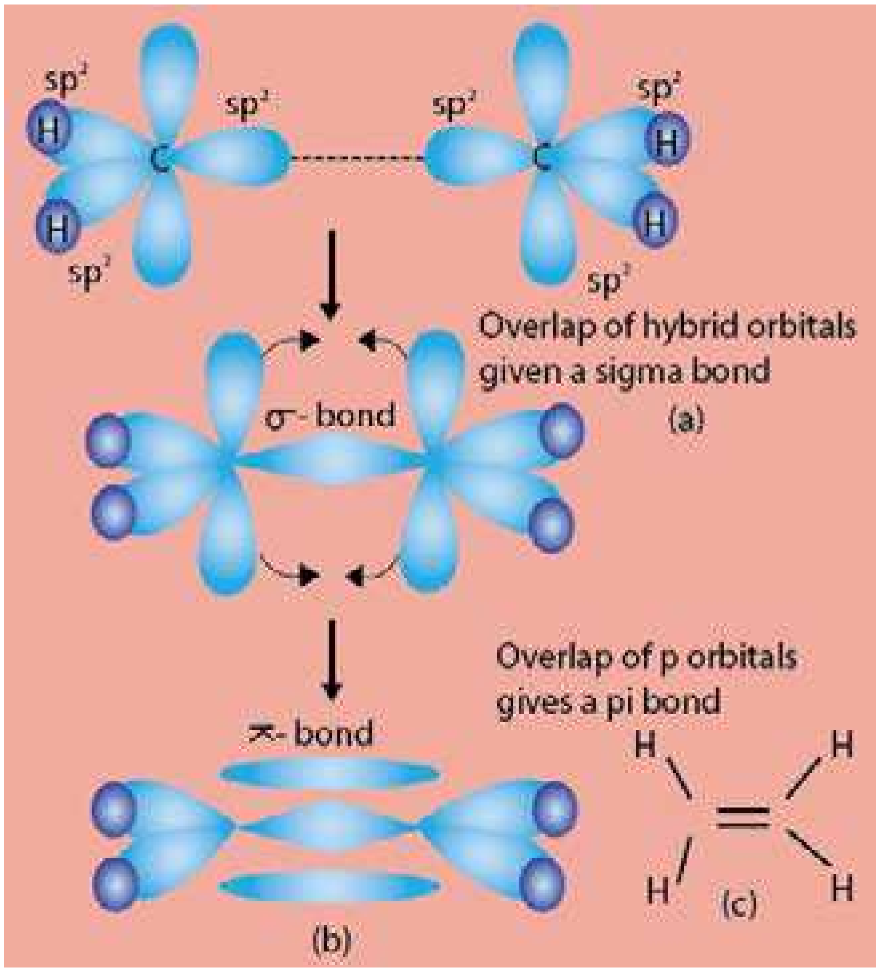


Fig. (6.16) Formation of one sigma between two carbon atoms and one π-bond in C_2H_4.

(iii) sp-Hybridization

In sp hybridization, one 's' and one 'p' orbitals.intermix to form two sp-hybrid orbital called sp hybrid orbitals.

Bonding and Structure of Beryllium Dichloride and Ethyne

(a) Beryllium Bichloride

Electronic configuration of ${}_4Be$ is

$_4$Be (ground state) $= \overset{\boxed{\uparrow\downarrow}}{1s}\ \overset{\boxed{\uparrow\downarrow}}{2s}\ \overset{0}{2p_x}\ \overset{0}{2p_y}\ \overset{0}{2p_z}$

$_4$Be (excited state) $= \overset{\boxed{\uparrow\downarrow}}{1s}\ \overset{\boxed{\uparrow}}{2s}\ \overset{\boxed{\uparrow}}{2p_x}\ \overset{0}{2p_y}\ \overset{0}{2p_z}$

$_4$Be (hybridized state) $= \overset{\boxed{\uparrow\downarrow}}{1s}\ \ \overset{\boxed{\uparrow}}{sp}\overset{\boxed{\uparrow}}{sp}$

The two sp hybrid orbitals lie in linear way, Fig (6.17). The sp hybridization explains the geometry of linear molecules such as beryllium chloride, $BeCl_2$. It is formed when two sp hybrid orbitals of Be atom overlap with the half filled p-orbitals of chlorine atoms. The outermost half filled $3p_z$ orbital of Cl has lobe shape.

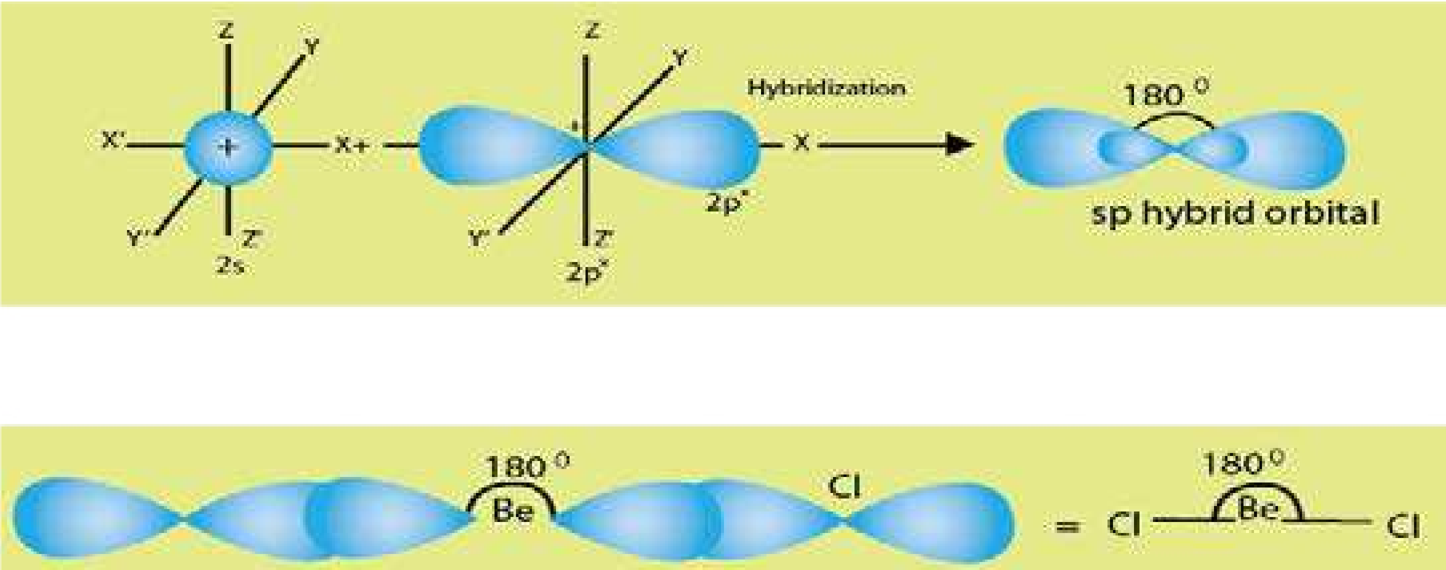


Fig. (6.17) sp-hybridization to form a linear structure

Be atom lies at the center and two Cl atoms on either side so that the Cl-Be-Cl angle is 180°.

(b) Ethyne (CH≡CH)

The electronic configuration of

$_6$C (ground state) $= \overset{\boxed{\uparrow\downarrow}}{1s}\ \overset{\boxed{\uparrow\downarrow}}{2s}\ \overset{\boxed{\uparrow}}{2p_x}\ \overset{\boxed{\uparrow}}{2p_y}\ \overset{0}{2p_z}$

$_6$C (excited state) $= \overset{\boxed{\uparrow\downarrow}}{1s}\ \overset{\boxed{\uparrow}}{2s}\ \overset{\boxed{\uparrow}}{2p_x}\ \overset{\boxed{\uparrow}}{2p_y}\ \overset{\boxed{\uparrow}}{2p_z}$

$_6$C (hybridized state) $= \overset{\boxed{\uparrow\downarrow}}{1s}\ \ \overset{\boxed{\uparrow}}{sp^2}\ \overset{\boxed{\uparrow}}{sp^2}\ \overset{\boxed{\uparrow}}{2p_y}\ \overset{\boxed{\uparrow}}{2p_z}$

Ethyne is formed as a result of sp hybridization of carbon atoms and subsequent formation of σ and π bonds. Each carbon atom undergoes sp-s overlap with one hydrogen atom and sp-sp overlap with other carbon atom. Each carbon atom is left with two unhybridized p orbitals perpendicular to the plane of sp hybrid orbitals. The two half filled p orbitals (on separate carbon atoms) are parallel to each other in one plane while the other two p orbitals are parallel to each other in another plane. The sideways π overlap between the p-orbitals in two planes results in the formation of two π bonds as shown in Fig.(6.18).

Ethyne molecule contains one σ and two π bonds between the two carbon atoms and each carbon atom is bonded with, one H atom through σ bond. Actually, four electronic clouds of two π-bonds intermix and they surround the sigma bond in the shape of a drum.

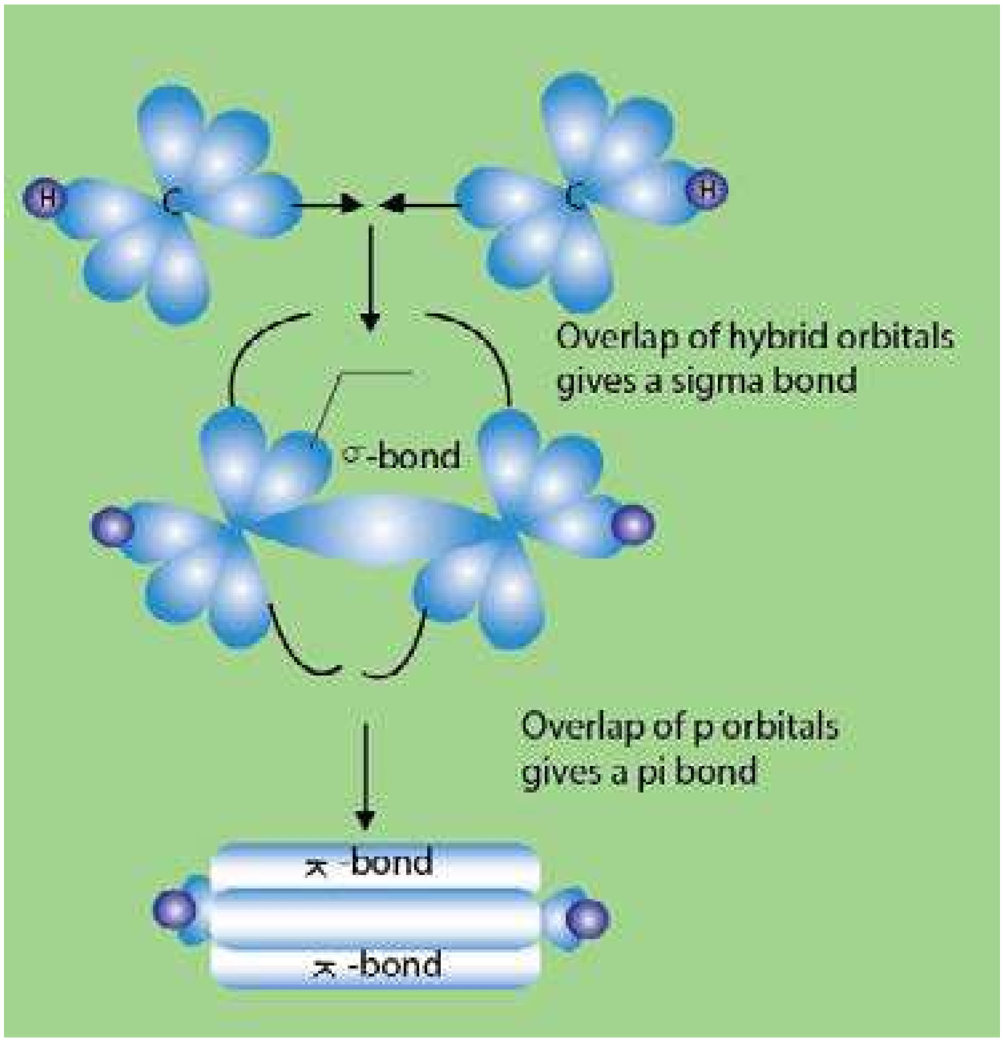


Fig. (6.18) Formation of one sigma and two pi-bonds in C_2H_2 (ethyne)

6.4.6. Molecular Orbital Theory

The molecular orbital approach considers the whole molecule as a single unit. It assumes that the atomic orbitals of the combining atoms overlap to form new orbitals called molecular orbitals which are characteristic of the whole molecule. The molecular orbital surrounds two or more nuclei of the bonded atoms. Two atomic orbitals, after overlapping, form two molecular orbitals which differ in energy. One of them, having lower energy, is called bonding molecular orbital while the other having higher energy is called anti-bonding molecular orbital.

The bonding molecular orbital is symmetrical about the axis joining the nuclei of the bonded atoms (molecular axis). It is designated as sigma (σ) bonding molecular orbital while the antibonding molecular orbital, is called σ^*. The process of formation of molecular orbitals from 1s atomic orbitals of hydrogen is shown in Fig (6.19).

The filling of electrons into the molecular orbitals takes place according to the Aufbau principle, Pauli's exclusion principle and Hund's rule.The two electrons (one from each hydrogen atom), thus fill the low energy σ_{1s}-orbital and have paired spin ($\boxed{\uparrow\downarrow}$), while the high energy σ^*_{1s} orbital remains empty.

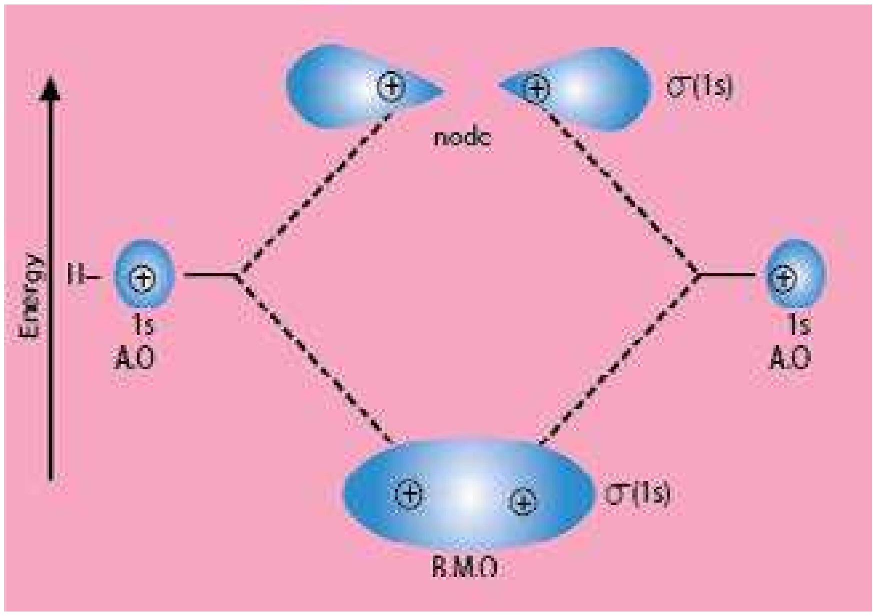
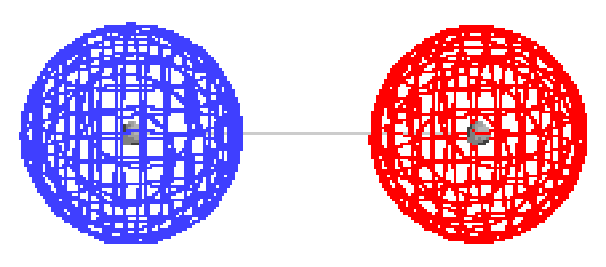


Fig (6.19). Formation of bonding and anti-bonding molecular orbitals for hydrogen molecule (H_2)



Animation 6.31: Molecular Orbital Theory
Source & Credit : andrew.cmu

So far, we have considered s and s orbital overlap for the formation of molecular orbitals of hydrogen molecule. Other types of overlaps occurring between p and p atomic orbitals to form molecular orbitals are described below. There are three 2p atomic orbitals directed along the three perpendicular x, y and z coordinates. For the formation of molecular orbitals from p- orbitals, two cases arise:

(a) Head on Approach

Here, the p-orbitals of the two atoms approach along the same axis (i.e. p_x axis) as shown in Fig. (6.20).

This combination of the atomic orbitals gives rise to $\sigma(2p_x)$ bonding and $\sigma^*(2p_x)$ antibonding molecular orbitals. Both are symmetrical about the nuclear axis.

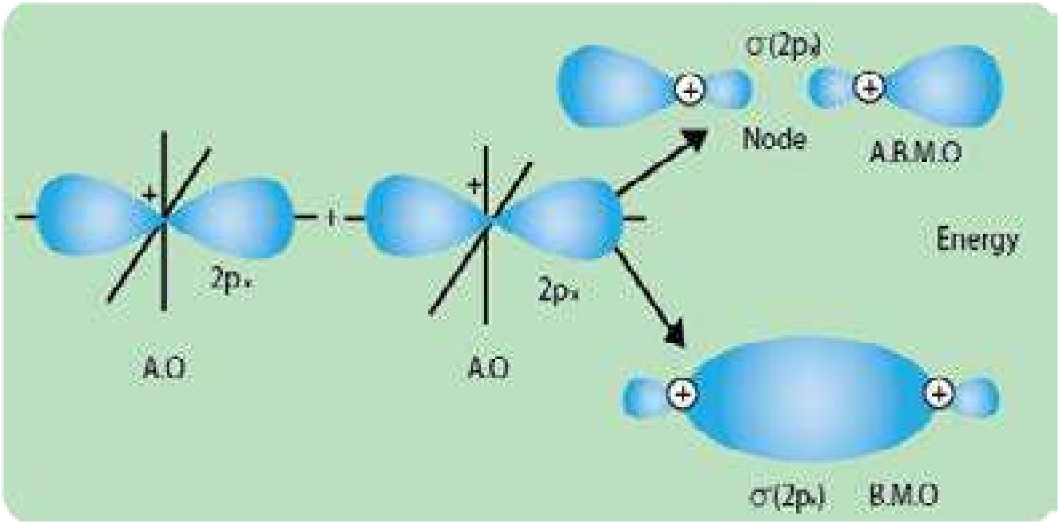


Fig. (6.20) Head on overlap of two p-orbitals

(b) Sideways Approach

When the axes of two p-orbitals (i.e p_y or p_z orbitals) are parallel to each other, they interact to form molecular orbitals as shown in Fig.(6.21).

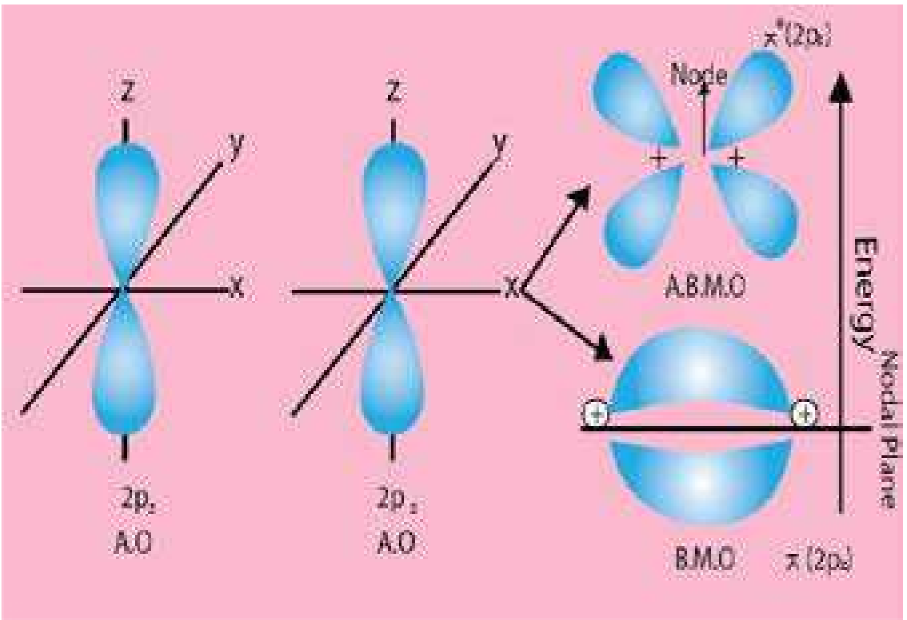


Fig. (6.21) Sideways overlap of two p-orbitals

The bonding molecular orbitals π($2p_y$) or π ($2p_z$) have zero electron density on the nuclear axis (called the nodal plane). The electron density is uniformly distributed above and below the nodal plane.

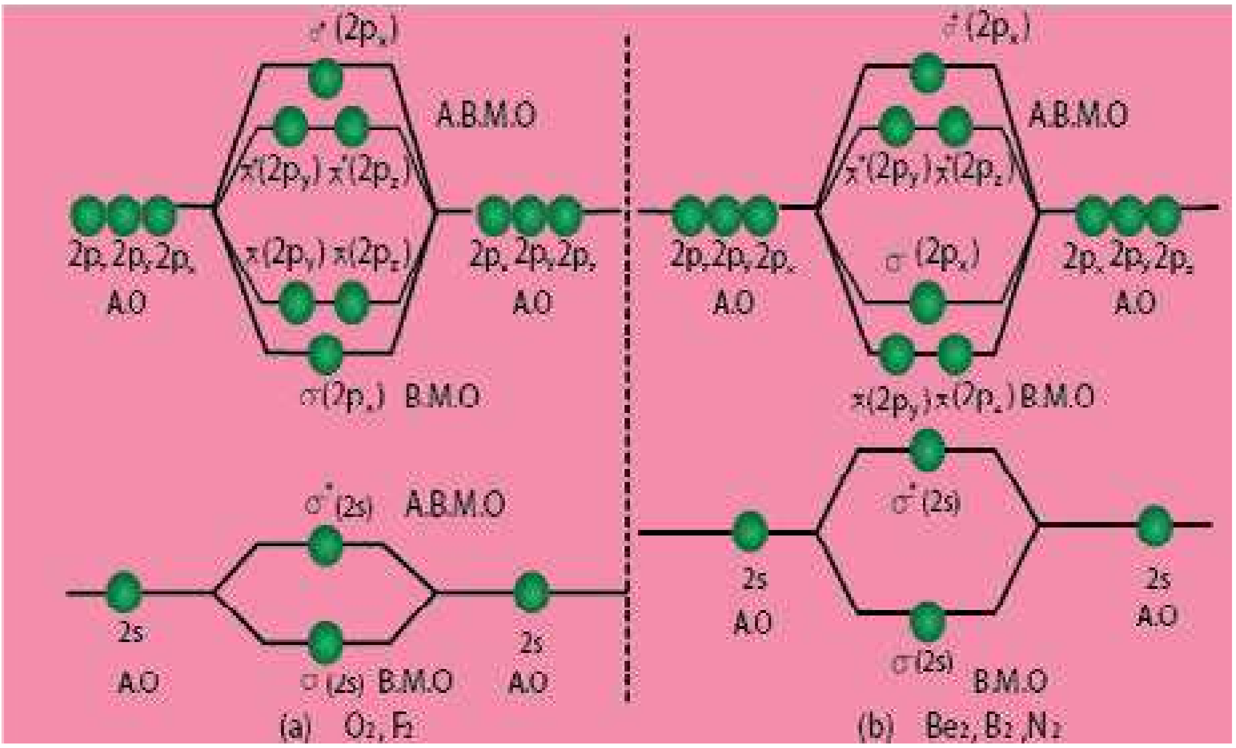
On the other hand, anti-bonding molecular orbitals π* ($2p_y$) and π* ($2p_z$) have the least electron density in the π inter-nuclear region. Since the 2py and 2pz atomic orbitals are degenerate (having the same energy), the π - molecular orbitals i.e. π ($2p_y$) and π ($2p_z$) are also degenerate. So,are also the π*($2p_y$) and π*($2p_z$) molecular orbitals.

Overall six molecular orbitals (three bonding and three anti-bonding) are formed from two sets of 2p atomic orbitals. The bond formed as a result of linear overlap is ó bond, while that formed as a result of sideways overlap is called a π (pi) bond. As there are three bonding molecular orbitals, the p-orbitals overlap can lead to the formation of at the most three bonds: one sigma and two π -bonds.

Relative Energies of the Molecular Orbitals

The relative energies of the molecular orbitals formed from 2s and 2p atomic orbitals in the case of homonuclear di-atomic molecules are shown in Fig. (6.22).

The energies of the molecular orbitals are determined by spectroscopic measurements. The molecular orbitals of diatomic molecules such as O_2, F_2 and their positive and negative ions can be arranged in the following-increasing order of energy (Fig 6.22a).



Fig(6.22)(a) Molecular orbital energy diagram for O_2, F_2 and their positive and negative ions
(b) Molecular orbital energy diagram.for Li_2, Be_2, B_2 and N_2.

$$\sigma(1s)<\sigma^*(1s)<\sigma(2s)<\sigma^*(2s)<\sigma(2p_x)<\pi(2p_y)=\pi(2p_z)<\pi^*(2p_y)=\pi(2p_z)<\sigma^*(2p_x)$$

The diatomic molecules, such as N_2 and other -lighter molecules like B_2, C_2 show slightly different energy order. See Fig. (6.22 b):

$$\sigma 1s<\sigma^* 1s<\sigma(2s)<\sigma^*(2s)<\pi(2p_z)=\pi(2p_z)<\sigma(2p_x)<\pi^*(2p_y)=\pi^*(2p_z)<\sigma^*(2p_x)$$

Reason

It has been observed that in case of B_2, C_2 and N_2 ,σ2p_x is higher in energy than π2p_y=π2p_x. MOs. This reversal is due to mixing of 2s and 2p_x atomic orbitals.

Actually, the energy difference of 2s and 2p atomic orbitals is small. There is a possibility of mixing of these orbitals (i.e. hybridization of A.O.) as a result of which σ2s and σ*2s MOs do not retain pure s-character. Similarly, σ2p_x and σ*2p_x MOs do not have pure p-character. All the four MOs acquire sp-character. Due to this mixing, their energies change'in such a way that MOs σ2s and σ*2s become more stable and are lowered in energy MOs as σ2p_x and σ*2p_x become less stable and are raised in energy. Since, πp-orbitals are not involved in mixing, so energy of π2p_y=π2p_z remains unchanged.σ 2p_x is raised to such an extend that it becomes higher in energy than π-bondings.

Anyhow, O_2 and F_2 do not do so. The reason is high energy difference of their 2s and 2p i.e. 1595 and 2078 kJmol^{-1}, for O_2 and F_2 , respectively. These values are 554kJmol^{-1} for boron, 846kJmol^{-1} for carbon, and 1195kJmol^{-1} for nitrogen. These energy differences have been calculated by spectroscopic techniques.

Bond Order

The number of bonds formed between two atoms after the atomic orbitals overlap, is called the bond order and is taken as half of the difference between the number of bonding electrons and anti-bonding electrons. The number of bonds formed between H-atoms in hydrogen molecule may be calculated as follows:

Number of electrons in the bonding orbitals = 2
Number of electrons in the anti-bonding orbitals = 0

Bond order $= \frac{2-0}{2} = 1$

It is a common practice that only MOs formed from valence orbital are considered in bond order calculations.

Molecular Orbital Structures of Some Diatomic Molecules

(i) Helium, He_2

The electronic configuration of He is $1s^2$. The 1s orbitals of He-atoms combine to form one bonding σ (1s) and one anti-bonding σ^* (1s) orbitals as shown in Fig (6.23).

Each He-atom contributes two electrons. Two electrons enter bonding molecular orbital σ (ls) and the remaining two go to antibonding σ^* (Is) molecular orbital.

The bond order for He_2 is zero i.e. $\frac{2-0}{2}$ picture of He_2 molecule is not formed.

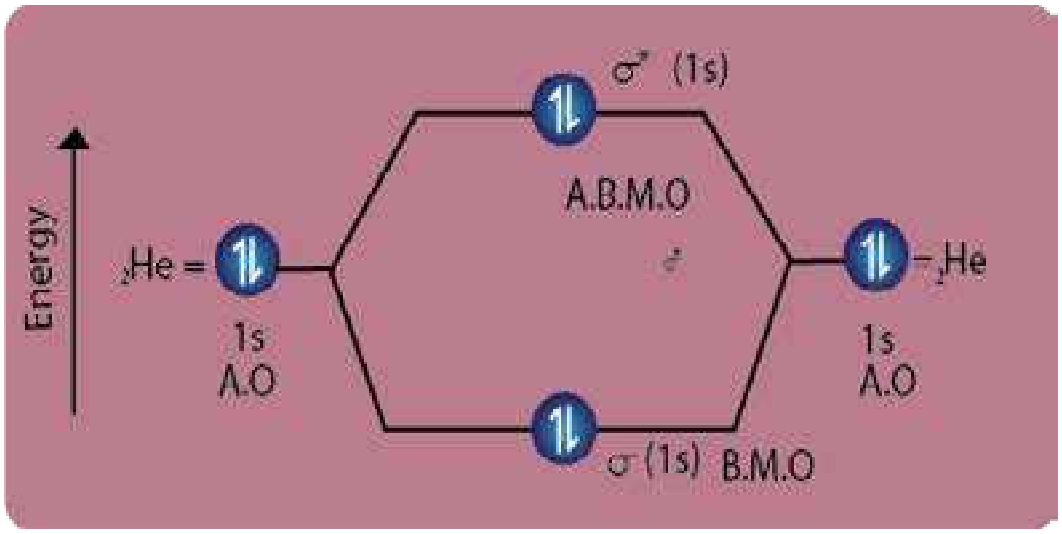


Fig Fig. (6.23) Hypothetical orbital picture of He_2 molecule.

(ii) Nitrogen, N_2

The molecular orbital structure of N_2 molecule is shown in Fig (6.24). Electronic configuration of N_2 molecule is

$$\sigma(1s^2)<\sigma^*(1s^2)<\sigma(2s^2)<\sigma^*(2s^2)<\pi(2p^2{}_y)=\pi(2p^2{}_z)<\sigma(2p^2{}_x)<\pi^*(2p_y)=\pi^*(2p_z)< \sigma^*(2p_x)$$

From the electronic configuration of N_2, it is clear that six electrons enter into three outermost bonding orbitals while no electrons enter into anti-bonding orbitals.

Thus, the bond order in N_2 molecule is $\frac{6-0}{2}=\frac{6}{2}$=3, which corresponds

to the triple bond consisting of one sigma and two π bonds. The bond dissociation energy of N_2 is very high, i.e. 941kJmol^{-1}.

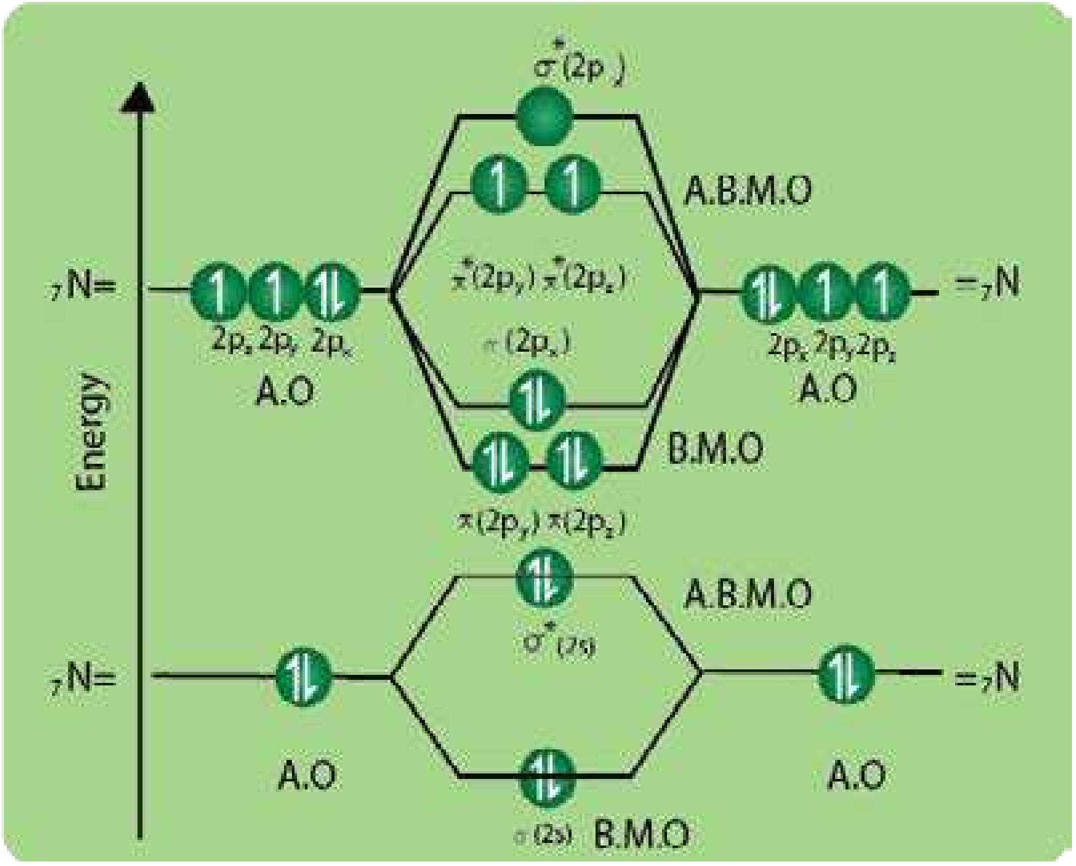


Fig. (6.24) Molecular orbitals picture of N_2 molecule.

(iii) Oxygen, 0_2

The formation of molecular orbitals in oxygen molecule is shown in Fig. (6.25). The electronic configuration of O_2 is

$$\sigma(1s)^2 < \sigma^*(1s)^2 < \sigma(2s)^2 < \sigma^*(2s)^2 < \sigma(2p_x) < \pi(2p_y)^2 = \pi(2p_z)^2 < \pi^*(2p_y)^1 = \pi_z^*(2p_z)^1 < \sigma^* 2p_x$$

The bond order in O_2, is $\frac{6-2}{2}$ =2, which corresponds to a double bond.

This is consistent with the large bond energy of 496kJ mol^{-1} of oxygen molecule. Fig(6.25) shows that the filling of molecular orbitals leaves two unpaired electrons in each of the $\pi^*(2p_y)$ and $\pi^*(2p_z)$ orbitals. Thus, the | electronic configuration of the molecular orbitals accounts admirably for the paramagnetic properties of oxygen. This is one of the greatest successes of the molecular orbital theory. Liquid O_2 is attracted towards the magnet.

Anyhow, when two more electrons are given to O_2, it becomes O_2^{2-}. The paragmanetism vanishes. Similarly, in O_2^{2+} the unpaired electrons are removed and paragmagnetic property is no more there. Bond order of O_2^{2-} are also different from O_2 and are one and three, respectively.

Similarly, M.O.T justifies that F_2 has bond order of one and Ne does not make a bond with Ne.

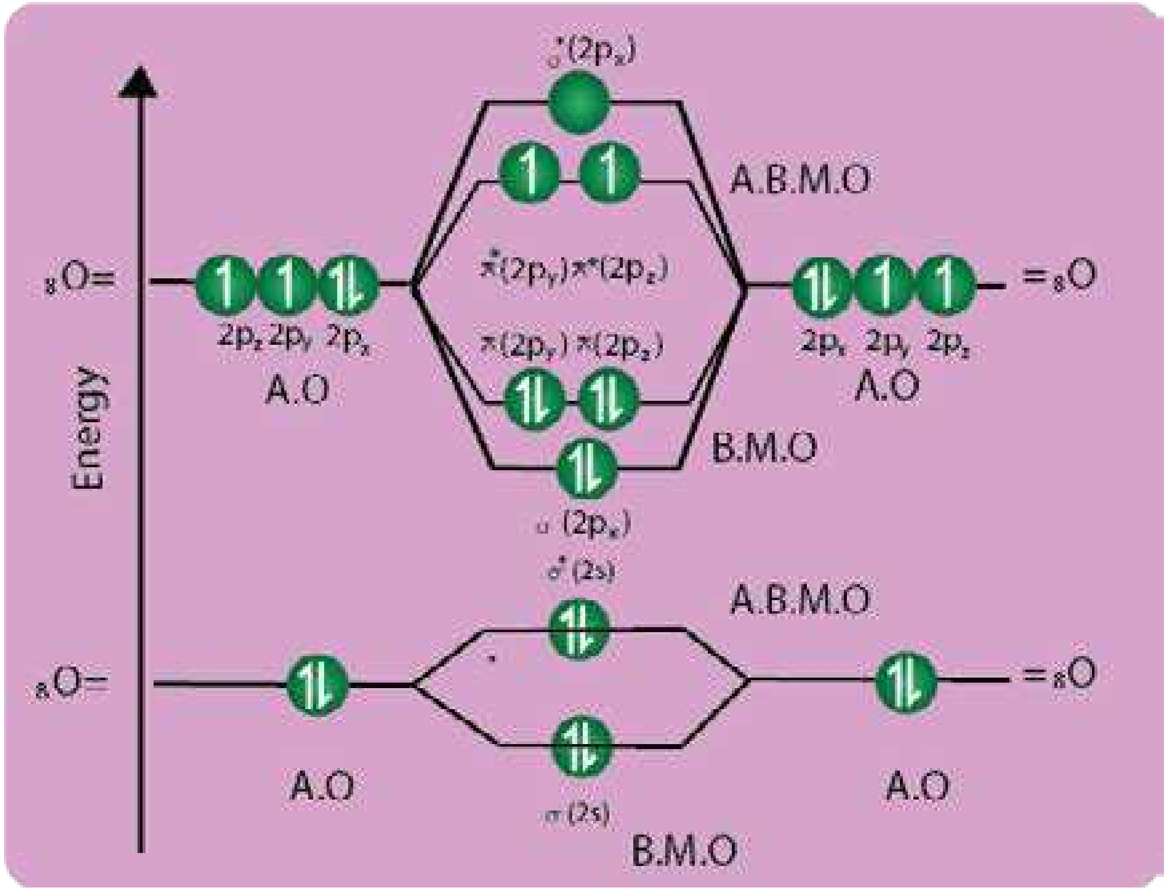


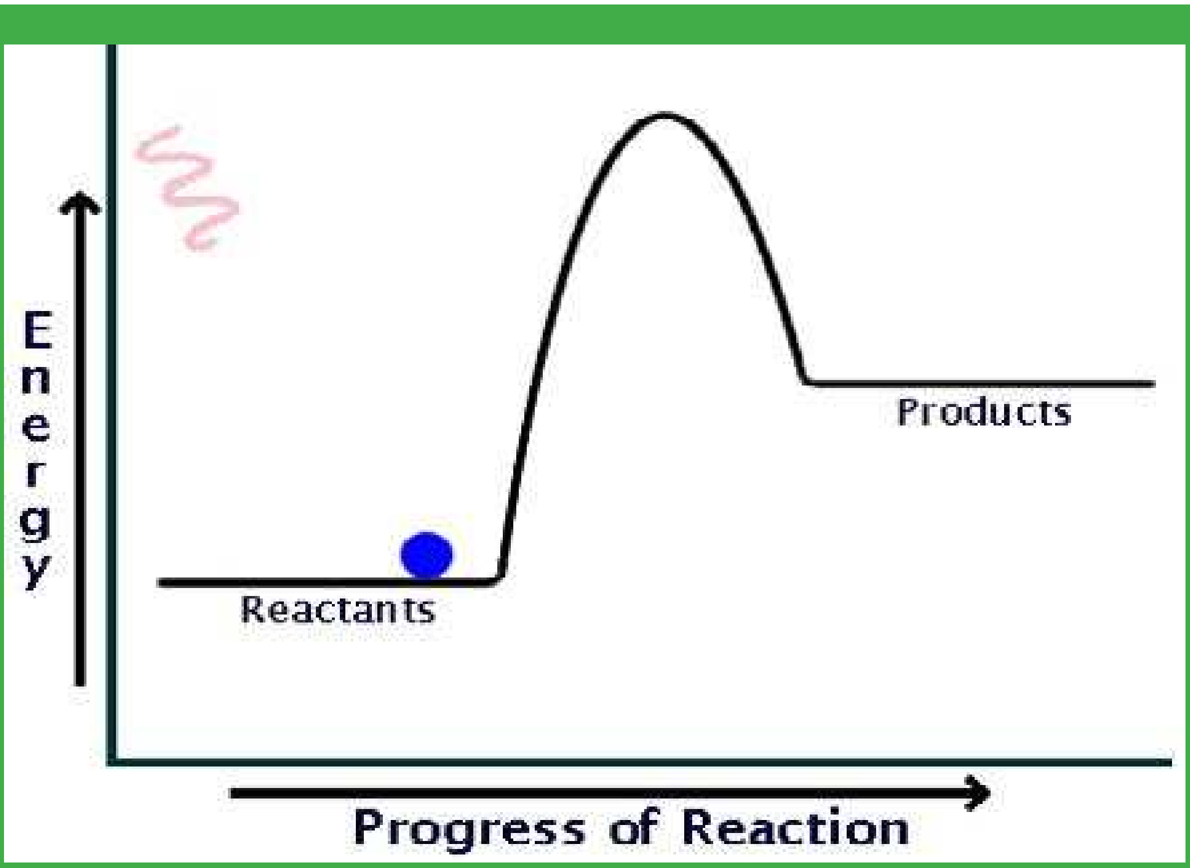
Fig. (6.25) Molecular orbitals in 0, molecule.

6.5 BOND ENERGY, BOND LENGTH AND DIPOLE MOMEN

6.5.1 Bond Energy (bond enthalpy)

When a bond is formed between two atoms, energy is released. The same amount of energy is absorbed when the bond is broken to form neutral atoms. So, the bond energy is the average amount of energy required to break all bonds of a particular type in one mole of the substance. It is determined experimentally, by measuring the heat involved in a chemical reaction. It is also called bond enthalpy, as it is a measure of enthalpy change at 298 K. The enthalpy change in splitting a molecule into its component atoms is called, enthalpy of atomization.

The bond energy is given in kJ mol^{-1} which is the energy required to break an Avogadro's number (6.02×10^{23}) of bonds. It is also released when an Avogadro's number of bonds are formed. Table (6.5).

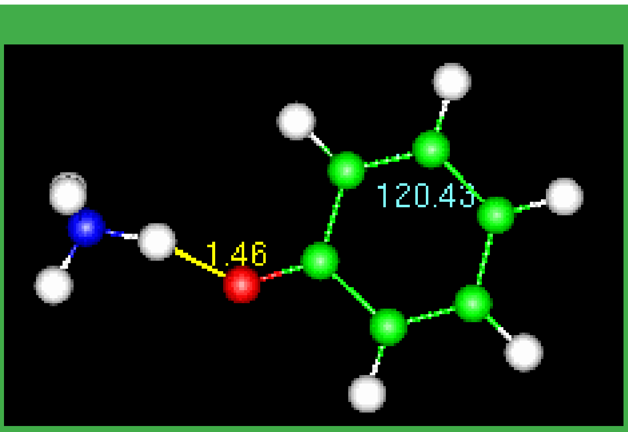


Animation 6.32: Bond Energy (bond enthalpy)
Source & Credit : packbackbooks

Table (6.5) Average bond enthalpies of some important bonds (kjmol^{-1}).

Bond	Bond energy (kJmol^{-1})	Bond	Bond energy (kJmol^{-1})	Bond	Bond energy (kJmol^{-1})	Bond	Bond energy (kJmol^{-1})
C-C	348	H-H	436	O-O	146	Si-H	323
C=C	614	H-F	567	O=O	495	Si-Si	226
C ≡ C	839	H-Cl	431	O-H	463	Si-C	301
C-H	413	H-Br	366	O-F	190	Si-O	368
C-N	293	H-I	299	O-Cl	203	F-H	155
C=N	615	N-N	163	O-I	234	Cl-F	253
C≡ N	891	N=N	418	S-S	266	Cl-Cl	242
C-O	358	N≡ N	941	S=S	418	Br-F	237
C=O	799	N-H	391	S=O	523	Br-Cl	218
C≡O	1072	N-O	201	S-H	339	Br-Br	193
C-F	485	N-F	272	S-F	327	I-Cl	208
C-Cl	328	N-Cl	200	S-Cl	253	I-Br	175
C-Br	276	N-Br	243	S-Br	218	I-I	151
C-I	240						
C-S	259						

It may be noted that energies of multiple bonds are greater than those of single bonds. But a double bond is not twice as a strong as a single bond or a triple bond is not thrice as strong as a single bond. It means that σ- bond is stronger than a π-bond. Similarly, a polar covalent bond is stronger than a non-polar covalent bond.



Animation 6.33: BOND ENERGY, BOND LENGTH AND DIPOLE MOMENT
Source & Credit : chem.utah

6.5.2 Ionic Character and Bond Energy

Bond energy is a measure of the strength of a bond. The strength of a bond depends upon the following factors.

(i) Electronegativity difference of bonded atoms (ii) Sizes of the atoms (iii)Bond length Let us consider, first the part played by electronegativity difference. Look at the bond energies of H-X type of compounds, where X=F, Cl, Br, I, Table (6.6).This data show that electrons are not equally shared between the bonded atoms i.e. HX. As halogen atom is more electronegative, the bonded pair is more attracted towards X atom and thereby polarity develops. This gives rise to additional attractive force for binding.

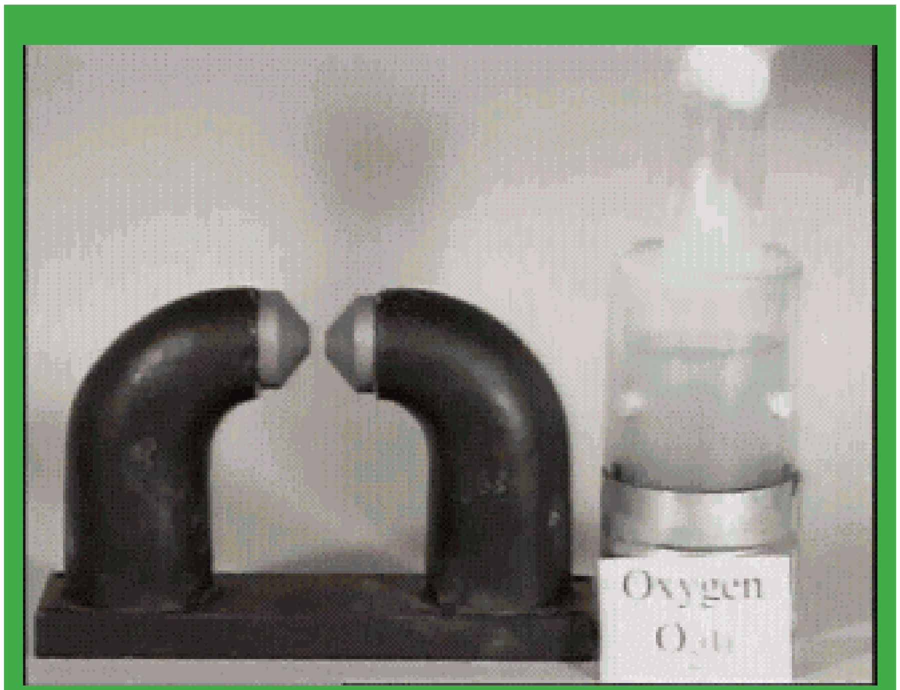
From the difference between experimental bond energies and those calculated by assuming equal sharing, it is possible to estimate relative electronegativities. The comparison of these values shows that the discrepancy is the greatest for HF and the least for HI, Table (6.9).

Let us calculate, the increase in the strength of H-Cl bond,due to the ionic character present in it.The H-H bond energy is 436 kJ mol^{-1}

It means 436 kJ of heat is required to break the Avogadro's number of H_2 molecules into individual atoms. Thus, bond energy per bond is 72.42 x 10^{-23}kJ. This is obtained by dividing 436 by 6.02 x 10^{23}. As the bonding electron pair is equally shared between the two H atoms, we can assume that each bonded H-atom contributes half of the bond energy i.e., 36.21x10^{-23}kJ.

Similarly, the bond energy for Cl_2 is 240 kJ mol^{-1}. Therefore, each Cl-atom should contribute 19.93 x 10^{-23} kJ to any bond, where sharing of an electron pair is equal.

$$H+H \rightarrow H_2 \qquad \Delta H=-436 kJmol^{-1}$$



Animation 6.34: Ionic Character and Bond Energy
Source & Credit : av8n

Table (6.6) Comparison of experimental and theoretical bond energies

Bond	Bond energies (kJmol^{-1})			
	X=F	X=Cl	X=Br	X=I
X-X	155	242	193	151
H-X (calculated)	293	336	311	291
H-X (observed)	567	431	366	299
difference	274	95	55	8

Let us, now consider, the bond in HCl. This bond is polar, but we consider the electron pair to be equally shared. On adding up the bond energy contributions of H-atom and Cl-atom, we expect the bond energy of H-Cl to be 56.14 x 10^{-23}kJ per molecule which is the sum of 36.21xl0^{-23}kJ and 19.93x10^{-23}kJ. For Avogadro's number of HCl molecules, the calculated bond energy is 337.96 kJmol^{-1} which is obtained by multiplying 56.14 x 10^{-23} with 6.02 x 10^{-23} The experimentally found bond energy for HCl is 431 kJmol^{-1}.The observed bond energy is significantly greater than the calculated value and that means a more stable H-Cl bond. This stability is due to the ionic character present in the molecule.The decreasing polarity from HF to HI shows a trend toward equal sharing of electrons which is consistent with decreasing electronegativity from F to I.

The bonds with higher bond energy values have shorter bond lengths. The bond energies of C to C bonds being in the order C ≡ C >C=C>C-C. Their bond lengths are in the reverse order i.e. C -C > C=C > C ≡ C.

6.5.3 Bond Length

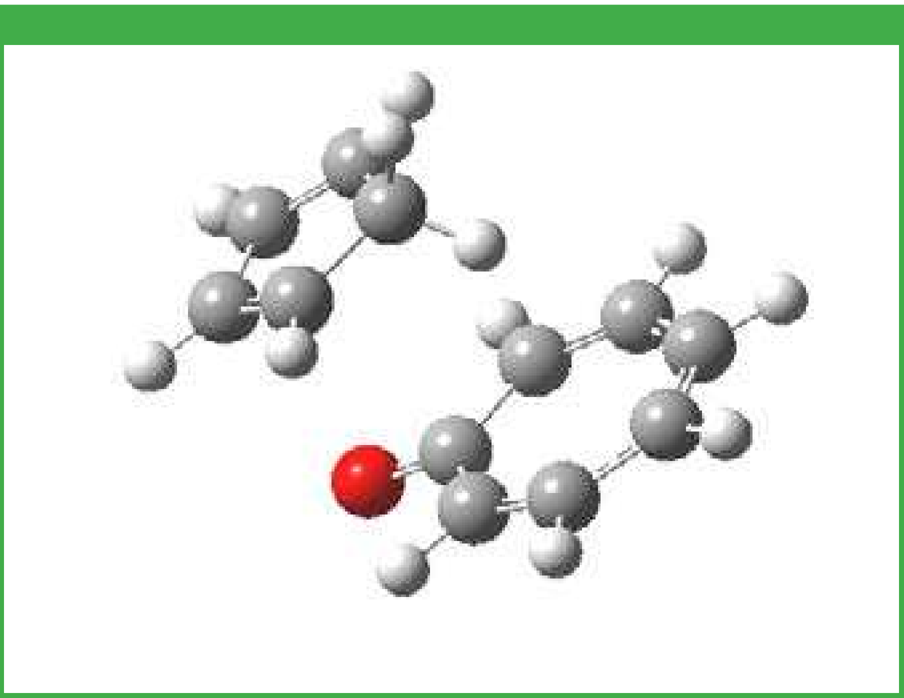
The distance between the nuclei of two atoms forming a covalent bond is called the bond length. The bond lengths are experimentally determined by physical techniques. The techniques may be electron diffraction, X-ray diffraction or spectral studies.

The covalent bond length between two atoms is often but not always independent of the nature of the molecules. For instance, in most of the aliphatic hydrocarbons, the C-C bond length is very close to 154 pm. The C-C bond length is also found to be the same in diamond.

The covalent radii for different elements are almost additive in nature. The single bond covalent radius of carbon is 77 pm which is half of the C-C bond length (154 pm). Similarly, the covalent radius of Cl is 99 pm i.e. one half of the Cl-Cl bond length (198 pm). So the bond length of C-Cl bond will be 77 + 99= 176 pm. Some selected bond lengths are given in Table (6.7).

Table (6.7) Some selected bond lengths alongwith and hybridization of central atom.

Compound	Hybridization	Bond	Bond length (pm)
BF_3 (Boron trifluoride)	sp^2	B-F	130
BCl_3 (Boron trifluoride)	sp^2	B-Cl	175
SiH_4 (Monosilane)	sp^3	Si-H	148
SiF_4 (silicon tetrafluoride)	sp^3	Si-F	155
C_2H_6 (Ethene)	sp^3	C-C	154
C_2H_4 (Ethene)	sp^2	C=C	133
C_2H_2 (Ethene)	sp	$C \equiv C$	120
$(CH_3)_2$ C=O (Acetone)	sp^2	C=O	122



Animation 6.35: Bond Length
Source & Credit : ch.ic.ac

With an increase in electronegativity difference between the bonded atoms, the bond becomes shortened. For example, Si-F bond length in SiF_4 is found to be 154-159 pm, whereas the addition of their covalent radii (Si=117 pm and F=64 pm) give Si-F bond length to be equal to 181 pm, Table (6.7). The calculated values are almost always higher due to electronegativity differences. The ionic character results in shortening of the bond length due to force of attraction between the polar ends.

Moreover, hybridization scheme involved, also explains the shortening of bonds due to the predominant participation of s-orbitals. Since, the 2s-orbital of carbon has smaller mean radius than the 2p-orbitals, it would be expected that greater the s character in the hybrid orbitals used, the shorter will be the bond distance. Thus, the C-C bond lengths are 154,133 and 120 pm for ethane, ethene and ethyne, respectively where s orbital contribution increases from sp^3 to sp. Further, p-bonding also reduces the internucleft bond distance.

The bond length increases, as we move from top to bottom in group IV-A of the periodic table. Thus, Si-Si bond length is more than C-C bond length in group IV-A and P-P bond length is much more than N-N bond length in group V-A. As the atomic radii increase in a group (N to P or C to Si), the effect of the effective nuclear charge decreases on electrons. As a result the bond length will increase. In the periodic table, shortening of bond lengths occurs from left to right in, a period. This can be attributed to the pull by nuclear charge with the same value of principal quantum number. Therefore, C-C bond length is greater than N-N bond length.

6.5.4 Dipole Moment

In heteronuclear molecules, e.g. HCl where the bonded atoms are of different elements, the molecule becomes polar due to the electronegativity difference. Partial positive and negative charges become separated on the bonded atoms. The se paration of these charges on the molecule is called a dipole and the molecule is said to have a dipole moment.

The dipole moment is a vector quantity, which has a magnitude as well as a direction.
Fig . (6.26) illustrates the dipole and its vecrtor representation. The dipole moment (m) is be defined as the product of the electric charge (q) and the distance between the positive and negative centres (r):

$$\mu = \mathbf{q \times r}$$

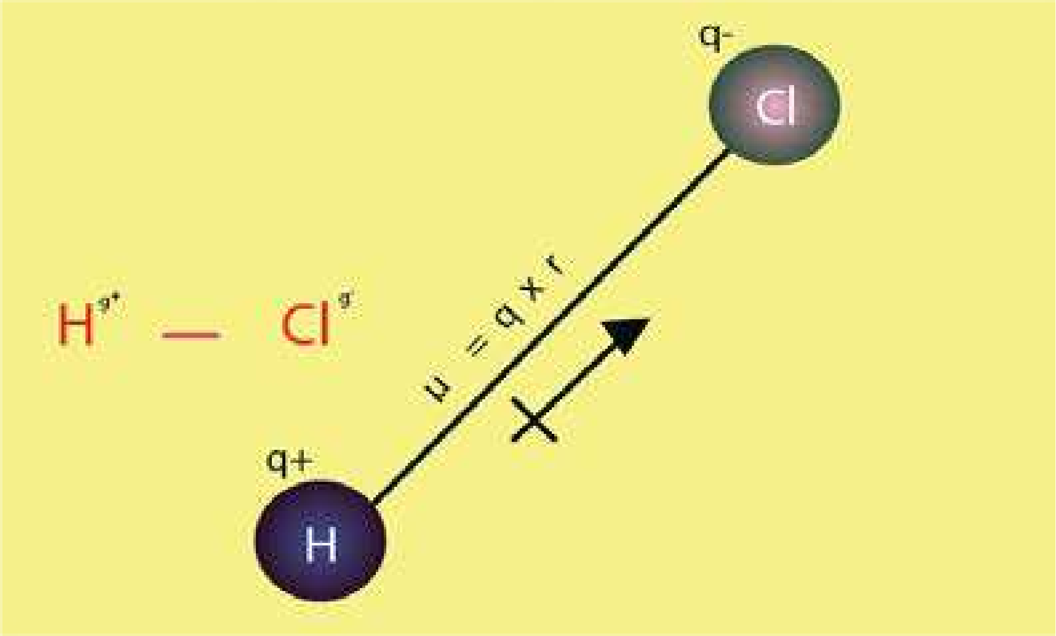
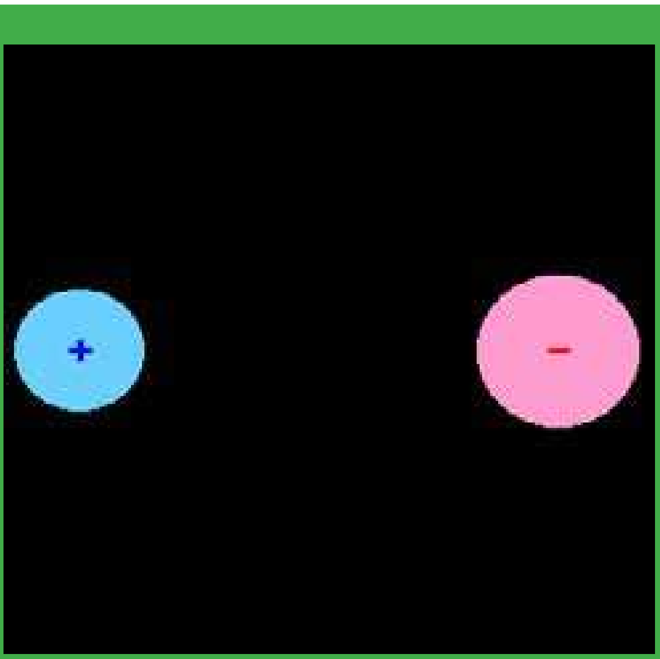


Fig. (6.26) Dipole moment and its vector representation

The dipole moments of simple heteronuclear diatomic molecules like HF, HCl, HBr. HI, CO, NO, etc. are directed from electropositive ends to electronegative ends.

The dipole moments are measured in Debye (D) units. Let us consider a hypothetical molecule (A^{*}—B^{-}), or a unit negative charge separated from a unit positive charge by distance r = 100 pm (1 Å)The dipole moment of such a molecule can be calculated by multiplying the distance 100pm to charge of one electron or proton is 1.6 or$\times 10^{-19}$C $\mu=(1.6022\times10^{-19}C)\times(100\times10^{-12}m) = 1.6022\times10^{-29}$ mC



Animation6.36: Dipole Moment
Source & Credit : chemwiki.ucdavis

Another unit of dipole moment is Debye. The equivalence of Debye and mC is 1 D = $3.336 \mathrm{x} 10^{-30}$mC. So, the dipole moment of the, above system in Debye units is

$$= \frac{1.6022 \mathrm{x} 10^{-29} \mathrm{mC}}{3.336 \mathrm{x} 10^{-30} \mathrm{mC}} = 4.8 \mathrm{~D}$$

The dipole moments of some substances in Debye units are given in Table (6.8). If the molecule is polyatomic and contains two or more dipoles, then the net dipole moment is the resultant of the vector addition of the individual bond moments. Examples of CO_2 and H_2O are shown in Fig (6.26).

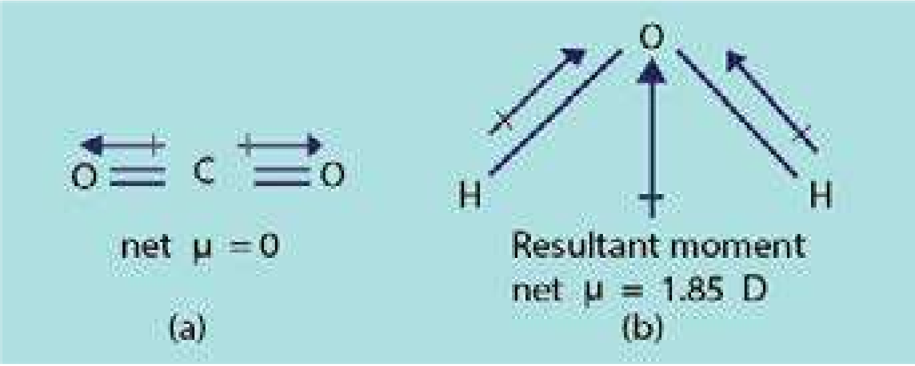


Fig (6.26) Vector addition of bond moments in
(a) linear $C0_2$ molecule and (b) angular H_20 molecular

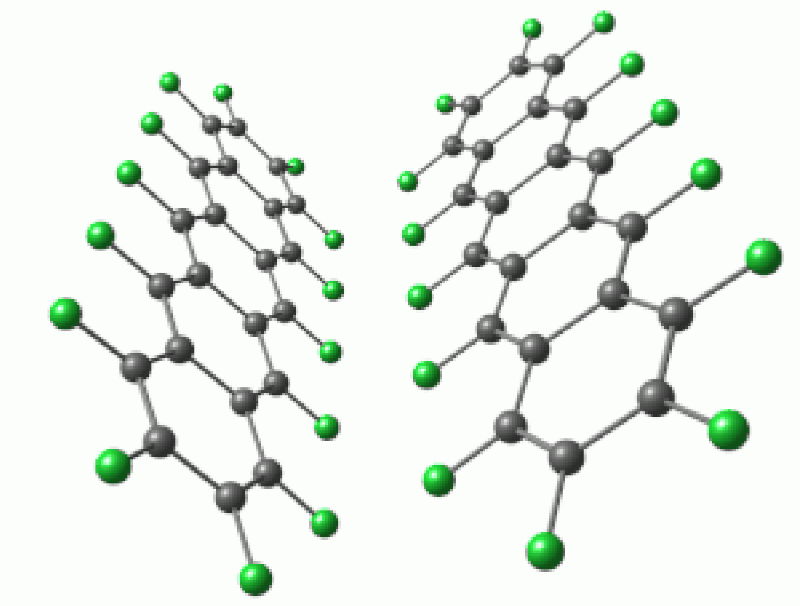
Table (6.8) Dipole moments of some substances in Debyes

Compound	Dipole moment (D)
H_2	0.00
HCl	1.03
HBr	0.78
HI	0.38
H_2O	1.85
H_2S	0.95
NH_3	1.49
SO_2	1.61
CO_2	0.00
CO	0.12
NO	0.16
H_2O_2	2.20
CH_4	0.00
CH_3F	1.81
CH_3Cl	1.45
CH_3Br	1.85
CH_3I	1.35
C_2H_5OH	1.69

6.5.5 Dipole Moments and Molecular Structure

Dipole moment provides two types of information about the molecular structure:

(i) Percentage ionic character of a bond
(ii) Angles between the bonds or the geometry of molecules



Animation 6.37: Dipole Moments and Molecular Structure
Source & Credit : uni-marburg

(1) Percentage Ionic Character

From the experimentally determined dipole moments, the percentage ionic character in a bond can be calculated. For this purpose, we should know the actual dipole moment μ_{obs} of the molecule and actual bond, length. The dipole moment of 100% ionic compound is represented as μ_{ionic}.

$$\%\text{age of ionic character} = \frac{\mu_{obs}}{\mu_{ionic}} x100$$

Example 1:

The observed dipole moment of HF is 1.90 D. Find the percentage ionic character in H-F bond. The distance between the charges is 0.917×10^{-10} m.
(Unit positive charge= 1.6022×10^{-19} C).

Solution:

Let us suppose that HF molecules is 100% ionic. It means that H has full positive charge and F has full negative charge.

To calculate its dipole moment multiply the bond length with full charge of electron or proton i.e. 1.6022 x 10^{-19} C. This dipole moment is called μ_{ionic}.

So, μ_{ionic} =qxr

=(1.6022×10^{-19}C)(0.917×10^{-10}m)

=1.469×10^{-29} mC

Scince 1 D =3.336×10^{-30} mC

So, $$= \mu_{ionic} = \frac{1.469 \times 10^{-29} m_c}{3.336 \times 10^{-30} m_c} = 4.4D$$

The actual dipole moment is given as it is observed.

$\mu_{observed}$=1.90 D

$$\%\text{ionic character} = \frac{\mu_{observed} \times 100}{\mu_{ionic}}$$

$$= \frac{1.90\,D \times 100}{4.4D} = \boxed{43.2\%}\text{Answer}$$

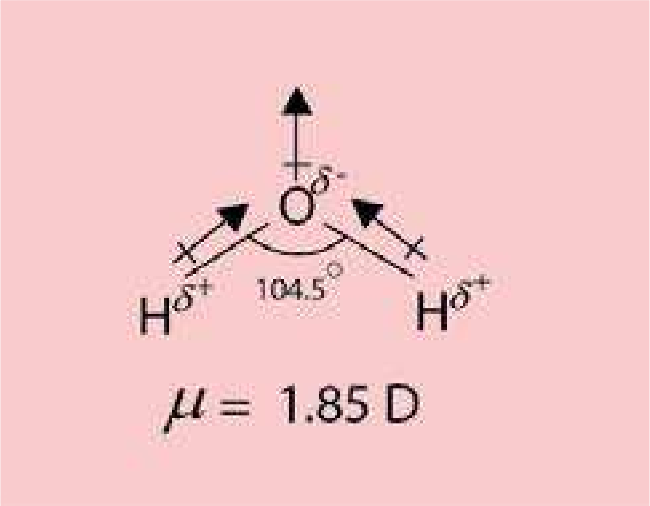
Hence, 43% of HF bond is ionic in nature and 57% covalent. The bond is predominantly covalent.

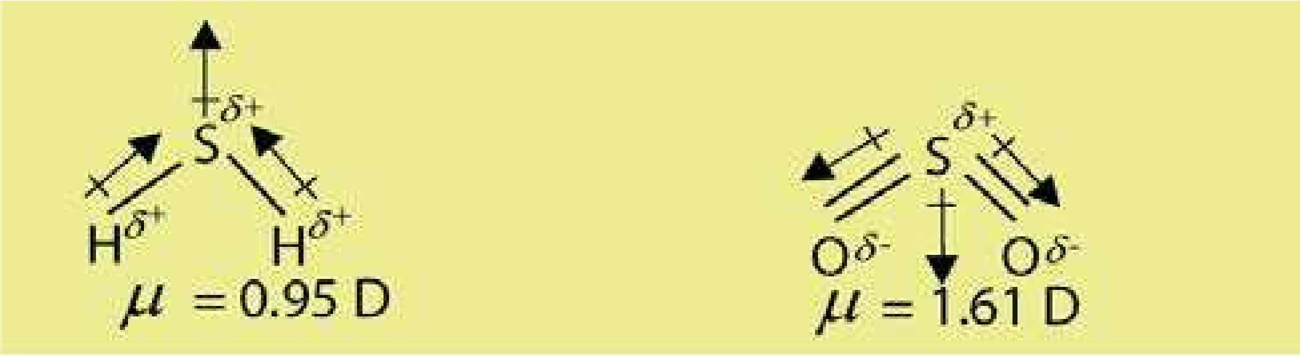
(ii) Bond Angles or the Geometry of Molecules

We can understand this aspect by taking some important examples.

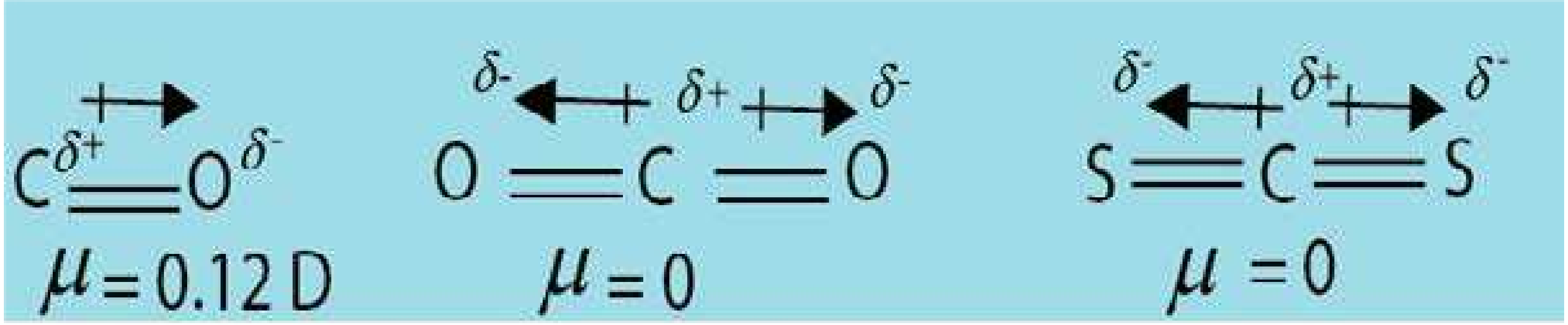
The dipole moment of water is 1.85 D which ruled out its linear structure. The calculations show that water has an angular structure with a bond angle 104.5° between the two O-H bonds. A linear H_2O molecule (H-O-H) would have zero dipole moment.

Similarly, the triatomic molecules H_2S or SO_2 etc. are also bent like H_2O.

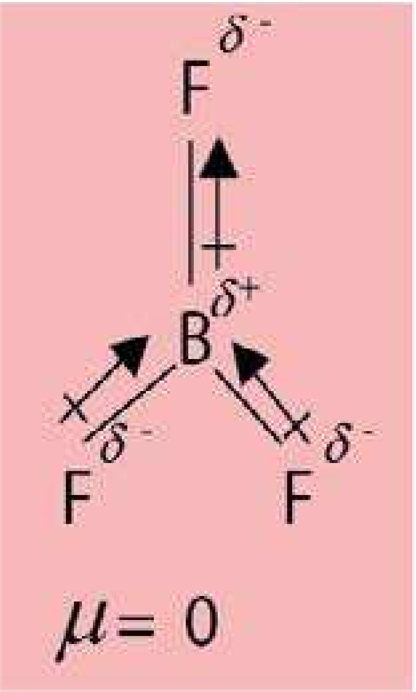


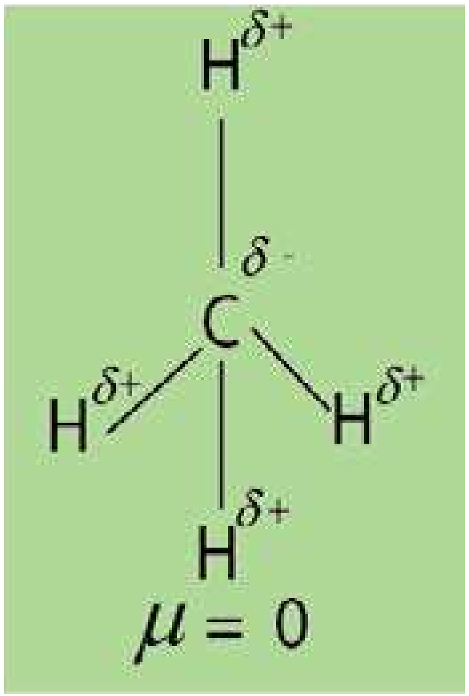


CO has a dipole moment while CO_2 does not have any. The reason is that CO_2 has a linear structure, where the dipoles being equal and opposite, cancel out each other's effect. Similarly, CS_2 has zero dipole moment.



Symmetrical triangular planar molecules of BF_3, $AlCl_3$ and perfectly tetrahedral molecules like CH_4, SiH_4, CCl_4 also have zero dipole moments. This is all due to the cancellation of individual bond moments.





6.6 THE EFFECT OF BONDING ON THE PROPERTIES OF COMPOUNDS

The properties of substances are characterized by the types of bonding present in them. Here, we shall consider the effects of the type of bond on physical and chemical properties of compounds.

(1) Solubility

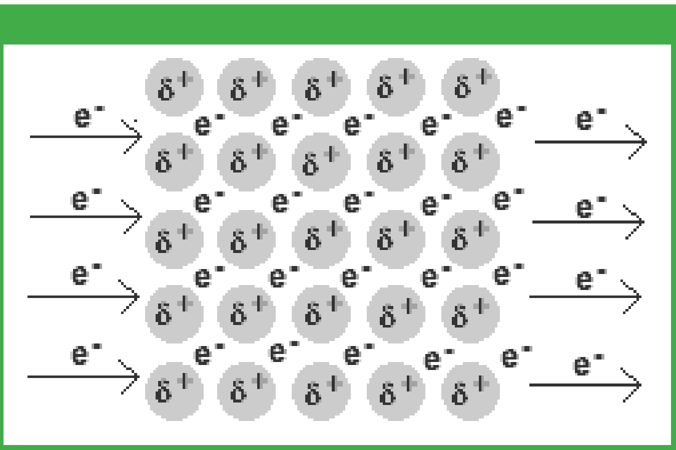
(a) Solubility of Ionic Compounds

Mostly, ionic compounds are soluble in water but insoluble in non-aqueous solvents. When a crystal of an ionic substance is placed in water, the polar water molecules detach the cations and anions from the crystal lattice by their electrostatic attraction. Thus, the ions are freed from the crystal lattice by hydration. This happens when the hydration energy is greater than the lattice energy and the ions are freed from their positions in the crystal. Many ionic compounds do not dissolve in water, as the attraction of water molecules cannot overcome the attraction between the ions. For the same reason, non-polar solvents like benzene and hexane do not dissolve, ionic compounds.

(b) Solubility of Covalent Compounds

In general, covalent compounds dissolve easily in non-polar organic solvent (benzene, ether, etc.)

Here, the attractive forces of solvent molecules are enough for overcoming the intermolecular forces of attraction. Mostly, covalent compounds are insoluble in water. However, some of them dissolve in water due to hydrogen bonding.



Animation 6.38: THE EFFECT OF BONDING ON THE PROPERTIES OF COMPOUNDS
Source & Credit : ausetute

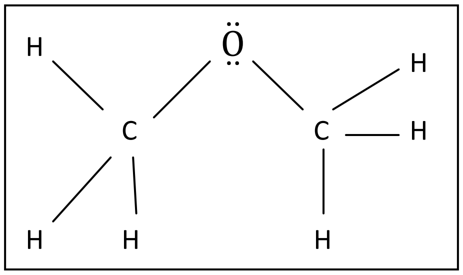
(2) Isomerism

(a) Non-Directional Nature of Ionic Bonds

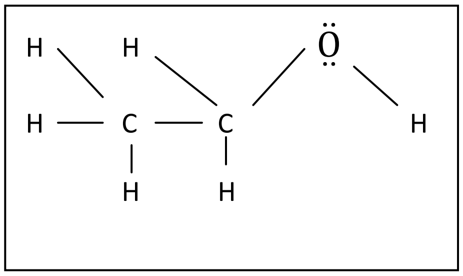
The ionic compounds involve electrostatic lines of forces between oppositely charged ions. Therefore, such bonds are non-rigid and non-directional. Because of this, ionic compounds do not exhibit the phenomenon of isomerism.

(b) Directional Nature of Covalent Bonds

Covalent compounds are rigid and directional. This leads to the possibility of a variety of isomerism. For example, the compounds, C_2H_6O, shows structural isomerism.



Dimethyl ether



Ethanol

(3) Reaction Kinetics:

(a) Speed of Reaction of Ionic Compounds

The ionic compounds exist in the form of ions in an aqueous solution. The chemical reaction between ions occur rapidly.

For example, addition of silver nitrate solution to sodium chloride solution produces a white precipitate of silver chloride instantaneously. The reaction is rapid because on mixing the solutions, no bonds have to be broken, only a new bond is formed. The ionic compounds have already been broken while forming their aqueous solutions.

(b) Speed of Reactions of Covalent Compounds

Since, there is no strong electrical force to speed up a chemical reaction (like in ionic reaction), the covalent bonds are generally much slower to react as they involve bond breaking and making of bonds. The molecules undergo a chemical change as a whole. Covalent bonds react in a variety of ways and their reactivity depends upon the way a reaction proceeds and the kind of a reaction.

KEY POINTS

1. Atoms combine together due to their inherent tendency to attain the nearest noble gas electronic configurations and the formation of a chemical bond always results in a decrease of energy.
2. The size of an atom is expressed in terms of atomic radius, ionic radius and covalent radius and van der Waals radius.
3. It is necessary to understand thermodynamic properties of elements. The minimum amount of energy required to remove an electron from an atom in gaseous state is called ionization energy. It depends upon the atomic size, nuclear charge and shielding effect of electrons. The electron affinity of an atom is the energy given out when an electron is added to a gaseous atom. The tendency of an atom to attract a shared pair of electrons to itself is called electronegativity. Fluorine, is the most electronegative atom and it has arbitrarily been given a value of 4.0.
4. The ionic bonds are formed by transfer of electron from one atom to another. Covalent bonds are formed by mutual sharing of electrons between combining atoms. After the formation of a coordinate covalent bond, there is no distinction between a covalent bond and a coordinate covalent bond.
5. A polar covalent bond is formed when atoms having different electronegativity values mutually share their electrons. Due to polarity, bonds become shorter and stronger and dipole moment may develop.
6. According to valence bond theory, the atomic orbitals overlap to form bonds but the individual character of the atomic orbitals are retained. The greater the overlap, the stronger will be the bond formed.
7. The VSEPR theory gives information about the general shapes and bond angles of molecules. It is based upon repulsion between bonding and lone pairs of electrons, which tend to remain at maximum distance apart so that interaction between them is minimum. The concept provides an alternate way to explain various geometrical shapes of molecules.
8. The geometrical shapes and bond angles are better explained by different hybridization schemes, where different atomic orbitals are mixed to form hybrid orbitals.
9. According to molecular orbital theory, atomic orbitals overlap to form molecular orbitals, n atomic orbitals combine to form n molecular orbitals. Half of them are bonding molecular orbitals and half antibonding molecular orbitals. In this combination, the individual atomic orbital character is lost in order to form an entirely new orbital that belongs to the whole molecule. The theory successfully explains bond order and paramagnetic property of O_2.
10. The bond energy in defined as the average amount of energy required to break all bonds of a particular type in one mole of the substance. It is a measure of the strength of the bond. Stronger the dipole of a bond, greater will be the bond energy.

11.The distance between the nuclei of two atoms forming a covalent bond is called bond length. In general, it is the sum of the covaleht radii of the combined atoms.

12. The dipole moment may be defined as the product of electric charge (q) and the distance (r) between the two oppositely charged centres. It is a vector quantity as it has magnitude and direction. It plays a major role, in determining the % age ionic character of a covalent bond and the shapes of molecules. It has magnitude and direction.

13. Properties of substances are characterized by the type of bonds present in them.

EXERCISE

Q.1 Select the correct statement

(i) An ionic compound A^+B^- is most likely to be formed when

(a) the ionization energy of A is high and electron affinity of B is low.
(b) the ionization energy of A is low and electron affinity of B is high.
(c) both the ionization energy of A andelectron affinity of B are high.
(d) both the ionization energy of A and electron affinity of B are low.

(ii) The number of bonds in nitrogen molecule is

(a) one ó and one π
(b) one ó and two π
(c) three sigma only
(d) two ó and one π

(iii) Which of the following statement is not correct regarding bonding molecular orbitals?

(a) Bonding molecular orbitals possess less energy than atomic orbitals from which they are formed.
(b) Bonding molecular orbitals have low electron density between the two nuclei.
(c) Every electron in the bonding molecular orbitals contributes to the attraction between atoms.
(d) Bonding molecular orbitals are formed when the electron waves undergo constructive interference.

(iv) Which of the following molecules has zero dipole moment?

(a) NH_3 (b) $CHCl_3$ (c)H_2O (d) BF_3

(v) Which of the hydrogen halides has the highest percentage of ionic character?

(a) HCl (b) HBr (c)HF (d)HI

(vi) Which of the following species has unpaired electrons in antibonding molecular orbitals.

(a) 0_2^{2+} (b) N_2^{2-} (c) B_2 (d) F_2

Q.2 Fill in the blanks

(i) The tendency of atoms to attain maximum ________ of electrons in the valence shell is called completion of octet.

(ii) The geometrical shape of $SiCl_4$ and PCl_3 can be explained on the basis of __________ and ________ hybridizations.

(iii) The VSEPR theory stands for__________________ .

(iv) For N_2 molecule, the energy of ó $(2p)_x$ orbital is________________ than $\pi(2p_y)$ orbital.

(v) The paramagnetic property of O_2 is well explained on the basis of MO theory in terms of the presence of_________________ electrons in two MO orbitals.

(vi) The values of dipole moment for CS_2 is __________while for SO_2 is __________

(vii) The bond order of N_2 is________________ while that of Ne_2 is _______________ .

Q.3 Classify the statements as true or false. Explain with reasons.

(i) The core of an atom is the atom minus its valence shell.

(ii) The molecules of nitrogen ($N \equiv N$) and acetylene ($HC \equiv CH$) are not isoelectronic.

(iii) There are four coordinate covalent bonds in NH_4^+ ion.

(iv) A ó-bond is stronger than a π-bond and the electrons of σ-bond are more diffused than π-bond.

(v) The bond energy of heteroatomic diatomic molecules increases with the decrease in the electronegativities of the bonded atoms.

(vi) With increase in bond order, bond length decreases and bond strength increases.

(vii) The first ionization energies of the elements rise steadily with the increasing atomic number from top to bottom ina group.

(viii) A double bond is stronger than a single bond and a triple bond is weaker than a double bond.

(ix) The bonds formed between the elements having electronegativity difference more than 1.7 are said to be covalent in nature.

(x) The re pulsive force between the two bonding pairs is less than that between the two lone pairs.

(xi) The number of covalent bonds an atom can form is related to the number of unpaired electrons it has.

(xii) The rules which govern the filling of electrons into the atomic orbitals also govern filling of electrons into the molecular orbitals.

Q.4 What is a chemical bond? Discuss the formation of ionic and covalent bonds. How does the electronegativity differences differentiate between ionic and covalent bond?

Q.5

(a) Define ionization energy and electron affinity. How these quantities change in the periodic table. What factors are responsible for their variation?

(b) Explain, what do you understand by the term electronegativity? Discuss its variations in the periodic table. How does it affect the bond strengths?

Q.6 Write the Lewis structures for the following compounds:

(i)HCN (ii)CCl_4 (iii) CS_2 (iv) $H_3N \rightarrow AlF_3$

(v)NH_4OH (vii)H_2SO_4 (vii)H_3PO_4 (viii) $K_2Cr_2O_7$

(ix)N_2O_5 (x) $Ag(NH_3)_2NO_3$

Q.7

(a) Explain qualitatively the valence bond theory. How does it differ from molecular orbital theory?

(b) How the bonding in the following molecules can be explained with respect to valence bond theory? Cl_2, O_2, N_2, HF, H_2S.

Q.8 Explain VSEPR theory. Discuss the structures of CH_4, NH_3, H_2O, $BeCl_2$, BF_3,$S0_2$, SO_3 with reference to this theory.

Q.9 The molecules NF_3 andBF_3 all have molecular formulae of the type XF_3. But they have different structural formulas. Keeping in view VSEPR theory sketch the shape of eachtnolecule and explain the origin of differing in shapes.

Q.10 The species NH_2^-, NH_3, NH_4^+ have bond angles of 105°, 107.5° and109.5^0 respectively. Justify these values by drawing their structures.

Q.11

(a) Explain atomic orbital hybridization with reference to sp^3, sp^2 and sp modes of hybridizations for PH_3, C_2H_4 and C_2H_2. Discuss geometries of CCl_4, PCl_3, and H_2S by hybridization of central atoms.

(b) The linear geometry of $BeCl_2$ suggests that central Be atom is sp-hybridized. What type of hybridization a central atom undergoes, when the atoms bonded to it are located at the corners of (a) an equilateral triangle (b) a regular tetrahedron and (c) triangular bipyramide?

Q.12

(a) Give the basis .of the molecular orbital theory and discuss the molecular orbital configurations of the following molecules?

(i)He_2 (ii)N_2 (iii) O_2 (iv)O_2^{2+} (v)O_2^{2-}

(b) How does molecular orbital theory explain the paramagnetic character of O_2,O_2^{2+} and O_2^{2-} species ?

Q.13

a) Sketch the molecular orbital pictures of

(i) $\pi(2p_x)$ and $\pi^*(2p_x)$ (ii) O_2, O_2^{2+} ,O_2^{2-} (iii) He_2 and Ne_2

b) Sketch the hybrid orbitals of the species, PCl_3, $SiCl_4$ and NH_4^+

Q.14

(a) Define bond energy. Explain the various parameters which determine its strength.

(b) How do you compare the bond strengths of

(i) Polar and non-polar molecules (ii) σ-and π-bonds?

(c) Calculate the bond energy of H-Br. The bond energy of H-H is 436 $kJmol^{-1}$ and that of Br- Br is 193 $kJmol^{-1}$.

(Ans : 314.5$kJmol^{-1}$)

Q.15

(a) Define dipole moment. Give its various units. Find relationship between Debye and mc. How does it help to find out the shapes of molecules?

(b) The bond length of H-Br is 1.4×10^{-10}m. Its observed dipole moment is 0.79D. Find the percentage ionic character of the bond. Unit positive charge = 1.6022×10^{-19}C and 1D = 3.336×10^{-30} mc.

(Ans: 11.7%)

Q.16 PF_3 is a polar molecule with dipole moment 1.02 D and thus the P-F bond is polar. Si, is in the proximity of P in the periodic table. It is expected that Si-F bond would also be polar, but SiF_4 has no dipole moment. Explain it?

Q.17 Which of the following molecules will be polar or non-polar, sketch the structures and justify your answer.

(i) CCl_4 (ii) SO_3 (iii)NF_3 (iv)SO_2

Q.18 Explain the following with reasons:

(i) Bond distance is the compromise distance between two atoms.

(ii) The distinction between a coordinate covalent bond and a covalent bond vanishes after bond formation in NH_4^+, H_3O^+ and $CH_3NH_3^+$.

(iii) The bond angles of H_2O and NH_3 are not 109.5° like that of CH_4. Although, O- and N-atoms are sp^3 hybridized.

(vi) π-bonds are more diffused than σ-bonds.

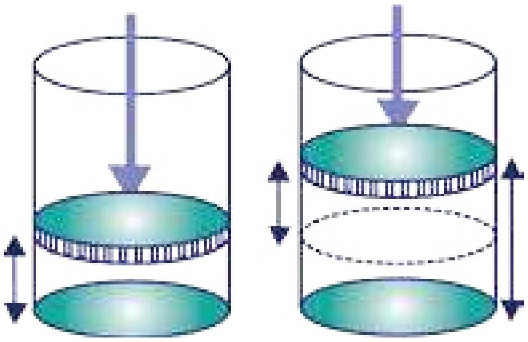
(v) The abnormality of bond length and bond strength in HI is less prominent than that of HCl.

(vi) The dipole moments of CO_2, and CS_2 are zero, but. that of $SO_2$1.61D.

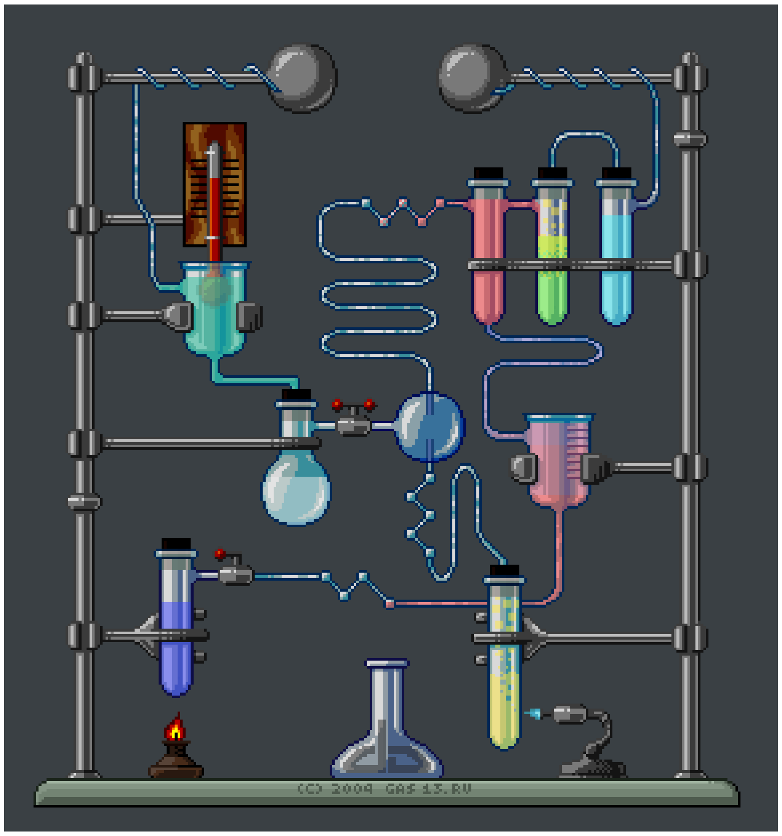
(vii) The melting points, boiling points, heat of vaporizations and heat of sublimations of electrovalent compounds are higher as compared with those of covalent compounds.

CHAPTER

7



THERMOCHEMISTRY



Animation 7.1: Thermochemistry
Source & Credit: wikispaces

7.0.0 INTRODUCTION

It is matter of common observation that energy in the form of heat, is either evolved or absorbed as a result of a chemical change. This is due mostly to the breaking of bonds in the reactants and formation of new bonds in the products. Bond breaking absorbs energy but bond making releases it. The overall energy change that occurs, results from the difference between energy supplied for the breaking of reactant bonds and that evolved in the making of product bonds. The study of heat changes accompanying a chemical reaction is known as thermochemistry.

Substances exist, because they possess energy. Different substances have different amounts of energy associated with them. Due to this reason, the total energy of the products is never equal to that of reactants. Hence, in a chemical change, the energy in the form of heat will either be evolved or absorbed and this is called heat of reaction.

Generally, in all chemical changes, energy is exchanged with the surroundings. When it is given out by the reaction, the change is said to be exothermic when it is absorbed, the reaction is endothermic.

When an exothermic reaction occurs, heat is given out by the system and the temperature of the system rises above the room temperature. Eventually, the temperature of the system falls to room temperature again as the heat produced is lost to the surroundings.

When an endothermic reaction occurs, the heat required for the reaction is taken from the reacting materials (system) and the temperature of the system falls below the initial temperature. Eventually, the temperature of the system rises to room temperature again as heat is absorbed from the surroundings.

The energy units in which heat changes, usually expressed in SI system are joule (J) and kilojoule (kJ).

Some of the examples of exothermic and endothermic reactions are given below.

(i) The combustion of carbon in oxygen is a common reaction.

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H = -393.7 \text{kJ mol}^{-1}.$$

The reaction is exothermic and 393.7kJmol ‘ of heat is evolved during the reaction.

(ii) The formation of water from hydrogen and oxygen is an exothermic reaction.

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)} \qquad \Delta H = -285.58 \text{kJ mol}^{-1}.$$

(iii) In the Haber’s process, the formation of ammonia is also an exothermic reaction.

$$N_{2(g)} + 3H_{2(g)} \quad \square \quad 2NH_{3(g)} \qquad \Delta H = -41.6 kJ\ mol^{-1}.$$

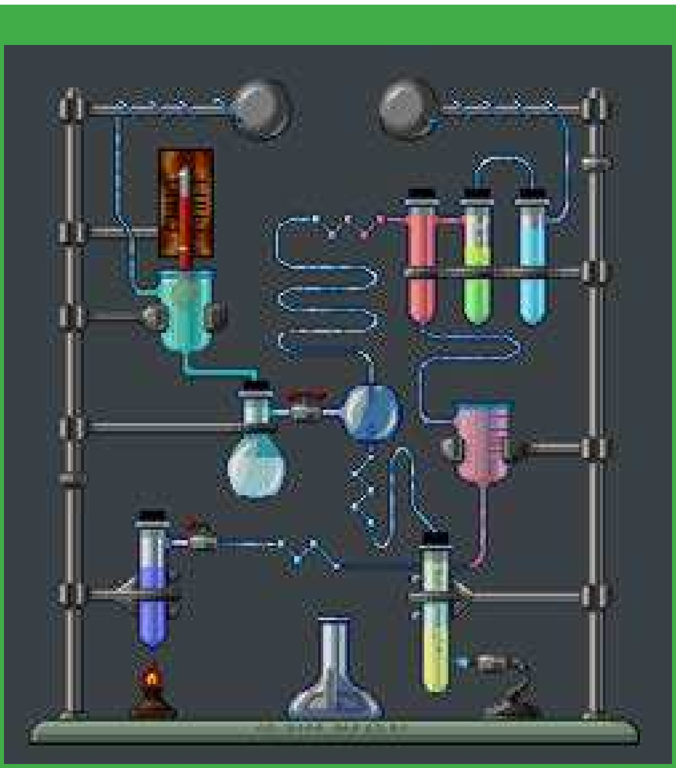
(iv) The decomposition of water into oxygen and hydrogen is an endothermic reaction.

$$H_2O_{(l)} \rightarrow H_{2(g)} + 1/2\ O_{2(g)} \qquad \Delta H = +285.58 kJ\ mol^{-1}.$$

(v) When one mole of nitrogen combines with one mole of oxygen to yield nitrogen oxide (NO), 180.51 kJ of heat is absorbed by the system and the reaction is endothermic.

$$N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)} \qquad \Delta H = +180.51 kJ\ mol^{-1}.$$

The subject matter of thermochemistry is based on the first law of thermodynamics. The subject has an important practical utility as it gives us information about the energy or heat contents of compounds, a knowledge of which is necessary for the study of chemical bonding and chemical equilibrium. The scope of thermochemistry is limited mainly, because only a few of many chemical reactions are such, whose heats of reaction can be accurately measured.



Animation 7.2 : Thermochemistry
Source & Credit : pamcox.wikispaces

7.1 SPONTANEOUS AND NON-SPONTANEOUS REACTIONS

A process which takes place on its own without any outside assistance and moves from a non-equilibrium state towards an equilibrium state is termed as spontaneous process or natural process. It is unidirectional, irreversible and a real process. Some examples of spontaneous processes are given below.

(i) Water flows from higher level to the lower level. The flow cannot be reversed without some external aid.

(ii) Neutralization of a strong acid with a strong base is a spontaneous acid-base reaction.

$$\mathrm{NaOH_{(aq)} + HCI_{(aq)} \quad \square \quad NaCl_{(aq)} + H_2\,O_{(l)}}$$

(iii) When a piece of zinc is added to the copper sulphate solution, blue colour of the solution disappears due to the spontaneous redox reaction.

$$\mathrm{CuSO_{4(aq)} + Zn_{(s)} \rightarrow ZnSO_{4(aq)} + Cu_{(s)}}$$

A reaction will also be called a spontaneous process, if it needs energy to start with, but once it is started, then it proceeds on its own. Burning of coal and hydrocarbon in air are examples of such spontaneous reactions. A piece of coal does not burn in air on its own rather the reaction is initiated by a spark and once coal starts burning, then the reaction goes spontaneously to completion.

Non-spontaneous process is the reverse of the spontaneous process. It does not take place on its own and does not occur in nature. Reversible processes constitute a limiting case between spontaneous and non-spontaneous processes. Some non-spontaneous processes, can be made to take place by supplying energy to the system from external source. Some examples of non-spontaneous processes are given below.

(i) Pumping of water uphill.

(ii) Transfer of heat from cold interior part nof the refrigerator to the hot surroundings.

(iii) When nitrogen reacts with oxygen, nitric oxide is formed. This reaction takes place by the absorbance of heat. Although, N_2 and O_2 are present in air, but they do not react chemically at ordinary conditions.The reaction takes place when the energy is provided by lightning.

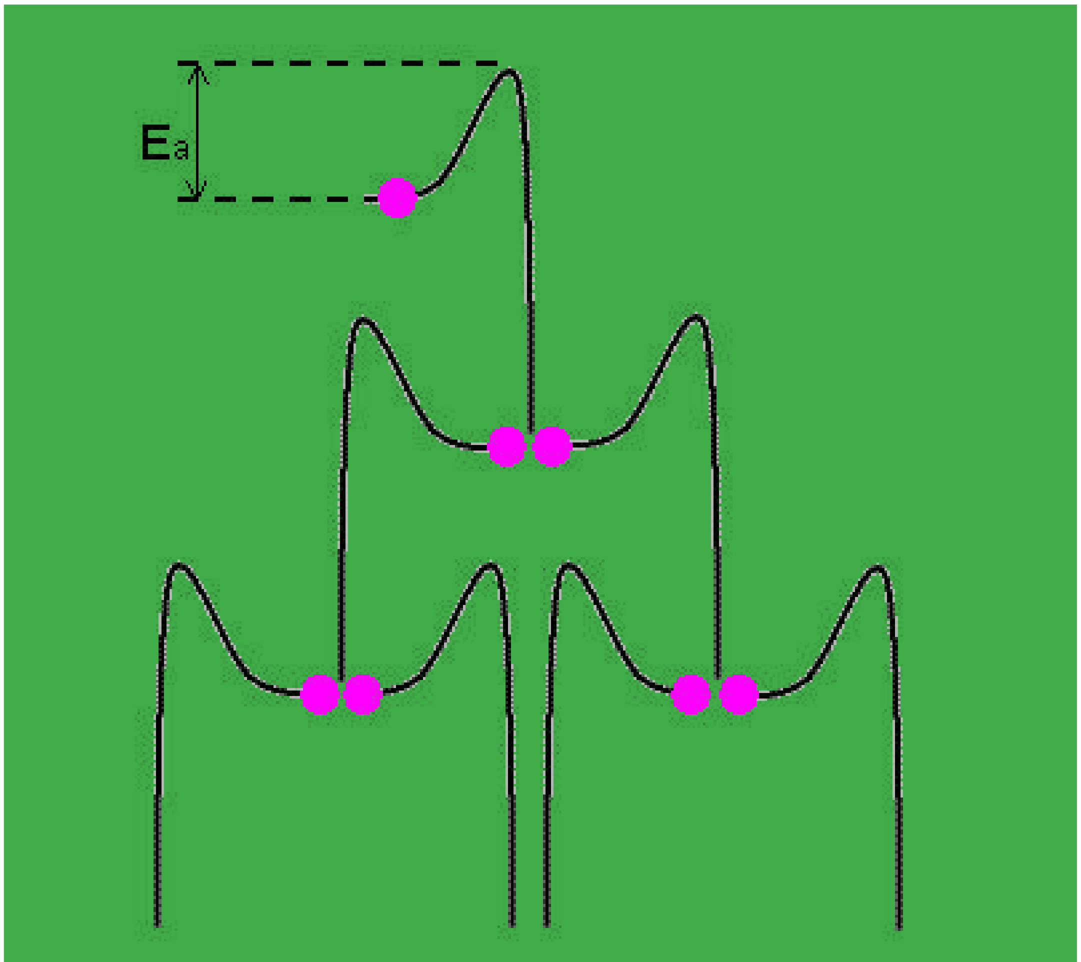
$$\mathrm{N_{2(g)} + O_{2(g)} \quad \square \quad 2NO_{(g)}} \qquad \text{(Non-spontaneous reaction)}$$

Our common experience, shows that spontaneous processes proceed with a decrease in energy. We might expect, therefore, that a chemical reaction would proceed spontaneously if the reaction system decreases in energy by transferring heat to its surroundings. In other words, we might expect all exothermic reactions to be spontaneous. This is usually true, but not always. There are many endothermic changes that proceed spontaneously although they absorb heat. For example,

Ammonium chloride dissolves in water and this process is also endothermic.

$$H_2O_{(l)} \rightarrow H_2O_{(g)} \qquad \Delta H = 44.0 kJmol^{-1}$$

$$NH_4Cl_{(s)} \rightarrow NH^+_{4(aq)} + Cl_{(aq)} \qquad \Delta H = 15.1 kJmol^{-1}$$



Animation 7.3: SPONTANEOUS AND NON-SPONTANEOUS REACTIONS
Source & Credit : thompsona.free.fr

Thus, energy change alone cannot help us to predict, whether a reaction will occur spontaneously or not. To predict whether a reaction will occur spontaneously or not it is necessary to study the free energy of the system. The concept of free energy can help us to understand the processes in terms of entropy change. Anyhow, its discussion is outside the scope of this book.

7.2 SYSTEM, SURROUNDING AND STATE FUNCTION

These are the terms employed in the study of thermochemistry. To understand the energy changes in materials, let us define these terms.

We shall be using them frequently later on. The term system is used for anything (materials) under test in the laboratory, or under consideration in the classroom for the purpose of argument. We can say that any portion of the universe which is under study is called a system and the remaining portion of the universe is known as its surroundings.

The real or imaginary surface separating the system from the surroundings is called the boundary, Fig. (7.1). In an experimental work, a specific amount of one or more substances constitute a system, e.g. one mole of oxygen confined in a cylinder fitted with a piston is a system. The cylinder, the piston and all other objects outside the cylinder are surroundings. Similarly, a cup of water is a system. The air surrounding it, the table on which it is lying, etc. are surroundings.

Consider, the reaction between Zn and $CuSO_4$ solution. This can be called a system under observation. The flask, the air, etc. are the surroundings, Fig (7.1).

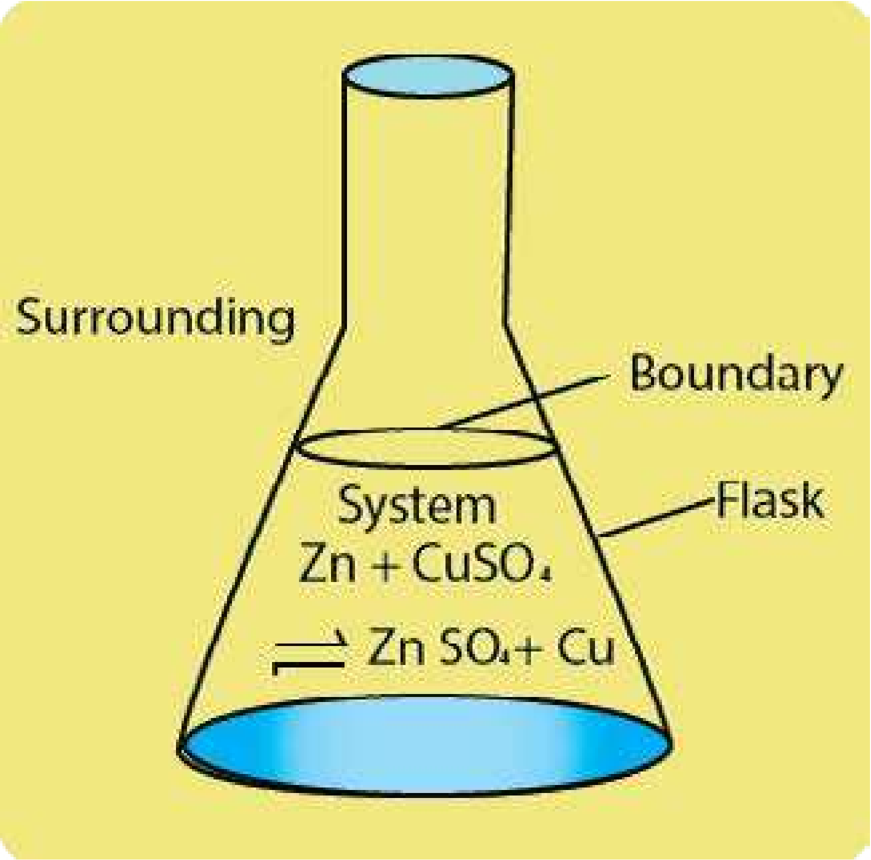


Fig (7.1) System and surroundings

The state of a system is the condition of a system. When any process is performed on a system its state is altered in some ways. Let us consider a beaker containing water. It will be a system having certain temperature and volume.

This initial condition of the system may be called the initial state. Suppose we heat the beaker. The system will undergo a change after heating. The final condition of the system may now be called the final state of the system. By comparing both initial and final states of the system, we can describe the.change taking place in the system.

Let T_1 and T_2 denote the temperatures of water before and after heating, respectively. The change in temperature ΔT, may then be represented as

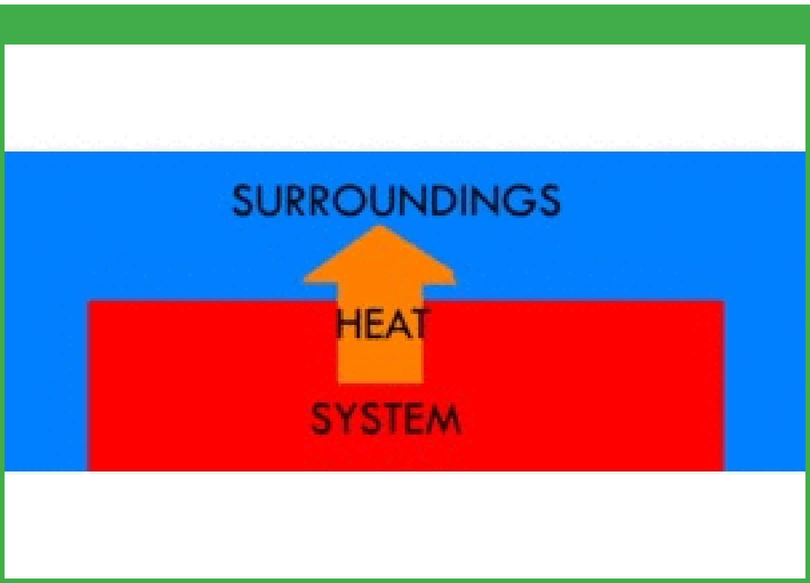
$$\Delta T = \text{Final temperature - Inital temperature}$$

$$\Delta T = T_2 - T_1$$

A state function is a macroscopic property of a system which has some definite values for initial and final states, and which is independent of the path adopted to bring about a change. By convention, we use capital letters as symbols for a state function, e.g. pressure (P), temperature (T), volume (V), internal energy (E) and enthalpy (H), are all state functions.

Let us suppose, that V_1 is the initial volume of a gas. A change is brought about in the gas and its final volume becomes V_2. The change in volume (ΔV) of the gas is given by

$$\Delta V = V_2 - V_1$$



Animation 7.4: SYSTEM, SURROUNDING AND STATE FUNCTION
Source & Credit : kastedu.weebly

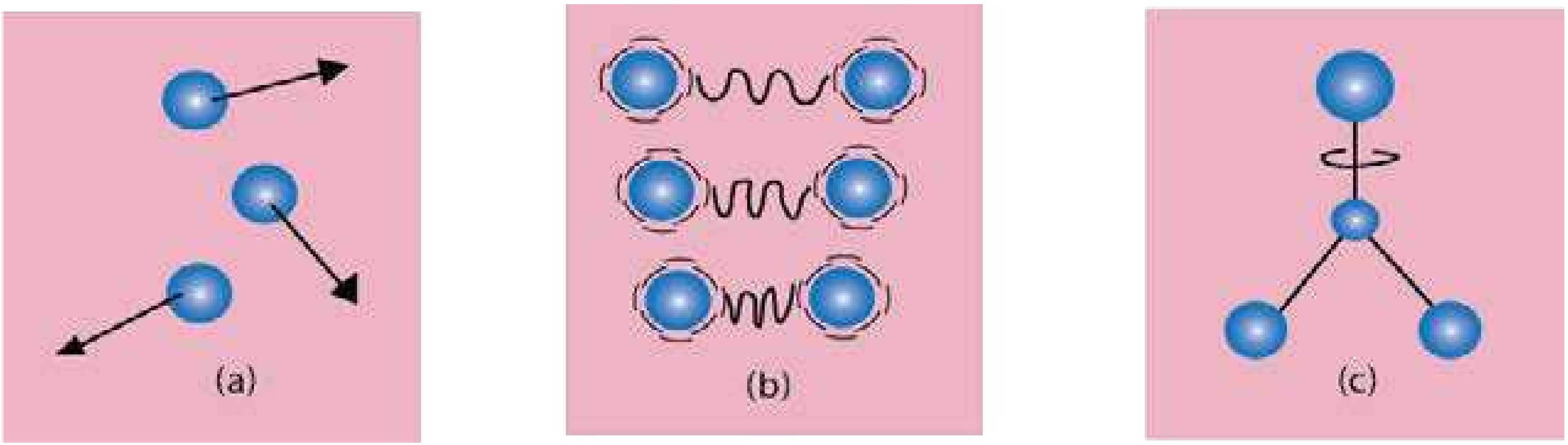
Now, this change in volume of the gas can be brought about either by changing temperature or pressure of the gas. Since V is a state function, so ΔV will be independent of the way the volume of the gas has been changed. It will only depend upon the initial and final volumes of the gas.

7.3 INTERNAL ENERGY AND FIRST LAW OF THERMODYNAMICS

A system containing some quantity of matter has definite amount of energy present in it. This energy is the sum of kinetic as well as the potential energies of the particles contained in the system. The kinetic energy is due to the translational, rotational and vibrational movements of particles, Fig (7.2). The potential energy accounts for all the types of attractive forces present in the system. These attractive forces, include all the types of bonds and the van der Waal's forces present among the particles.

The total of all the possible kinds of energies of the system is called its internal energy, E. The change in internal energy of the system ΔE is a state function.

It is not possible, to measure the absolute value of internal energy of a system, but it is often possible to measure the value of ΔE for a change in the state of the system.



Translational motion of He gas molecules

A diatomic molecule H_2 is vibrating

A tetra-atomic molecule say BF_3 is rotating on an axis

Fig (7.2) Translational, vibrational and rotational movements of molecules. Diatomic molecules have translational motions as well. Anyhow triatomic and higher molecules have translational, vibrational and rotational motions.

There are two fundamental ways of transferring energy to or from a system. These are heat and work. Heat is not a property of a system. It is therefore not a state function. It is defined as the quantity of energy that flows across the boundary of a system during a change in its state due to the difference in temperature between the system and the surroundings. Heat evolved or absorbed by the system is represented by a symbol q. Work is also a form in which energy is transfered from one system to another. It is defined as the product of force and distance i.e. $W = F \times S$. Work is measured in Joules in SI units. There are different kinds of work. The type of work we most commonly encounter in thermochemistry is pressure-volume work. For example, expansion can occur when a gas is evolved during a chemical reaction Fig (7.3).

In such cases, the work W done by the system is given by

$W = -P \Delta V$ (In pressure volume work, force becomes pressure and distance becomes volume change where P is the external pressure and ΔV is the change in volume. Work is not a state function. The sign of W is positive when work is done on the system and it is negative when work is done by the system.

Similarly the sign of q is positive when heat is absorbed by the system from surroundings, and it is negative when heat is absorbed by the surroundings from the system.

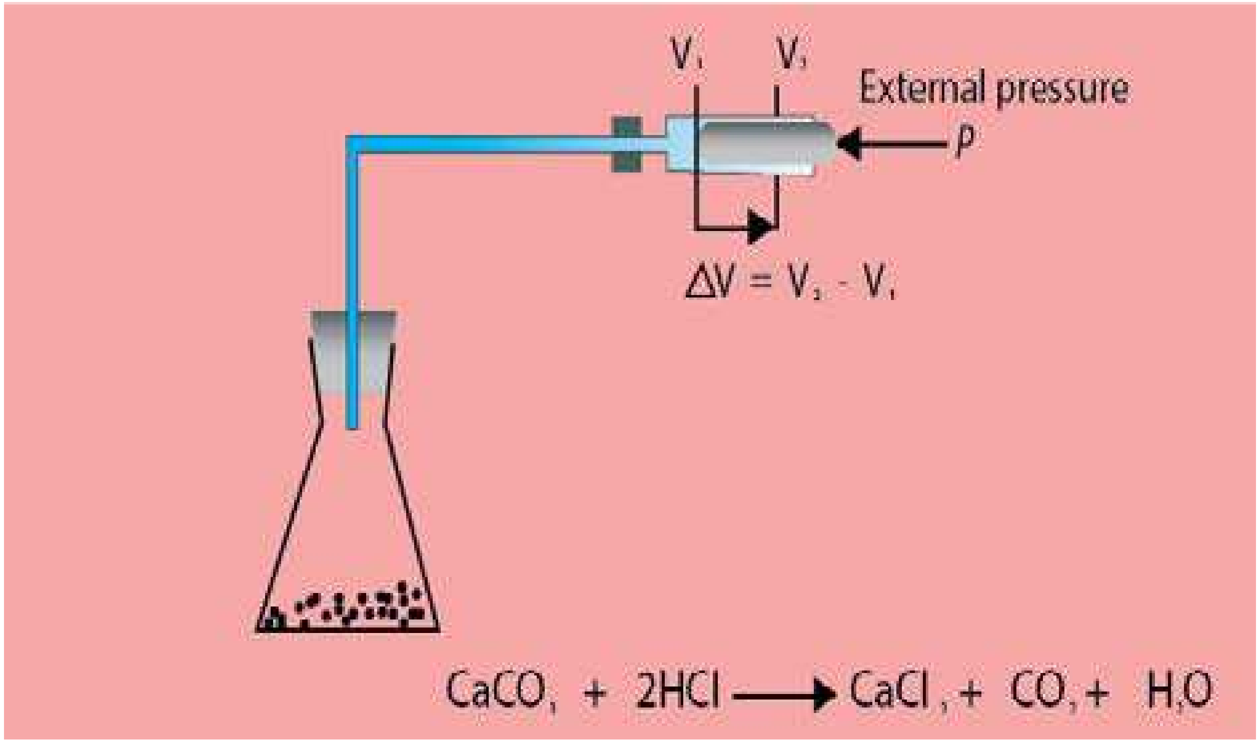


Fig (7.3) Pressure-volume work during expansion of a gas.

Animation 7.5: INTERNAL ENERGY AND FIRST LAW OF THERMODYNAMICS
Source & Credit : ashamedparents

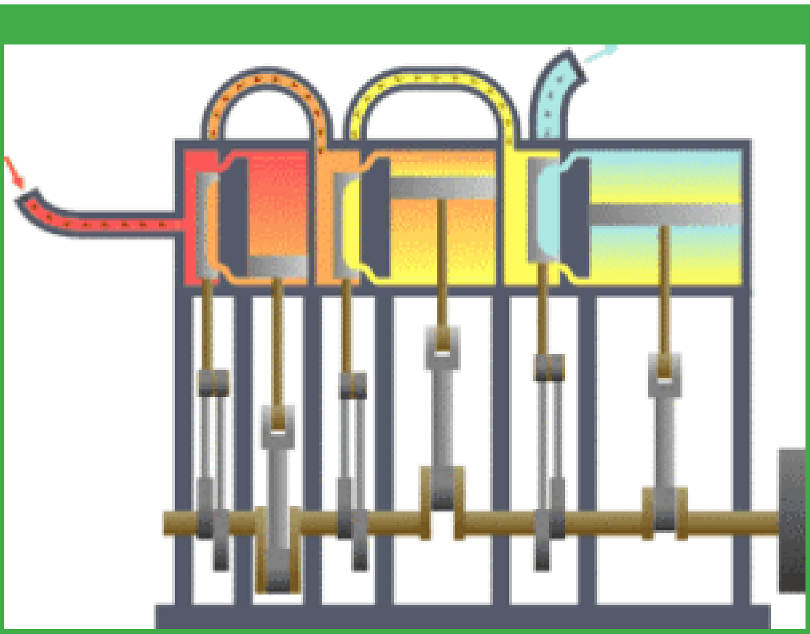
7.3.1 First Law of Thermodynamics

The first law of thermodynamics, also called the law of conservation of energy, states that energy can neither be created nor destroyed, but can be changed from one form to another. In other words, a system cannot destroy or create energy. However, it can exchange energy with its surroundings in the form of heat and work. Thus, the energy change is the sum of both heat and work, so that the total energy of the system and its surroundings remains constant.

Consider, a gas enclosed in a cylinder having a frictionless piston Fig (7.4). When a quantity of heat 'q' is supplied to the system, its internal energy E_1 changes to E_2 and piston moves upwards. The change in internal energy ΔE is given by the following equation.

$$\Delta E = E_2 - E_1 = q + w$$

$$\Delta E = q + w$$



Animation 7.6: First Law of Thermodynamics
Source & Credit : docsity

In this equation ‘q’ represents the amount of heat absorbed by the system and V is the work done by the system in moving the piston up, Fig (7.4).

If ‘w‘ is pressure-volume work, then the above expression assumes the following form

$$\Delta E = q - P\Delta V \quad \text{............} \quad (2)$$

When the piston is kept in its original position or the volume of the gas is not allowed to change, then $\Delta V = 0$ and equation (2) will take the following form.

$$\Delta E = q_v \quad \text{.............} \quad (3)$$

This shows that a change in internal energy of a system, at constant volume is equal to heat absorbed by the system (q_v).

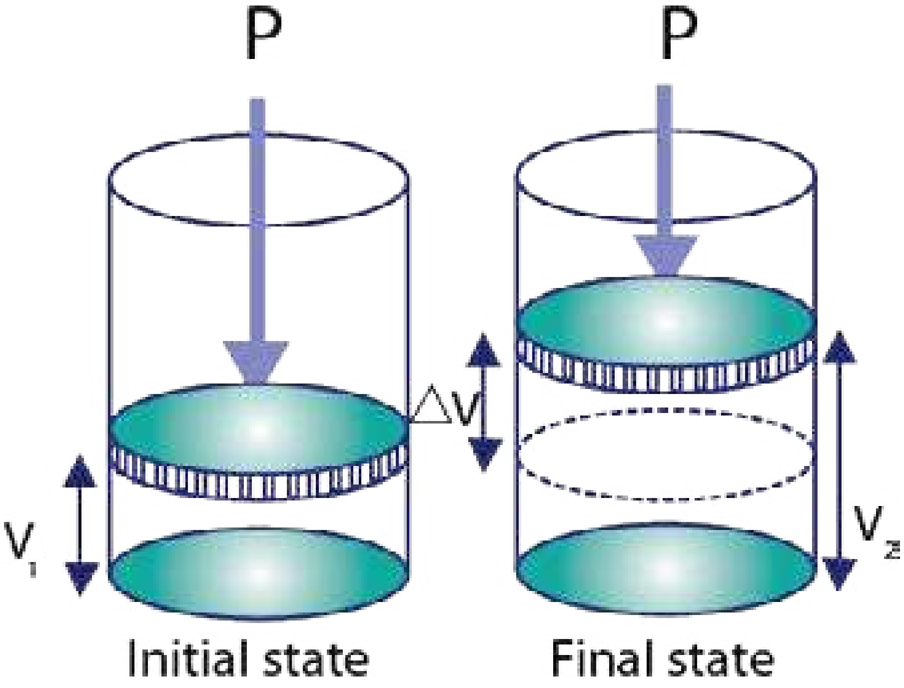
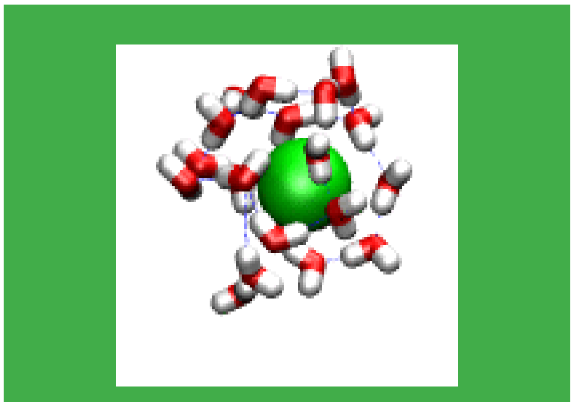


Fig (7.4) Expansion of a gas and pressure-volume work.

7.4 ENTHALPY

Again consider the same process as described above. A quantity of heat q is given to the system (gas) which is now kept at constant atmospheric pressure.



Animation 7.7: ENTHALPY
Source & Credit : physik.fu-berlin.de

A part of this heat is used to increase the internal energy of the gas and the rest is used to do work on the surroundings. This work is done by the gas, when it expands against a constant pressure. To take account of increase in internal energy and accompanying work done by the gas, there is another property of the system called enthalpy or heat content. It is represented by H. In general, enthalpy is equal to the internal energy, E plus the product of pressure and volume (PV).

$$H = E + PV$$

Enthalpy is a state function. It is measured in joules. It is not possible, to measure the enthalpy of a system in a given state. However, change in enthalpy (ΔH) can be measured for a change in the state of system . A change in enthalpy of a system can be written as:

$$\Delta H = \Delta E + \Delta(PV)$$

or $$\Delta H = \Delta E + V\Delta P + P\Delta V$$

Since, the gas is kept at constant pressure, = 0

Hence $$\Delta H = \Delta E + P\Delta V \qquad \text{..........} \quad (4)$$

In case of liquids and solids, the changes in state do not cause significant volume change i.e. $\Delta V = 0$. For such process, ΔH and ΔE are approximately the same i.e. $\Delta H \approx \Delta E$

According to first law of thermodynamics:

$$\Delta E = q + w$$

If w is pressure - volume work done by the system, then:

$$w = - P\Delta V$$

So $$\Delta E = q - P\Delta V$$

Putting the value of ΔE in equation (4) we get:

$$\Delta H = q - P\Delta V + P\Delta V$$
$$\Delta H = q$$

Since the pressure is constant, therefore,

$$\Delta H = q_p \qquad \text{.........} \qquad (5)$$

This shows that change in enthalpy is equal to heat of reaction at constant pressure. The reactions are carried out at constant pressure more frequently than at constant volume. So, working with ΔH is more convenient rather than ΔE.

Example 1:

When 2.00 moles of H_2 and 1.00 mole of O_2 at 100°C and 1 torr pressure react to produce 2.00 moles of gaseous water, 484.5 kJ of energy are evolved. What are the values of (a) ΔH (b) ΔE for the production of one mole of H_2O (g)?

Solution:

(a) The reaction is occurring at constant pressure.

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)}$$

The enthalpy change for one mole of water vapours is

$$\Delta H = \frac{-484.5\text{kJ}}{2\text{ moles of }H_2O} = \boxed{-242.2\text{kJ mol}^{-1}}\text{ Answer}$$

The minus sign shows that the reaction is exothermic for the production of 1 mole of water,

(b) To calculate ΔE from ΔH, we use the equation (4)

$$\Delta H = \Delta E + P\Delta V$$

Let us, first calculate the value of $P\Delta V$ using the ideal gas equation

$$PV = nRT$$

Or $$P\Delta V = \Delta nRT$$

Now, Δn = No. of moles of the products - No. of moles of the reactants

$$= 2\text{moles} - 3\text{moles} = -1\text{mole}$$

$$R = 8.314\text{JK}^{-1}\text{mol}^{-1}$$

$$T = 373\text{K}$$

$$P\Delta V = \Delta nRT \quad .... \quad (6)$$

$$P\Delta V = -1\text{ mole x }8.314\text{J mol K}^{-1}\text{ x }373\text{K}$$

$$P\Delta V = -3100\text{J} = -3.10\text{kJ}$$

This is the value for 2 moles of water. For the formation of 1 mole of water,

$$P\Delta V = \frac{-3.10}{2} = -1.55\text{kJmol}^{-1}$$

On substituting, these values into equation (4).

$$\Delta H = \Delta E + P\Delta V$$

$$\Delta E = \Delta H - P\Delta V$$

$$= -242.2-(-1.55) \quad = -242.2+1.55$$

$$\Delta E = \boxed{-240.6\text{kJ mol}^{-1}} \quad \text{Answer}$$

7.4.1 Enthalpy of a Reaction (ΔH^o)

In an exothermic reaction, the heat content or enthalpy of the products H_2 is less than that of the reactants H_1. Since, the system has lost heat, we can say the enthalpy change for the reaction ΔH is negative, Fig (7.5 a)

In an endothermic reaction, the enthalpy of products H_2, is greater than that of the reactants H_1 and the enthalpy change, ΔH is positive. These enthalpy changes are represented in Fig (7.5 b).

The standard enthalpy of a reaction ΔH^o is the enthalpy change which occurs when the certain number of moles of reactants as indicated by the balanced chemical equation, react together completely to give the products under standard conditions, i.e 25 °C (298K) and one atmosphere pressure. All the reactants and products must be in their standard physical states. Its units are kJ mol^{-1}.

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(\ell)} \qquad \Delta H^o = -285.8\text{kJmol}^{-1}$$

-285.8 kJmol^{-1} is standard enthalpy of reaction.

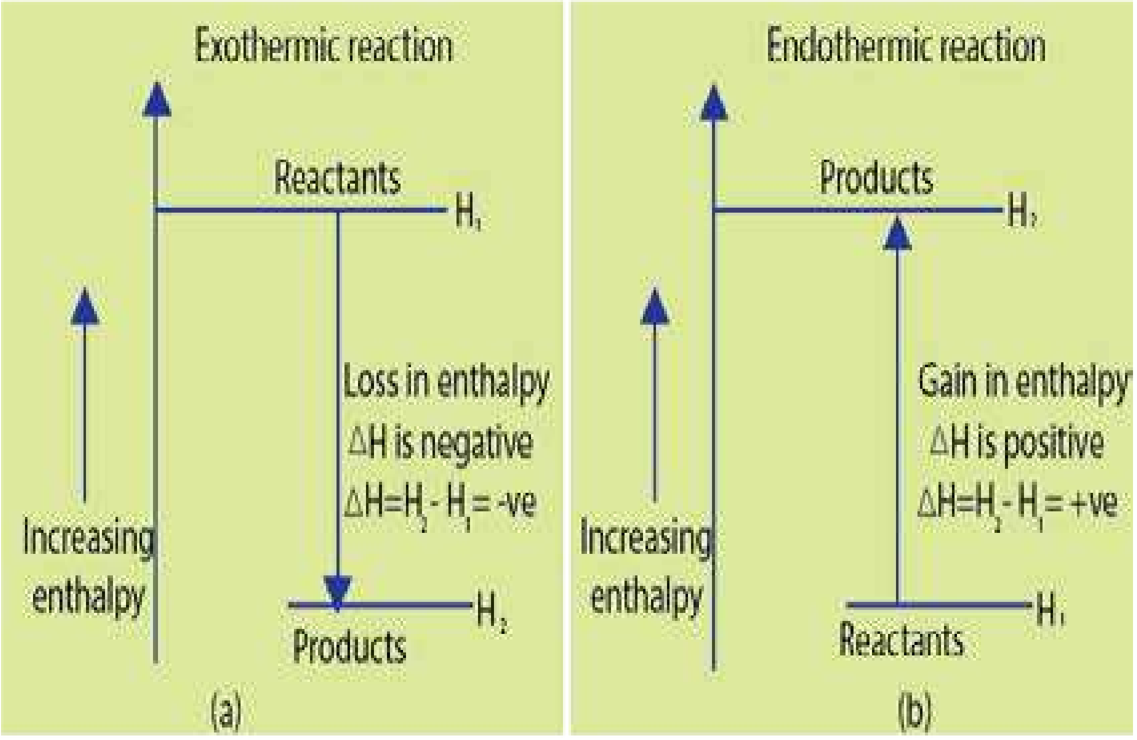
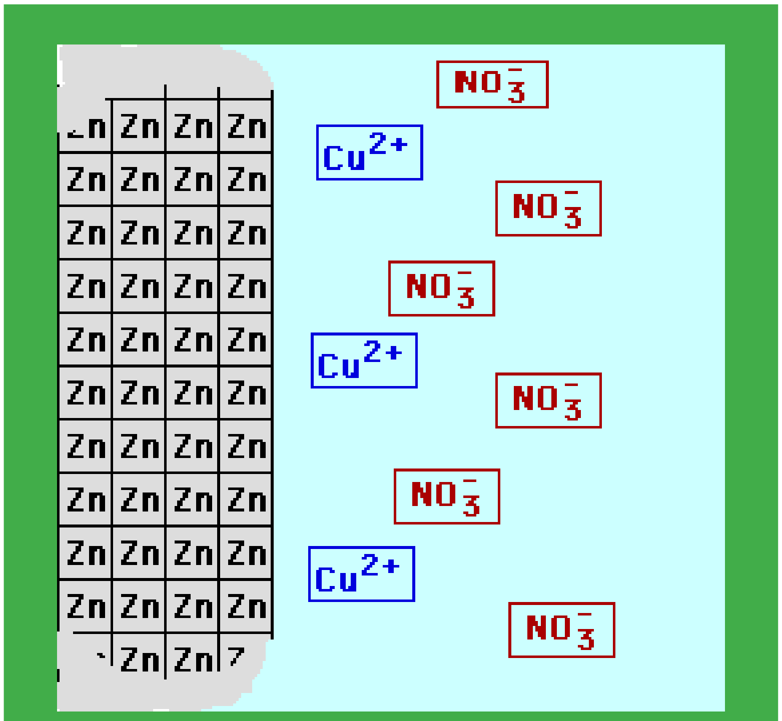


Fig (7.5) Enthalpy changes in thermochemical reactions



Animation 7.8: Enthalpy of a Reaction (DH)
Source & Credit : web.mst

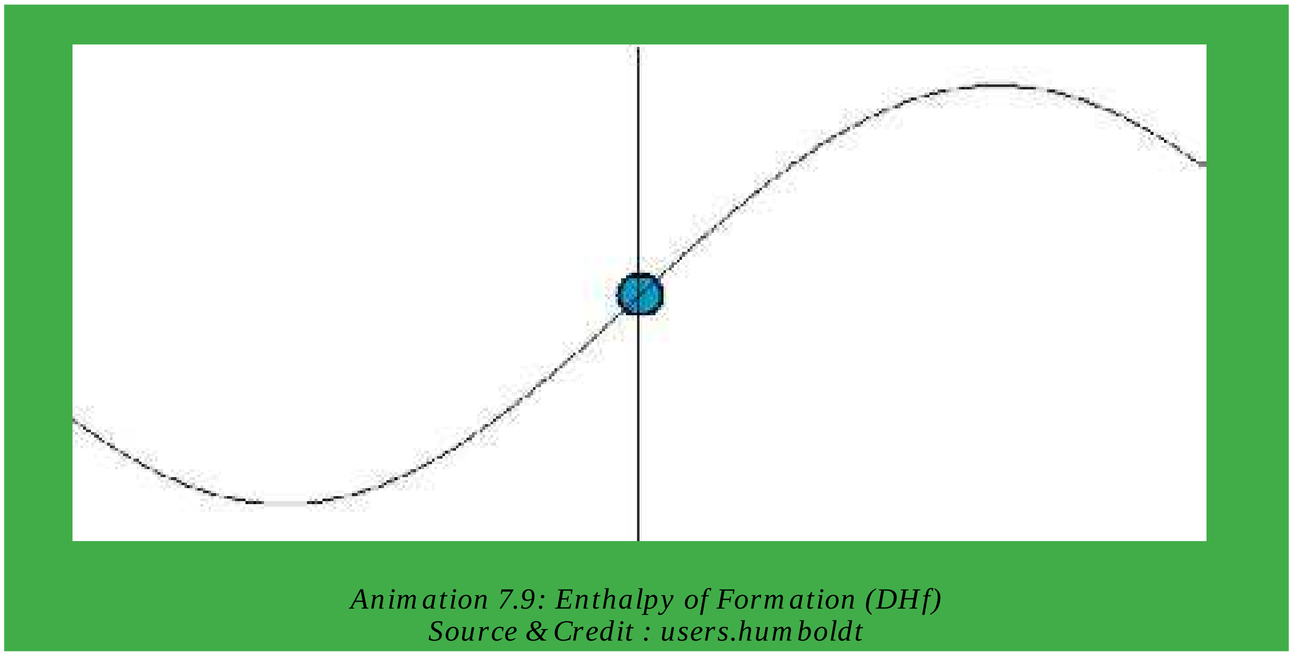
7.4.2 Enthalpy of Formation ($\Delta H^0{}_f$)

The standard enthalpy of formation of a compound is the amount of heat absorbed or evolved when one mole of the compound is formed from its elements. It is denoted by $\Delta H°_f$. All the substances involved are in their standard physical states and the reaction is carried out under standard conditions i.e. at 25°C (298 K) and one atm. pressure. Its units are kJ mol^{-1}. For example, the enthalpy of formation, ($\Delta H°_f$) for MgO(s) is - 692 kJ mol^{-1}

$$Mg_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow MgO_{(s)} \qquad \Delta H^o{}_f = -692 kJ\ mol^{-1}$$

Similarly, when carbon reacts with oxygen to form CO_2, 393.7 kJ mol^{-1} of energy is released. It is $\Delta H°_f$, of CO_2(g).

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H^o{}_f = -393.7 kJ\ mol^{-1}$$



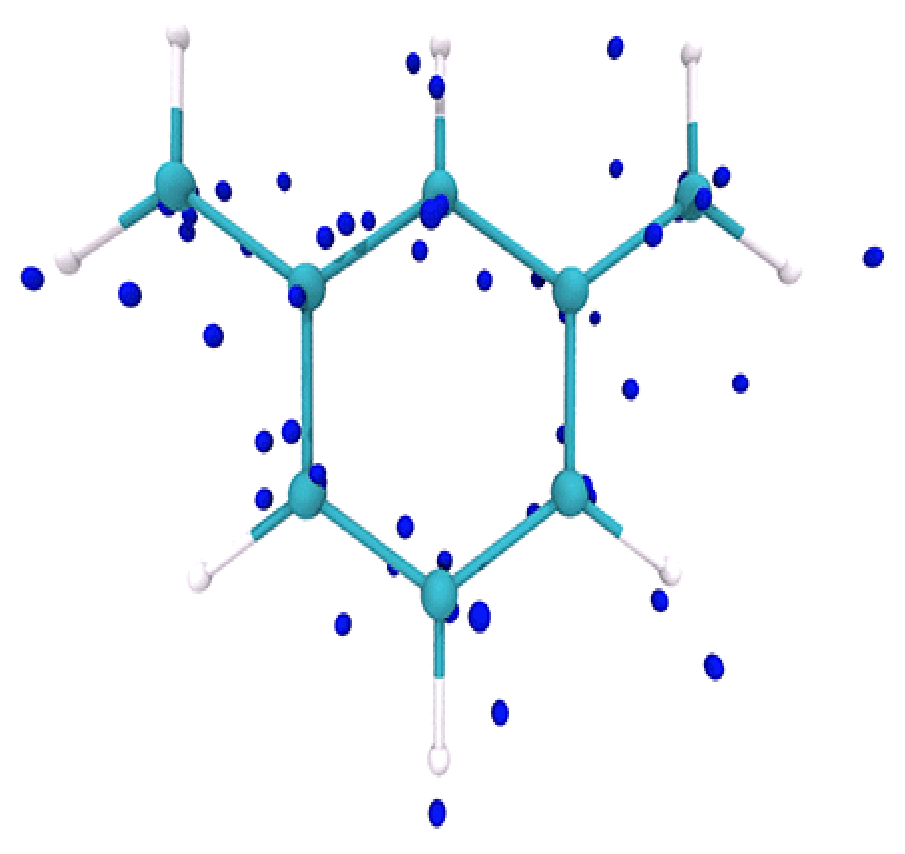
Animation 7.9: Enthalpy of Formation (DHf)
Source & Credit : users.humboldt

7.4.3 Enthalpy of Atomization (ΔH^{o}_{at})

The standard enthalpy of atomization of an element is defined as the amount of heat absorbed when one mole of gaseous atoms are formed from the element under standard conditions. It is denoted by H^{o}_{at}. For example, the standard enthalpy of atomization of hydrogen is given below.

$$\frac{1}{2}H_{2(g)} \rightarrow H_{(g)} \qquad \Delta H^{o}_{at} = 218 \text{kJ mol}^{-1}$$

A wide range of experimental techniques, are available for determining enthalpies of atomization of elements.



Animation 7.10: Enthalpy of Atomization (DHat)
Source & Credit : github

7.4.4 Enthalpy of Neutralization (ΔH°_n)

The standard enthalpy of neutralization is the amount of heat evolved when one mole of hydrogen ions [H^+] from an acid, react with one mole of hydroxide ions from a base to form one mole of water. For example, the enthalpy of neutralization of sodium hydroxide by hydrochloric (OH^-) acid is -57.4 kJ mol^{-1}. Note that a strong acid HCl and a strong base, NaOH, ionize completely in dilute solutions as follows.

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

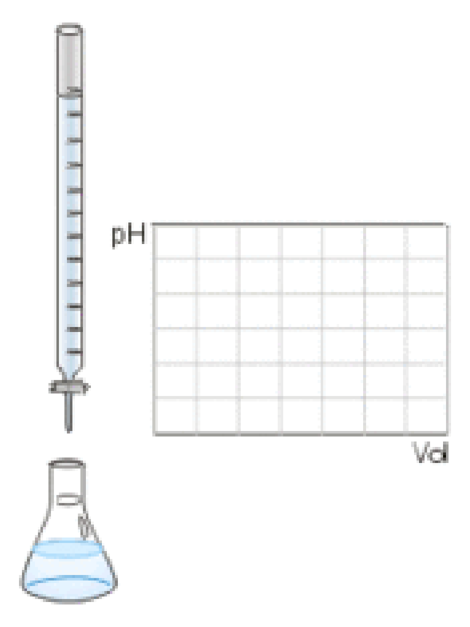
$$NaOH_{(aq)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$$

When these solutions are mixed together during the process of neutralization, the only change that actually occurs is the formation of water molecules leaving the sodium ions and the chloride ions as free ions in solution. Thus, the enthalpy of neutralization is merely the heat of formation of one mole of liquid water from its ionic components,

$$H^{+}_{(aq)} + Cl^{-}_{(aq)} + Na^{+}_{(aq)} + OH^{-}_{(aq)} \rightarrow Na^{+}_{(aq)} + Cl_{(aq)} + H_2O_{(\ell)}$$

Or

$$H^{+}_{(aq)} + OH^{-}_{(aq)} \rightarrow H_2O_{(\ell)} \qquad \Delta H^{o}_{n} = -57.4 kJ\ mol^{-1}$$



Animation 7.11: Enthalpy of Neutralization (DHn)
Source & Credit : Wiki

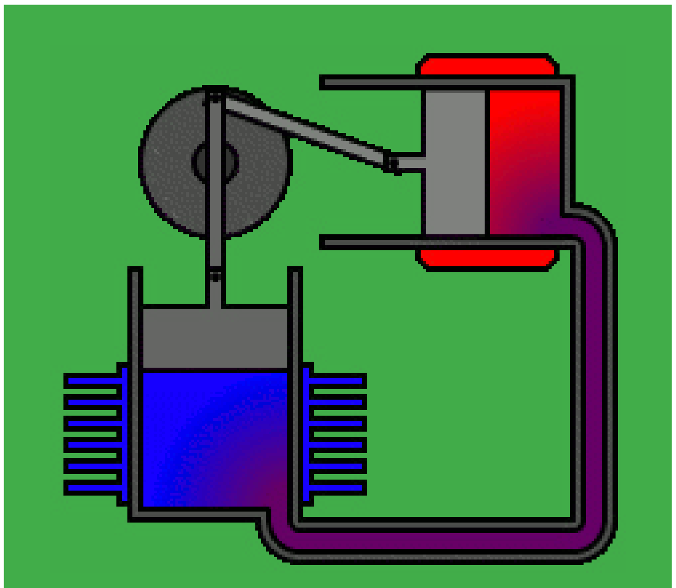
Enthalpy of neutralization for any strong acid with a strong base is approximately the same i.e. -57.4 kJ mole^{-1}.

7.4.5 Enthalpy of Combustion (ΔH^{o}_{c})

The standard enthalpy of combustion of the substance is the amount of heat evolved when one mole of the substance is completely burnt in excess of oxygen under standard conditions. It is denoted by ΔH^{o}_{c}.

For example, standard enthalpy of combustion of ethanol ΔH^0_c is -1368kJ mol^{-1}. The reaction is represented by the following equation.

$$C_2H_5OH(\ell) + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(\ell)} \qquad \Delta H^o_c = -1368kJ\ mol^{-1}$$

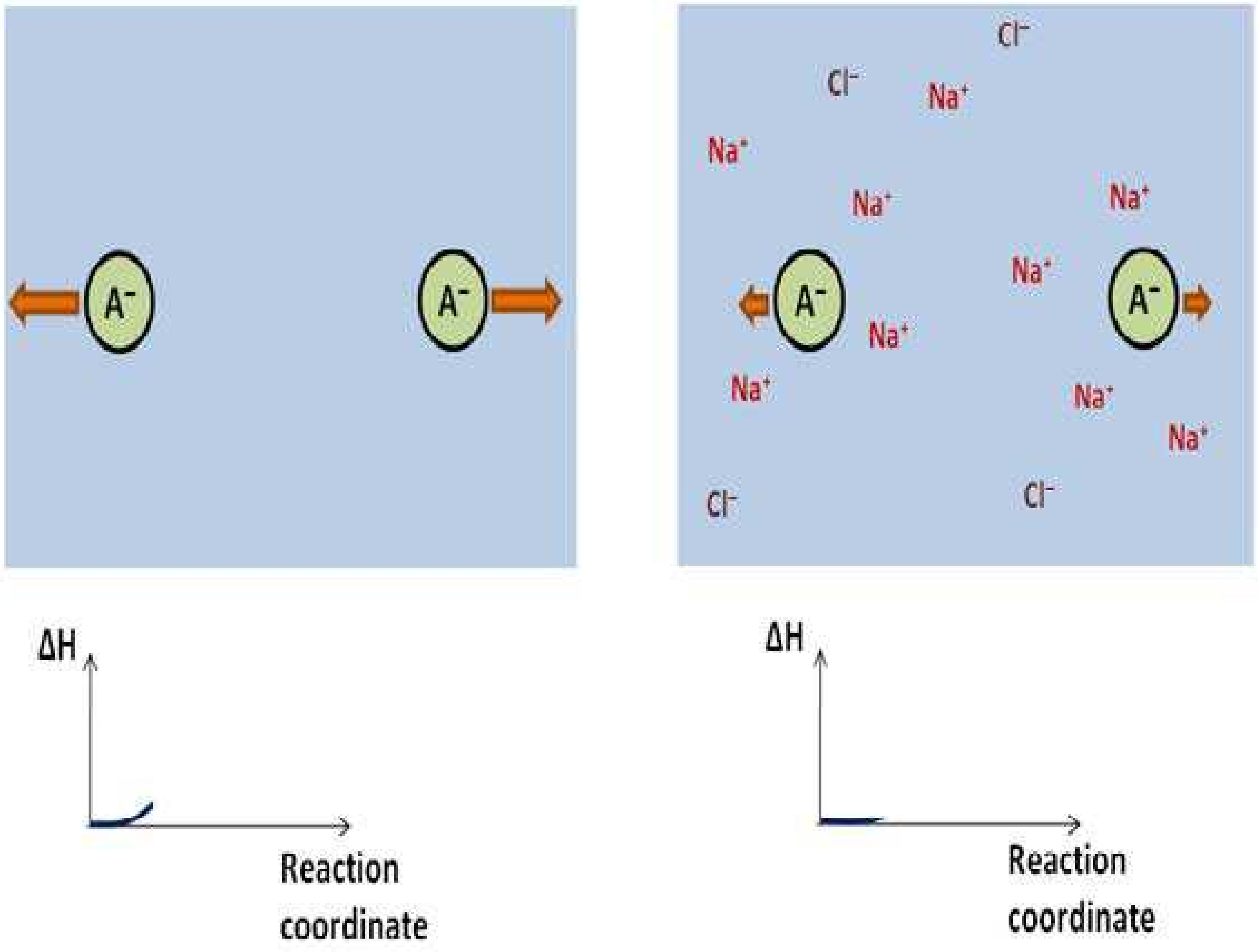


Animation 7.12: Enthalpy of Combustion (DHc)
Source & Credit : wikipedia

7.4.6 Enthalpy of Solution ($\Delta H^o_{sol.}$)

The standard enthalpy of a solution is the amount of heat absorbed or evolved when one mole of a substance is dissolved in so much solvent that further dilution results in no detectable heat change.

For example, enthalpy of solution ($\Delta H^o_{sol.}$) of ammonium chloride is +16.2 kJmol^{-1} and that of sodium carbonate is -25.0 kJmol^{-1}. In the first case, heat absorbed from the surroundings is indicated by cooling of the solvent (water), an endothermic process. While in the second case, the temperature of the solvent rises showing that the process is exothermic.



Animation 7.13: Enthalpy of Solution (DHsol.)
Source & Credit : commons.wikimedia

7.4.7 Measurement of Enthalpy of a Reaction

Exothermic and endothermic reactions can easily be detected by observing the temperature of the reaction vessel before and after the reaction, as long as the heat of reaction evolved or absorbed is considerable. More accurate values of ΔH can be determined by using calorimeters as described below.

(i) Glass Calorimeter

For most purposes, an ordinary glass calorimeter can be used to determine the value of ΔH. This usual type of calorimeter, is basically an insulated container with a thermometer and a stirrer, Fig (7.6).

Reactants in stoichiometric amounts are placed in the calorimeter. When the reaction proceeds, the heat energy evolved or absorbed will either warm or cool the system. The temperature of the system is recorded before and after the chemical reaction. Knowing the temperature change the mass of reactants present and the specific heat of water, we can calculate the quantity of heat q evolved or absorbed during the reaction. Thus:

$$q = m \times s \times \Delta T \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$

Where m = mass of reactants, s = specific heat of the reaction mixture and ΔT is the change in temperature. The product of mass and specific heat of water is called heat capacity of the whole system.

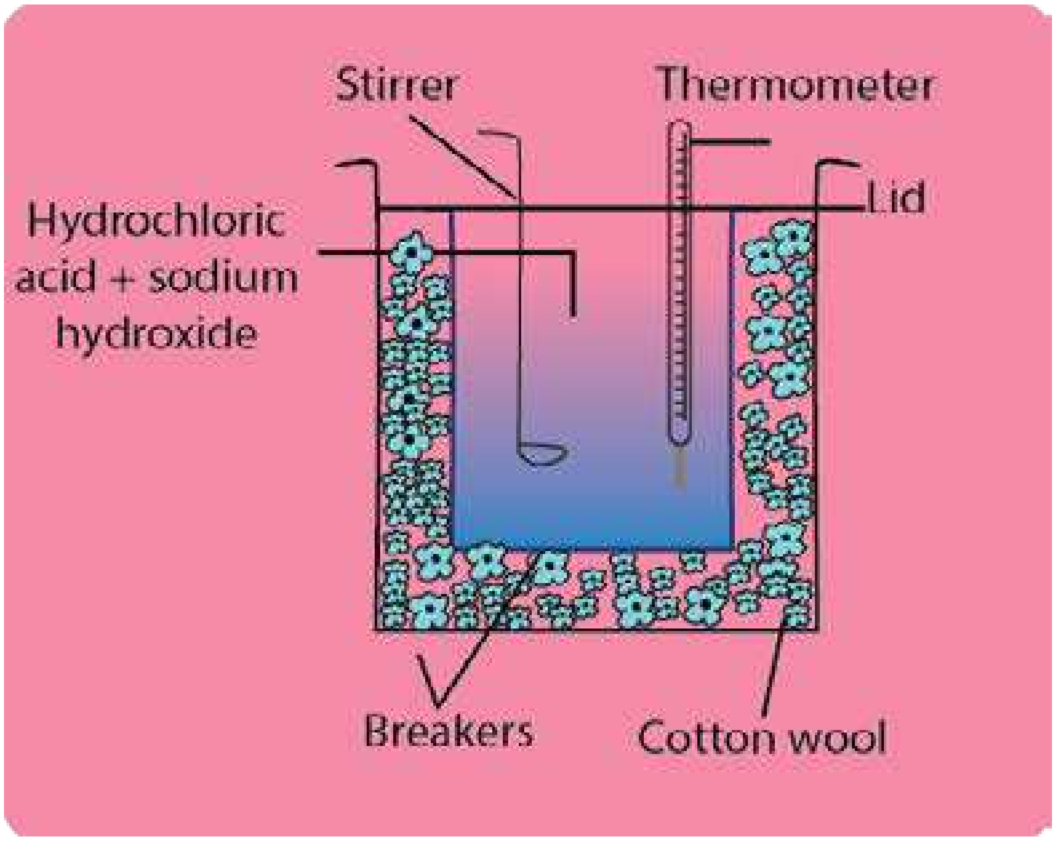
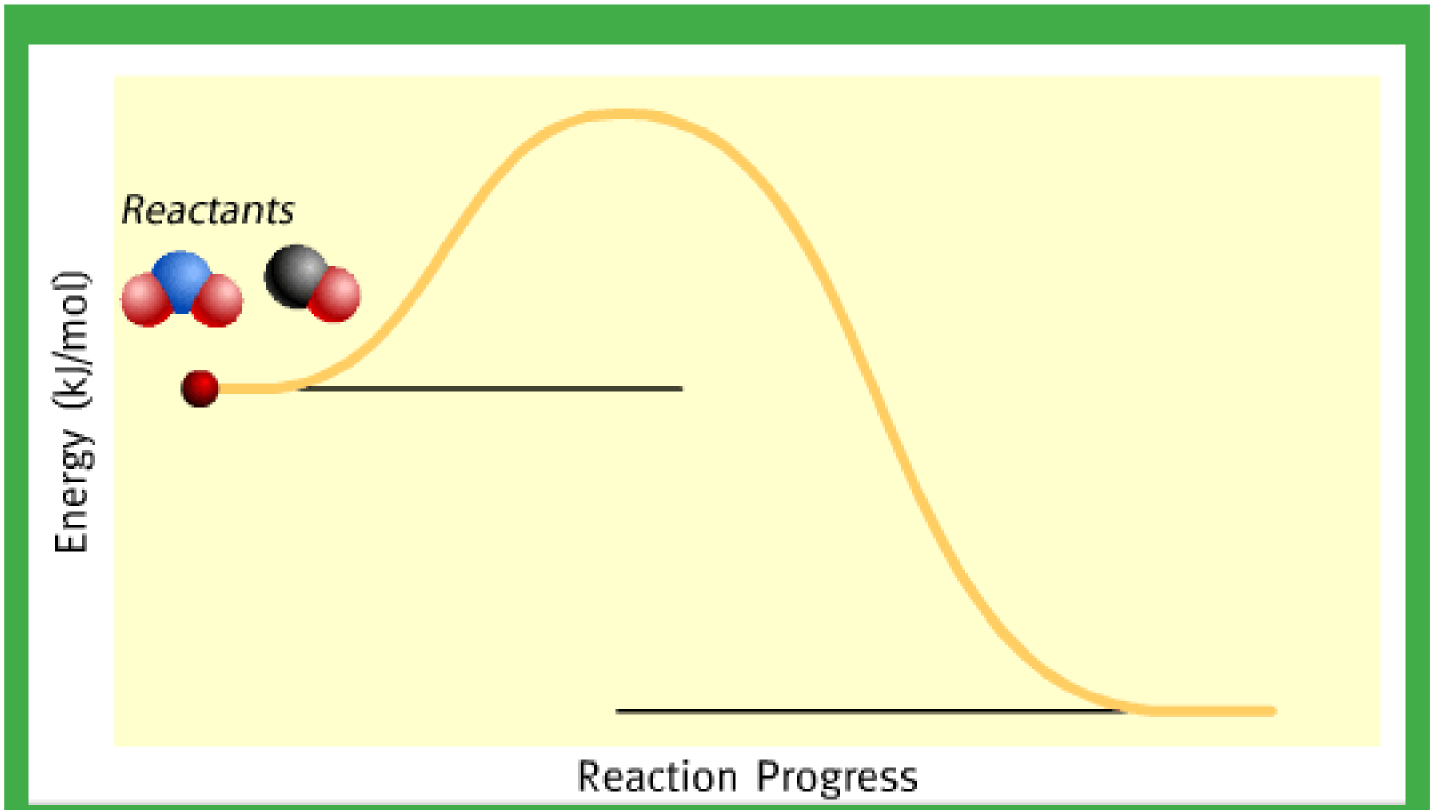


Fig (7.6) Glass calorimeter to measure enthalpy change of reactions.

Example 2:

Neutralization of 100 cm^3 of 0.5 M NaOH at 25^0C with 100 cm^3 of 0.5 M HCl at 25^0C raised the temperature of the reaction mixture to 28.5^0C. Find the enthalpy of neutralization. Specific heat of water = 4.2 J $K^{-1}g^{-1}$



Animation 7.14: Measurement of Enthalpy of a Reaction
Source & Credit : 3ddrawing.online

Solution:

Specific heat of water, s = 4.2 $JK^{-1}g^{-1}$

Density of H_2O is around $1gcm^{-3}$, so 200 cm^3 of total solution is approximately = 200g

Hence, total mass of the reaction mixture = 200g

Rise in temperature, ΔT = 28.5-25.0 = 3.5^0C = 3.5 K

$100 cm^3$ of 0.5 M NaOH = $100 cm^3$ of 0.5 MHCl

0.5 M solution means that $1000 cm^3$ of solution has 0.5 moles of solute

So $100 cm^3$ of 0.5 M solutions =0.05 moles of HCl and NaOH, respectively

Amount of total heat evolved, (q) = m x s x ΔT

= 200g x 4.2 $Jg^{-1}K^{-1}$ x 3.5 K = 2940 J

=2940 J = 2.94 kJ

Since, the reaction is exothermic

So, q =-2.94kJ

When this heat is divided by number of moles, then ΔH_n^0 is for one mole

Enthalpy of neutralization. (ΔH_n^0)

$$= \frac{-2.94\text{kJ}}{0.05\text{ mol}} = \boxed{-58.8\text{kJ mol}^{-1}} \quad \text{Answer}$$

(ii) Bomb Calorimeter

A bomb calorimeter is usually used for the accurate determination of the enthalpy of combustion for food, fuel and other compounds.

A bomb calorimeter is shown in Fig (7.7). It consists of a strong cylindrical steel vessel usually lined with enamel to prevent corrosion. A known mass (about one gram) of the test substance is placed in a platinum crucible inside the bomb. The lid is screwed on tightly and oxygen is provided in through a valve until the pressure inside is about 20 atm. After closing the screw valve, the bomb calorimeter is then immersed in a known mass of water in a well insulated calorimeter.

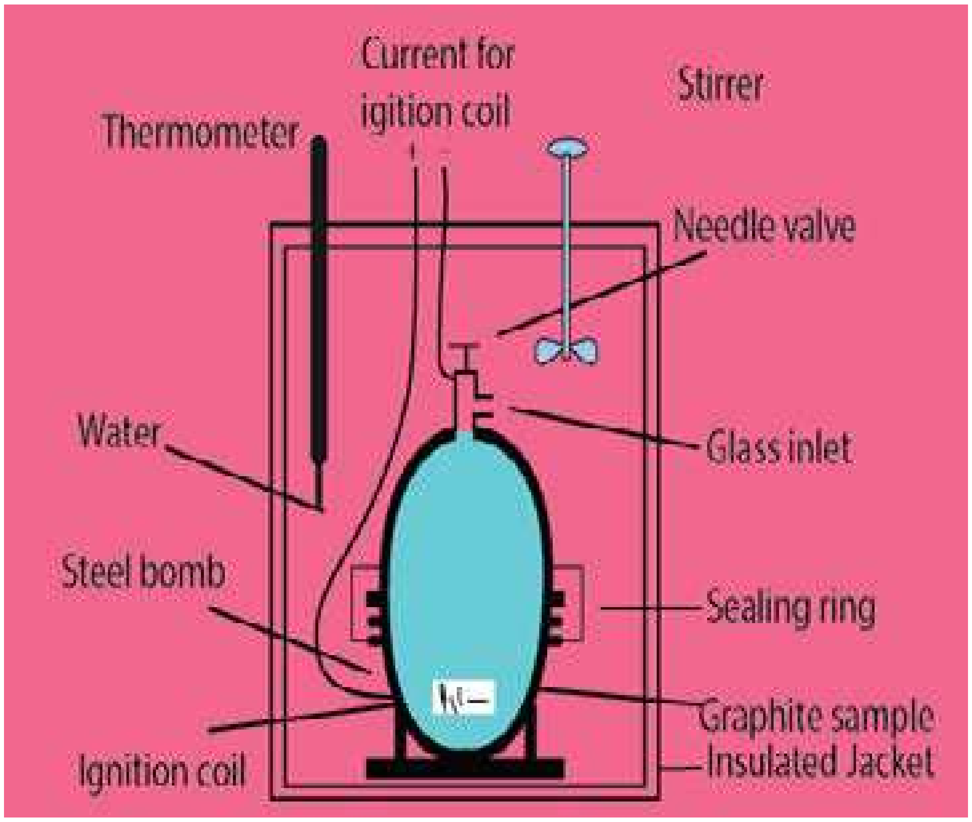


Fig (7.7) Bomb calorimeter

Then, it is allowed to attain a steady temperature. The initial temperature is measured, by using the thermometer present in the calorimeter. The test substance is then, ignited, electrically by passing the current through the ignition coil. The temperature of water, which is stirred continuously, is recorded at 30 sec intervals.

From the increase of temperature ΔT, heat capacity (c) in kJK^{-1} of bomb calorimeter including bomb, water etc., we can calculate the enthalpy of combustion.

The heat capacity 'c' of a body or a system is defined as the quantity of heat required to change its temperature by 1 kelvin.

$$q = c \times \Delta T$$

Example 3:

10.16g of graphite is burnt in a bomb calorimeter and the temperature rise recorded is 3.87K. Calculate the enthalpy of combustion of graphite, if the heat capacity of the calorimeter (bomb, water, etc.) is 86.02 $kJ\ K^{-1}$

Solution:

Heat capacity of bomb calorimeter =86.02 kJK^{-1}

Rise in temperature of the calorimeter and its contents = 3.87 K

Heat gained by the system (bomb calorimeter and water etc.) q $= c \times \Delta T$

$= 86.02\ \text{kJK}^{-1} \times 3.87\text{K}$

$= 332.89\ \text{kJ}$

This heat is evolved by burning 10.16g of graphite $= \frac{10.16}{12}$ mole of graphite

= 0.843 mole of graphite

Hence enthalpy of combustion of graphite per mole $= \frac{332.89}{0.843}\ \text{kJmol}^{-1}$

= 395kJmol^{-1}

Since heat is evolved during combustion, so the sign of the answer would be negative.

$= \boxed{-395\ \text{kJmol}^{-1}\ \ \text{Answer}}$

7.5.0 HESS'S LAW OF CONSTANT HEAT SUMMATION

There are many compounds, for which ΔH cannot be measured directly by calorimetric method. The reason is, that some compounds like tetrachloromethane (CCl_4), cannot be prepared directly by combining carbon and chlorine. Similarly, it does not decompose easily into its constituent elements. In the same way, boron oxide (B_2O_3) and aluminium oxide (Al_2O_3) provide problems for the measurement of standard enthalpies of their formation. In these cases, it is difficult to burn these elements completely in oxygen, because a protective layer of oxides covers the surface of the unreacted element. Similarly, heat of formation of CO cannot be measured directly due to the formation of CO_2 with it.

As a result, of above mentioned problems, the chemists had to look for methods of obtaining standard enthalpies of formation indirectly. The energy cycle shows two routes for converting graphite and oxygen to CO_2, whilst the alternative route goes via CO. It would seem reasonable that the overall enthalpy change for the conversion of graphite to CO is independent of the route taken, that is,

$$\Delta H = \Delta H_1 + \Delta H_2 \text{ ....} \quad (8)$$

If the enthalpy of combustion for graphite to form CO_2 and the enthalpy of combustion of CO to form CO_2 are known, we can determine the enthalpy of formation for CO. To clear the idea look at the following cycle. The oxidation of carbon (graphite) can be written as follows.

$$C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H_{\ (graphite)} = -393.7\text{kJ mol}^{-1}$$

$$CO_{(gas)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H_2(CO) = -283\text{kJ mol}^{-1}$$

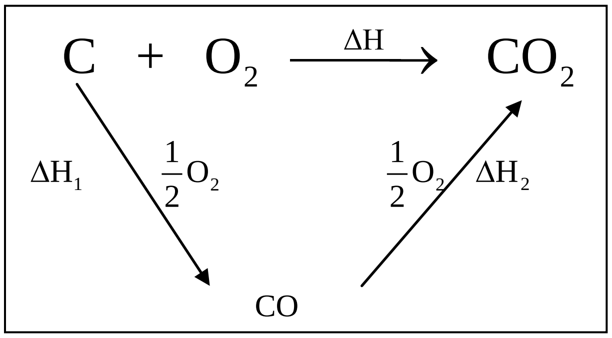
$$C_{(graphite)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)} \qquad \Delta H_1(CO) = ?$$

Applying equation (8) $\Delta H = \Delta H_1 + \Delta H_2$

or $\Delta H_1 = \Delta H - \Delta H_2$

$= -393 - (-283)$

$= -110\text{kJ mol}^{-1}$



So, the enthalpy change for the formation of CO(g) is -110.0 kJmol^{-1}.

The method we have just used in obtaining equation (8), is a specific example of Hess's law of constant heat summation. This law states that

If a chemical change takes place by several different routes, the overall energy change is the same, regardless of the route by which the chemical change occurs, provided the initial and final conditions are the same.

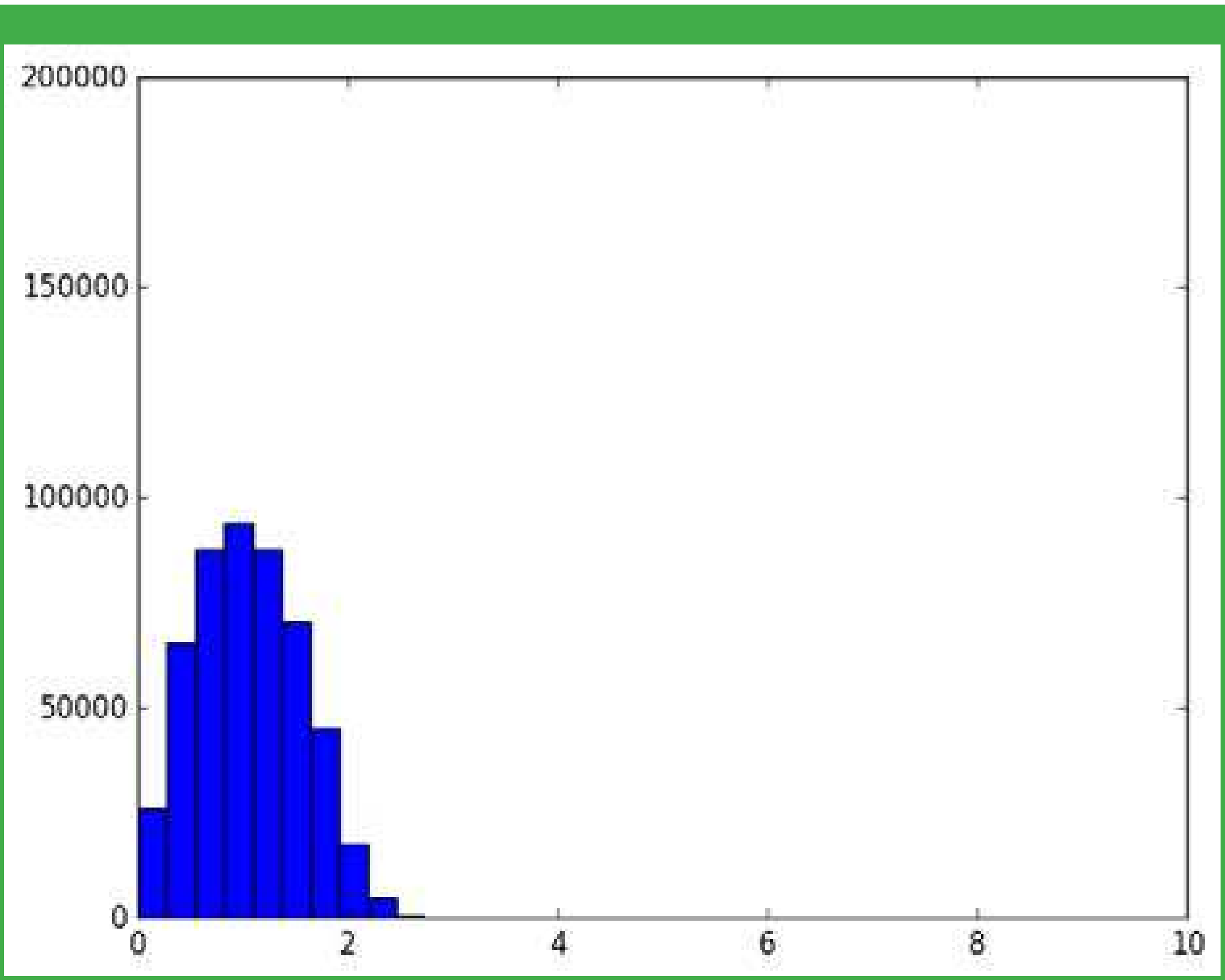
Let A can be converted to D directly in a single step and heat evolved is ΔH. If the reaction can have a route from $A \rightarrow B \rightarrow C$ as shown below.

$$\begin{tikzcd} A \arrow[r, "\Delta H"] \arrow[d, "\Delta H_1"] & D \\ B \arrow[r, "\Delta H_2"'] & C \arrow[u, "\Delta H_3"'] \end{tikzcd}$$

According to Hess's law, $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$

Mathematically, $\sum \Delta H(\text{cycle}) = 0$

Of course, Hess's law is simply an application of the more fundamental law of conservation of energy. So, $\Sigma\Delta H$ (cycle) = 0



Animation 7.15: HESS'S LAW OF CONSTANT HEAT SUMMATION
Source & Credit : jeremykun

It means that if one goes form A to D directly and comes back to A through B and C then $\Delta H = 0$.

The formation of sodium carbonate, is another example for the verification of Hess's law. The formation of sodium carbonate may be studied as a single step process, or in two steps as via sodium hydrogen carbonate.

Single Step Process

$$2NaOH_{(aq)} + CO_{2(g)} \rightarrow Na_2CO_{3(aq)} + H_2O_{(l)} \qquad \Delta H = -89.08 \text{ kJ}$$

Two Step Process

$$NaOH_{(aq)} + CO_{2(g)} \rightarrow NaHCO_{3(aq)} \qquad \Delta H_1 = -48.06 \text{ kJ}$$

$$NaHCO_{3(aq)} + NaOH_{(aq)} \rightarrow Na_2CO_{3(aq)} + H_2O_{(\ell)} \qquad \Delta H_2 = -41.02 \text{ kJ}$$

According to Hess's law,

$$\Delta H = \Delta H_1 + \Delta H_2 \quad .... \quad (8)$$

Putting the values of ΔH, ΔH_1, ΔH_2, in equation (8)

$$-89.08 = -48.06 - 41.02$$
$$-89.08 = -89.08$$

This illustrates, how heats of reactions may be added algebraically and this proves Hess's law. Hess's law finds its best applications in Born-Haber cycle.

7.5.1 The Bom-Haber Cycle

This cycle has wide applications. It finds its special applications in Hess's law. It states that energy change in a cyclic process is always zero. It enables us, to calculate the lattice energies of binary ionic compounds such as M^+X^-.

The lattice energy of an ionic crystal is the enthalpy of formation of one mole of the ionic compound from gaseous ions under standard conditions.

Thus, the lattice energy of NaCl corresponds to the following process.

$$Na^+_{(g)} + Cl^-_{(g)} \rightarrow Na^+Cl^-_{(s)} \qquad \Delta H^o_{Latt} = -787 \text{ kJ mol}^{-1}$$

Lattice energies cannot be determined directly but values can be obtained indirectly by means of an energy cycle. In Fig (7.8), an energy triangle of sodium chloride is shown.

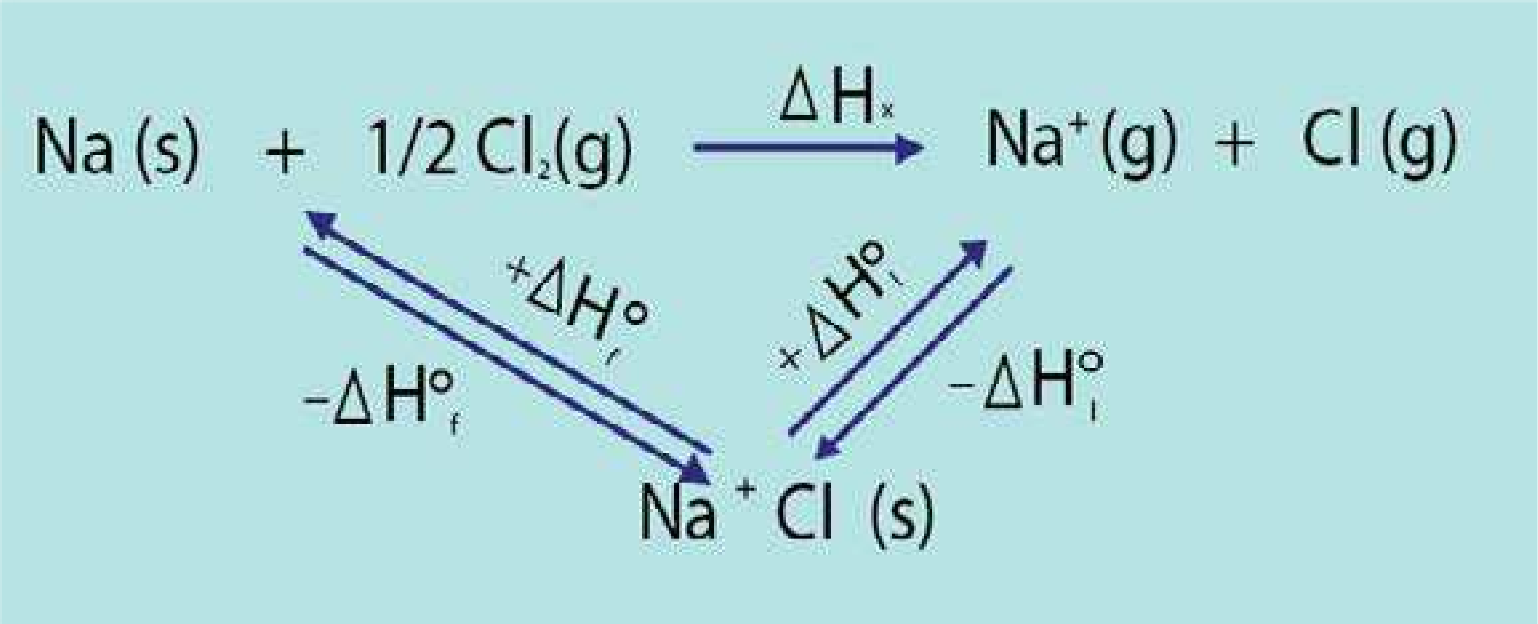


Fig (7.8) Energy triangle for sodium chloride

Since, ΔH°_f, the standard enthalpy of formation of sodium chloride, can be measured conveniently in a calorimeter. ΔH°_l, can be obtained if ΔH_x, which is the total energy involved in changing sodium and chlorine from their normal physical states to gaseous ions, can be calculated.

In Fig (7.9), the previous energy triangle has been extended to show the various stages involved in finding ΔH_x. The complete energy cycle is called a Born -Haber cycle.

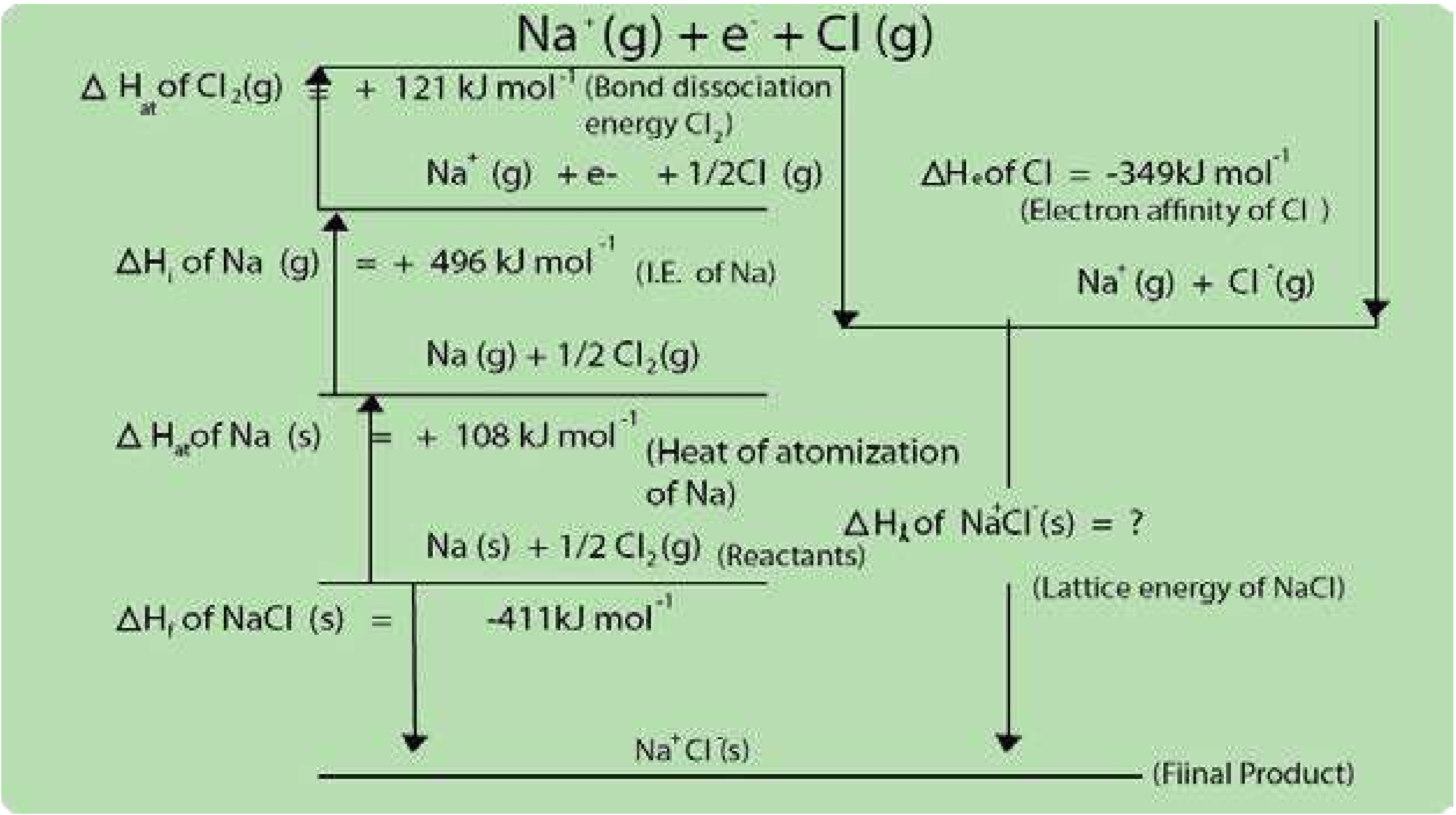


Fig (7.9) Born-Haber cycle

It is clear from the picture of Born-Haber cycle in Fig (7.9) that

$$\Delta H_x = \Delta H_{at(Na)} + \Delta H_{i(Na)} + \Delta H_{at(Cl)} + \Delta H_{e(Cl)}$$

The first two stages in this process involve atomizing and the ionizing of sodium. The heat of atomization of sodium can be obtained from values of its heat of fusion, heat of vaporization and specific heat capacity. The first ionization energy of sodium can be determined spectroscopically.

$$Na_{(s)} \rightarrow Na_{(g)} \qquad \Delta H_{at} = 108 \text{kJ mol}^{-1}$$

$$Na_{(g)} \rightarrow Na_{(g)} + 1e^- \qquad \Delta H_i = 496 \text{kJ mol}^{-1}$$

The third and fourth stages in the expression for ΔH_x above, involve the atomization of chlorine and the conversion of chlorine atoms to chloride ions, respectively. The later process is, of course, called the electron affinity of chlorine.

The heat of atomization of chlorine can be obtained from spectroscopic studies:

$$\frac{1}{2}Cl_{2(g)} \rightarrow Cl_{(g)} \qquad \Delta H_{at} = 121 \text{ kJ mol}^{-1}$$

whilst, the electron affinity for chlorine can also be found by similar methods.

$$Cl_{(g)} + e^{-} \rightarrow Cl^{-}_{(g)} \qquad \Delta H_e = -349 \text{ kJ mol}^{-1}$$

Thus $$\Delta H_x = (108+496+121-349) = 376 \text{ kJ mol}^{-1}$$

The lattice energy for sodium chloride can thus be obtained:

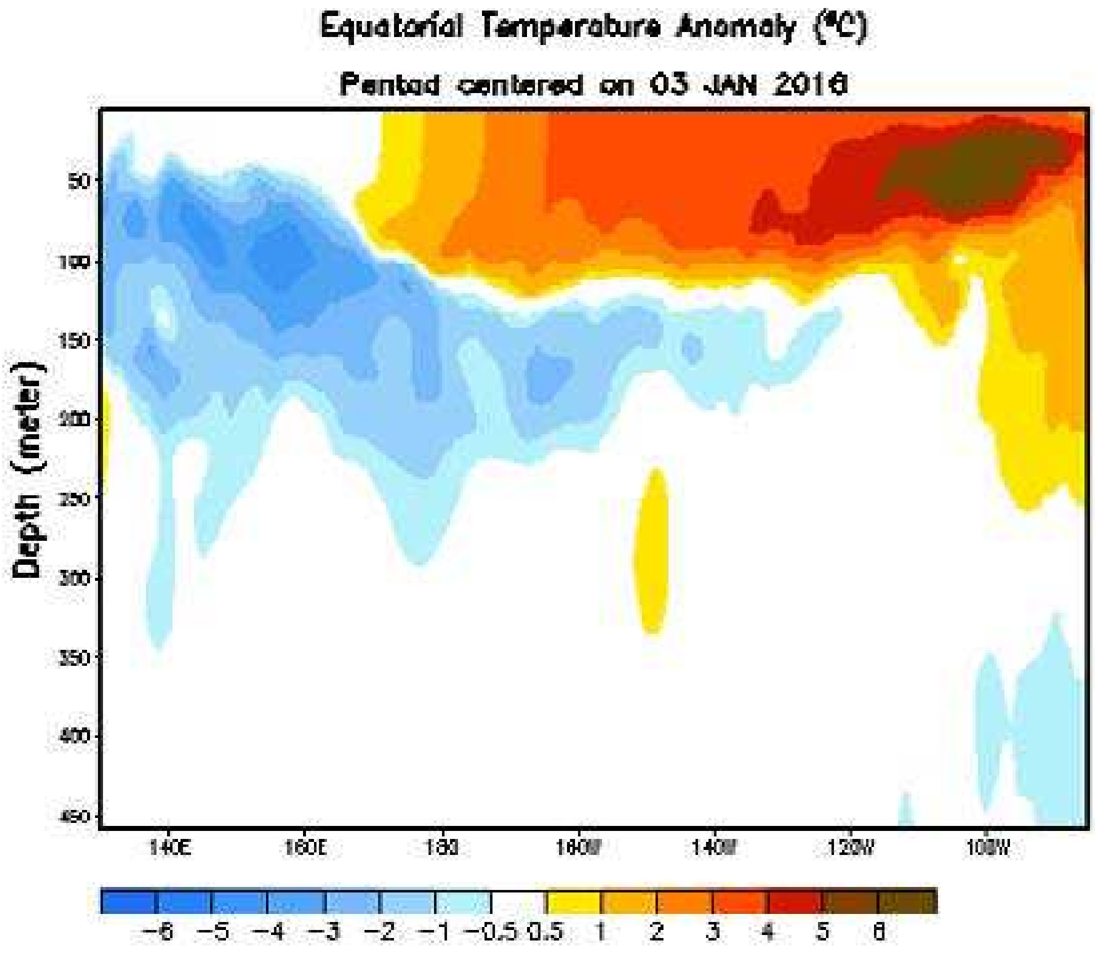
$$\Delta H^o_f = \Delta H^o_\ell + \Delta H_x$$

$$\Delta H^o_\ell = \Delta H^o_f - \Delta H_x$$

Using the values from Fig (7.9)

$$\Delta H_\ell = -411-376 = -787 \text{ kJ mol}^{-1}$$

The lattice energy, gives us some idea of the force of attraction between Na^+ and Cl^- ions in crystalline sodium chloride. Lattice energies are very helpful in discussing the structure, bonding and properties of ionic compounds.



Animation 7.16: The Bom -H aber Cycle
Source & Credit : climate.gov

KEY POINTS

1. Substances exist because they possess energy. Energy can be transformed in form of heat and the study of heat changes accompanying a chemical reaction is called thermochemistry.
2. Whenever, a reaction happens, then the driving force is the enthalpy change, along with the entropy change. Both these parameters decide upon spontaneity of reaction.
3. Most of the thermodynamic parameters are state functions.
4. First law of themodynamics is the law of conservation of energy and helps us to understand the equivalence of heat and work.
5. When heat is supplied to the system at constant pressure, then it is the enthalpy change of the system. Anyhow, at constant volume, the heat supplied is just equal to internal energy change.
6. There is difference between heat and temperature. The amount of heat evolved or absorbed can be measured in laboratory by using glass calorimeter or bomb calorimeter. The amount of heat is calculated from mass of the reactants, specific heat and change of temperature. Hess's law of heat summation is another form of first law of thermodynamics. It helps us to determine the enthalpy changes of those chemical reactions, which can not be carried out in laboratory or heat changes are difficult to measure.
7. According to Born-Haber cycle, another form of Hess's law, the energy change in a cyclic process is always equal to zero. With the help of this cycle, we can calculate lattice energy of ionic crystals.

EXERCISE

Q.1 Select the suitable answer from the given choices.

(i) If an endothermic reaction is allowed to take place very rapidly in the air, the temperature of the surrounding air

(a) remains constant (b) increases
(c) decreases (d) remains unchanged

(ii) In endothermic reactions, the heat content of the
(a) products is more than that of reactants
(b) reactants is more than that of products
(c) both (a) and (b)
(d) reactants and products are equal

(iii) Calorie is equivalent to
(a) 0.4184J (b) 41.84J (c) 4.184J (d) 418.4J

(iv) The change in heat energy of a chemical reaction at constant temperature and pressure is called

(a) enthalpy change (c) heat of sublimation
(b) bond energy (d) internal energy change

(v) Which of the following statements is contrary to the first law of thermodynamics?
(a) Energy can neither be created nor destroyed.
(b) One form of energy can be transferred into an equivalent amount of other kinds of energy.
(c) In an adiabatic process, the work done is independent of its path.
(d) Continuous production of mechanical work without supplying an equivalent amount of heat is possible.

(vi) For a given process, the heat changes at constant pressure (q_p) and at constant volume (q_v) are related to each other as

(a) $q_p = q_v$ (b) $q_p < q_v$ (c) $q_p > q_v$ (d) $q_p = q_v / 2$

(vii) For the reaction: $NaOH + HCl \rightarrow NaCl + H_2O$ the change in enthalpy is called
(a) heat of reaction (b) heat of formation
(c) heat of neutralization (d) heat of combustion

(viii) The net heat change in a chemical reaction is same,whether it is brought about in two or more different ways in one or several steps. It is known as

(a) Henry's law (b) Joule's principle
(c) Hess's law (d) Law of conservation of energy

(ix) Enthalpy of neutralization of all the strong acids and strong bases has the same value because
  (a) neutralization leads to the formation of salt and water.
  (b) strong acids and bases are ionic substances.
  (c) acids always give rise to H^+ ions and bases always furnish OH^- ions.
  (d) the net chemical change involve the combination of H^+ and OH^- ions to form water.

Q.2 Fill in the blanks with suitable words.
(i) The substance undergoing a physical or a chemical change forms a chemical .
(ii) The change in internal energy_________ be measured.
(iii) Solids which have more than one crystalline forms possess_______ values of heats of formation.
(iv) A process is called________ if it takes place on its own without any external assistance.
(v) A________ is a macroscopic property of a system which is__________ of the path adopted to bring about that change.

Q.3 Indicate the true or false as the case may be.
(i) It is necessary that a spontaneous reaction should be exothermic.
(ii) Amount of heat absorbed at constant volume is internal energy change.
(iii) The work done by the system is given the positive sign.
(iv) Enthalpy is a state function but internal energy is not.
(v) Total heat content of a system is called enthalpy of the system.

Q.4 Define the following terms and give three examples of each
(i) System
(ii) Surroundings
(iii) State function
(iv) Units of energy
(v) Exothermic reaction
(vi) Endothermic reaction
(vii) Internal energy of the system
(viii) Enthalpy of the system

Q.5
(a) Differentiate between the following:
  (i) Internal energy and enthalpy
  (ii) Internal energy change and enthalpy change
  (iii) Exothermic and endothermic reactions
(b) Define the following enthalpies and give two examples of each.
  (i) Standard enthalpy of reaction
  (ii) Standard enthalpy of combustion
  (iii) Standard enthalpy of atomization
  (iv) Standard enthalpy of solution

Q.6 (a) What are spontaneous and non-spontaneous processes. Give examples.

(b) Explain that burning of a candle is a spontaneous process.

(c) Is it true that a non-spontaneous process never happens in the universe? Explain it.

Q.7 (a) What is the first law of thermodynamics. How does it explain that

(i) $q_v = \Delta E$ (ii) $q_p = \Delta H$

(b) How will you differentiate between ΔE and ΔH? Is it true that ΔH and ΔE have the same values for the reactions taking place in the solution state.

Q.8

(a) What is the difference between heat and temperature? Write a mathematical relationship between these two parameters.

(b) How do you measure the heat of combustion of a substance by bomb calorimeter.

Q.9 Define heat of neutralization. When a dilute solution of a strong acid is neutralized by a dilute solution of a strong base, the heat of neutralization is found to be nearly the same in all the cases. How do you account for this?

Q. 10

(a) State the laws of thermochemistry and show how are they based on the first law of thermodynamics.

(b) What is a thermochemical equation. Give three examples. What information do they convey?

(c) Why is it necessary to mention the physical states of reactants and products in a thermochemical reaction? Apply, Hess's law to justify your answer.

Q .11

(a) Define and explain Hess's law of constant heat summation. Explain it with examples and give its application.

(b) Hess's law helps us, to calculate the heats of those reactions, which cannot be normally carried out in a laboratory. Explain it.

Q.12

(a) What is lattice energy? How does Born-Haber cycle help to calculate the lattice energy of NaCl?

(b) Justify that heat of formation of compound is the sum of all the other enthalpies.

Q. 13 50 cm^3 of 1.0 M HCl is mixed with 50 cm^3 of 1.00 M NaOH in a glass calorimeter. The temperature of the resultant mixture increases from 21.0°C to 27.5°C. Assume, that calorimeter losses of heat are negligible. Calculate the enthalpy change mole^{-1} for the reactions. The density of solution to be considered is 1gcm^{-3} and specific heat is 4.18Jg^{-1}k^{-1}.

(Ans: -54 kJ mol^{-1})

Q .14 Hydrazine (N_2H_4) is a rocket fuel. It burns in O_2 give N_2 and H_2O.

$$N_2H_{2(\ell)} + O_{2(g)} \rightarrow N_{2(g)} + 2H_2O_{(g)}$$

1.00 g of N_2H_4 is burned in a bomb calorimeter. An increase of temperature 3.51^{0}C is recorded. The specific heat of calorimeter is 5.5kJK^{-1}g^{-1}. Calculate the quantity of heat evolved. Also, calculate the heat of combustion of 1 mole of N_2H_4.

(Ans: -19.3kJ, -618kJmol^{-1})

Q. 15 Octane (C_8H_{18}) is a motor fuel. 1.80 g of a sample of octane is burned in a bomb calorimeter having heat capacity 11.66 kJK^{-1}. The temperature of the calorimeter increases from 21.36^{0}C to 28.78^{0}C. Calculate the heat of combustion for 1.8g of octane. Also, calculate the heat for 1 mole of octane.

(Ans: 86.51kJ, -5478.84kJmol^{-1})

Q.16 By applying, Hess's law calculate the enthalpy change for the formation of an aqueous solution of NH_4Cl from NH_3 gas and HCl gas. The results for the various reactions are as follows.

(i)

(ii) $NH_{3(g)} + aq \rightarrow NH_{3(aq)}$ $\Delta H = -35.16$kJ mol^{-1}

(iii) $HCl_{(g)} + aq \rightarrow HCl_{(aq)}$ $\Delta H = -72.41$kJ mol^{-1}

$NH_{3(aq)} + HCl_{(aq)} \rightarrow NH_4Cl_{(aq)}$ $\Delta H = -51.48$kJ mol^{-1}

(Ans: -159.08 kJ mol^{-1})

Q.17 Calculate the heat of formation of ethyl alcohol from the following information

(i) Heat of combustion of ethyl alcohol is -1367 kJ mol^{-1}

(ii) Heat of formation of carbon dioxide is-393.7 kJ mol^{-1}

(iii) Heat of formation of water is -285.8 kJ mol^{-1}

(Ans:-278.4 kcal mol^{-1})

Q.18 If the heats of combustion of C_2H_4, H_2 and C_2H_6 are -337.2, -68.3 and -372.8k calories respectively, then calculate the heat of the following reaction.

$$C_2H_{4(g)} + H_{2(g)} \rightarrow C_2H_{6(g)}$$

Q.19 Graphite and diamond are two forms of carbon. The enthalpy of combustion of graphite at 25°C is -393.51 kJ mol^{-1} and that of diamond is -395.41 kJ mol^{-1}. What is the enthalpy change of the process?

Graphite → Diamond at the same temperature?

(Ans: 1.91 kJmol^{-1})

Q.20 What is the meaning of the term enthalpy of ionization? If the heat of neutralization of HCl and NaOH is -57.3 kJ mol^{-1} and heat of neutralization of CH_3COOH with NaOH is -55.2 kJ mol^{-1}, calculate the enthalpy of ionization of CH_3COOH.

(Ans: 2.1 kJmol^{-1})

Q.21

(a) Explain what is meant by the following terms.

  (i) Atomization energy

  (ii) Lattice energy

(b) Draw a complete, fully labeled Born-Haber cycle for the formation of potassium bromide.

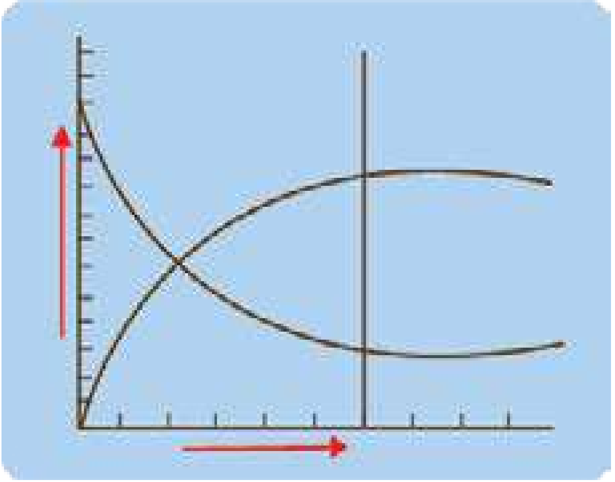
(c) Using the information given in the table below, calculate the lattice energy of potassium bromide.

Reactions	$\Delta H/kJ\ mol^{-1}$
$K_{(s)} + 1/2Br_{2(\ell)} \rightarrow K^+Br^-_{(s)}$	-392
$K_{(s)} \rightarrow K_{(g)}$	+90
$K_{(g)} \rightarrow K^+_{(g)} + e^-$	+420
$1/2Br_{2(\ell)} \rightarrow Br_{(g)}$	+112
$Br_{(g)} + e^- \rightarrow Br^-_{(g)}$	-342

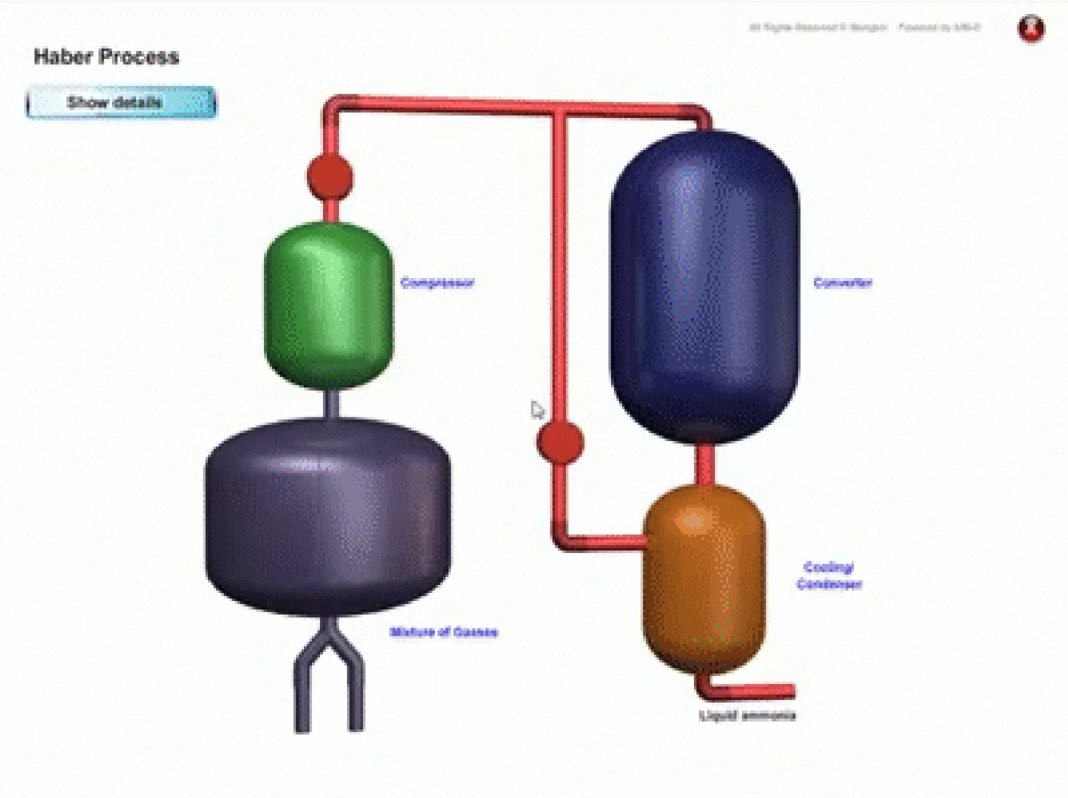
(Ans: -672 kJ mol^{-1})

CHAPTER

8



CHEMICAL EQUILIBRIUM



Animation 8.1: Haber's Process
Source & Credit: makeagif

8.1.0 REVERSIBLE AND IRREVERSIBLE REACTIONS

A chemical reaction can take place in both directions, i.e. forward and reverse, but in some cases the tendency of reverse reaction is very small and is negligible. For example, sodium reacts with water to form sodium hydroxide and hydrogen gas.

$$2Na(s)+2H_2O(\ell) \rightarrow 2NaOH(aq)+H_2(g)$$

The tendency for hydrogen to react with sodium hydroxide to form sodium and water is negligible at normal temperature. This is an example of irreversible reaction.

Let us take another example of the reaction between two parts of hydrogen and one part of oxygen by means of an electric spark at normal temperature and pressure. The reaction occurs stoichiometrically according to the following chemical equation.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell)$$

If hydrogen and oxygen are present in correct proportion, there will be no residual gases i.e. hydrogen and oxygen. If the product is heated to a temperature of 1500^{0}C, a noticeable quantity of H_2O decomposes, producing hydrogen and oxygen. It means that reverse reaction does occur, but only at higher temperature. It is very likely that the reverse reaction occurs at low temperature, but it is too small to be noticeable. The reaction between stoichiometric amounts of hydrogen and oxygen proceeds to completion in the presence of electric spark. Such reactions are called irreversible reactions and they take place in one direction only.

Now, consider a reaction between nitrogen and hydrogen at 450^{0}C under high pressure in the presence of iron as a catalyst.

$$N_2(g) + 3H_2(g) \xrightleftharpoons[\text{high pressure}]{\text{Fe/450}^0\text{C}} 2HN_3(g)$$

There action mixture, after some time, will contain all the three species i.e. nitrogen, hydrogen and ammonia. No matter, how long the reaction is allowed to continue, the percentage composition of species present remains constant. The conditions are favourable for the forward as well as for a reverse reaction to occur to a measurable extent. This type of reaction is described as a reversible reaction.

8.1.1 State of Chemical Equilibrium

If a reversible reaction is allowed to continue for a considerable long time, without changing the conditions, there is no further change in composition of the reaction mixture. The reaction is said to have attained a state of chemical equilibrium. Once this equilibrium has been established, it will last forever if undisturbed.

To illustrate an example of the attainment of equilibrium, let us consider a general reaction in which A reacts with B to produce C and D.

$$A(g) + B(g) \rightleftharpoons C(g) + D(g)$$

Suppose that all the substances are in gaseous state.

Let the initial concentrations of A and B be equal. As time goes on, concentrations of A and B decrease, at first quite rapidly but later slowly. Eventually, the concentrations of A and B level off and become constant.

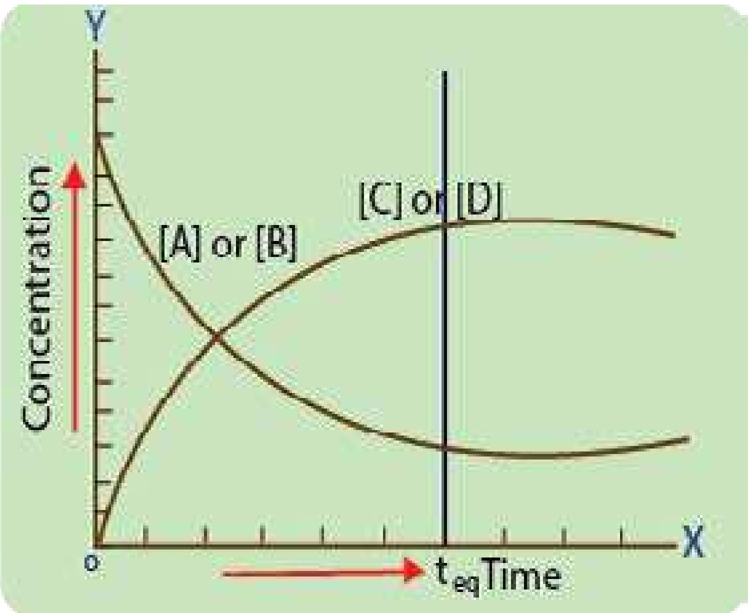


Fig (8.1) Reversible reaction and state of equilibrium

The graph is plotted between time and concentrations for reactants and products, Fig(8.1). The initial concentrations of C and D are zero. As the time passes the products C and D are formed. Their concentrations increase rapidly at first and then level off. At the time of equilibrium concentrations become constant. This is how the chemical equilibrium is attained and state of equilibrium is reached.

Now, let us consider the example of a reversible reaction between hydrogen gas and iodine vapours to form hydrogen iodide at 425^0 C. At equilibrium three components will be present in definite proportions in the reaction m ixture Fig (8.2). The equilibrium is established when the rising curve of product HI and the falling curve of reactants [H_2] and [I_2] become parallel to time axis.

$$H_2(g) + I_2(g) \xrightleftharpoons{425^0C} 2HI(g)$$

The same equilibrium mixture is obtained irrespective whether the reaction starts by mixing hydrogen and iodine or by decomposition of hydrogen iodide. The situation suggests two possibilities of the state of reaction at equilibrium

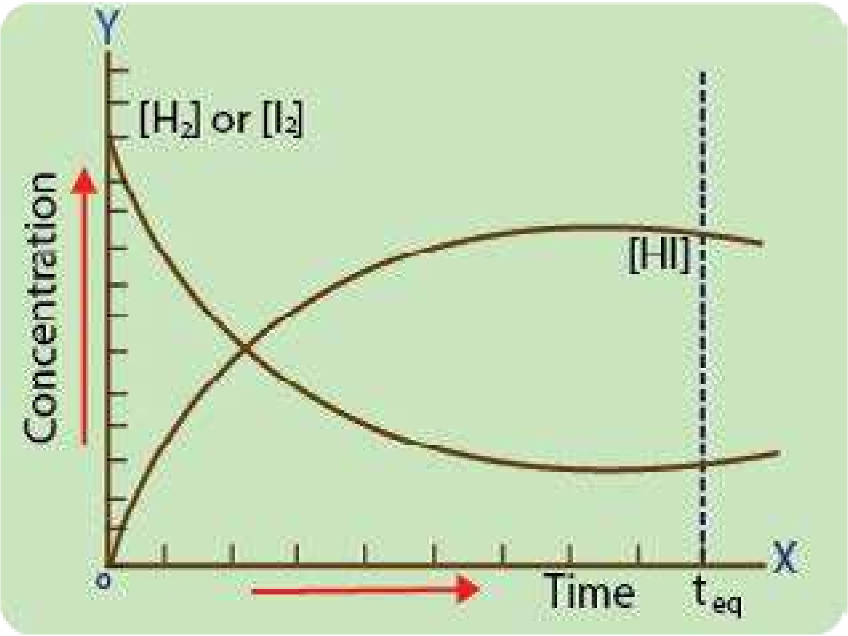
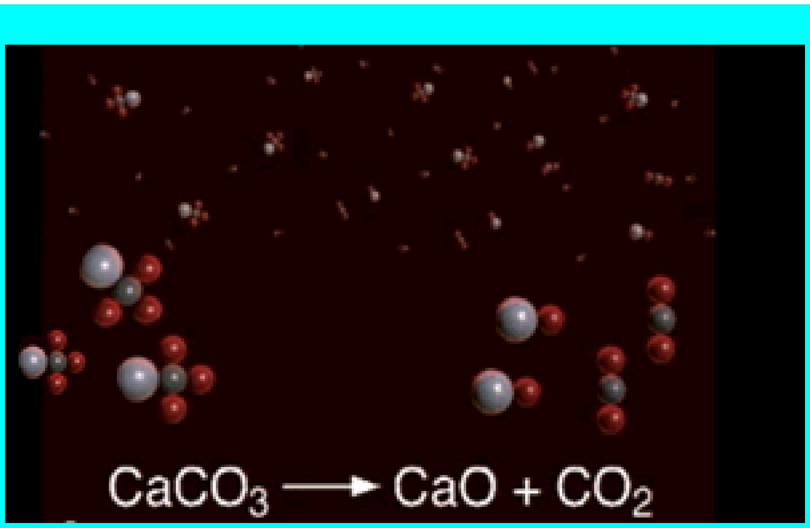


Fig (8.2) State of dynamic equilibrium

(i) All reactions cease at equilibrium so that the system becomes stationary.
(ii) The forward and reverse reactions are taking place simultaneously at exactly the same rate.

It is now universally accepted that the later conditions prevail in a reversible reaction at equilibrium stage of reaction. It is known as the state of dynamic equilibrium.



Animation 8.2: Chemical Equilibrium
Source & Credit : dynamicscience

8.1.2 Law of Mass Action

A state of dynamic equilibrium helps to determine the composition of reacting substances and the products at equilibrium. We use the relationship which was derived by C.M. Guldberg and R Waage in 1864. **It is known as the law of mass action. It states that the rate at which the reaction proceeds is directly proportional to the product of the active masses of the reactants.**

The term active mass represents the concentration in mole dm^{-3} of the reactants and products for a dilute solution.

Now, consider a general reaction in which A and B are the reactants and C and D are the products. The reaction is represented by the following chemical equation.

$$A + B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} C + D$$

The equilibrium concentrations of A, B, C and D are represented in square brackets like [A], [B], [C] and [D] respectively and they are expressed in moles dm^{-3}. According to the law of mass action, the rate of the forward reaction, is proportional to the product of molar concentrations of A and B.

$$\text{Rate of forward reaction } (R_f) \propto [A][B]$$

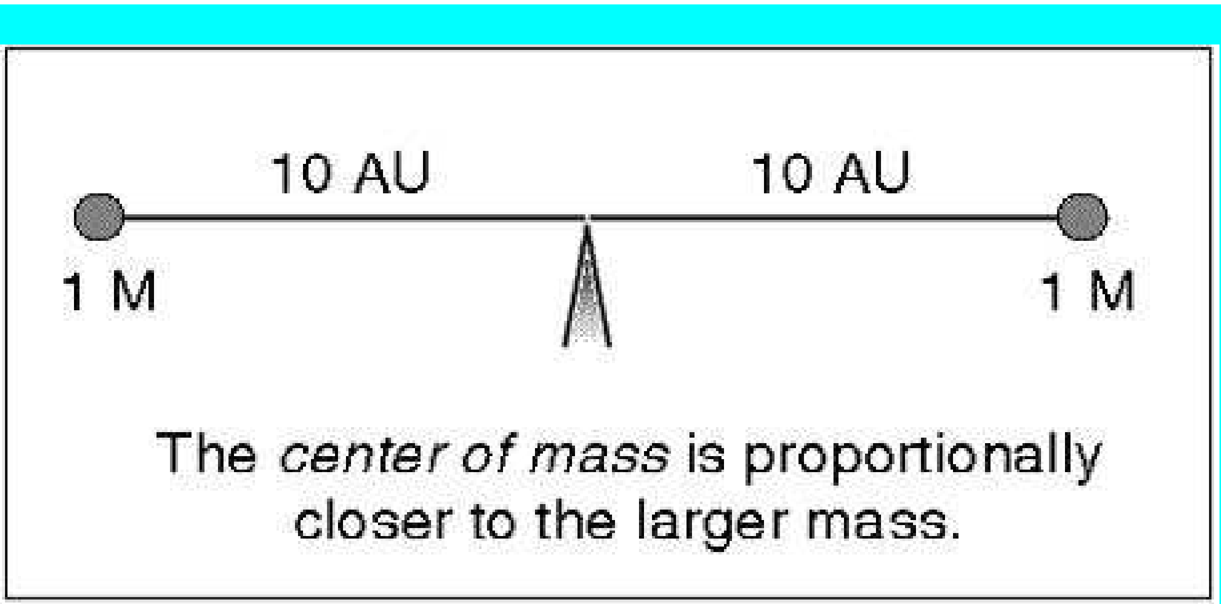
or $$R_f = k_f[A]\,[B]$$

k_f is the proportionality constant and is called rate constant for forward reaction and R_f is the rate of forward reaction. Similarly, the rate of reverse reaction (R_r) is given by

$$\text{Rate of reverse reaction } (R_r) \propto [C][D]$$

$$R_r = k_r[C]\,[D]$$

Where kr is the proportionality constant and is called the rate constant for backward reaction. Remember that C and D are the reactants for backward step.



Animation 8.3: Mass Action
Source & Credit : astronomynotes

At equilibrium,

$$R_f = R_r$$

or $$k_f[A]\,[B] = k_r[C]\,[D]$$

On rearranging, we get

$$\frac{k_f}{k_r} = \frac{[C][D]}{[A][B]}$$

Let $$\frac{k_f}{k_r} = K_c$$

So, $$K_c = \frac{[C][D]}{[A][B]}$$

The constant K_c is called the equilibrium constant of the reaction. K_c is the ratio of two rate constants.

Conventionally, while writing equilibrium constant, the products are written as numerator and reactants as denominator.

$$K_c = \frac{[\text{products}]}{[\text{reactants}]} \quad \text{or} \quad K_c = \frac{\text{rate constant for forward step}}{\text{rate constant for reverse step}}$$

For a more general reaction

$$aA + bB \underset{k_r}{\overset{k_f}{\rightleftharpoons}} cC + dD$$

Where a, b, c and d are the coefficients of balanced chemical equation. They are number of moles of A, B, C and D, respectively in the balanced equation.
The equilibrium constant is given by

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Hence, the coefficients in the equation appear as exponents of the terms of concentrations in the equilibrium constant expression.

Units of Equilibrium Constants

Equilibrium constant is the ratio of the products of the concentrations of the products to the product of concentrations of the reactants. If the reaction has equal number of moles on the reactant and product sides, then equilibrium constant has no units. When the number of moles is unequal then it has units related to the concentration or pressure. But it is a usual practice that we don't write the units with K_p or K_c values.

Following are some important reversible reactions. Their units of K_c are expressed as

(i) $CH_3COOH(aq) + C_2H_5OH(aq) \rightleftharpoons CH_3COOC_2H_5(aq) + H_2O(\ell)$

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} = \frac{[\text{moles dm}^{-3}][\text{moles dm}^{-3}]}{[\text{moles dm}^{-3}][\text{moles dm}^{-3}]} = \text{no units}$$

(ii) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{[\text{moles dm}^{-3}]^2}{[\text{moles dm}^{-3}][\text{moles dm}^{-3}]^3} = \text{moles}^{-2}\text{dm}^{+6}$$

In the expression of K_c, we have ignored the physical states for the sake of convenience.

Example 1:

The following reaction was allowed to reach the state of equilibrium.

$$2A(aq) + B(aq) \rightleftharpoons C(aq)$$

The initial amounts of the reactants present in one dm^3 of solution were 0.50 mole of A and 0.60 mole of B. At equilibrium, the amounts were 0.20 moles of A and 0.45 mole of B and 0.15 mole of C. Calculate the equilibrium constant K_c.

Solution

Equation: $$2A(aq) + B(aq) \underset{k_r}{\overset{k_f}{\rightleftharpoons}} C(aq)$$

K_c for the reaction is given by

$$K_c = \frac{[C]}{[A]^2[B]}$$

$$2A(aq) + B(aq) \rightleftharpoons C(aq)$$

Initial concentrations	0.50 mol	0.60 mol	0.00 mol
Equilibrium concentrations	0.20 mol	0.45 mol	0.15 mol

Since $$K_c = \frac{[C]}{[A]^2[B]}$$

Putting values of concentrations, which are present at equilibrium stage

So, $$K_c = \frac{(0.15)}{(0.20)x(0.20)x(0.45)}$$

$$K_c = \frac{1}{0.20x0.20x3} == \frac{1}{0.12} \qquad \boxed{8.3} \text{ Answer}$$

The units have been ignored for the sake of convenience.

8.1.3 Equilibrium Constant Expressions for Some Important Reactions

i. Formation of Ester from an Organic Acid and Alcohol (aqueous phase reaction)

This is a well known reversible reaction in the solution state.

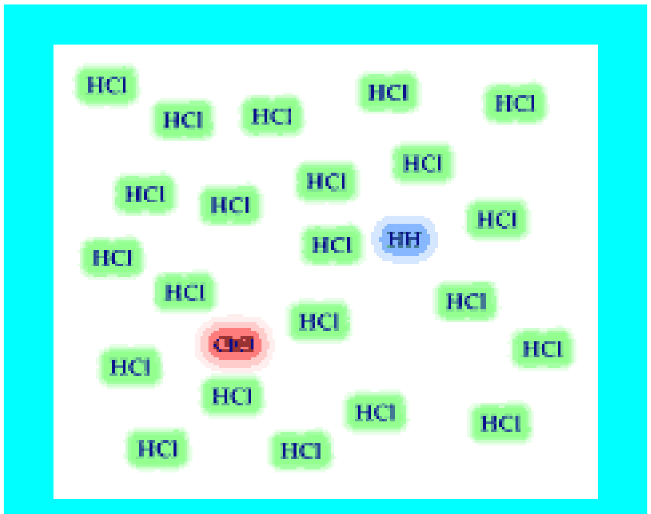
$$CH_3COOH(aq) + C_3H_2OH(aq) \overset{H_3O^+}{\rightleftharpoons} CH_3COOC_2H_5(aq) + H_2O(\ell)$$

acid alcohol ester water

Let us suppose that ‘a’ moles of CH_3COOH and ‘b’ moles of C_2H_5OH are initially taken in a vessel in the presence of small amount of a mineral acid as a catalyst.

The progress of the reaction can be studied by finding out the concentrations of acetic acid after regular intervals.

A very small portion of the reaction mixture is withdrawn and the concentration of acetic acid is determined by titrating it against a standard solution of sodium hydroxide. The concentration of acetic acid will decrease until the attainment of state of equilibrium, when it will become constant. At equilibrium stage, x moles of ester and ‘x’ moles of H_2O are produced. The number of moles of acid and alcohol left behind are ‘a-x’ moles and ‘b-x’ moles respectively. If the volume of reaction mixture at equilibrium stage is ‘V’ dm³, then



Animation 8.4: Equilibrium Constant
Source & Credit : mainstreet

$$\begin{array}{llcllll} CH_3COOH(aq) + & C_2H_5OH(aq) & \rightleftharpoons & CH_3COOC_2H_5(aq) + & H_2O(\ell) & \\ \text{'a' moles} & \text{'b' moles} & \rightleftharpoons & \text{'0' moles} & \text{'0' moles} & t=0sec \\ \text{(a-x) moles} & \text{(b-x) moles} & \rightleftharpoons & \text{'x' moles} & \text{'x' moles} & t=t_{eq} \end{array}$$

When number of moles are divided by total volume of the reaction mixture, we get concentration of each species at equilibrium stage in moles dm^{-3}.

$$\left(\frac{a-x}{V}\right)\text{moles dm}^{-3}+\left(\frac{b-x}{V}\right)\text{moles dm}^{-3} \rightleftharpoons \left(\frac{x}{V}\right)\text{moles dm}^{-3}+\left(\frac{x}{V}\right)\text{moles dm}^{-3}$$

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

Since

Brackets [ ] denote the concentrations in moles dm^{-3}.

Putting concentrations at equilibrium

$$K_c = \frac{\frac{X}{V}\cdot\frac{X}{V}}{\frac{(a-x)}{V}\cdot\frac{(b-x)}{V}}$$

Simplifying the right hand side, we get

$$K_c = \frac{X^2}{(a-x)(b-x)}$$

In this expression of K_c, the factor of volume is cancelled out. So, the change of volume at equilibrium stage does not affect the K_c value or equilibrium position of reaction.

ii. Dissociation of PCl_5 (gaseous phase reaction)

The dissociation of PCl_5 into PCl_3 and Cl_2, is a well known homogeneous gaseous phase reaction. This reaction has unequal number of moles of reactants and products.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Let ‘a’ moles of PCl_5 present initially are decomposed by ‘x’ moles. So, at equilibrium stage, ‘a-x’ moles of PCl_5 are left behind while ‘x‘ moles of PCl_3 and ‘x’ moles of Cl_2 are produced. If the volume of equilibrium mixture is ‘V’ dm^3, then

$PCl_5(g)$	$\rightleftharpoons$	$PCl_3(g)$	$+$	$Cl_2(g)$	
‘a’moles		‘O’moles		‘O’moles	t = 0sec
(a - x) moles		‘x‘ moles		‘x‘ moles	$t = t_{eq}$

Dividing the number of moles by total volume of reactants and products at equilibrium.

$$\left(\frac{a-x}{V}\right)\text{moles dm}^{-3} \rightleftharpoons \left(\frac{x}{V}\right)\text{moles dm}^{-3} + \left(\frac{x}{V}\right)\text{moles dm}^{-3}$$

Since $$K_c = \frac{[PCl_3][Cl_2]}{PCl_5}$$

Putting the concentrations at equilibrium

$$K_c = \frac{\frac{X}{V}.\frac{X}{V}}{\frac{(a-x)}{V}}$$

Simplifying the right hand side, we get

$$K_c = \frac{x^2}{V(a-x)}$$

The final expression is not independent of the factor of volume. So, the change of volume at equilibrium stage disturbs the equilibrium position of the reaction. We will discuss this reaction in Le-Chatelier’s principle with reference to effect of volume change and its effect on change of equilibrium position.

iii. Decomposition of N_2O_4 (gaseous phase reaction)

Similarly, for decomposition of N_2O_4 (g). the expression of K_c involves the factor of volume.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

$$K_c = \frac{4x^2}{(a-x)V}$$

'a' is the initial number of moles of N_2O_4 'x' is number of moles of N_2O_4 decomposed and 'V' is total volume of N_2O_4 , and NO_2 at equilibrium stage.

iv. Synthesis of NH_3 (gaseous phase reaction)

For the synthesis of ammonia,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

the expression of K_c is

$$K_c = \frac{4x^2V^2}{(a-x)(b-3x)^3}$$

Where 'a' and 'b' are the initial number of moles of N_2 and H_2 and 'x' is number of moles of N_2, decomposed at equilibrium stage. 'V' is the total volume of N_2, H_2 and NH_3 at equilibrium. The final expression involves V^2 in the numerator:

Hence, it depends upon the coefficients of balanced equation that whether the factor of volume will appear in numerator or denominator.

8.1.4 Relationship Between Equilibrium Constants

The expressions of equilibrium constants depend upon the concentration units used. Mostly the concentrations are expressed in mole dm^{-3}. Let us consider the following reversible reaction.

$$aA + bB \rightleftharpoons cC + dD$$

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad \text{or} \quad K_c = \frac{C_C{}^c D_D{}^d}{A_A{}^a B_B{}^b}$$

The square brackets represent the concentration of species in moles dm^{-3}. Anyhow, the capital C is also used for molar concentrations.

If the reactants A, B, and the products C, D of the reaction under consideration are ideal gases, then molar concentration of each gas is proportional to its partial pressure . When the concentrations are expressed in terms of partial pressures, the expression of K_p is,

$$K_p = \frac{p_C{}^c p_D{}^d}{p_A{}^a p_B{}^b}$$

Here P_A, P_B, P_C and P_D are partial pressures of A, B, C, D respectively at equilibrium position. As long as the number of moles of products and reactants, which are in the gaseous state, are equal, the values of K_C and K_P remain the same. Otherwise, the following relationship between K_P and K_C can be derived by using Dalton’s law of partial pressures.

$$K_p = K_c(RT)^{\Delta n}$$

Where ‘Δn’ is the difference between number of moles of the gaseous products and the number of moles of gaseous reactants.

Δn = no. of moles of products - no. of moles of reactants

‘R’ is the general gas constant and ‘T’ is absolute temperature at which the reaction is being carried out

Where, $\Delta n = 0$, then all the equilibrium constants have the same values.

Example 2:

N_2 (g) and H_2 (g) combine to give NH_3 (g). The value of K_c in this reaction at 500 °C is 6.0×10^{-2}. Calculate the value of K_p for this reaction.

Solution:

The reaction for the synthesis of NH_3 is

$$N_2(g) + 3H_2(g) \quad \quad 2NH_3(g)$$

This reaction takes place with decrease in the number of moles. The relationship of K_p and K_c is

$$K_p = K_c(RT)^{\Delta n}$$

Now $K_p = 6.0 \times 10^{-2}$

Temperature $= 500 + 273 = 773$ K

Δn = no of moles of products - no of moles of reactants

$$\Delta n = 2 - 4 = -2$$

$$R = 0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$$

Substituting these values in the expression

$$K_p = 6.0 \times 10^{-2} (773 \times 0.0821)^{-2} \quad = 6.0 \times 10^{-2} (63.5)^{-2}$$

$$K_p = \frac{6.0\text{x}10^{-2}}{(63.5)^2}$$

$$K_p = \boxed{1.5\text{x}10^{-5}} \quad \text{Answer}$$

In this case the value of K_p is smaller than K_c . Those reactions, which take place with the increase in the number of moles mostly have greater K_p than K_c.

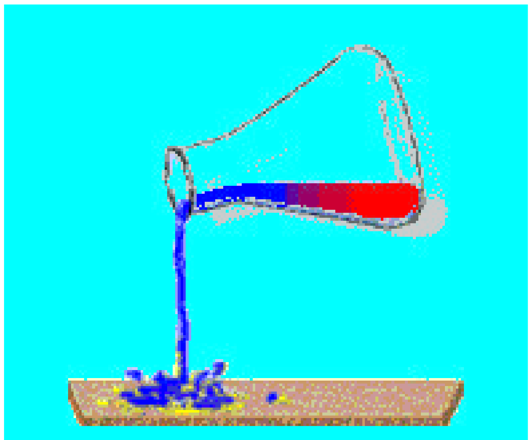
8.1.5 APPLICATIONS OF EQUILIBRIUM CONSTANT

The value of equilibrium constant is specific and remains constant at a particular temperature.

The study of equilibrium constant provides us the following informations:

(i) Direction of reaction (ii) Extent of reaction

(iii) Effect of various factors on equilibrium constant and equilibrium position.



Animation 8.5: APPLICATIONS OF EQUILIBRIUM CONSTANT
Source & Credit : oocities

(i) Direction of Reaction

we know that, $K_c = \dfrac{[\text{Products}]}{[\text{Reactants}]}$ for any reaction.

The direction of a chemical reaction at any particular time can be predicted by means of [products] / [reactants] ratio, calculated before the reaction attains equilibrium. The value of [product] / [reactants] ratio leads to one of the following three possibilities.

(a) The ratio is less than K_c. This implies that more of the product is required to attain the equilibrium, therefore, the reaction will proceed in the forward direction.

(b) The ratio is greater than K_c. It means that the reverse reaction will occur to attain the equilibrium.

(c) When the ratio is equal to K_c, then the reaction is at equilibrium.

Example 3:

Esterification reaction between ethanol and acetic acid was carried out by mixing definite amounts of ethanol and acetic acid alongwith some mineral acid as a catalyst. Samples were drawn out of the reaction mixturq to check the progress of the esterification reaction. In one of the samples drawn after time t, the concentrations of the species were found to be $[CH_3COOH] = 0.025$ mol dm^{-3}, $[C_2H_5OH] = 0.032$ mol dm^{-3}, $[CH_3COOC_2H_5] = 0.05$ mol dm^{-3}, and $[H_20] = 0.04$ mol dm^{-3}. Find out the direction of the reaction if K_c for the reaction at 25°C is 4.

Solution:

Esterification reaction is represented by the following stoichiometric equation.

$$CH_3COOH + C_2H_5OH \overset{H^+}{\rightleftharpoons} CH_3COOC_2H_5 + H_2O$$

All the substances are present in the same volume of solution, therefore K_C is given by

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

The various values of concentrations, at time t are substituted to get the ratio

$$K_c = \frac{0.05 \text{x} 0.04}{0.025 \text{x} 0.032} = \boxed{2.50} \text{ Answer}$$

The given value of K_c for this reaction is 4 and 2.5 is less than K_c. Therefore, the reaction will proceed in the forward direction to attain the equilibrium.

(ii) Extent of Reaction

(a) If the equilibrium constant is very large, this indicates that the reaction is almost complete.

(b) If the value of K_c is small, it reflects that the reaction does not proceed appreciably in the forward direction.

(c) If the value of K_c is very small, this shows a very little forward reaction.

Examples:

Equilibrium constant for the decomposition of ozone to oxygen is 10^{55} at 25°C.

i.e., $2O_3 \rightleftharpoons 3O_2, \quad K_c = 10^{55} \quad \text{at } 25^{\circ}C$

It infers that at room temperature 0_3 is unstable and decomposes very rapidly to 0_2. This reaction is almost complete.

On the other hand the value of equilibrium constant for the decomposition of HF at 2000°C is 10^{-13}.

$$2HF(g) \rightleftharpoons H_2(g) + F_2(g) \quad K_c = 10^{-13} \quad \text{at } 2000^{\circ}C$$

It indicates high stability and slow decomposition of HF, even at 2000°C.

(iii) The Effect of Conditions on the Position of Equilibrium

Equilibrium constant and position of equilibrium are two different entities. K_c is equilibrium constant and has constant value at a particular temperature whereas the ratio of products to reactants in equilibrium mixture is described as the position of equilibrium and it can change if the external conditions e.g. temperature, pressure and concentrations are altered. If K_c is large the position of equilibrium lies on the right and if it is small, the position of the equilibrium lies on the left, for a reversible reaction.

Chemists are interested in finding the best conditions to obtain maximum yield of the products in reversible reaction, by favourably shifting the position of equilibrium of a reaction. For this purpose, we have to discuss an important principle in this respect i.e.Le-Chatelier’s principle.

8.1.6 The Le-Chatelier's Principle

Le-Chatelier studied the effects of concentration, pressure and temperature on equilibria.

This principle states that if a stress is applied to a system at equilibrium, the system acts in such a way so as to nullify, as far as possible, the effect of that stress.

The system cannot completely cancel the effect of change, but will minimize it. The Le-Chatelier’s principle has wide range of applications for ascertaining the position and composition of the physical and chemical equilibria.

Animation 8.6: The Le-Chatelier’s Principle
Source & Credit : Anotherequilibriumsite

(a) Effect of Change in Concentration

In order to understand the effect of change in concentration on the reversible reaction, consider the reaction in which $BiCl_3$ reacts with water to give a white insoluble compound BiOCl.

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$$

The equilibrium constant expression for above reaction can be written as

$$K_c = \frac{[BiOCl][HCl]^2}{[BiCl_3][H_2O]}$$

Aqueous solution of $BiCl_3$ is cloudy, because of hydrolysis and formation of BiOCl. If a small amount of HCl is added to this solution, it will disturb the equilibrium and force the system to move in such a way so that effect of addition of HCl is minimized. The reaction will move in the backward direction to restore the equilibrium again and a clear solution will be obtained. However, if water is added to the above solution the system will move in the forward direction and the solution will again become cloudy. The shifting of reaction to forward and backward direction by disturbing the concentration is just according to Le-Chatelier's principle.

So, in general, we conclude that addition of a substance among the reactants, or the removal of a substance among the products at equilibrium stage disturbs the equilibrium position and reaction is shifted to forward direction. Similarly, the addition of a substance among the products or the removal of a substance among the reactants will derive the equilibrium towards the backward direction. Removing one of the products formed can therefore increase the yield of a reversible reaction. The value of K however remains constant. This concept is extensively applied in common ion effect and follows the Le-Chatelier's principle.

(b) Effect of Change in Pressure or Volume

The change in pressure or volume are important only for the reversible gaseous reactions where the number of moles of reactants and products are not equal. Le-Chatelier's principle plays an important role, to predict the position and direction of the reaction. Take the example of formation of SO_3 gas from SO_2 gas and O_2 gas.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

This gas phase reaction proceeds with the decrease in the number of moles and hence decreases in volume at equilibrium stage. When the reaction approaches the equilibrium stage, the volume of the equilibrium mixture is less than the volume of reactants taken initially. If one decreases the volume further at equilibrium stage, the reaction is disturbed. It will move to the forward direction to minimize the effect of disturbance. It establishes a new equilibrium position while K_c remains constant. The reverse happens when the volume is increased or pressure is decreased at equilibrium stage.

(c) Quantitative Effect of Volume on Equilibrium Position

The quantitative effect of change of volume or pressure can be inferred from the mathematical expression of K_c for SO_3 (g) synthesis.

$$2SO_2(g) + O_2(gas) \rightleftharpoons 2SO_3(g)$$

$$K = \frac{4x\ V}{(a\text{-}2x)\ (b\text{-}x)}$$

Where 'V' is the volume of reaction mixture at equilibrium stage, 'a' and 'b' are the number of moles of SO_2 and O_2 present initially and Y are the number of moles of oxygen which has reacted at equilibrium. According to the above equation, when volume is increased, then 'x' has to be decreased to keep K_c constant. The decrease of x means that reaction is pushed to the backward direction. From the amount of the increase in volume, we can calculate the amount of x which has to be decreased to keep K_c constant

Similarly,increasing the pressure on the above reaction at equilibrium, will decrease tlie volume and hence the value of K_c will increase. In order to keep the value of K_c constant, the reaction will move in the forward direction.

In the same way, we can explain the effect of change of pressure on the equilibrium positions for the dissociation of PCl_5 and N_2O_4 reactions. These reactions are homogenous gaseous phase reactions.

PCl_5 dissolves to give PCl_3 and Cl_2

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

K_c for this reaction is as follows:

$$K_c = \frac{x^2}{V(a\text{-}x)}$$

The dissociation of N_2O_4 gives NO_2 gas

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

The K_c for this reaction is as follows

$$K_c = \frac{4x^2}{V(a-x)}$$

Both these reactions have the factor of volume present in the denominator. The reason is that numbers of moles of products are greater than those of reactants. So, increase in pressure will decrease x to keep the value of K_c constant and the reaction will be pushed to the backward direction. The equilibrium position is disturbed but not the K_c value.

Remember that, those gaseous reactions in which number of moles of reactants and products are same, are not affected by change in pressure or volume. Same is the case for reactions in which the participating substances are either liquids or solids.

(d) Effect of Change in Temperature

Most of the reversible chemical reactions are disturbed by change in temperature. If we consider heat as a component of equilibrium system, a rise in temperature adds heat to the system and a drop in temperature removes heat from the system. According to Le-Chatelier's principle, therefore, a temperature increase favours the endothermic reactions and a temperature decrease favours the exothermic reactions.

The equilibrium constant changes by the change of temperature, because the equilibrium position shifts without any substance being added or removed. Consider the following exothermic reaction in gas phase at equilibrium taking place at a known temperature.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \qquad \Delta H = -41.84\ kJ\ mole^{-1}$$

At equilibrium stage, if we take out heat and keep the system at this new lower temperature, the system will readjust itself, so as to compensate the loss of heat energy. Thus, more of CO and H_2O molecules will react to form CO_2 and H_2 molecules, thereby, liberating heat because reaction is exothermic in the forward direction. It means by decreasing temperature, we shift the initial equilibrium position to the right until a new equilibrium position is established. On the contrary, heating the reaction at equilibrium will shift the reaction to the backward direction because the backward reaction is endothermic.

An interesting feature of Le-Chatelier's principle is the effect of temperature on the solubility. Consider a salt such as KI. It dissolves in water and absorbs heat.

$$KI(s) \rightleftharpoons KI(aq) \qquad \Delta H = 21.4 kJ\ mol^{-1}$$

Let us have a saturated solution of KI in water at a given temperature. It has attained equilibrium at this temperature. A rise in temperature at equilibrium favours more dissolution of the salt.

Equilibrium is shifted to the forward direction. On the other hand, cooling will favour crystallization of salt. Hence the solubility of KI in water must increase with increase in temperature. For some salts the heat of solution is close to zero (heat is neither evolved or absorbed). The solubility of these salts in water is not affected by the change in temperature. Formation of aqueous solution of NaCl is an example of such a salt.

Those substances, whose heats of solutions are negative (exothermic), decrease their solubilities by increasing temperature, as LiCl and Li_2CO_3 etc.

(e) Effect of Catalyst on Equilibrium Constant

In most of the reversible reactions the equilibrium is not always reached within a suitable short time. So, an appropriate catalyst is added. A catalyst does not affect the equilibrium position of the reaction. It increases the rates of both forward and backward reactions and this reduces the time to attain the state of equilibrium.

Actually, a catalyst lowers the energy of activation of both forward and reverse steps by giving new path to the reaction.

8.2 APPLICATIONS OF CHEMICAL EQUILIBRIUM IN INDUSTRY

Concept of chemical equilibrium is widely applicable for preparation of certain materials on industrial scale. Let us discuss the manufacture of NH_3 and SO_3 gases on industrial scale.

8.2.1 Synthesis of Ammonia by Haber's Process

The process of ammonia synthesis was developed by German chemist F. Haber and first used in 1933. This process provides an excellent setting in which to apply equilibrium principle and see the compromises needed to make an industrial process economically worth while. The chemical equation is as follows.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92.46 kJ$$

When we look at the balanced chemical equation it is inferred, from Le-Chatelier's principle that one can have three ways to maximize the yield of ammonia.

(i) By continual withdrawl of ammonia after intervals, the equilibrium will shift to forward direction in accordance with Le-Chatelier's principle. To understand it look at the effect of change of concentration in Le-Chatelier's principle.

ii) In crease the pressure to decrease the volume of the reaction vessel. Four moles of the reactants combine to give two moles of the products. High pressure will shift the equilibrium position to right to give more and more ammonia.

(iii) Decreasing the temperature will shift it to the forward direction according to Le-Chatelier's principle.

Table (8.2) Effect of temperature on K_c for ammonia synthesis

T(K)	K_c
200	$7.7x10^{15}$
300	$2.69x10^{8}$
400	$3.94x10^{1}$
500	$1.72x10^{2}$
600	$4.53x10^{0}$
700	$2.96x10^{-1}$
800	$3.96x10^{-2}$

So high pressure, low temperature and continual removal of ammonia will give the maximum yield of ammonia. Table (8.2) shows the effect of the rise in temperature on the value of Kc and the Fig. (8.3) shows the optimum conditions to get maximum yield of ammonia. Fig (8.3) shows percent yield of ammonia vs. temperature (^{0}C) at five different operating pressures.

At very high pressure and low temperature (top left), the yield of NH_3 is high but the rate of formation is low. Industrial conditions denoted by circle are between 200 and 300 atmospheres at about 400^{0}C.

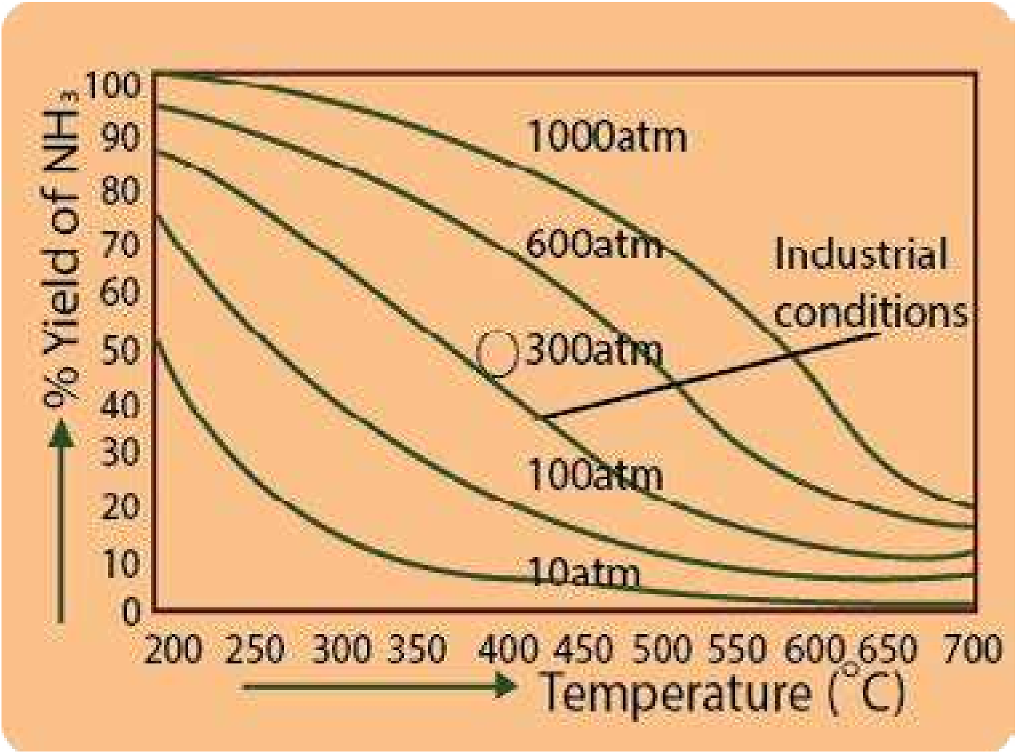
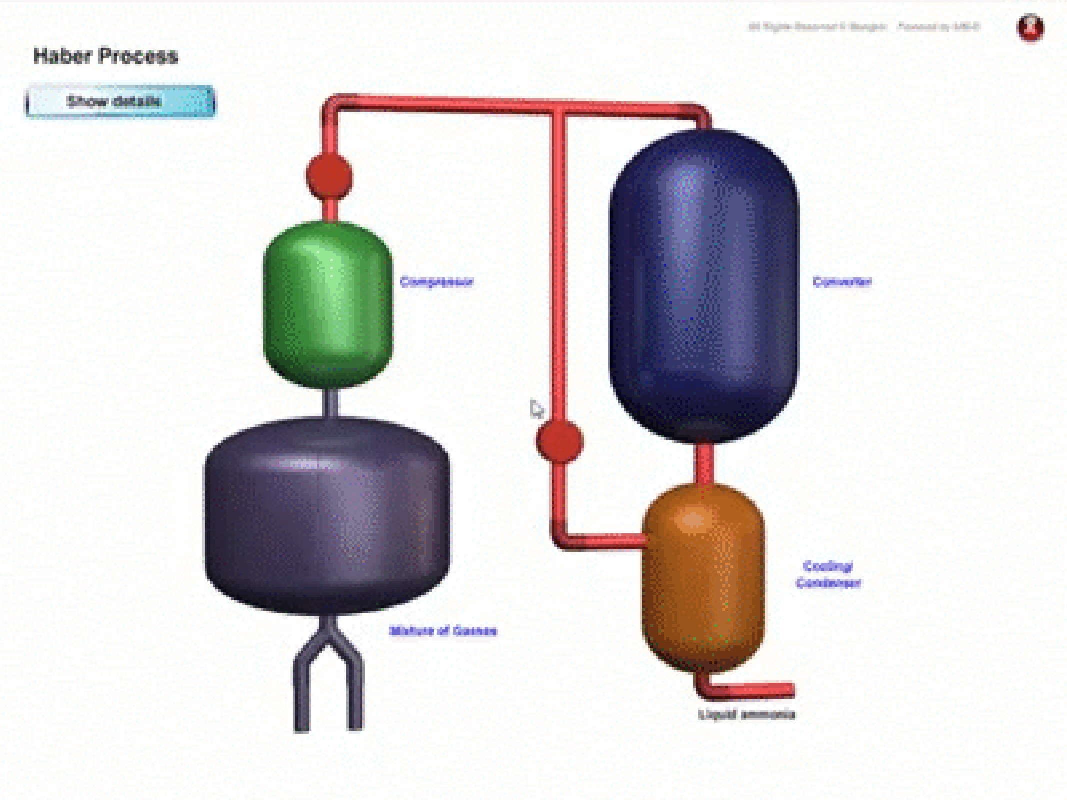


Fig (8.3). Graphical representation of temperature and pressure for NH_3 synthesis.

No doubt, the yield of NH_3 is favoured at low temperature, but the rate of its formation does not remain favourable. The rate becomes so slow and the process is rendered uneconomical. One needs a compromise to optimize the yield and the rate. The temperature is raised to a moderate level and a catalyst is employed to increase the rate. If one wants to achieve the same rate without a catalyst, then it requires much higher temperature, which lowers the yield. Hence the optimum conditions are the pressure of 200-300 atm and temperature around 673 K (400^{0}C). The catalyst is the pieces of iron crystals embedded in a fused mixture of MgO, Al_2O_3 and SiO_2.

The equilibrium mixture has 35% by volume of ammonia. The mixture is cooled by refrigeration coils until ammonia condenses (B.P = -33.4^{0}C) and is removed. Since, boiling points of nitrogen and hydrogen are very low, they remain in the gaseous state and are recycled by pumps back into the reaction chamber.

Nearly 13% of all nitrogen fixation on earth is accomplished industrially through Haber's process. This process synthesizes approximately 110 million tons of ammonia in the world. About 80% of this is used for the production of fertilizers and some is used in manufacture of explosives or the production of nylon and other polymers.



Animation 8.7: Haber's Process
Source & Credit : makeagif

8.2.2 Preparation of Sulphur Trioxide

In the contact process for manufacture of H_2SO_4, the conversion of SO_2 to SO_3 is achieved in a reversible reaction.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -194 kJ/mol$$

The temperature and pressure are the most essential factors for controlling the rate of this reaction. The principles involved here are the same as those discussed previously for Haber's process. At low temperature, the equilibrium constant for formation of SO_3 is large but equilibrium is reached very slowly. As the temperature is raised the rate increases but the yield of SO_3 drops off according to Le-Chatelier's principle. High pressure tends to increase yield of SO_3. However, instead of using high pressure, the concentration of O_2 (air) is increased to increase the yield of SO_3. Table (8.3) helps to understand the effect of different conditions on the yield of SO_3. During the process pressure is kept at one atmosphere.

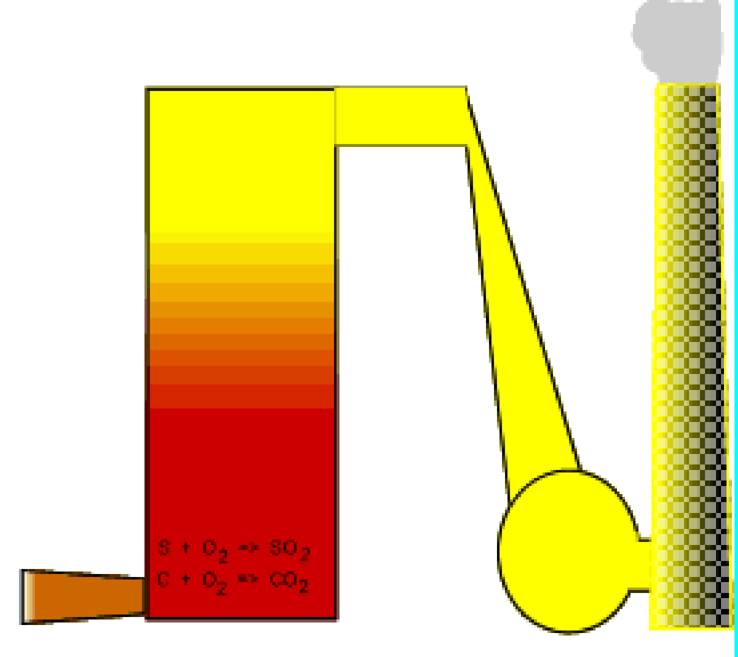
To have the best possible yield of SO_3 within a Table (8.3) Effect of temperature reasonable time, a mixture of SO_2 and O_2 (air) at 1 atm pressure is passed over a solid catalyst at 650^{0}C.

Table (8.3) Effect of temperature on the yield of SO_3

Temp. ^{0}C	K_c	Mole% of SO_3
200	5500	98
300	690	91
400	160	75
500	55	61
600	25	46
700	13	31

The equilibrium mixture is then recycled at lower temperature, 400 to 500^{0}C, to increase the yield of SO_3. The most effective catalysts are V_2O_5 and finely divided platinum. SO_3 is dissolved in H_2SO_4 to get oleum, which is diluted to get H_2SO_4.

H_2SO_4 is the king of chemicals. A country's industrial progress is measured by the amount of H_2SO_4 manufactured each year.



Animation 8.8: Preparation of Sulphur Trioxide
Source & Credit : dynamicscience

8.3.0 IONIC PRODUCT OF WATER

Pure water is a very poor conductor of electricity but its conductance is measurable. Water undergoes self ionization as follows and the reaction is reversible.

$$H_2O + H_2O \quad \quad H_3O^+ + OH^-$$

or

$$H_2O \quad \quad H^+ + OH^-$$

The equilibrium constant for this reaction can be written as follows.

$$K_c = \frac{[H^+][OH^-]}{H_2O} = 1.8 \text{ x } 10^{-16} \text{moles dm}^{-3}$$

The concentration of H_2O i.e.$[H_2O]$ in pure water may be calculated to be 1000gdm^3 divided by 18gmol^{-1} giving 55.5 moles dm^{-3}

Since, water is present in very large excess and very few of its molecules undergo ionization, so its concentration remains effectively constant. Constant concentration of water is taken on L.H.S. and multiplied with K_c to get another constant called K_w.

$$1.8 \text{ x } 10^{-16} \text{ x } 55.5 = 1.01\text{x}10^{-14} = [H^+][OH^-]$$

This 1.01x10^{-14} is called K_w of water of 25^{0}C

$$K_c[H_2O] = [H^+][OH^-]$$

So, $$K_w = [H^+][OH^-] = 10^{-14} \text{at } 25^oC.$$

K_w is called ionic product of water or dissociation constant of water. The value of K_w increases almost 75 times when temperature is increased from 0°C to 100°C. Anyhow, the increase in K is not regular. The effect of temperature on K. is shown in Table (8.4).

Table (8.4) K_w at various temperatures.

Temp. (^{0}C)	K_w
ne0	0.11x10^{-14}
10	0.30x10^{-14}
25	1.0x10^{-14}
40	3.00x10^{-14}
100	7.5x10^{-14}

When ever some quantity of acid or base is added in water, then K_w remains the same, but $[H^+]$ and $[OH^-]$are no more equal. Anyhow, in neutral water

$$[H^+] = [OH^-]$$

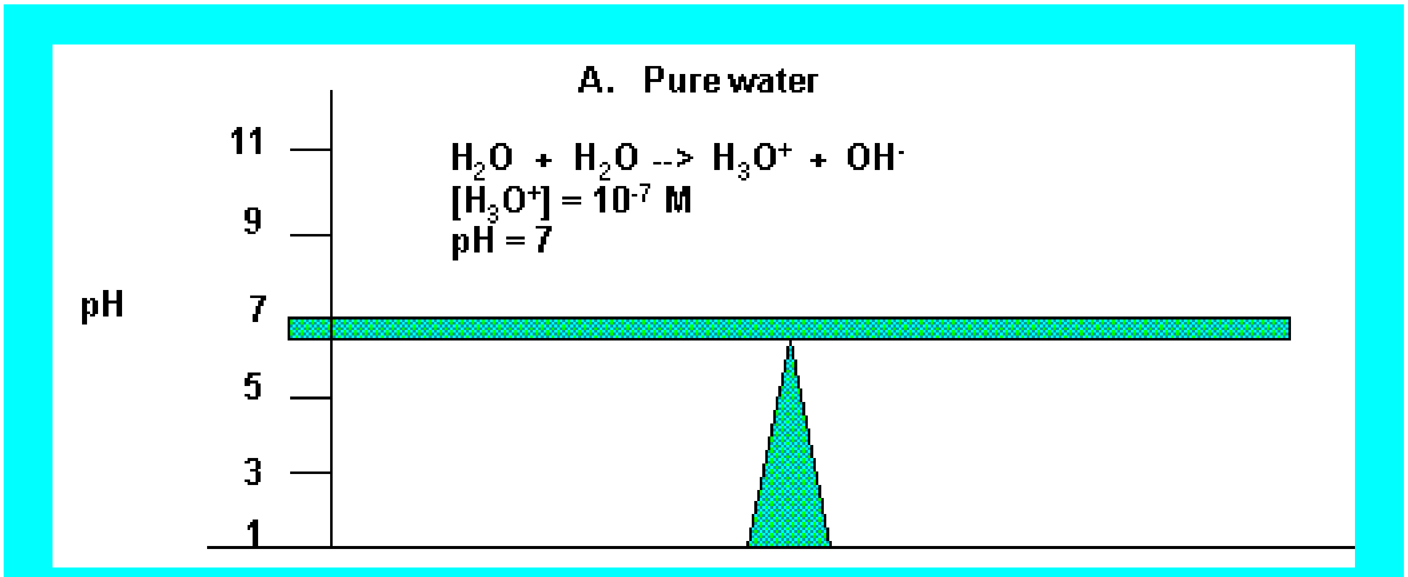
or $$[H^+][H^+] = 10^{-14}$$

$$[H^+]^2 = 10^{-14}$$

$$[H^+] = 10^{-7}\text{moles dm}^{-3}$$

and $$[OH^-] = 10^{-7}\text{moles dm}^{-3}$$

This means that out of 55.5 moles of pure water in one dm^3 of it, only 10^{-7} moles of it have dissociated into ions. This shows that water is a very weak electrolyte. At 40^0C, the $[H^+] = [OH^-]$ but the values are more than 10^{-7} moles dm^{-3} and pure water is again neutral at 40°C. Similarly, pure water is neutral at 100^0C. $[H^+]$ and $[OH^-]$ are greater than those at 40°C.



Animation 8.9: IONIC PRODUCT OF WATER
Source & Credit : employees.csbsju

In case of addition of small amount of an acid

$$[H^+] > [OH^-]$$

While in the case of addition of few drops of a base

$$[OH^-] > [H^+]$$

During both of these additions, the value of K_w will remain the same i.e. 10^{-14} at 25^0C.

pH and pOH

Actually, in all the aqueous solutions, the concentration of H^+ and OH^- are too low to be conveniently expressed and used in calculations. In 1909, Sorenson, a Danish biochemist, introduced the term pH and pOH. So, the scales of pH and pOH have been developed. pH and pOH are abbreviations of negative log of hydrogen ion concentration and negative log of hydroxide ion concentration, respectively.

$$pH = -\log[H^+]$$

and

$$pOH = -\log[OH^-]$$

For neutral water, $pH = -\log 10^{-7} = 7$

$$pOH = -\log 10^{-7} = 7$$

when

$pH = 7, \rightarrow$ solution is neutral

$pH < 7, \rightarrow$ solution is acidic

$pH > 7, \rightarrow$ solution is basic

If we take the negative log of K_w, then it is called pK_w.

$$pK_w = -\log K_w$$

$$= -\log 10^{-14}$$

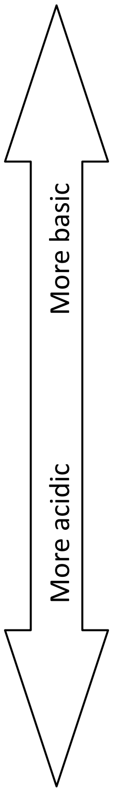
$$pK_w = 14\log 10$$ Since (log 10=1)

$$pK_w = 14x1 = 14 (\text{at } 25^{\circ}C)$$

The value of pK_w is less than 14 at higher tem peratures i.e. at 40^0Cand 100^0C.

The value of pH normally varies between 0 → 14 at 25°C. Solutions of negative pH and having values more than 14 are also known. Table (8.5) shows the relationship among $[H^+]$,$[OH^-]$, pH and pOH of various solutions.

Table (8.5) Relationship of $[H_30^+]$, $[OH^-]$, pH and pOH



	$[H_3O^+]$	pH	$[OH^-]$	pOH
Basic	$1x10^{-14}$	14.0	1x10	0.0
	$1x10^{-13}$	13.0	$1x10^{-1}$	1.0
	$1x10^{-12}$	12.0	$1x10^{-2}$	2.0
	$1x10^{-11}$	11.0	$1x10^{-3}$	3.0
	$1x10^{-10}$	10.0	$1x10^{-4}$	4.0
	$1x10^{-9}$	9.0	$1x10^{-5}$	5.0
	$1x10^{-8}$	8.0	$1x10^{-6}$	6.0
Neutral	$1x10^{-7}$	7.0	$1x10^{-7}$	7.0
Acidic	$1x10^{-6}$	6.0	$1x10^{-8}$	8.0
	$1x10^{-5}$	5.0	$1x10^{-9}$	9.0
	$1x10^{-4}$	4.0	$1x10^{-10}$	10.0
	$1x10^{-3}$	3.0	$1x10^{-11}$	11.0
	$1x10^{-2}$	2.0	$1x10^{-12}$	12.0
	$1x10^{-1}$	1.0	$1x10^{-13}$	13.0
	$1x10^{-0}$	0.0	$1x10^{-14}$	14.0

The pH values of some familiar aqueous solutions are shown inTable (8.6). This table can help you to understand the acidic or basic nature of commonly used solutions.

Table (8.6) Approximate pH and pOH of some common materials at 25°C

Material	pH	pOH	Material	pH	pOH
1.0 M HCl	0.1	13.9	bread	5.5	8.5
0.1 M HCl	1.1	12.9	potatoes	5.8	8.2
0.1 M CH_3COOH	2.9	11.10	rainwater	6.2	7.8
gastric juice	2.0	12.00	milk	6.5	7.5
lemons	2.3	11.7	saliva	6.5-6.9	7.5-7.1
vinegar	2.8	11.2	pure water	7.0	7.00
soft drinks	3.0	11.00	eggs	7.8	6.2
apples	3.1	10.9	0.1 M $NaHCO_3$	8.4	5.6
grapefruit	3.1	10.9	seawater	8.5	5.5
oranges	3.5	10.5	milkofmagnesia	10.5	3.5
tomatoes	4.2	9.8	0.1 M NH_3	11.1	2.9
cherries	3.6	10.4	0.05 M Na_2CO_3	11.6	2.4
bananas	4.6	9.4	0.1 M NaOH	13.0	1.00

8.4.0 IONIZATION CONSTANTS OF ACIDS (K_a)

Acids and bases when dissolved in water may or may not be completely dissociated. Many acids are weak electrolytes and they ionize to an extent which is much less than 100%. The value of K_a called the dissociation constant of acid, is the quantitative measure of the strength of the acid. Suppose we have an acid HA dissolved in water, in a reversible manner

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

K_c for the reversible reaction will be written as follows.

$$K_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

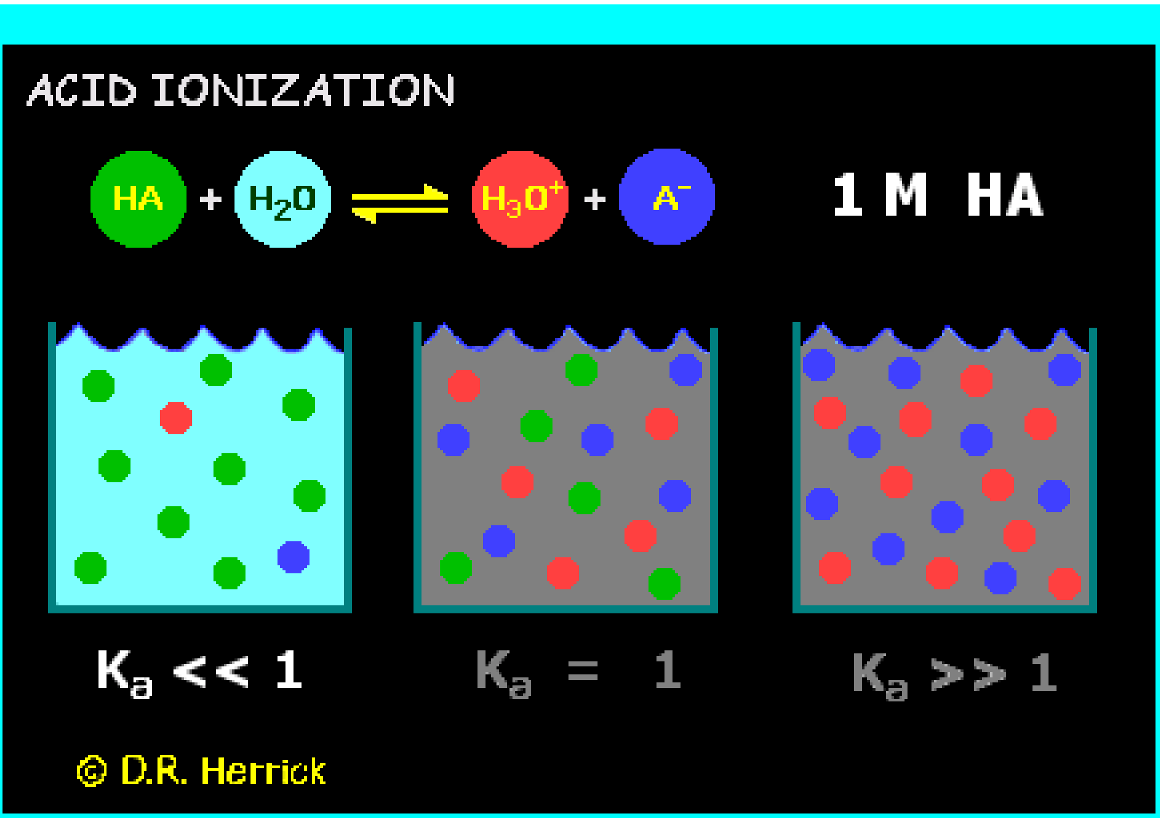
At the equilibrium stage, the concentration of water is almost the same as at the initial stages because it has been taken in large excess. A reasonable approximation, therefore, is to take the concentration of water to be effectively constant and take it on the left-hand side with K_c.

$$K_c[H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

Let $K_c[H_2O] = K_a$

K_a is another constant

Hence $K_a = \frac{[H_3O^+][A^-]}{[HA]}$



Animation 8.10: IONIZATION CONSTANTS OF ACIDS (K_a)
Source & Credit : eechem3

This equation can be used to calculate K_a for any acid solution if we know the pH or $[H^+]$ of that solution and the initial concentration of acid [HA] dissolved. This can also be used to calculate the equilibrium concentration of H_3O^+ and A^- produced if we know the initial concentration of acid HA and its K_a value.

When $K_a < 10^{-3}$ acid is weak

$K_a = 1 \text{ to } 10^{-3}$ acid is moderately strong

$K_a > 1$ acid is strong

The values of K_a for some acids are given in the Table (8.7)

Table (8.7) Dissociation constants of some acids at 25^0C and their relative strength

Acid	Dissociation	K_a	Relative strength
HCl	$HCl \rightleftharpoons H^+ + Cl^-$	very large(10^{+7})	Very strong
HNO_3	$HNO_3 \rightleftharpoons H^+ + NO_3^-$	very large(10^{+3})	Very strong
H_2SO_4	$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$	Large(10^{+2})	Very strong
HSO^-_4	$HSO^-_4 \rightleftharpoons H^+ + SO_4^{2-}$	$1.3x10^{-4}$	Strong
HF	$HF \rightleftharpoons H^+ + F^-$	$6.7x10^{-5}$	Weak
CH_3COOH	$CH_3COOH \rightleftharpoons H^+ + CH_3COOH^-$	$1.85x10^{-5}$	Weak
H_2CO_3	$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$	$4.4x10^{-7}$	Weak
H_2S	$H_2S \rightleftharpoons H^+ + HS^-$	$1.0x10^{-7}$	Weak
NH_4^+	$NH_4 \rightleftharpoons H^+ + NH_3$	$5.7x10^{-10}$	Weak
HCO_3^-	$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	$4.7x10^{-11}$	Weak
H_2O	$H_2O \rightleftharpoons H^+ + OH^-$	$1.8x10^{-16}$	Very weak

Percentage of Ionization of Acids

We can calculate the percentage ionization of weak acid and the formula is as follows:

$$\%\text{ionization}=\frac{\text{Amount of acid ionized}}{\text{Amount of acid initially available}}\ x\ 100$$

The percentage ionization of weak acids depend upon the extent of dilution of their aqueous solutions. Table (8.8) shows the change in percentage ionization of acetic acid at different concentrations. Lesser the molarity, diluted the solution, greater the chances for electrolyte to be dissociated. When 0.1 mole of CH_3COOH is dissolved in $1000cm^3$ of solution, then 1.33 molecules are dissociated out of 100, and 13.3 out of 1000. When the 0.001 moles are dispersed per dm^3 of solution then 12.6 molecules of CH_3COOH get dissociated out of 100. Remember that K_a remains the same at all dilutions at a constant temperature.

Table (8.8) Percentage ionization and ionization constants of acetic acid at 25^{0}C

Molarity	% Ionized	$[H_3O^+]$	$[CH_3COOH]$	K_a
0.10000	1.33	0.001330	0.098670	1.79×10^{-5}
0.0500	1.89	0.000945	0.049060	1.82×10^{-5}
0.0100	4.17	0.000417	0.009583	1.81×10^{-5}
0.0050	5.86	0.000293	0.004707	1.81×10^{-5}
0.0010	12.60	0.000126	0.000874	1.72×10^{-5}

Example 4:

What is the percentage ionization of acetic acid in a solution in which 0.1 moles of it has been dissolved per dm^3 of the solution.

Solution:

$$CH_3-\overset{\overset{O}{||}}{C}-O-H \rightleftharpoons CH_3-\overset{\overset{O}{||}}{C}-O^- + H^+$$

$K_a = 1.85\times10^{-5}$

Initial conc. 0.10 moles 0 moles 0 moles t = 0 sec.

Change in concentration due to ionization

$(0.1=x)$ moles $\rightleftharpoons$ xmoles + xmoles t=equilibrium

Concentration at equilibrium

$(0.1-x) \approx 0.10 \rightleftharpoons$ xmoles + xmoles t=equilibrium

(0.1 - x) is approximately 0.1, because the value of x is very small as compared to 0.1. The reason is that CH_3COOH is a much weak electrolyte.

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{x.x}{0.1}$$

Putting the value of K_a

$$1.85\text{x}10^{-5}=\frac{x^2}{0.1}$$

or $x^2=0.1\text{x}1.8\text{x}10^{-5}=1.8\text{x}10^{-6}$

Taking square root on both sides

x = $0.1 \text{ x } 1.8 \text{ x } 10^{-5} = 1.8\text{x}10^{-6}$

In other words $[H^+]$ = $1.3 \text{ x } 10^{-3}$ mole dm^{-3} (amount of acid ionized)

$$\%\text{ionization}=\frac{\text{concentration of ionized acid}}{\text{original concentration}}\text{ x }100$$

$$\%\text{ionization}=\frac{1.3\text{x}10^{-3}\text{x}100}{0.1}=\boxed{1.3}\text{ Answer}$$

Hence, out of 1000 molecules of acetic acid only 13 are dissociated into ions, when 0.1 molar solution is prepared. In other words when 6 g of CH_3COOH i.e 0.1 moles is dissolved in 1000 cm^3 of solution only 13 molecules ionize out of energy 1000 CH_3COOH molecules.

This is known as Ostwald's dilution law, that dilution increases the degree of dissociations.

8.5.0 IONIZATION CONSTANT OF BASES (K_b)

Unlike, strong bases weak Bronsted bases which are proton acceptors, usually consist of molecules or ions. They react with water, remove a proton from it, and generate OH^- ions. Take the examples of NH_3 and CO_3^{2-}.

$$NH_3(aq) + H_2O(\ell) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$CO_3^{2-}(aq) + H_2O(\ell) \rightleftharpoons HCO_3^{1-}(aq) + OH^-(aq)$$

NH_3 and $C0_3^{2-}$ have acted as bases in above reactions. They have different abilities to accept protons from water molecules. We compare these abilities of bases by knowing the equilibrium constant K_b, which is called base ionization constant of a base.

Let the base is represented by B. Then

$$B(aq) + H_2O(\ell) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

$$K_c = \frac{[BH^+][OH^-]}{[B][H_2O]}$$

Since, the concentration of H_2O constant, being in large excess

So, $$K_c\ [H_2O] = \frac{[BH^+][OH^-]}{[B]}$$

Put $$K_c[H_2O] = K_b$$

Hence $$K_b = \frac{[BH^+][OH^-]}{[B]}$$

K_b value of a base is the quantitative measurement of strength of a base Smaller the K_b value, weaker the base. Table (8.9) gives the K_b values for some bases.

Table (8.9) K_b of some important bases

Base	Dissociation	K_b	Relative strength
NaOH	$NaOH \rightleftharpoons Na^+ + OH^-$	Very high	Very strong
KOH	$KOH \rightleftharpoons K^+ + OH^-$	Very high	Very strong
$Ca(OH)_2$	$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH$	High	Very strong
NH_4OH	$NH_4OH \rightleftharpoons NH_4^+ + OH^-$	1.81×10^{-5}	Weak
CH_3NH_2 (Mathyl amine)	$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$	4.38×10^{-4}	Weak
$C_6H_5NH_2$ (Aniline)	$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$	4.7×10^{-10}	Very weak

pK_a and pK_b

Table (8.7) and (8.9), we conclude that the values of K_a and K_b for weak acids and bases are small numbers usually expressed in exponential form. It is convenient to convert them into whole numbers by taking their negative log. Thus we obtain pK_a and pK_b values of acids and bases.

$$pK_a = -\log K_a$$

$$pK_b = -\log K_b$$

Larger the pK_a, weaker is the acid and vice versa. Similarly, larger the pK_b, weaker is the base. If the difference of pK_a values of the two acids is one, then acid with smaller pK_a is ten times stronger than the other. If the difference is two, then one is hundred times stronger than the other.

8.6.0 LOWRY BRONSTED ACID AND BASE CONCEPT

According to this concept, acids are those species which donate the proton or have a tendency to donate and bases are those species which accept the proton or have a tendency to accept the proton.

Whenever, a weak acid or a weak base is dissolved in water, the conjugate acid base pair is produced. There is a close relationship between K_a of the acid, K_b of the conjugate base and K_w of water. Let us have an acid HA, and it gives protons to water in a reversible manner. H_3O^+ gives proton to A^- and is an acid, but A^- accepts H^+ from H_3O^+ and act as a conjugate base of HA.

$$\underset{\text{acid}}{HA} + \underset{\text{base}}{H_2O} \rightleftharpoons \underset{\substack{\text{conjugate acid}\\ \text{of } H_2O}}{H_3O^+} + \underset{\substack{\text{conjugate base}\\ \text{of HA}}}{A^-}$$

Now,

$$K_c = \frac{[H_3O^+][A^-]}{[H_2O][HA]} \quad \text{or} \quad K_a = \frac{[H^+][A^-]}{[HA]}$$

In case A^- is dissolved in water, the equation for hydrolysis of conjugate base A^- will be,

$$\underset{\text{base}}{A^-} + \underset{\text{acid}}{H_2O} \rightleftharpoons \underset{\text{acid}}{HA} + \underset{\text{base}}{OH^-}$$

So, its

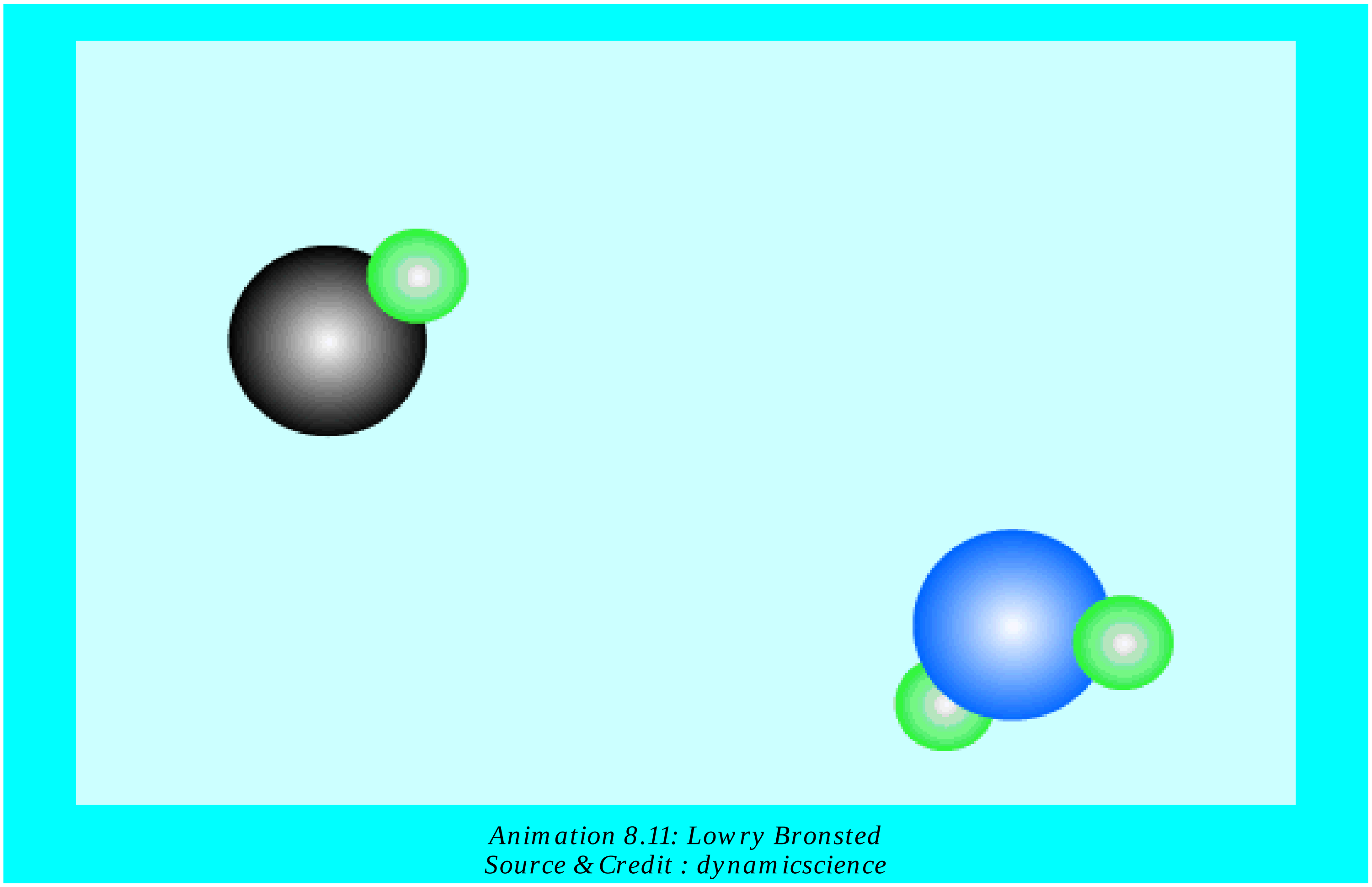
$$K_b = \frac{[HA][OH^-]}{[A^-]}$$

Let us multiply two expressions for K_a and K_b

$$K_a x K_b = \frac{[H^+][A^{1-}]}{[HA]} \times \frac{[OH^-][HA]}{[A^{1-}]}$$

Or $$K_a x K_b = [H^+][OH^-]$$

Or $$K_a x K_b = K_w$$



Animation 8.11: Lowry Bronsted
Source & Credit : dynamicscience

This equation is useful in the sense that if we know K_a of the acid, we can calculate K_b for the conjugate base and vice versa. The value of K_w is a constant at a given temperature. i.e 10^{-14} at 25c°

Let us take the log of above equation

$$\log(K_a x K_b) = \log(K_w)$$

or $$\log K_a + \log K_b = \log K_w$$

Multiply both sides by '-1'

$$-\log K_a - \log K_b = -\log K_w$$

Since $pK_a = -\log K_a$ and $pK_b = -\log K_b$

or $pK_a + pK_b = pK_w$

Since $pK_w=14$, at 25⁰C hence pK_a and pK_b of conjugate acid base pair has a very simple relation with each other.

$$pK_a + pK_b = 14 \text{ at } 25^{o}C$$

This equation proves the following facts.

(a) Conjugate base of a very weak acid is relatively very strong base.

(b) Conjugate acid of a very strong base is relatively very weak acid.

So $K_a \propto \frac{1}{K_b}$

We can calculate the pK_b of CH_3COO^-, if we know pK_a of CH_3COOH. Similarly, if we know pK_b of NH_3, we can calculate pK_a of NH_4^+ .

8.7 COMMON ION EFFECT

The suppression of ionization of a weak electrolyte by adding a common ion from outside is called common ion effect.

We are familiar with purification of sodium chloride by passing hydrogen chloride gas through saturated brine. Sodium chloride is fully ionized in the solution. Equilibrium constant expression for this process can be written as follows:

$$NaCl(s) \rightleftharpoons Na^+(aq) + Cl^-(aq)$$

$$K_c = \frac{[Na^+][Cl^-]}{[NaCl]}$$

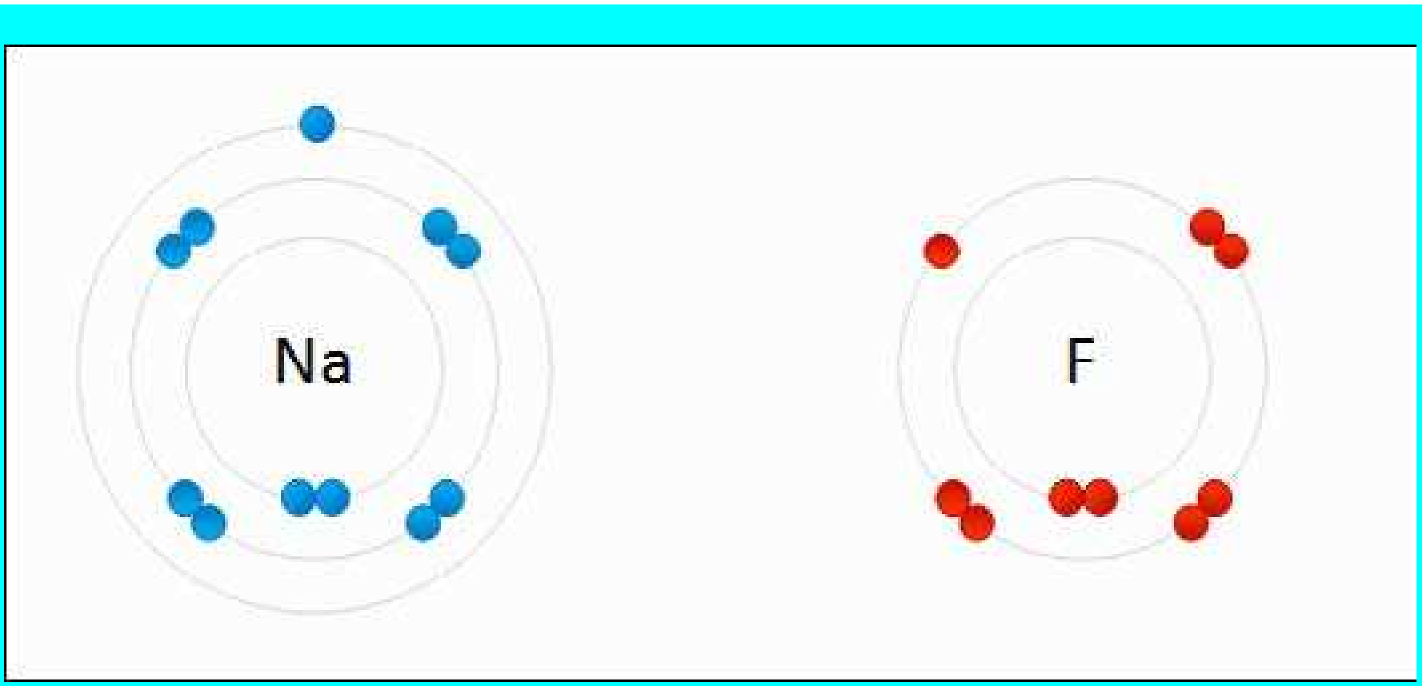
HCl also ionizes in solution

$$HCl \rightleftharpoons H^+(aq) + Cl^-(aq)$$

On passing HCl gas, concentration of Cl^- ions is increased, therefore NaCl crystallizes out of the solution to maintain the constant value of the equilibrium constant.

This type of effect is called the common ion effect. The addition of a common ion to the solution of a less soluble electrolyte suppresses its ionization and the concentration of unionized species increases, which may come out as a precipitate.

$$Na^+(aq) + Cl^-(aq) \rightleftharpoons NaCl(s)$$



Animation 8.12: COMMON ION
Source & Credit : boundless

More Examples of Common Ion Effect

(i) The solubility of a less soluble salts $KClO_3$ in water is suppressed by the addition of a more soluble salt KCl by common ion effect. K^+ is a common ion. The ionization of $KClO_3$ is suppressed and it settles down as precipitate.

$$KClO_3(s) \ \square \ K^+(aq) + ClO^-_3(aq)$$

$$KCl \ \square \ K^+(aq) + Cl^-(aq)$$

(ii) Similarly, the dissociation of a weak acid H_2S in water can be suppressed by the addition of stronger acid HCl. H^+ is a common ion. H_2S becomes less dissociated in acidic solution. In this way low concentration of S^{-2} ion is developed.

$$H_2S \ \square \ 2H^+(aq) + S^{2-}(aq)$$

This low concentration of S^{-2} ions helps to do the precipitation of radicals of second group basic radicals during salt analysis.

$$HCl(aq) \ \square \ H^+(aq) + Cl^-(aq)$$

(iii) An addition of NH_4Cl in NH_4OH solution suppresses the concentration of OH^- (aq) due to the presence of a large excess of NH_4^+ from NH_4Cl. Actually, NH_4Cl is a strong electrolyte. The combination of these two substances is used as a group reagent in third group basic radicals

$$NH_4Cl(aq) \ \square \ NH_4^+(aq) + Cl^-(aq)$$

$$NH_4OH(aq) \ \square \ NH_4^+(aq) + OH^-(aq)$$

(iv) Common ion effect finds extensive applications in the qualitative analysis and the preparation of buffers.

8.8.0 BUFFER SOLUTIONS

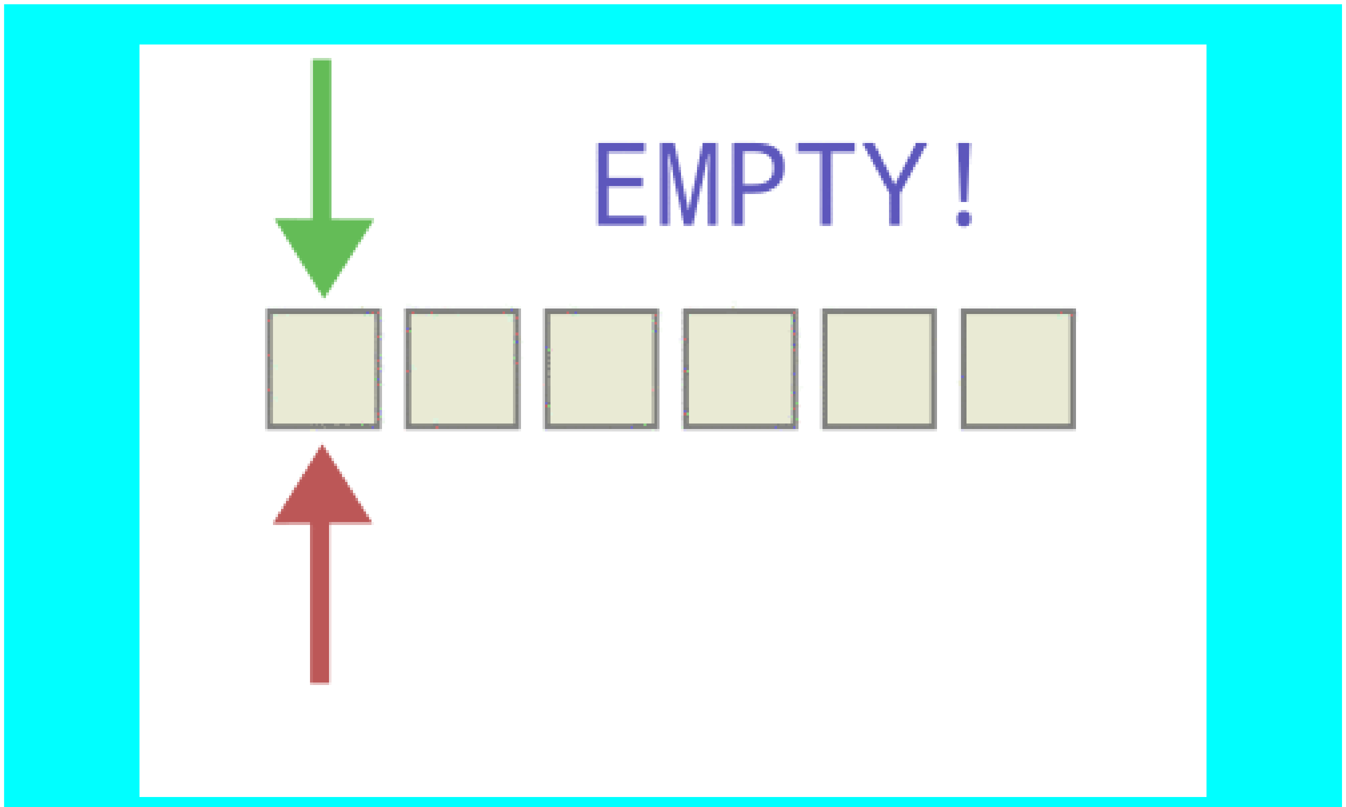
Those solutions, which resist the change in their pH when a small amount of an acid or a base is added to them, are called buffer solutions. They have a specific constant value of pH and their pH values do not change on dilution and on keeping for a long time. Buffer solutions are mostly prepared by mixing two substances.

(i) By mixing a weak acid and a salt of it with a strong base. Such solutions give acidic buffers with pH less than 7. Mixture of acetic acid and sodium acetate is one of the best examples of such a buffer.

(ii) By mixing a weak base and a salt of it with a strong acid. Such solutions will give basic buffers with pH more than 7. Mixture of NH_4OH and NH_4Cl is one of the best examples of such a basic buffer.

(a) Why Do We Need Buffer Solution?

It is a common experience that the pH of the human blood is maintained at pH 7.35, if it goes to 7.00 or 8.00, a person may die.



Animation 8.13: BUFFER
Source & Credit : hackaday

Sometimes one wants to study a reaction under conditions that would suffer any associated change in the pH of the reaction mixture. So, by suitable choice of the solutes, a chemist can ensure that a solution will not experience more than a very small change in pH, even if a small amount of a strong acid or a strong base is added. Buffers are important in many areas of chemistry and allied sciences like molecular biology, microbiology, cell biology, soil sciences, nutrition and the clinical analysis.

Buffer is not a new concept at this stage of our discussion, it is just the application of common ion effect.

(b) How Do the Buffers Act?

Let us take the example of an acidic buffer consisting of CH_3COOH and CH_3COONa. Common ion effect helps us to understand how the buffer will work. CH_3COOH, being a weak electrolyte undergoes very little dissociation. When CH_3COONa, which is a strong electrolyte, is added to CH_3COOH solution, then the dissociation of CH_3COOH is suppressed, due to common ion effect of CH_3COO^- .

$$CH_3COOH(aq)+H_2O(\ell) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

$$CH_3COONa(aq) \rightleftharpoons CH_3COO^-(aq) + Na^+(aq)$$

If one goes on adding CH_3COONa in CH_3COOH solution, then the added concentrations of CH_3COO^- decrease the dissociation of CH_3COOH and the pH of solution increases. The table (8.10) tells us how the pH value of a mixture of two compounds is maintained. Greater the concentration of acetic acid as compared to CH_3COONa, lesser is the pH of solution.

Table (8.10) Effect of addition of acetate ions on the pH of acetic acid solution

$[CH_3COOH]$ (mole dm^{-3})	$[CH_3COO^-]$ (mole dm^{-3})	% Dissociation	pH
0.10	0.00	1.3	2.89
0.10	0.05	0.036	4.44
0.10	0.10	0.018	4.74
0.10	0.15	0.012	4.92

Actually a buffer mentioned above is a large reservoir of CH_3COOH and CH_3COO^- components. When an acid or H_3O^+ ions are added to this buffer, they will react with CH_3COO^- to give back acetic acid and hence the pH of the solution will almost remain unchanged. The reason is that CH_3COOH being a week acid will prefer to remain undissociated. Similarly, the puffer solution consisting of NH_4Cl and NH_4OH, can resist the change of pH and pOH, when acid or base is added from outside. When a base or OH^- ions are added in it, they will react with H_3O^+ to give back H_2O and the pH of the solution again will remain almost unchanged.

Calculating the pH of a Buffer

Let us try to learn, how a buffer of definite pH can be prepared. Consider a weak acid HA and its salt NaA with a strong base say NaOH. The reversible reactions for dissociation of HA are as follows:

$$HA \rightleftharpoons H^+ + A^-$$

$$NaA \rightleftharpoons Na^+ + A^-$$

The dissociation constant of a weak acid HA is given by:

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

Rearranging the equation,

$$[H^+] = \frac{K_a[HA]}{[A^-]}$$

The concentration of A in the reaction mixture is predominantly being supplied by NaA which is a stronger electrolyte than HA, and the ionization of HA is being suppressed by common ion effect (A^- is the common ion in this buffer solution). Taking log of this equation.

$$\log[H^+] = \log\frac{K_a[HA]}{[A^-]}$$

$$\log[H^+] = \log(K_a) + \log\frac{[HA]}{[A^-]}$$

Multiplying with (-1) on both sides

$$-\log[H^+] = -\log(K_a) - \log\frac{[HA]}{[A^-]}$$

Since - $-\log[H^+] = pH$ and $-\log(K_a) = pK_a$

So, $pH = pK_a - \log\frac{[HA]}{[A^-]}$

$[A^-]$ refers to the concentration of the salt. Actually, maximum possible concentrate of A^- is given by NaA, being a strong electrolyte

$$pH = pK_a - \log\frac{[acid]}{[salt]}$$

Interchanging the numerator and denominator the sign of log changes

or
$$pH = pK_a + \log\frac{[salt]}{[acid]}$$

This relationship is called Henderson's equation. This equation shows that two factors evidently govern the pH of a buffer solution. First is the pK_a of the acid used and second is the ratio of the concentrations of the salt and the acid. The best buffer is prepared by taking equal concentration of salt and acid.

So, pH is controlled by pK_a of the acid. For example, for acetic acid sodium acetate buffer, if

$$[CH_3COOH] = [CH_3COONa]$$

then
$$pH = pK_a + \log\frac{[CH_3COONa]}{[CH_3COOH]}$$

$$pH = pK_a + \log(1)$$

so
$$pH = pK_a + 0 = pK_a$$

$$pH = 4.74.$$

It means that the pH of this buffer is just equal to the pK of the acid. Similarly for formic acid sodium formate buffer, if

$$[HCOOH] = [HCOONa]$$

then
$$pH = pK_a + 0 = pK_a$$

so
$$pH = 3.78.$$

To prepare a buffer of definite pH, we need a suitable acid for that purpose. We can also manage the buffer of our own required pH by suitably selecting the concentration ratio of the salt and the acid. If $[CH_3COOH]$ is 0.1 mole dm and that of $[CH_3COONa]$ is 1.0 mole dm^{-3} then

$$pH= 4.74 + \log \frac{[salt]}{[acid]}$$

$$pH= 4.74 + \log \frac{1.0}{0.1} = 4.74 + \log 10$$

Since $\log 10 = 1$

$$pH = 4.74 + 1 = 5.74$$

$$pH = 5.74$$

Similarly, if $[CH_3COOH]$ is 1.0 mole dm^{-3} and $[CH_3COONa]$ is 0.1 moles dm^{-3} , then

$$pH= 4.74 + \log \frac{0.1}{1}$$

$$pH= 4.74 + \log \frac{1}{10} \qquad =4.74+\log 10^{-1}$$

$$pH = 4.74 - 1 = 3.74$$

or $pH = 3.74$

Anyhow, the above mentioned combination can be used to prepare buffers from 3.74 to 5.74. The buffer beyond this range will not be good buffers and will have small buffer capacities.

Just like acidic buffers, the basic buffer have their own Henderson equation. For this purpose, let us use the mixture of NH_4OH and NH_4Cl. NH_4OH is a solution of NH_3 in water and it can be represented as follows:

$$NA_3(aq) + H_2O(\ell) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$K_b = \frac{[NH_4^+][OH^{-1}]}{[NH_3]}$$

Taking the log, multiplying with negative sign and rearranging, we get

$$pOH \quad = pK_b + \log\frac{[salt]}{[base]}$$

Using this relationship, we can prepare a basic buffer of the required pOH or pH by suitably selecting a base and adj usting the ratio of [salt] / [base].

Example :

Calculate the pH of a buffer solution in which 0.11 molar CH_3COONa and 0.09 molar acetic acid solutions are present. K_a for CH_3COOH is 1.85×10^{-5}

Solution:

0.11M CH_3COONa solution means that 0.11 moles are dissolved in 1 dm^3 of solution.

$$[CH_3COONa] \quad = 0.11M$$

$$[CH_3COOH] \quad = 0.09M$$

$$K_a \text{ of } CH_3COOH \quad = 1.85x10^{-5}$$

$$pK \quad = -\log(1.8x10^{-5}) = 4.74$$

$$pH \quad = pK_a + \log\frac{[salt]}{[acid]}$$

$$pH \quad = pK_a + \log\frac{0.11}{0.09}$$

$$pH \quad = 4.74 + 0.087 = \boxed{4.83} \text{ Answer}$$

Since, the concentration of CH_3COONa is more than that of CH_3COOH, so pH of buffer is greater than 4.74. In other words, the solution has developed the properties of a base, because CH_3COONa has Na^+ ion which is from a strong base.

8.8.1 Buffer Capacity

The buffer capacity of a solution is the capability of a buffer to resist the change of pH. It can be measured quantitatively that how much extra acid or base, the solution can absorb before the buffer is essentially destroyed. Buffer capacity of a buffer solution is determined by the sizes of actual molarities of its components. So,a chemist must decide before making the buffer solution, what outer limits of change in its pH can be tolerated.

Let us do some calculations to check the effectiveness of a buffer system. Consider, that we have a buffer having 0.11 molar CH_3COONa and 0.09 molar acetic acid. Its pH will be 4.83. Let us add 0.01 moles of NaOH in one dm^3 of the buffer solution (remember that addition of 0.01 moles NaOH per dm^3 of solution will change the pH from 7.00 to 12.00 in pure water).

Since NaOH is a strong base and it is 100% dissociated, it generates 0.01 moles OH^-. Out of 0.09 mole of CH_3COOH, 0.01 mole will react with OH^- and 0.08 moles of CH_3COOH is left behind in one dm^3 of solution. This neutralization of course makes the identical change in the amount of CH_3COONa and its concentration will increase from 0.11 mole to 0.12 mole.

Henderson equation is, $\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\text{salt}]}{[\text{acid}]}$

Putting the new concentrations of salt and acid after addition of NaOH.

$$\mathrm{pH} = 4.74 + \log\frac{0.12}{0.08}$$

$$\mathrm{pH} = 4.74 + \log(1.5)$$

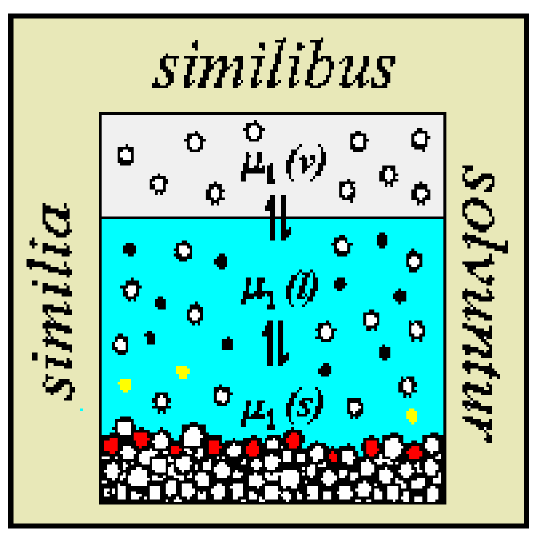
$$\mathrm{pH} = 4.74 + 0.176$$

$$\mathrm{pH} = \boxed{4.92}\ \text{Answer}$$

It means that there is a very small change in pH from 4.83 to 4.92, that is only a difference of 0.1. So we reach the conclusion that a buffer does not hold the pH exactly constant. But it does a very good job in limiting the change in pH to a very small amount.

8.9.0 EQUILIBRIA OF SLIGHTLY SOLUBLE IONIC COMPOUNDS (SOLUBILITY PRODUCT)

When a soluble ionic compound is dissolved in water, like NaCl, it dissociates completely into ions. But for slightly soluble salts the dissociation is not complete at equilibrium stage. For example, when $PbCl_2$ is shaken with water the solution contains Pb^{2+}, Cl^- and undissociated $PbCl_2$. It means that equilibrium exists between solid solute, $PbCl_2$ and the dissolved ions, Pb^{2+} and Cl^-.



Animation 8.14: SOLUBILITY
Source & Credit : iupac

$$PbCl_2(s) \rightleftharpoons PbCl_2(aq) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$

According to law of mass action $K_c = \dfrac{[Pb^{2+}_{(aq)}][Cl^-_{(aq)}]^2}{[PbCl_2]}$

Lead sulphate is a well known sparingly soluble compound and it dissociates to a very small extent like $PbCl_2$.

$$PbSO_4(s) \rightleftharpoons PbSO_4(aq) \rightleftharpoons Pb^{2+}(aq) + SO_4^{2-}(aq)$$

Law of mass action applied to the dissociation of $PbSO_4$ gives equilibrium constant K_c

$$K_c = \frac{[Pb^{2+}][SO_4^{\ 2-}]}{[PbSO_4]}$$

Being a sparingly soluble salt the concentration of lead sulphate ($PbSO_4$) almost remains constant. Bring $[PbSO_4]$ on L.H.S. with K_c

$$K_c[PbSO_4] = [Pb^{2+}][SO_4^{\ 2-}]$$

if $\quad K_c[PbSO_4] = K_{sp}$

then $\quad K_{sp} = [Pb^{2+}(aq)][SO_4^{\ 2-}(aq)] = 1.6\text{x}10^{-8}$ at 25°C

K_{sp} is called the solubility product of $PbSO_4$. It is the product of molar solubilities of two ions at equilibrium stage.

Similarly,for $\quad PbCl_2 \qquad K_{sp} = [Pb^{2+}(aq)][Cl^{-}(aq)]^2$

K_{sp} is usually a very small quantity at room temperature. The value of K_{sp} is temperature dependent. For a general, sparingly soluble substance, A_xB_y.

$$A_xB_y \rightleftharpoons xA^{+y} + yB^{-x}$$

$$K_{sp} = [A^{+y}]^x + [B^{-x}]^y$$

So, the solubility product is the product of the concentrations of ions raised to an exponent equal to the co-efficient of the balanced equation. The value of K_{sp} is a measure of how far to the right dissolution proceeds at equilibrium i.e. saturation. The following Table (8.10) shows us the K_{sp} values of slightly soluble ionic compounds.

Smaller the value of K_{sp}, lesser the capability to be dissociated.

Table (8.10) K_{sp} values for some ionic compounds (compounds are arranged alphabetically).

Salt	Ion Product	K_{sp}	Salt	Ion Product	K_{sp}
AgBr	$[Ag^+][Br^-]$	$5.0x10^{-13}$	CuS	$[Cu^{2+}][S^{2-}]$	$8x10^{-34}$
Ag_2CO_3	$[Ag^+]^2[CO_3^{\ 2-}]$	$8.1x10^{-12}$	FeS	$[Fe^{2+}][S^{2-}]$	$6.3x10^{-18}$
AgCl	$[Ag^+][Cl^-]$	$1.8x10^{-10}$	Fe_2S_3	$[Fe^{3+}][S^{2-}]^3$	$1.4x10^{-85}$
Agl	$[Ag^+][I^-]$	$8.3x10^{-17}$	$Fe(OH)_3$	$[Fe^{3+}][OH^-]^3$	$1.6x10^{-39}$
Ag_2S	$[Ag^+]^2[S^{2-}]$	$8x10^{-48}$	HgS	$[Hg^{2+}][S^{2-}]$	$2x10^{-50}$
$Al(OH)_3$	$[Al^{3+}][OH^-]^3$	$3x10^{-34}$	$MgCO_3$	$[Mg^{2+}][CO_3^{\ 2-}]$	$3.5x10^{-8}$
$BaCO_3$	$[Ba^{2+}][CO_3^{\ 2-}]$	$2x10^{-9}$	$Mg(OH)_2$	$[Mg^{2+}][OH^-]^2$	$6.3x10^{-10}$
$BaSO_4$	$[Ba^{2+}][SO_4^{\ 2-}]$	$1.1x10^{-10}$	MnS	$[Mn^{2+}][S^{2-}]$	$3x10^{-11}$
CdS	$[Cd^{2+}][S^{2-}]$	$8.0x10^{-27}$	$PbCl_2$	$[Pb^{2+}][Cl^-]^2$	$1.6x10^{-5}$
$CaCO_3$	$[Ca^{2+}][CO_3^{\ 2-}]$	$3.3x10^{-9}$	$PbCrO_4$	$[Pb^{2+}][CrO_4^{\ 2-}]$	$2.3x10^{-13}$
CaF_2	$[Ca^{2+}][F^-]^2$	$3.2x10^{-11}$	$PbSO_4$	$[Pb^{2+}][SO_4^{\ 2-}]$	$1.6x10^{-8}$
$Ca(OH)_2$	$[Ca^{2+}][OH^-]^2$	$6.5x10^{-6}$	PbS	$[Pb^{2+}][S^{2-}]$	$8.0x10^{-28}$

8.9.1 Applications of solubility product

(a) Determination of K_{sp}, from solubility

From the solubility of the compounds, we can calculate K_{sp} of the salt. The solubility for most of the compounds are given in terms of the grams of the solute per 100 g of water. Since the quantity of solute is very very small, so 100 g of water solution is considered to be 100 ml of solution. The reason is that the density of water is very close to unity. Hence, we get the concentration in moles dm^{-3}. The number of moles of solute dm^{-3} of the solution is calculated by dividing the mass of solute by its molar mass. Then by using the balanced equation, we find the molarity of each ion and then find K_{sp}.

Example 6 :

The solubility of PbF_2 at 25^{0}C is 0.64 gdm^{-3}. Calculate K_{sp} of PbF_2.

Solution:

First of all convert the concentration from g dm 1 to moles dm 3;

Mass of PbF_2 dessolved dm^{-3} = 0.64g

Molecular mass of PbF_2 = 245.2g mol^{-1}

Number of moles of $PbF_2 = \dfrac{0.64\text{gdm}^{-3}}{245.2\text{gmol}^{-1}} = 2.6\text{x}10^{-3}$

The balanced equation for dissociation of PbF_2 is,

$PbF_2(s) \rightleftharpoons Pb^{2+}(aq) + 2F^{1-}(aq)$

$2.6\text{x}10^{-3}$M 0 + 0 t = 0 sec

"zero" moles $2.6\text{x}10^{-3}$moles + $2\text{x}2.6\text{x}10^{-3}$moles t=equilibrium

The expression of K_{sp} is

$$K_{sp} = [Pb^{2+}][F^-]^2$$

Putting values of concentration

$$K_{sp} = 2.6\text{x}10^{-3}\text{x}(2\text{x}2.6\text{x}10^{-3})^2 = \boxed{7.0\text{x}10^{-8}}\text{Answer}$$

(b) Determination of Solubility from K_{sp}

For this purpose we need the formula of the compound and K_{sp} value. Then the unknown molar solubility S is calculated and the concentration of the ions are determined. Table (8 .11) shows the relationship between the K_{sp} values and the solubility of some sparingly soluble compounds.

Table (8.11) Relationship between K_{sp} and the solubility of some compounds.

Formula	No. of ions	Cation / Anion	K_{sp}	Solubility gdm^{-3}
$MgCO_3$	2	1 / 1	3.61×10^{-8}	1.9×10^{-4}
$PbSO_4$	2	1 / 1	1.69×10^{-8}	1.3×10^{-4}
$BaCrO_4$	2	1 / 1	1.96×10^{-10}	1.4×10^{-5}
$Ca(OH)_2$	3	1 / 2	6.5×10^{-6}	1.175×10^{-2}
BaF_2	3	1 / 2	1.35×10^{-5}	7.2×10^{-3}
CaF_2	3	1 / 2	3.2×10^{-11}	2.0×10^{-4}
Ag_2CrO_4	3	2 / 1	2.6×10^{-12}	8.7×10^{-5}

Example 7 :

$Ca(OH)_2$ is a sparingly soluble compound. Its solubility product is 6.5×10^{-6} Calculate the solubility of $Ca(OH)_2$.

Solution:

Let the solubility is represented by S in terms of moles dm^{-3}.
The balanced equation is

$$Ca(OH)_2 \rightleftharpoons Ca^{2+}(aq) + 2OH^{-}(aq)$$

$Ca(OH)_2 \rightleftharpoons \quad 0 \quad + \quad 0$ Initial stage

$Ca(OH)_2 \rightleftharpoons \quad S \quad + \quad 2S$ Equilibrium stage

The K_{sp}=6.5x10^{-6}

The concentration of OH^- is double than the concentration of Ca^{2+}, so

$$K_{sp} = [Ca^{2+}][OH^-]^2 = S \times (2S)^2$$

$$4S^3 = 6.5 \times 10^{-6}$$

So, $$S = \left(\frac{6.5x10^{-6}}{4}\right)^{1/3} = (1.625x10^{-6})^{1/3}$$

$$S = (1.625)^{1/3} x10^{-2}$$

$$S = 1.175 x10^{-2}$$

Hence, at equilibrium stage 1.175 x 10^{-2} moles dm^{-3} of Ca^{2+} and 2x1.175 x 10^{-2} = 2.75 x 10^{-2} moles dm^{-3} OH^- are present in the solution. In this way, we have calculated the individual concentrations of Ca^{2+} and OH^- ion from the solubility product of $Ca(OH)_2$.

Effect of Common Ion on Solubility

The presence of a common ion decreases the solubility of a slightly soluble ionic compound. In order to explain it, consider a saturated solution of $PbCrO_4$, which is a sparingly soluble ionic salt.

$$PbCrO_4(aq) \rightleftharpoons Pb^{2+}(aq) + CrO_4^{2-}(aq)$$

Now add Na_2CrO_4 which is a soluble salt. CrO_4^{2-} is the common ion. It combines with Pb^{2+} to form more insoluble $PbCrO_4$. So equilibrium is shifted to the left to keep K_{sp} constant.

KEY POINTS

1. There versible chemical reactions can achieve a state in which the forward and the reverse processes are occurring at the same rate. This state is called state of chemical equilibrium. The concentrations of reactants and products are called equilibrium concentrations and the mixture is called equilibrium mixture.
2. Law of mass action provides the relationship among the concentrations of reactants and products of a system at equilibrium stage.The ratio of concentrations of the products to the concentrations of reactants is called equilibrium constant. The equilibrium constants are expressed as K_c, K_p, K_n and K_x.
3. The value of equilibrium constant can predict the direction and extent of a chemical reaction.
4. The effect of change of concentration, temperature, pressure or catalyst in a reaction can be s adied witii the help of Le-Chatelier's principle. Increasing concentrations of reactants or decreasing concentrations of products or heating of the endothermic reactions shifts the reaction to the forward direction. The change of temperature disturbs the equilibrium position and the equilibrium constant of reaction. A catalyst decreases the time to reach the equilibrium and does not alter the equilibrium position and equilibrium constant under the given conditions.
5. Water is a very weak electrolyte and ionizes to a slight degree. The extent of this a autoionization is expressed by ionic product of water called K_w, having a value 10^{-14} at 25^0C. The addition of an acid or a base changes the $[H^+]$ and $[OH^-]$, but the ionic product remains the same at 25^0C.
6. The concentration of H^+ is expressed in terms of pH and that of $[OH^-]$ in terms of pOH. Neutral water has a pH = 7 and pOH= 7.The value of pK_w is 14 at 25^0C.
7. According to Lowry-Bronsted concept of an acid and a base the conjugate base of a strong acid is always weak. So $pK_a + pK_b = pK_w$ Where pK_a and pK_b are the parameters to measure the strengths of acids and bases.
8. Those solutions which resist the change of pH are called buffer solutions. Buffer solutions of pH below 7 are prepared by mixing a weak acid and salt of it with a strong base while basic buffers can be prepared by combining a weak base and salt of it with a strong acid. Hendersen's equation guides us quantitatively to have the buffer solutions of good buffer capacity and to select the pair of compounds for this purpose.
9. The solubility of sparingly soluble substances are calculated from the solubility product data. This data provides us the information about the selective precipitation and fractional precipitation.
10. Common ion effect operates best in buffer solutions, and purification of certain substances. It is one of the best applications of Le-Chatelier's principle.

EXERCISE

Q1. Multiple choice questions

i) For which system does the equilibrium constant, K_c has units of (concentration)’?

(a) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

(b) $H_2 + I_2 \rightleftharpoons 2HI$

(c) $2NO_2 \rightleftharpoons N_2O_4$

(d) $2HF \rightleftharpoons H_2 + F_2$

ii) Which statement about the following equilibrium is correct

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ ÄH= -188.3kJ mol $^{-1}$

(a) The value of K_p falls with a rise in temperature

(b) The value of K_p falls with increasing pressure

(c) Adding V_2O_5 catalyst increase the equilibrium yield of sulphur trioxide

(d) The value of K_p is equal to K_c.

iii) The pH of 10^{-3} mol dm^{-3} of an aqueous solution of H_2SO_4 is

(a) 3.0 (b) 2.7 (c) 2.0 (d) 1.5

iv) The solubility product of AgCl is 2.0×10^{-10} mol^2 dm^{-6}. The maximum concentration of Ag^+ ions in the solution is

(a) 2.0×10^{-10} mol dm^{-3} (b) 1.41×10^{-5} mol dm^{-3}

(c) 1.0×10^{-10} mol dm^{-3} (d) 4.0×10^{-20} mol dm^{-3}

v) An excess of aqueous silver nitrate is added to aqueous barium chloride and precipitate is removed by filtration. What are the main ions in the filtrate?

(a) Ag^+ and NO_3^- only (b) Ag^+ and Ba^{2+} and NO_3^-

(c) Ba^{2+} and NO_3^- only (d) Ba^{2+} and NO_3^- and Cl^-

Q2. Fill in the blanks

i) Law of mass action states that the__________ at which a reaction proceeds, is directly proportional to the product of the active masses of the __________.

ii) In an exothermic reversible reaction,_______ temperature will shift the equilibrium towards the forward direction.

iii) The equilibrium constant for the reaction $2O_3 \rightleftharpoons 3O_2$ is 10^{55} at 25^{0}C, it tells that ozone is_________ at room temperature.

iv) In a gas phase reaction, if the number of moles of reactants are equal to the number of moles of the products, K_c of the reaction is__________ to the K_p.

v) Buffer solution is prepared by mixing together a weak base and its salt with or a weak acid and its salt with__________.

Q3. Label the sentences as True or False.

i) When a reversible reaction attains equilibrium both reactants and products are present in a reaction mixture.

ii) The K_c of the reaction

$$A + B \rightleftharpoons C + D$$

is given by

$$K_c = \frac{[C][D]}{[A][B]}$$

therefore it is assumed that

$$[A] = [B] = [C] = [D]$$

iii) A catalyst is a substance which increases the speed of the reaction and consequently increases the yield of the product.

iv) Ionic product K_w of pure water at 25^0C is 10^{-14} $mol^2\ dm^{-6}$ and is represented by an expression $K_w = [H^+][OH^-] = 10^{-14}$ $mol^2\ dm^{-6}$

v) AgCl is a sparingly soluble ionic solid in water. Its solution produces excess of Ag^+ and Cl^- ions.

Q4 (a) Explain the term s" reversible reaction" and "state of equilibrium".

(b) Define and explain the Law of mass action and derive the expression for the equilibrium constant(K_c).

(c) Write equilibrium constant expression for the following reactions

(i) $Sn^{+2}(aq)+2Fe^{3+}(aq) \rightleftharpoons Sn^{4+}(aq)+2Fe^{2+}(aq)$

(ii) $Ag^+(aq)+Fe^{2+}(aq) \rightleftharpoons Fe^{3+}(aq)+Ag(s)$

(iii) $N_2(g)+O_2(g) \rightleftharpoons 2NO(g)$

(iv) $4NH_3(g)+5O_2(g) \rightleftharpoons 4NO(g)+6H_2O(g)$

(v) $PCl_5(g) \rightleftharpoons PCl_3(g)+Cl_2(g)$

Q5 (a) Reversible reactions attain the position of equilibrium which is dynamic in nature and not static. Explain it.

(b) Why do the rates of forward reactions slow down when a reversible reaction approaches the equilibrium stage?

Q6 When a graph is plotted between time on x-axis and the concentrations of reactants and products on y-axis for a reversible reaction, the curves become parallel to time axis at a certain stage.

(a) At what stage the curves become parallel ?

(b) Before the curves become parallel, the steepness of curves falls! Give reasons.

(c) The rate of decrease of concentrations of any of the reactants and rate of increase of concentrations of any of the products may or may not be equal, for various types of reactions, before the equilibrium time. Explain it.

Q7 (a) Write down the relationship of different types of equilibrium constants i.e. K_c and K_p for the following general reaction.

$$aA + bB \rightleftharpoons cC + dD$$

(b) Decide the comparative magnitudes of K_c and K_p for the following reversible reactions.

i) Ammonia synthesis ii) Dissociation of PCl_5

Q8 (a) Write down K_c for the following reversible reactions. Suppose that the volume of reaction mixture in all the cases is 'V' dm^3 at equilibrium stage.

i) $CH_3COOH + CH_3CH_2OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

ii) $H_2 + I_2 \rightleftharpoons 2HI$

iii) $2HI \rightleftharpoons H_2 + I_2$

iv) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

v) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

(b) How do you explain that some of the reactions mentioned above are affected by change of volume at equilibrium stage.

Q9 Explain the following two applications of equilibrium constant. Give examples

i) Direction of reaction ii) Extent of reaction

Q10 Explain the following with reasons.

(a) The change of volume disturbs the equilibrium position for some of the gaseous phase reactions but not the equilibrium constant.

(b) The change of temperature disturbs both the equilibrium position and the equilibrium constant of a reaction.

(c) The solubility of glucose in water is increased by increasing the temperature.

Q11 (a) What is an ionic product of water? How does this value vary with the change in temperature? Is it true that its value increase 75 times when the temperature of water is increased form 0^0C to $100\ ^0C$.

(b) What is the justification for the increase of ionic product with temperature?

(c) How would you prove that at 25^0C, $1dm^3$ of water contains 10^{-7} moles of H_3O^+ and10^{-7} moles of OH

Q12 (a)Define pH and pOH. How are they related with pK_w.

(b) What happens to the acidic and basic properties of aqueous solutions when pH varies from zero to 14?

(c) Is it true that the sum of pK_a and pK_b is always equal to 14 at all temperatures for any acid? If not why?

Q13 (a) What is Lowry Bronsted idea of acids and bases? Explain conjugate acid and bases.

(b) Acetic acid dissolves in water and gives proton to water, but when dissolved in H_2SO_4, it accepts protons. Discuss the role of acetic acid in both cases.

Q14 In the equilibrium

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \qquad \Delta H=+90kJ\ mol^{-1}$$

What is the effect on

(a) the position of equilibrium (b) equilibrium constant? if

i) temperature is increased ii) volume of the container is decreased

iii) catalyst is added iv) chlorine is added

Explain your answer.

Q15. Synthesis of ammonia by Haber's process is an exothermic reaction.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92.46\ kJ$$

(a) What should be the possible effect of change of temperature at equilibrium stage?
(b) How does the change of pressure or volume shifts the equilibrium position of this reaction?
(c) What is the role of the catalyst in this reaction?
(d) What happens to equilibrium position of this reaction if NH_3 is removed from the reaction vessel from time to time?

Q16 Sulphuric acid is the king of chemicals. It is produced by the burning of SO_2 to SO_3 through an exothermic reversible process.
(a) Write the balanced reversible reaction.
(b) What is the effect of pressure change on this reaction?
(c) Reaction is exothermic but still the temperature of 400-500^{0}C is required to increase the yield of SO_3. Give reasons.

Q17 (a) What are buffer solutions? Why do we need them in daily life?
(b) How does the mixture of sodium acetate and acetic acid give us the acidic buffer?
(c) Explain that a mixture of NH_4OH and NH_4Cl gives us the basic buffer.
(d) How do you justify that the greater quantity of CH_3COONa in acetic acid decreases the dissociating power of acetic acid and so the pH increases.
(e) Explain the term buffer capacity.

Q18 (a) What is the solubility product? Derive the solubility product expression for sparingly soluble compounds, AgCl, Ag_2CrO_4 and $PbCl_2$.
(b) How do you determine the solubility product of a substance when its solubility is provided in grams/100 g of water?
(c) How do you calculate the solubility of a substance from the value of solubility product?

Q19 K_c value for the following reaction is 0.016 at 520^{0}C

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

Equilibrium mixture contains [HI] = 0.08 M, [H_2] = 0.01M, [I_2] = 0.01M. To this mixture more HI is added so that its new concentration is 0.096M. What will be the concentration of [HI], [H_2] and [I_2] when equilibrium is re-established.

(Ans: 0.0926 mole, 0.01168 mole, 0.01168 mole)

Q20 The equilibrium constant for the reaction between acetic acid and ethyl alcohol is 4.0. A mixture of 3moles of acetic acid and one mole of C_2H_5OH is allowed to come to equilibrium. Calculate the amount of ethyl acetate at equilibrium stage in number of moles and grams. Also calculate the masses of reactants left behind.

(Ans: 79.5g,126g,4.6g)

Q21 Study the equilibrium

$$H_2O(g)+CO(g) \rightleftharpoons H_2(g)+CO_2(g)$$

(a) Write an expression of K_p

(b) When 1.00 mole of steam and 1.00 mole of carbon monoxide are allowed to reach equilibrium, 33.3 % of the equilibrium mixture is hydrogen. Calculate the value of K_p. State the units of K_p.

(Ans: 4, K, has no unit)

Q22 Calculate the pH of

(a) 10^{-4} mole dm^{-3} of HCl (Ans: 4)

(b) 10^{-4} mole dm^{-3} of $Ba(OH)_2$ (Ans: 10.3)

(c) 1.0 mole dm^{-3} of H_2X, which is only 50% dissociated. (Ans: zero)

(d) 1.0 mole dm^{-3} of NH_4OH which is 1% dissociated. (Ans: 12)

Q23

(a) Benzoic acid, C_6H_5COOH, is a weak mono-basic acid (K_a= 6.4 x 10^{-5} mol dm^{-3}). What is the pH of a solution containing 7.2 g of sodium benzoate in one dm^3 of 0.02 mole dm^{-3} benzoic acid.

(Ans: 4.59)

(b) A buffer solution has been prepared by mixing 0.2 M CH_3COONa and 0.5 M CH_3COOH in 1 dm^3 of solution. Calculate the pH of solution. pK_a of acid = 4.74 at 25^{0}C. How the values of pH will change by adding 0.1 mole of NaOH and 0.1 mole of HCl separately.

(Ans: 4.34, 4.62, 3.96)

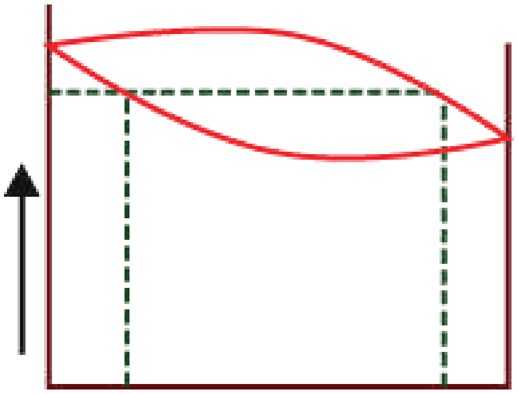
Q24 The solubility of CaF, in water at 25°C is found to be 2.05 x 10 1 mol dm f. What is the value of K_{sp} at this temperature.

(Ans: 3.446 x 10^{-11})

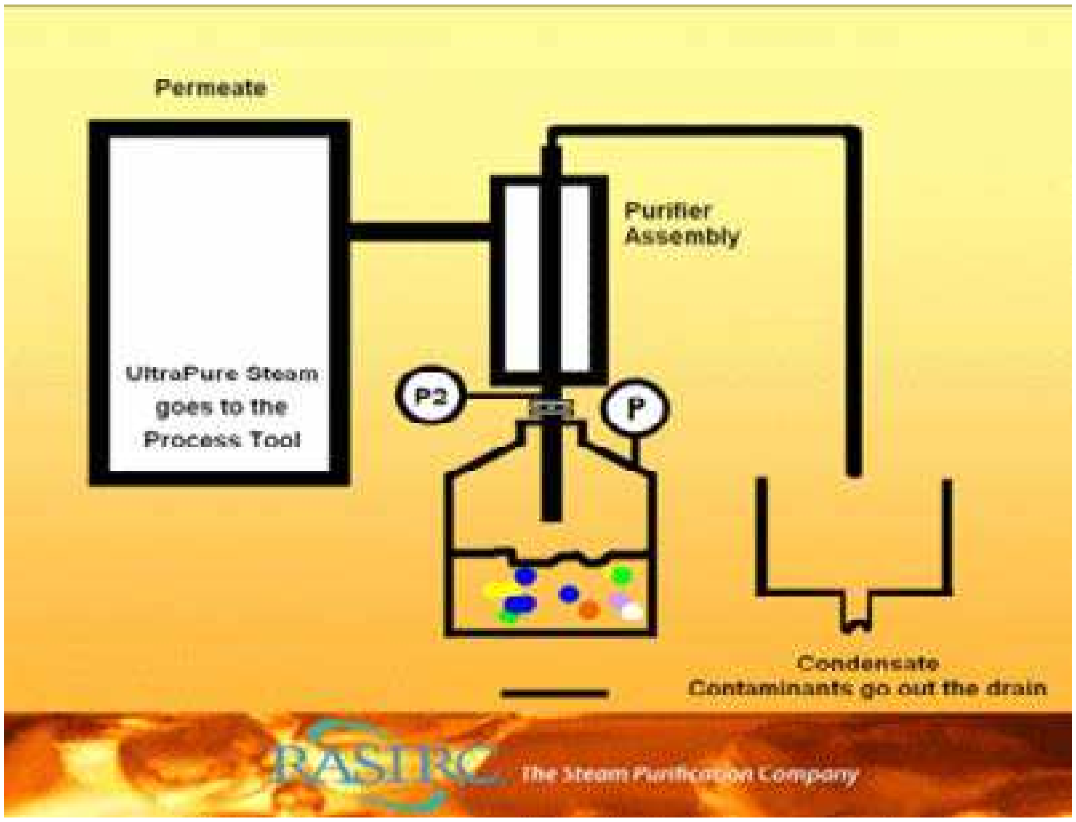
Q25 The solubility product of Ag_2CrO_4 is 2.6 x 10^{-2} at 25^{0}C. Calculate the solubility of the compound.

(Ans: 0.1866 mol dm^{-3})

CHAPTER
9



SOLUTIONS

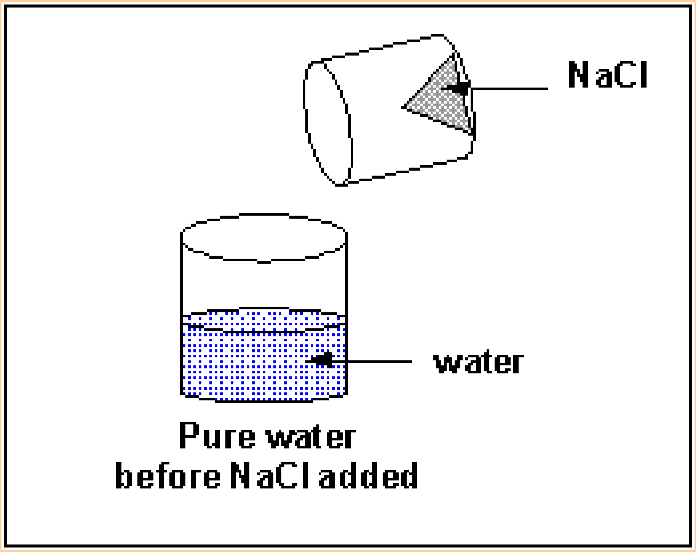


Animation 9.1: RAOULT'S LAW
Source & Credit: rasirc

9.0.0 CONCEPT OF A SOLUTION

Every sample of matter with uniform properties and a fixed composition is called a phase. For example, water at room temperature and normal pressure exists as a single liquid phase, that is, all the properties of water are uniform throughout this liquid phase. If a small amount of sugar is added to this sample of water, the sugar dissolves but the sample remains as a single liquid pha. se. However, the properties and composition of this new liquid phase, now the sugar solution, are different from those of pure water. As this solution of sugar in water is containing two substances (binary solution), so it is a mixture and since its properties are uniform, therefore, it is homogeneous in character.

A solution, on average, is a homogeneous mixture of two or more kinds of different molecular or ionic substances. The substance which is present in large quantity is called a solvent and the other component in small quantity is called a solute.



Animation 9.2: CONCEPT OF A SOLUTION
Source & Credit: employees.csbsju

For a given solution, the amount of solute dissolved in a unit volume of solution (or a unit amount of solvent) is termed as the concentrat ion of the solution. Solutions containing relatively lower concentrations of solute are called dilute solutions, whereas those containing relatively higher concentrations of solutes are called concentrated solutions.

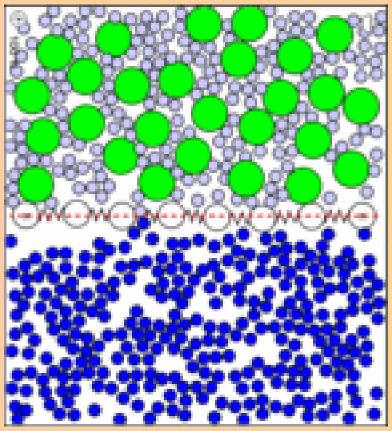
9.1.0 CONCENTRATION UNITS OF SOLUTIONS

There are various types of concentration units of solutions. They are discussed as follows.

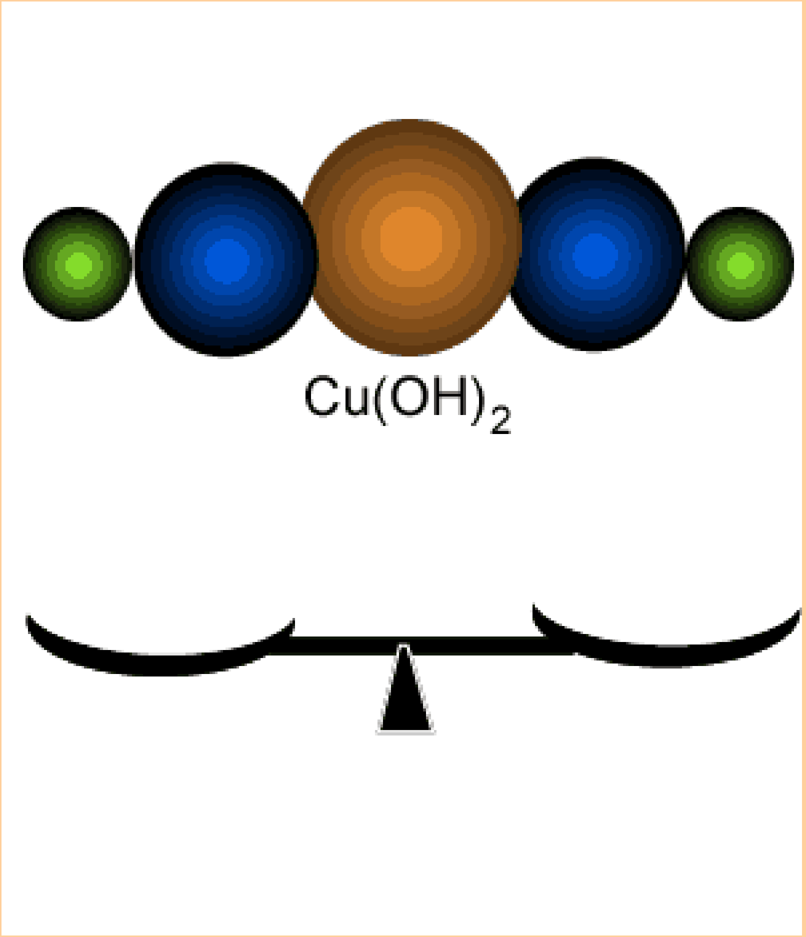
9.1.1 Percentage composition

The amounts of solute and solvent can be expressed in percentage composition by four different ways.

a. Percentage weight/weight
b. Percentage weight/volume
c. Percentage volume/weight
d. Percentage volume/volume



Animation 9.3: CONCENTRATION UNITS OF SOLUTIONS
Source & Credit: chempaths.chemeddl



Animation 9.4: Percentage composition
Source & Credit: dynamicscience

(a) Percentage weight / weight

It is the weight of a solute dissolved per 100 parts by weight of solution. 5% w/w sugar solution will contain 5 g of sugar dissolved in 100 g of solution in water. This solution contains 95 g of water.

$$\%\text{ by weight} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \text{x}100$$

Example (1):

Calculate the percentage by weight of NaCl, if 2.0g of NaCl is dissolved in 20 g of water.

Solution:

Weight of NaCl = 2.0g

Weight of sovent = 20.0g

Weight of solution = 20+2 = 22g

$$\% \text{ of NaCl by weight} = \frac{2.0g}{22.0g} \times 100 = \boxed{9.09\%} \text{ Answer}$$

(b) Percentage Weight/Volume

It is the weight of a solute dissolved per 100 parts by volume of solution. 10 g of glucose dissolved in 100 cm^3 of solution is 10% w/v solution of glucose. The quantity of the solvent is not exactly known. In such solutions, the total volume of the solution is under consideration.

(c) Percentage Volume /Weight

It is the number of cm^3 of a solute dissolved per 100 g of the solution. If we dissolve 10 cm^3 of alcohol in water and the total weight of the solution is 100 g, then it is 10% v/w solution of alcohol in water. In such type of solutions, we don’t know the total volume of the solution.

(d) Percentage Volume / Volume

It is the volume of a solute dissolved per 100 cm^3 of the solution. This unit of concentration is best applicable to the solutions of liquids in liquids. A 12 % alcohol beverage is 12 cm^3 of alcohol per 100 cm^3 of solution. In such solutions, the total volume of the solution may not be necessarily equal to the sum of volumes of solute and the solvent.

9.1.2 Molarity (M)

Molarity is the number of moles of solute dissolved per dm^3 of the solution. To prepare one molar solution of glucose in water, we take 180 g of glucose and add sufficient water to make the total volume 1 dm^3 (llitre) in a measuring flask.

M 0 mol/L
% 0 w/w
m 0 mol/kg
% 0 w/v
x 0
d 0.9991 g/mL

Animation 9.5: Molarity (symbol, M)
Source & Credit: chembuddy

In case of one molar solution of sucrose, 342 g of sucrose are dissolved in water to make it 1 dm³. Since the volume of 342 g of sucrose is greater than 180 g of glucose so the volume of water in 1 molar sucrose solution is less than that of 1 molar glucose solution. Anyhow, to calculate the volume of the solvent, we need to know the density of the solute. Following formula is used to prepare the solution of any molarity.

$$\text{Molarity(M)} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \text{x} \frac{1}{\text{Volume of soultion (dm}^3\text{)}}$$

or $$\text{Molarity(M)} = \frac{\text{Number of moles of solute}}{\text{Volume of soultion (dm}^3\text{)}}$$

Examples (2):

Calculate the molarity of a solution containing 20.7 g of K_2CO_3 dissolved in 500 cm³ of the given solution.

Solution:

$$\text{Mass of } K_2CO_3 = 20.7\text{g}$$

$$\text{Molar mass of } K_2CO_3 = 138\text{gmol}^{-1}$$

$$\text{volume of solution} = 500\text{cm}^3 = 0.5\text{dm}^3$$

Formula: $$\text{Molarity} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \text{x} \frac{1}{\text{Volume of soultion in dm}^3}$$

$$\text{Molarity} = \frac{20.7\text{g}}{138\text{gmol}^{-1}} \text{x} \frac{1}{0.5\text{dm}^3} = 0.3\text{mol dm}^{-3} = \boxed{0.3\text{mol dm}^{-3}} \text{ Answer}$$

9.1.3 Molality (m)

Molality is the number of moles of solute in 1000 g (1 kg) of the solvent. In order to prepare molal solutions, we don't have to take any flask. 180 g of glucose when dissolved in 1000 g of water gives one molal solution of glucose. The total mass of the solution is 1180 g. We don't know the volume of the solution. In order to know the volume we need the density of the solution. For one molal sucrose solution, 342 g of sucrose are dissolved in 1000 g of H_2O.

So,one molal solution of different solutes in water have their own masses and volumes. In order to get the molality of any solution, we use the following equation.

$$\text{Molality(m)} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \text{x} \frac{1}{\text{Mass of solvent in kg}}$$

or

$$\text{Molality(m)} = \frac{\text{Number of moles of solute}}{\text{Mass of solvent in kg}}$$

Example (3):

What is the molality of a solution prepared by dissolving 5g of toluene (C_7H_8) in 250g of benzene.

Solution:

Mass of toluene = 5g

Mass of benzene = 250g = 0.25kg

Molar mass of toluene = 12x7+1x8=92

Formula used

$$\text{Molality(m)} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \text{x} \frac{1}{\text{Mass of solvent in kg}}$$

$$\text{Molality(m)} = \frac{5\text{g}}{92\text{g mol}^{-1}} \text{x} \frac{1}{0.250\text{ kg}}$$

$$= \frac{5}{92\text{x}0.25} \text{mol kg}^{-1} = \boxed{0.217\text{mol kg}^{-1}} \text{ Answer}$$

$$=0.217\text{m}$$

The molality of a solution is indirect expression of the ratio of the moles of the solute to the moles of the solvent. The molal aqueous solution of a solute say glucose or NaOH is dilute in comparison to its molar solution. The reason is that in molal solution the quantity of the solvent is comparatively greater.

The value of concentration given in the units of molality does not change with temperature but that of molarity does. The reason is that the volume of liquids are affected by the variation in temperature.

9.1.4. Mole Fraction (x)

This unit of concentration may be for any type, of solution i.e. gas in gas, liquid in liquid or solid in liquid, etc. This unit is also applicable to a solution having more than two components.

The mole fraction of any component in a mixture is the ratio of the number of moles of it to the total number of moles of all the components present.

Let there be three components A, B, C making a solution. The number of moles are n_a, n_b, n_c respectively. If the mole fraction of A, B and C are denoted by x_a, x_b, x_c respectively, Then,

$$X_A = \frac{n_A}{n_A + n_B + n_C}$$

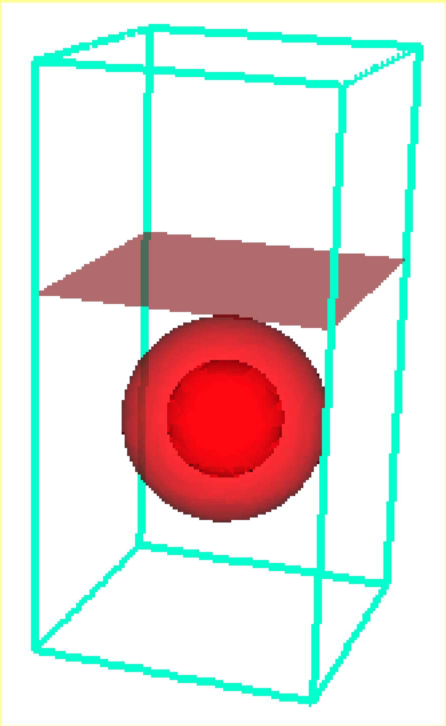
$$X_B = \frac{n_B}{n_A + n_B + n_C}$$

$$X_C = \frac{n_C}{n_A + n_B + n_C}$$

The sum of the mole fractions of all the components of a solution must be equal to one. There are no formal units of mole fraction. Anyhow, we sometimes multiply mole fraction by 100 to get mole percent.

Example (4):

Calculate the mole fraction and mole percent of each component in a solution having 92 g of ethyl alcohol, 96 g of methyl alcohol and 90 g of water.



Animation 9.6: Mole Fraction (symbol, x)
Source & Credit: ima.umn

Solution:

First of all get the number of moles of each component.

$$\text{Number of moles of the substance} = \frac{\text{Mass in grams of the substance}}{\text{Molecular mass in grams}}$$

$$\text{Molar mass of ethyl alchohol } (C_2H_5OH) = 46\ \text{gmol}^{-1}$$

$$\text{Number of moles of ethyl alchohol} = \frac{92\text{g}}{46\ \text{gmol}^{-1}} = 2\ \text{mol}$$

$$\text{Molar mass of methyl alchohol } (CH_3OH) = 32\ \text{gmol}^{-1}$$

$$\text{Number of moles of methyl alchohol} = \frac{96\text{g}}{32\ \text{gmol}^{-1}} = 3\ \text{mol}$$

$$\text{Molar mass of water}(H_2O) = 18\ \text{gmol}^{-1}$$

$$\text{Number of moles of water} = \frac{90\text{g}}{18\ \text{gmol}^{-1}} = 5\ \text{mol}$$

The mole fraction of any components is ratio of its moles to total number of moles.

$$X_{\text{ethyl alcohol}} = \frac{2}{2+3+5} = \frac{2}{10} = \boxed{0.2}\ \text{Answer}$$

$$X_{\text{methyl alcohol}} = \frac{3}{2+3+5} = \frac{2}{10} = \boxed{0.3}\ \text{Answer}$$

$$X_{H_2O} = \frac{5}{2+3+5} = \frac{5}{10} = \boxed{0.5}\ \text{Answer}$$

Now, multiply the mole fractions with 100, to get mole percent.

Moles % of ethyl alcohol = 0.2x100 = $\boxed{20}$ Answer

Moles % of methyl alcohol = 0.3x100 = $\boxed{30}$ Answer

Moles % of H_2O = 0.5x100 = $\boxed{50}$ Answer

In the case of mixture of gases, one can determine the mole fraction from the partial pressure data of the mixture. Hence

$$X_A = \frac{p_A}{p_A + p_B + p_C} \quad , X_B = \frac{p_B}{p_A + p_B + p_C} \quad , X_C = \frac{p_C}{p_A + p_B + p_C}$$

Where p_a, p_b, p_c are the partial pressures of various gases in the mixture.

Generally, we can say that

$$\text{Mole fraction of any gas} = \frac{\text{Partial pressure of that gas}}{\text{Total pressure of the mixture of gases}}$$

9.1.5. Parts Per Million (ppm)

It is defined as the number of parts (by weight or volume) of a solute per million parts (by weight or volume) of the solution.

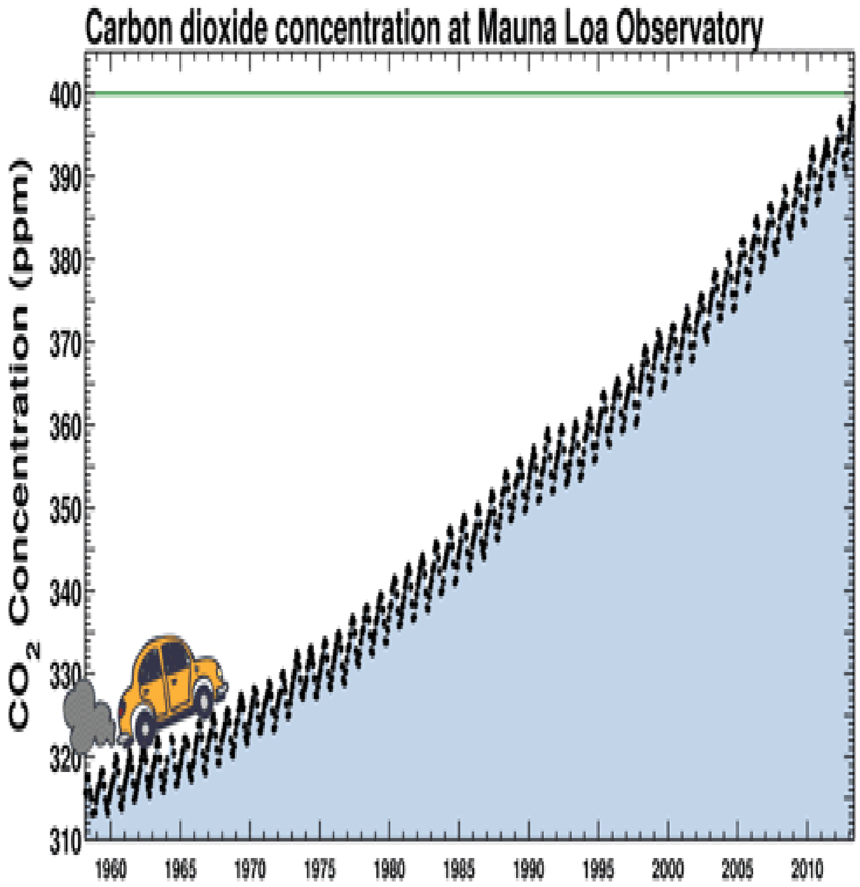
This unit is used for very low concentrations of solutions, e.g. to express the impurities of substances in water.

$$\text{Parts per million (ppm)} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$$

Example (5):

Sea water has 5.65 x 10^{-3} g of dissolved oxygen in one kg of water. Calculate the concentration of oxygen in sea water in parts per million

$$\text{ppm of oxygen in sea water} = \frac{5.65\times10^{-3}\text{g}}{1000\text{g}} \times 10^6 = \boxed{5.65 \text{ ppm}} \text{ Answer}$$



Animation 9.7: Parts Per Million (symbol, p p m)
Source & Credit: media.tumblr

9.1.6 Interconversion of Various Concentration Units of Solutions

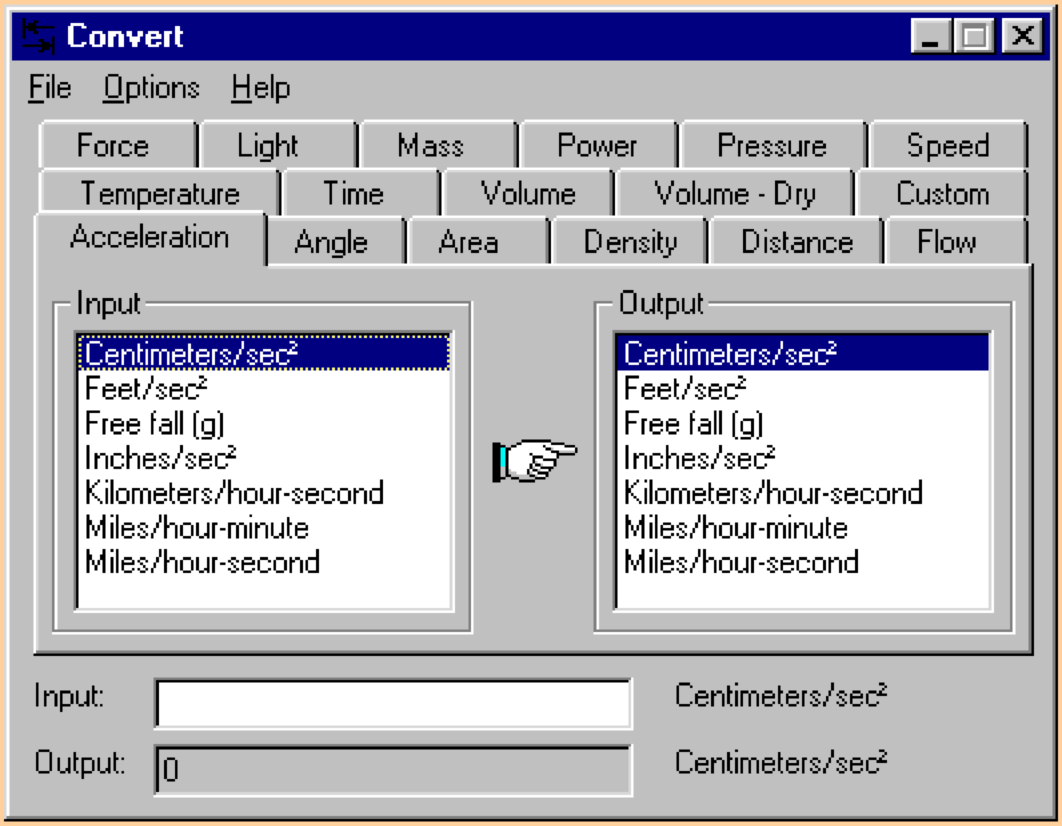
Sometimes, we get prepared solutions from the chemical supply houses. For example, we are working with a solution whose molarity is given by the supplier, but we need to know its molality or w/w percentage. For such purpose, we need to convert one unit of concentration into other. These conversions are usually done if we know the formula masses and the densities of the solutes or solutions. Following table shows the five important chemicals whose w/w%, molarities and densities are given.

One should be able to interconvert these concentration units into each other and moreover to molalities and mole fractions for laboratory work Let us do some calculations in this respect.

Name of Acid	% (w/w)	Molarity (M dm^{-3})	Density (gcm^{-3})
H_2SO_4	98%	18	1.84
H_3PO_4	85.5%	4.8	1.70
HNO_3	70.4%	15.9	1.42
HCl	37.2%	12.1	1.19
CH_3COOH	99.8%	17.4	1.05

Example (6):

Calculate the molality of 8% w/w NaCl solution.



Animation 9.8: Interconversion of Various Concentration Units of Solutions
Source & Credit: mechanicaldesignforum

It means that 0.1367 moles of NaCl is dissolved in 0.092 kg of water.

$$\text{Molality(m)}=\frac{\text{Number of moles of solute}}{\text{Mass of solvent in kg}}=\frac{0.1367\text{ moles}}{0.092\text{ kg}}$$

$$=\boxed{1.487\text{ m}}\ \text{Answer}$$

The given solution is 1.487 molal.

Example (7):

Hydrochloric acid available in the laboratory is 36% (w/w). The density of HCl solution is 1.19 g cm^{-3}. Determine the molarity of HCl solution.

Solution:

36% (w/w) HCl solution means that 36g of HCl dissolved in 100g of solution.

Mass of HCl =36g

Mass of solution =100g

In case of molarity, the final volume of solution is 1000 cm^3. Convert this volume into mass, by using density of 1.19 gcm^{-3}.

Mass of 1000cm^3 of HCl solution =1000x1.19 =1190g

Since, (Mass=volume x density)

100g of solution has HCl =36g

so, mass of HCl in 1190g of solution $=\frac{1190x36}{100g}$ =428.4g

Molar mass of HCl =36.5g mol^{-1}

Number of moles of HCl, in 428.4g of HCl $=\frac{428.4g}{36.5gmol^{-1}}$ =11.73

So, 1000 cm^3 solution of HCl has 11.73 moles of HCl

Hence, molarity of HCl =11.73mol dm^{-3} Answer

Example (8):

9.2 molar $HClO_4$ is available in the market. The density of this solution is 1.54gcm^3. What is the percentage by weight of $HClO_4$.

Solution:

Molarity of $HClO_4$ = 9.2g moles dm^{-3}

Density of solution = 1.54 gcm^{-3}

Let us calculate the mass of solution which is $1dm^3$ in volume and has 9.2moles of $HClO_4$ in it.

Since, Mass = volume x density
Mass of $1000cm^3$ solution $=1000cm^3 x 1.54gcm^{-3}=1540g$

Molar mass of $HClO_4$ =100.5gm mol^{-1}

9.2 moles of $HClO_4$, can be converted to its mass

Mass of $HClO_4$ $=100.5g\ mol^{-1}\ x\ 9.2mol = 924.6\ g$

Mass of $H_2$0 = mass of solution - mass of $HClO_4$ = 1540-924.6 = 615.4 g

% of $HClO_4$ by weight $=\frac{\text{mass of HClO}_4}{\text{mass of solution}} x100 = \frac{924.6}{1540g} x100 = 60.04$

% of H_2O by weight = 100-mass of $HClO_4$ $=100-60.04= \boxed{39.96}$ Answer

9.2 TYPES OF SOLUTIONS

Most commonly, we come across solutions, where solute is a solid and the solvent is a liquid. As a matter of fact, all the three states of matter i.e. solid, liquid or gas can act as solute or solvent. Examples for nine possible types of solution are given in Table (9.2).

Table (9.2) Common types and examples of solutions

State of Solute	State of Solvent	Example
Gas	Gas	Air
Gas	Liquid	O_2 in water, CO_2 in water.
Gas	Solid	H_2 adsorbed by palladium
Liquid	Gas	Mist, fog, clouds, liquid air pollutants.
Liquid	Liquid	Alcohol in water, milk, benzene in toluene.
Liquid	Solid	Mercury in silver, butter, cheese.
Solid	Liquid	Sugar in water, jellies, paints.
Solid	Gas	Dust particles in smoke.
Solid	Solid	Metal alloys pearls, opals, carbon in iron (steel).

Animation 9.9:TYPES OF SOLUTIONS
Source & Credit: blobs

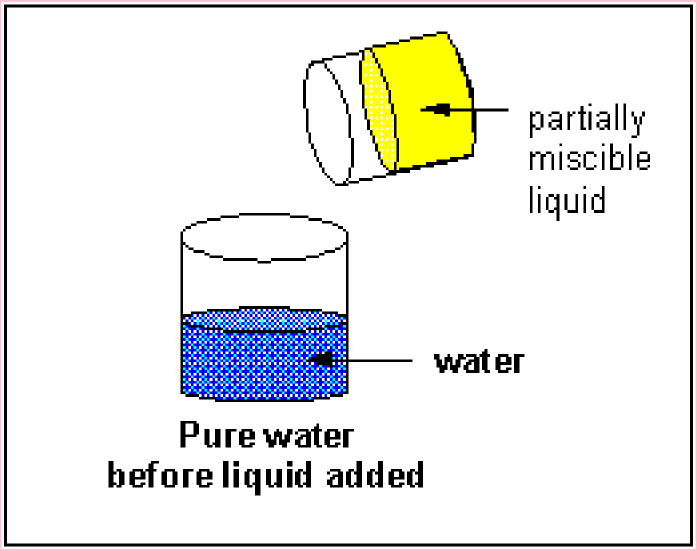
9.2.1 Solutions of Solids in Liquids

When a solid comes in contact with a suitable liquid, it dissolves forming a solution i.e. a homogeneous mixture. This process of dissolution can be explained in terms of attraction between the particles of a solute and that of a solvent. The molecules or ions in solids are arranged in such a regular pattern that the inter-molecular or inter-ionic forces are at a maximum.

The process of dissolution is to overcome these forces of attraction holding together the solute molecules or ions in the crystal lattice, by the solute-solvent forces. In molecular crystals, the inter-molecular forces of attraction are either dipole-dipole or London dispersion type. These forces are relatively weak and can easily be overcome. Hence, non-polar or less polar molecular crystals usually dissolve in non-polar solvents like benzene.

In the crystal lattice, the inter-molecular or inter-ionic forces of attraction between highly polar molecules or ions are quite strong, hence the polar solids fail to dissolve in nonpolar solvents. These strong electrostatic forces cannot be overcome or shattered by the weak solute-solvent attractions. Take the case of cane sugar. Due to hydrogen bonding, it has tightly bound molecules, so it will not be dissolved by solvents like kerosene oil, petrol, benzene, etc. It will be dissolved readily in water, because water attracts sugar molecules almost in the same way as the sugar molecules attract one another.

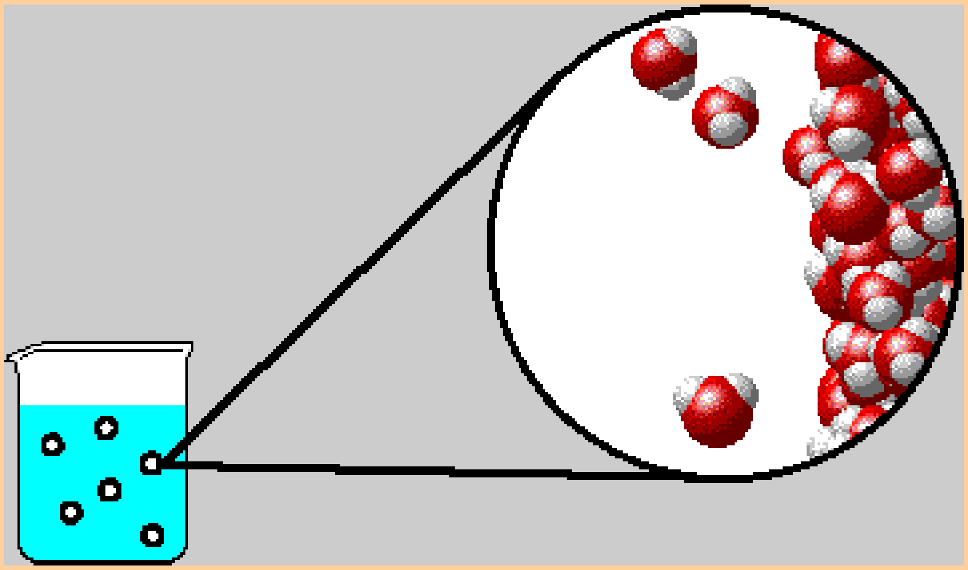
The inter-ionic forces of attraction are very strong in ionic solids so, equally strong polar solvents are needed to dissolve them. Such solids cannot be dissolved by moderately polar solvents e.g. acetone. A moderately polar solvent, fails to dissolve sodium chloride, which is an ionic solid. Thus the solubility principle is that “ like dissolves like’ .



Animation 9.10: Solutions of Solids in Liquids
Source & Credit: employees.csbsju

9.2.2 Solutions of Liquids in Liquids

The solutions of liquids in liquids may be divided into three classes.



Animation 9.11: Solutions of Liquids in Liquids
Source & Credit: chem.purdue

(i) Completely Miscible Liquids

Liquids like alcohol and water or alcohol and ether mix in all proportions. However, the properties of such solutions are not strictly additive. Generally, the volume decreases on mixing but in some cases it increases. Heat may be evolved or absorbed during the formation of such solutions. These types of solutions can usually be separated by fractional distillation.

(ii) Partially Miscible Liquids

A large number of liquids are known which dissolve into one another up to a limited extent. For example, ether $C_2H_5-O-C_2H_5$ dissolves water to the extent of about 1.2 % and water dissolves ether up to the extent of about 6.5%.

As the mutual solubilities are limited, the liquids are only partially miscible. On shaking equal volumes of water and ether, two layers are formed. Each liquid layer is a saturated solution of the other liquid. Such solutions are called conjugate solutions. The mutual solubility of these conjugate solutions is affected by temperature changes. Typical examples of such systems are:

a. Phenol-water system
b. Triethylamine-water system
c. Nicotine-water system

Phenol-Water System ($H_2O + C_6H_5OH$)

The example of phenol in water is interesting. If equal volumes of water and phenol are mixed together, they show partial miscibility. It has been observed that around room temperature, phenol will dissolve in a lot of water giving us the upper layer and water will dissolve in a lot of phenol giving us the lower layer.

At 25^{0}C the upper layer is 5% solution of phenol in water and the lower layer is 30% water in phenol. These two solutions are conjugate solutions to each other. The lower layer has a greater density due to greater percentage of phenol. Water acts as a solute in the lower layer while phenol is a solute in the upper layer. When the temperature of water-phenol system is increased, the compositions of both layers change. Water starts travelling from upper to the lower layer and phenol travels from lower to the upper layer.

When the temperature of this system approaches 65.9^{0}C, a homogeneous mixture of two components is obtained. This homogeneous mixture contains 34% phenol and 66% water. The temperature of 65.9^{0}C at which two conjugate solutions merge into one another, is called critical solution temperature or upper consulate temperature. Some other partially miscible pairs of liquids have their own consulate temperatures with definite compositions.

For example, water-aniline system has a single layer at 167.0^0 C with 15% water. Methanol-cyclohexane system has consulate temperature of 49.1^0 C with 29% methanol.

(iii) Liquids Practically Immiscible

Those liquids which do not dissolve into each other in any proportion are immiscible.

Examples: (i) Water and benzene ($H_20 + C_6H_6$)

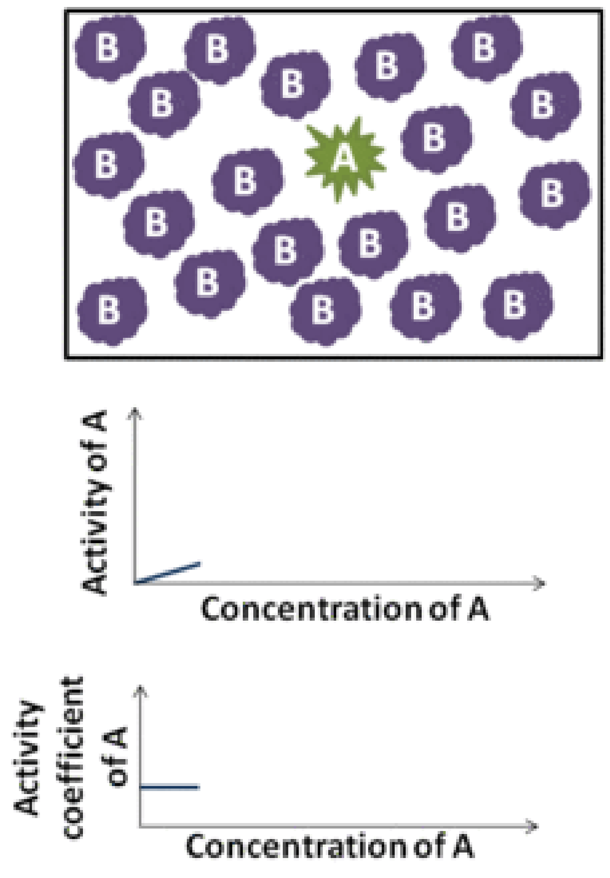
(ii) Water and carbon disulphide ($H_2O + CS_2$)

9.3.0 IDEAL AND NON-IDEAL SOLUTIONS

When two or more than two liquid substances are mixed, the solutions may be ideal or non-ideal. To distinguish between such solutions we look at the following aspects:-

i. If the forces of interactions between the molecules of different components are same as when they were in the pure state, they are ideal solutions, otherwise non-ideal.
ii. If the volume of solution is not equal to the sum of the individual volumes of the components, the solution is non-ideal.
iii. Ideal solutions have zero enthalpy change as their heat of solution.
iv. If the solutions obey Raoult's law, then they are ideal. This is one of the best criterion for checking the ideality of a solution

Let us first study, the Raoults's law and then try to understand ideality of solutions, the process of fractional distillation and the formation of azeotropes.



Animation 9.12: Ideal and Non-Ideal Solutions
Source & Credit: wikipedia

9.3.1 RAOULT'S LAW

Raoult's law can be defined in these ways:

The vapour pressure ol a solvent above a solution is equal to the product of the vapour pressure of pure solvent and the mole fraction of solvent in solution.

Mathematically, it can be written in equation form as follows:

$$p = p^o x_1 \qquad .... \qquad (1)$$

Where p is the vapour pressure of solvent in the solution, p° is the vapour pressure of pure solvent and x_1 is the mole fraction of solvent.

We also known that

$X_1 + X_2 = 1$ (x_2 is the mole fraction of solute)

or $X_1 = 1 - X_2$

Putting the value of x_1 in equation (1)

$$p = p^o(1 - X_2)$$

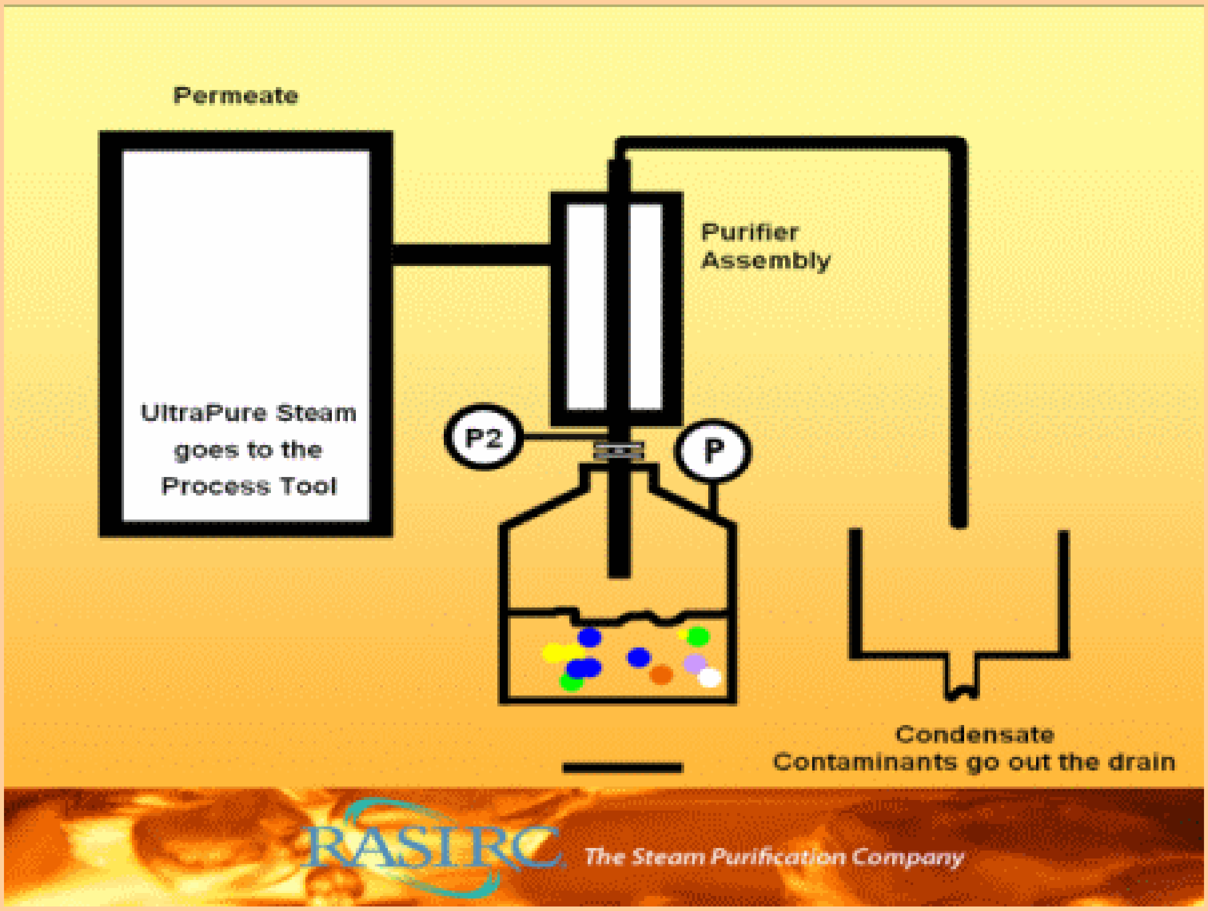
or $p = p^o - p^o X_2$

or $p^o - p = p^o X_2$

or $\Delta p = p^o X_2$ ....(2)

Equation (2) gives another definition of Raoult's law. "The lowering of vapour pressure is directly proportional to the mole of fraction of solute." Now rearrange equation (2) to get equation (3).

$$\frac{\Delta p}{p^o} = X_2 \qquad .... \qquad (3)$$



Animation 9.13: RAOULT'S LAW
Source & Credit: rasirc

Δp/p° is called relative lowering of vapour pressure and it is more important than actual lowering of vapour pressure (Δp). The equation (3) gives us another definition of Raoult's law. "The relative lowering of vapour pressure is equal to the mole fraction of solute".

The relative lowering of vapour pressure:

(i) is independent of the temperature
(ii) depends upon the concentration of solute.
(iii) is constant when equimolecular proportions of different solutes are dissolved in the same mass of same solvent.

Example (9):

The vapour pressure of water at 30° C is 28.4 torr. Calculate the vapour pressure of a solution containing 70g of cane sugar ($C_{12}H_{22}O_{11}$) in 1000g of water at the same temperature. Also calculate the lowering of vapour pressure.

Solution:

Mass of cane sugar dissolved =70g

Molar mass of cane sugar $= 342 \text{ g mole}^{-1}$

Number of moles of a compound $= \dfrac{\text{mass}}{\text{molar mass}}$

Number of moles of sugar, $C_{12}H_{22}O_{11}$ (n_2) $= \dfrac{70\text{g}}{342\text{g/mol}} = 0.20$

Mass of H_2O in solution =1000g

Number of moles of water, H_20 (n_1) $= \dfrac{1000\text{g}}{18.02\text{g/mol}} = 55.49$

Total number of moles $= 0.20 + 55.49 = 55.69$

Mole fraction of sugar, $C_{12}H_{22}O_{11}$(x_2) $= \dfrac{n_2}{n_1+n_2} = \dfrac{0.2}{55.69} = 0.0036$

Mole fraction of water, H_2O (x_1) $= \dfrac{n_1}{n_1+n_2} = \dfrac{55.49}{55.69} = 0.9964$

Vapour pressure of pure water =28.4 torr

Applying the formula for vapour pressure of solution

$$p = p^{o}X_1 = (28.4)(0.9964) = 28.29 \text{ torr}$$

So, vapour pressure of solution $= \boxed{28.29 \text{ torr}}$ Answer

Lowering of vapour pressure, Δp $= 28.4 - 28.29 = \boxed{0.11 \text{ torr}}$ Answer

9.3.2 Raoult's Law (when both components are volatile)

Raoult's law can be applied to understand the relationship between mole fractions of two volatile components and their vapour pressures before making the solution and after making the solution. Consider two liquids 'A' and 'B' with vapour pressures $p°_A$ and $p°_B$ in the pure state at a given temperature. After making the solution, the vapour pressures of both liquids are changed. Let the vapour pressures of these liquids in solution state be p_A and p_B with their mole fractions x_A and x_B respectively.

Applying Raoult's law to both components

$$p_A = p^o{}_A x_A$$

$$p_B = p^o{}_B x_B$$

$P_t = p_A + p_B = p^o{}_A x_A + p^o{}_B x_B$ where P_t is total vapour pressure)

since $x_A + x_B = 1$

$$x_B = 1 - x_A$$

$$P_t = p^o_A x_A + p^o_B(1 - x_A)$$

$$P_t = p^o_A x_A + p^o_B - p^o_B x_A$$

$$P_t = (p^o_A - p^o_B)x_A + p^o_B \quad \ldots\ldots\ldots\ldots \quad (4)$$

The component A is low boiling liquid and B is high boiling liquid. The vapour pressure of A is more than B at a given temperature.

Equation (4) is a equation of straight line If a graph is plotted between $x_B$or mole % of B on x-axis and P_t on y-axis, a straight line will be obtained Fig (9.1).

Only those pairs of liquids give straight lines which form ideal solutions. So, Raoult's law is one of the best criterion to judge whether a solution is ideal or not.

All the possible solutions of two components A and B have their vapour pressures on the straight line connecting $p°_A$ with $p°_B$. All such solutions will be ideal. Each point on this straight line represents the vapour pressure of a solution, at a given temperature, with the corresponding contribution of both the components A and B. The two dotted lines represent the partial pressures of the individual components of solution. They show the increase of vapour pressure of a component with increase in its mole fraction in solution.

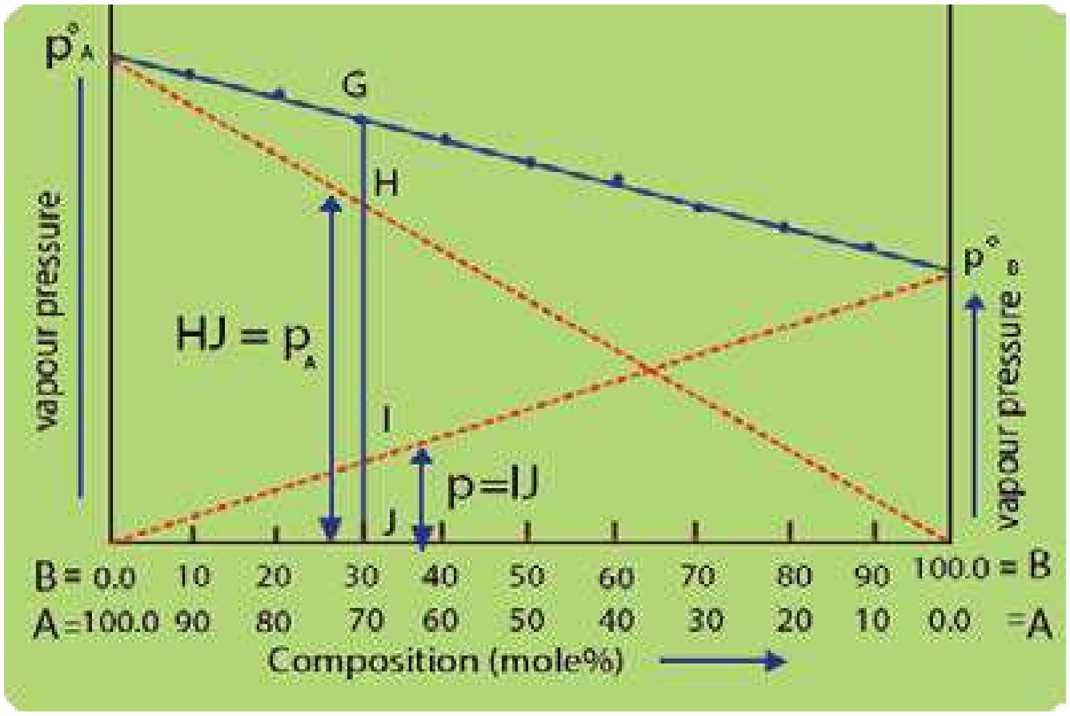


Fig. (9.1) Graph between composition
and vapour pressure

In order to explain it, consider a point G on the straight line. This point represents the vapour pressure of solution with 30% moles contribution of the component B and 70% of component A.

Since, A is more volatile component, so its contribution towards the vapour pressure of solution is represented by p_A.

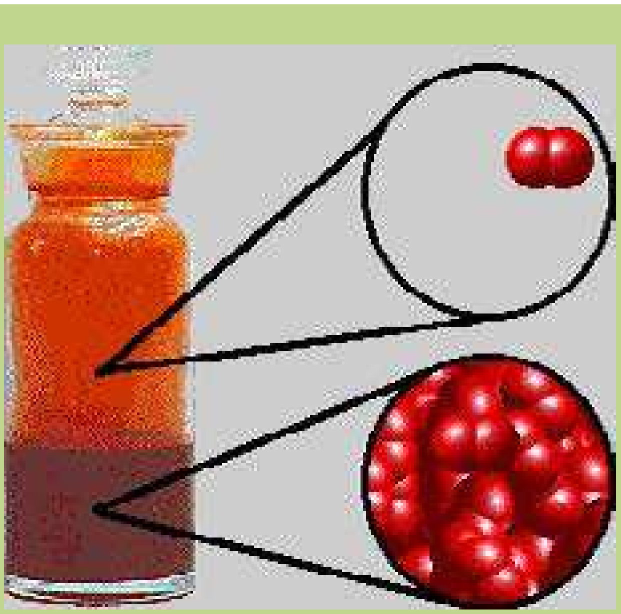
The contribution of the less volatile component B is represented by p_B. Similarly, we can calculate the relative contributions of A and B towards the total vapour pressure of solution by taking other points along the line joining p^o_A to p^o_B.

The total vapour pressure of the solution (P_t) corresponding to the point G will be equal to the sum of the vapour pressures of the individual components ($p_A + p_B$) as shown in the Fig. (9.1).

9.4 VAPOUR PRESSURES OF LIQUID -LIQUID SOLUTIONS

Binary mixtures of miscible liquids may be classified as (i) ideal (ii) non-ideal or real solutions.

The vapour pressures of solutions provides a simple picture about their behaviour. Let us discuss the vapour pressures of ideal and real solutions one by one.



Animation 9.14:VAPOUR PRESSURES OF LIQUID LIQUID SOLUTIONS
Source & Credit: chem.purdue

(i) Ideal solutions

An ideal solution is that which obeys Raoult's law. Some typical ideal solution forming liquid pairs are: benzene-toluene, benzene-ether, chlorobenzene-bromobenzene, ethyl iodide-ethyl bromide, etc.

Fractional Distillation of Ideal Mixture of Two Liquids

Let us have two liquids A and B which form a completely miscible solution. A is a more volatile component so its boiling point is less than B. If we have various solutions of these two components and a graph is plotted between compositions on x-axis and temperature on y-axis, then two curves are obtained as shown in the Fig. (9.2).

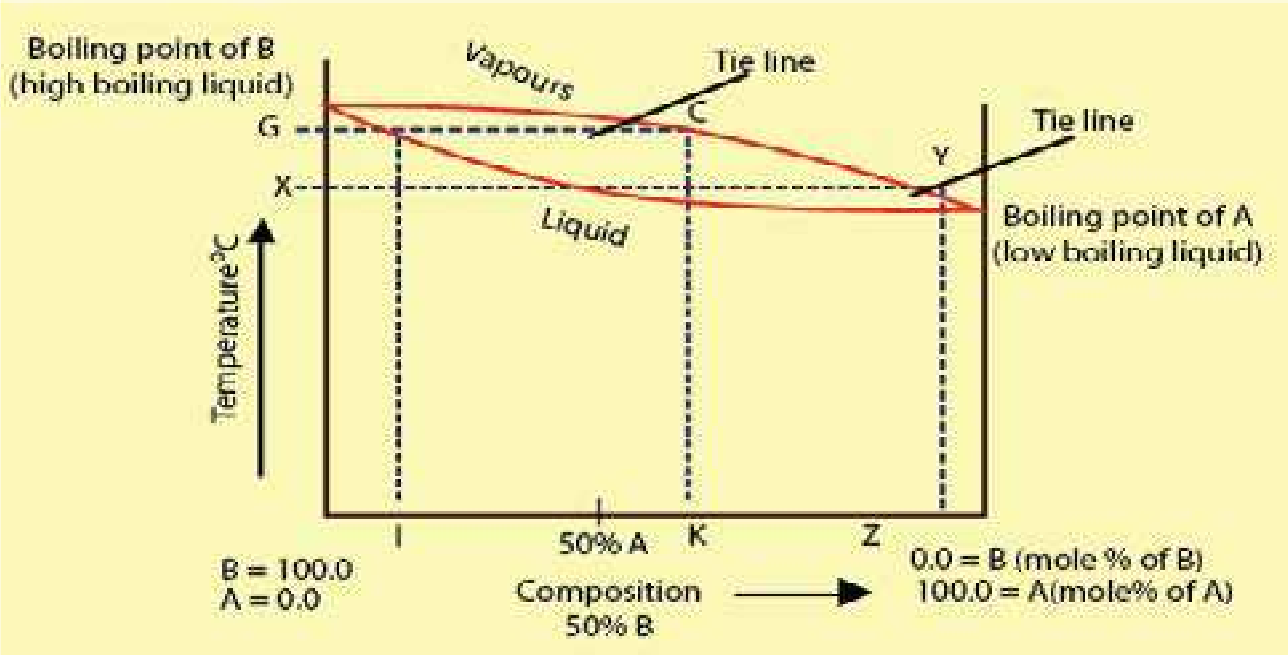


Fig (9.2) Composition - temperature curve of an ideal solution.

The upper curve represents the composition of the vapours of different solutions while the lower curve represents the composition of the liquid mixtures. The reason is that at any temperature the composition of vapours is different from the composition of liquid mixture.

Consider the temperature, corresponding to the point G. It is the boiling point of solution corresponding to composition I. It meets liquid curve at point H and the vapour curve at the point C. The composition of liquid mixture corresponding to the point H is shown by the point I. At point I the mixture has greater percentage of B and less percentage of A. While at the same temperature the vapours of the mixture have the composition K. At the point K, the percentage of A is comparatively greater than B when we compare it with composition of liquid mixture corresponding to point I. Because A is a low boiling liquid, it is present in the vapour state in greater percentage than at point I.

If the temperature of the mixture is maintained corresponding to point G, the distillate will have greater percentage of A and the residue will have greater percentage of B. The reason is that the fraction going to distillate is that which is in vapour state and it has greater % of A. The distillate of composition K is again subjected to distillation. Its boiling point is X, and at this temperature the distillate of composition Z is obtained. This distillate of composition Z is further distilled. In this way, the distillate becomes more and more rich in A and residue is more and more rich in B. So, process of distillation is repeated again and again to get the pure component A. Thus we can completely separate the components by fractional distillation. Such liquid mixtures, which distil with a change in composition, are called zeotropic mixtures. For example, methyl alcohol-water solution can be separated into pure components by distillation.

ii. Non-Ideal Solutions (azeotropic mixtures)

Many solutions do not behave ideally. They show deviations from Raoult's Law due to differences in their molecular structures i.e. size, shape and intermolecular forces. Formation of such solutions is accompanied by changes in volume and enthalpy. The vapour pressure deviations may be positive or negative in such solutions.

Azeotropic mixtures are those which boil at constant temperature and distil over without change in composition at any temperature like a pure chemical compound. Such mixtures can not be regarded as chemical compounds as changing the total pressure alongwith the boiling point changes their composition. Whereas, for a chemical compound, the composition remains constant over a range of temperature and pressure.

The deviations of solutions are of two types:

(a) Positive deviations
(b) Negative deviations

(a) Positive Deviations

If a graph is plotted between composition and vapour pressure of a solution which shows positive deviation from Raoult's law, the total vapour pressure curve rises to a maximum. The vapour pressure of some of solutions are above the vapour pressure of either of the pure components.

Let us consider the mixture of A and B components at point C in Fig (9.3). At the point C Fig (9.3), the mixture has the highest vapour pressure and, therefore, the lowest, boiling point.

On distilling this type of solution, the first fraction will be a constant boiling point mixture i.e. azeotropic mixture having a fixed composition corresponding to the maximum point. For this type of solution, it is not possible to bring about complete separation of components by fractional distillation. Ethanol-water mixture is an example of this type. It boils at 78.1°C with 4.5% water and 95.5 % alcohol. 78.1°C is lower than the boiling point of ethanol (78.5°C) and water (100°C).

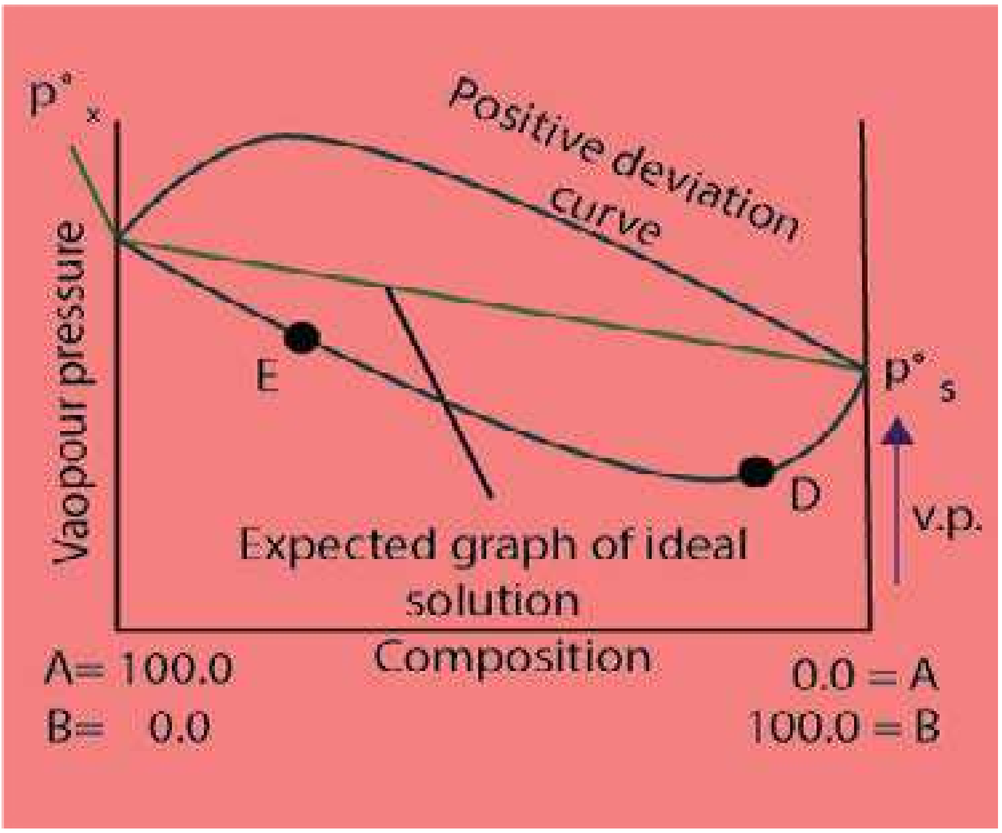


Fig (9.3) Non-ideal solutions and azeotropic mixtures for positive deviation

(b) Negative Deviations

For this type of solution, the vapour pressure curve shows a minimum. Let us consider a point E in Fig (9.3). Here, the more volatile component A is in excess. On distilling this solution, the vapours will contain more of A and the remaining mixture becomes richer in less volatile component B'. Finally, we reach the point D where vapour pressure is minimum and the boiling point is maximum. At this point, the mixture will distill over unchanged in composition.

Therefore, it is not possible to separate this type of solution completely into its components. We can give the example of hydrochloric acid solution in water for this type of solutions. HCl forms an azeotropic mixture with water, boiling at 110°C and containing 20.24% of the acid.

9.5 SOLUBILITY AND SOLUBILITY CURVES

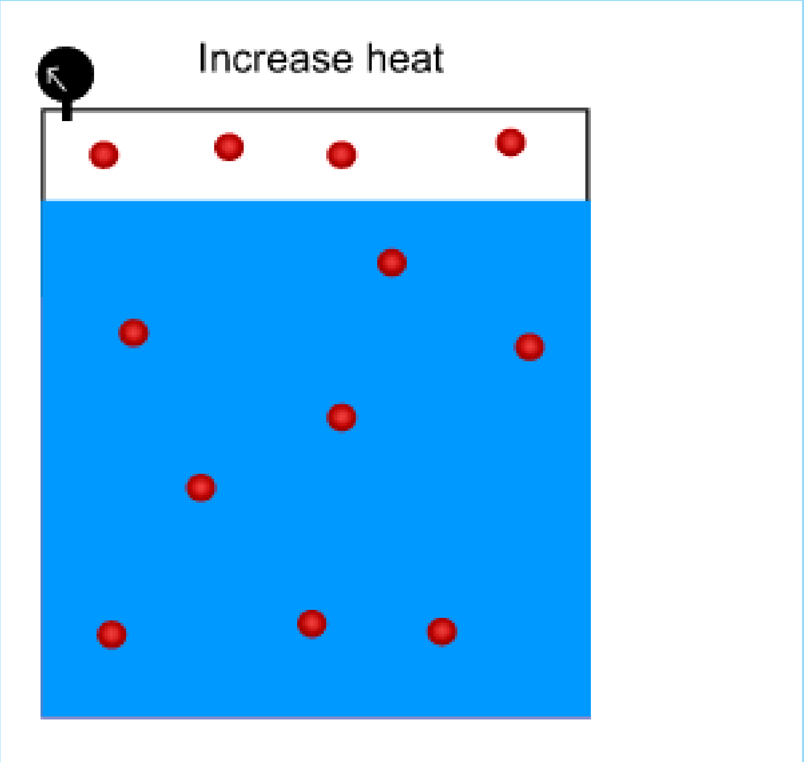
Whenever a solid solute is put in a liquid solvent then the molecules or ions break away from the surface of the solid and pass into the solvent. These particles of solid are free to diffuse throughout the solvent to give a uniform solution. The solute and solvent molecules are constantly moving about in the solution phase because of kinetic energy possessed by them. In this way some of the particles of the solute may come back towards the solid due to collisions. These molecules or ions are entangled in its crystal lattice and get deposited on it. This is called re-crystallization or precipitation.If excess of solid is present in the solution then the rate of dissolution and rate of crystallization become equal. This is a state of dynamic equilibrium.

The concentration of the solute at equilibrium with the solution is constant for a particular solvent and at a fixed temperature. The solution thus obtained is called saturated solution of the solid substance and the concentration of this solution is termed as its solubility.

So the solubility is defined as the concentration of the solute in the solution when it is in equilibrium with the solid substance at a particular temperature.

Solubility is expressed in terms of number of grams of solute in 1000g of solvent. At a particular temperature, saturated solution of NaCl in water at 0°C contains 37.5g of NaCl in lOOg of water. Similarly the solubility of $CuSO_4$ in water at 0°C is 14.3g/100g, while at 100°C it is 75.4g/100g.

To determine the solubility of substance, a saturated solution of a solid is prepared at a constant temperature. Then this solution is filtered. A known volume of this solution is evaporated in a china dish and from the mass of the residue, the solubility can be calculated.



Animation 9.15: SOLUBILITY AND SOLUBILITY CURVES
Source & Credit: dynamicscience

Solubility Curves

Temperature has a marked effect on the solubility of many substances. A grafical representation between temperature and solubility of solution is called solubility curves.There are two types of solubility curves.

(a) Continuous solubility curves

(b) Discontinuous solubility curves

(a) Continuous Solubility Curves

Continuous solubility curves don't show sharp breaks anywhere. According to Fig.(9.4). $KClO_3$, $K_2Cr_2O_7$, $Pb(NO_3)_2$ and $CaCl_2$ are showing continuous solubility curves. The solubility curves of KCl, NaCl and $NaNO_3$ give the straight lines. NaCl shows a very small change of solubility from 0°C to 100°C increase of temperature.

$Ce_2(SO_4)_3$ shows the exceptional behaviour whose solubility decreases with the increase in temperature and becomes constant from 40°C onwards. Anyhow, it shows continuous solubility curve.

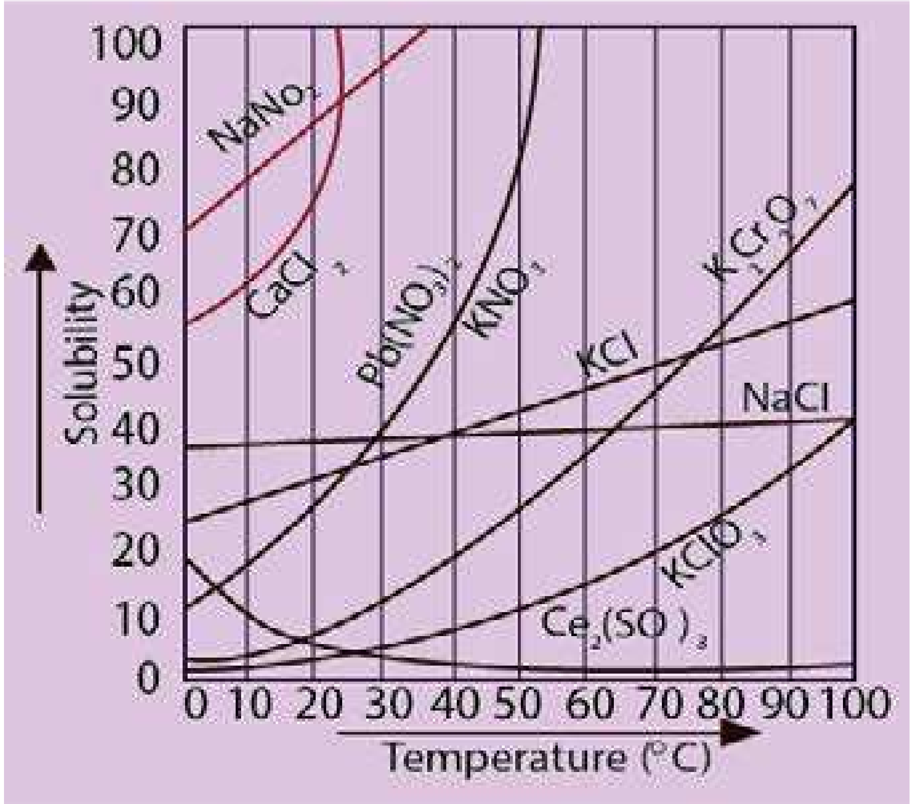


Fig (9.4) Continuous solubility curves

(b) Discontinuous Solubility Curves

Sometimes, the solubility curves show sudden changes of solubilities and these curves are called discontinuous solubility curves. The best examples in this reference are $Na_2SO_4.10\ H_20$, $CaCl_2.6\ H_2O$. Actually, these curves are combination of two or more solubility curves. At the break a new solid phase appears and another solubility curve of that new phase begins. It is the number of molecules of water crystallization which changes and hence solubility changes, Fig (9.5).

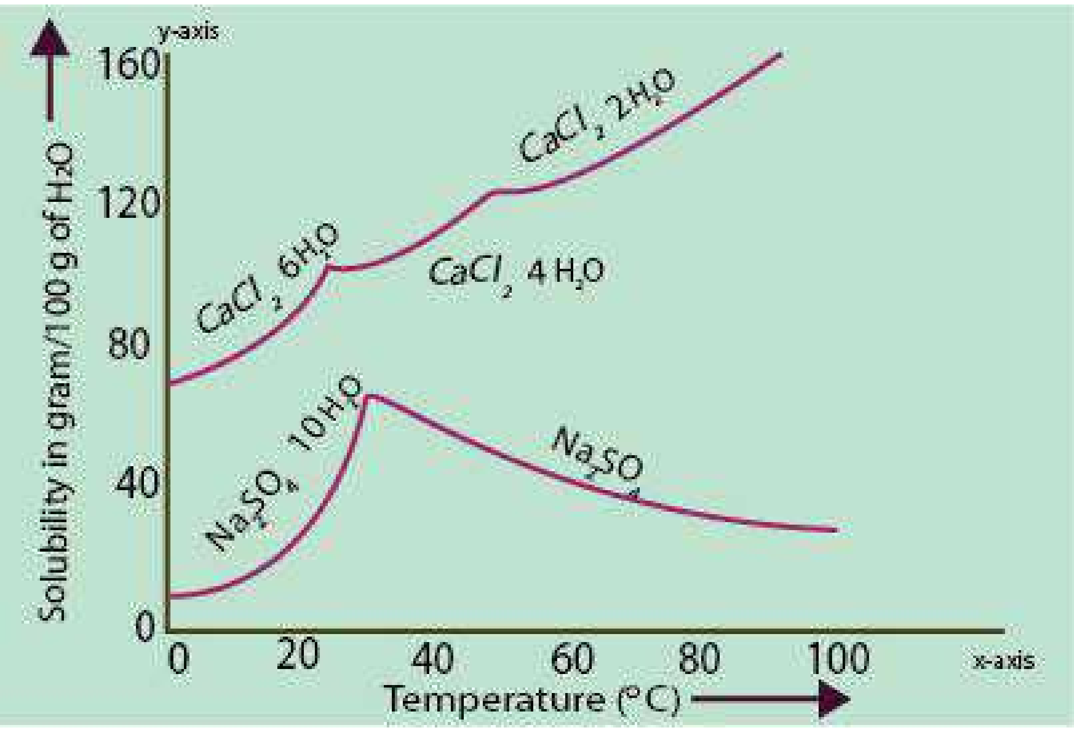
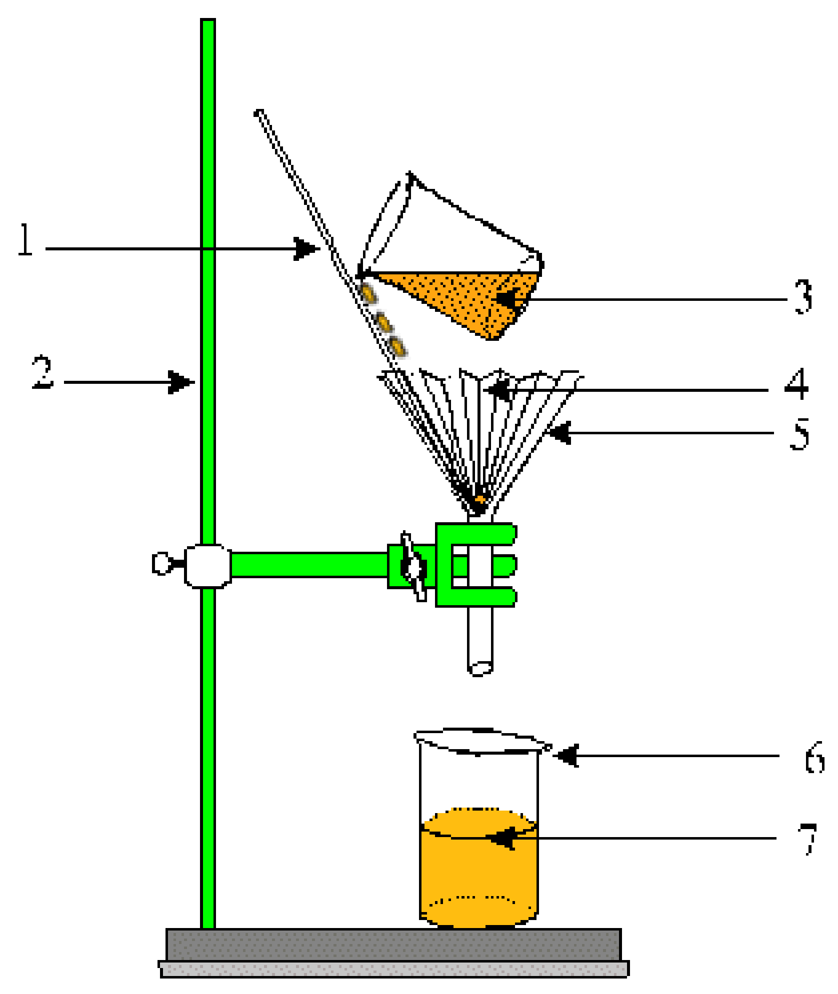


Fig (9.5) Discontinuous solubility curves

9.5.1 Fractional Crystallisation

The curves in Fig (9.4) show that the variation in solubility with temperature is different for different substances. For example, the change in solubility in case of KNO_3 is very rapid with changing temperature, while such a change is more gradual in other cases like KBr, KCl, alanine, etc.
These differences in the behaviour of compounds provide the basis for fractional crystallisation, which is a technique for the separation of impurities from the chemical products.

By using the method, the impure solute is dissolved in a hot solvent in which the desired solute is less soluble than impurities. As the hot solution is cooled, the desired solute being comparatively less soluble, separates out first from the mixture, leaving impurities behind. In this way, pure desired product crystallizes out from the solution.



Animation 9.16: Fractional Crystallisation
Source & Credit: mind42

9.6 COLLIGATIVE PROPERTIESOF SOLUTIONS

The colligative properties are the properties of solution that depend on the number of solute and solvent molecules or ions. Following are colligative properties of dilute solution.

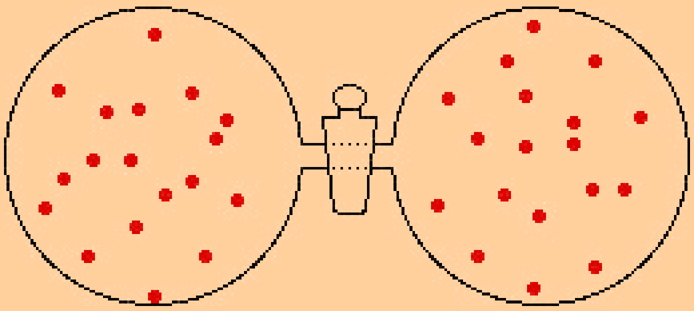
(i) Lowering of vapour pressure
(ii) Elevation of boiling point
(iii) Depression of freezing point
(iv) Osmotic pressure

The practical applications of colligative properties are numerous. The study of colligative properties has provided us with methods of molecular mass determination and has also contributed to the development of solution theory.

Animation 9.17: COLLIGATIVE PROPERTIESOF SOLUTIONS
Source & Credit: web.mst

9.6.1 Why Some of the Properties are Called Colligative

The reason for these properties to be called colligative can be explained by considering three solutions. Let us take 6 g of urea, 18 g of glucose and 34.2 g of sucrose and dissolve them separately in 1 kg of H_20.



Animation 9.18: Why Some of the Properties are Called Colligative
Source & Credit: web.mst

This will produce 0.1 molal solution of each substance. Pure H_2O has certain value of vapour pressure at a given temperature. In these three solutions, the vapour pressures will be lowered. The reason is that the molecules of a solute present upon the surface of a solution decrease the evaporating capability. Apparently, it seems that sucrose solution should show the maximum lowering of vapour pressure while urea should have the minimum lowering of vapour pressure. The reality is that the lowering of vapour pressure in all these solutions will be same at a given temperature. Actually, the number of particles of the solute in all the solutions are equal. We have added 1/10th of Avogadro's number of particles (6.02×10^{22}). The lowering of vapour pressure depends upon the number of solute particles and not upon their molar mass and structures. Well, it should be kept in mind that these three solutes are non-volatile and non-electrolyte.

The boiling points of these solutions are higher than that of pure solvent. It is observed that the boiling point elevation of these three solutions is 0.052 °C. Similarly, freezing points will be depressed for these solutions and the value of depression in these three cases is 0.186°C. The reason again is that the elevation of boiling point and the depression of freezing point depend upon number of particles of solute.

Now, let us deduce the values of elevation of the boiling point and the depression of the freezing point of water for 1 molal solutions. For that purpose, try to dissolve 60 g of urea. 180 g of glucose and 342 g of sugar separately in 1 kg of water. If, it is possible then the elevation of boiling point and depression of freezing point of water will be 0.52 °C and 1.86 °C, respectively. All the three solutions will boil at 100.52 °C and freeze at -1.86 °C. These values of elevation of boiling point and depression of freezing point are called molal boiling point constants and molal freezing point constants of H_2O denoted by K_b and K_f respectively.

These are also named as ebullioscopic and cryoscopic constants, respectively. These constants depend upon the nature of solvent and not upon the nature of solute. Following Table (9.3) give the values of K_b and K_f for some common solvents.

Table (9.3) K_b and K_f values for some solvents

Solvent	B.P.(°C)	K_b(°C/m)	F.P.(°C)	K_f(°C/m)
H_2O	100	0.52	0	1.86
Ether	34.4	2.16	-116.3	1.79
Aceticacid	118	3.07	17	3.90
Ethanol	79	1.75	-114.5	1.99
Benzene	80	2.70	5.5	5.10

To observe the colligative properties, following condition should be fulfilled by the solutions.

(i) Solution should be dilute

(ii) Solute should be non-volatile

(iii) Solute should be non-electrolyte.

Now, let us discuss these colligative properties one by one. (We will not discuss osmotic pressure over here).

9.6.2 Lowering of Vapour Pressure

The particles can escape from all over the surface of a pure solvent Fig. (9.6a). When the solvent is containing dissolved non-volatile non-electrolyte solute particles, the escaping tendency of solvent particles from the surface of the solution decreases and its vapour pressure is lowered Fig (9.6 b)

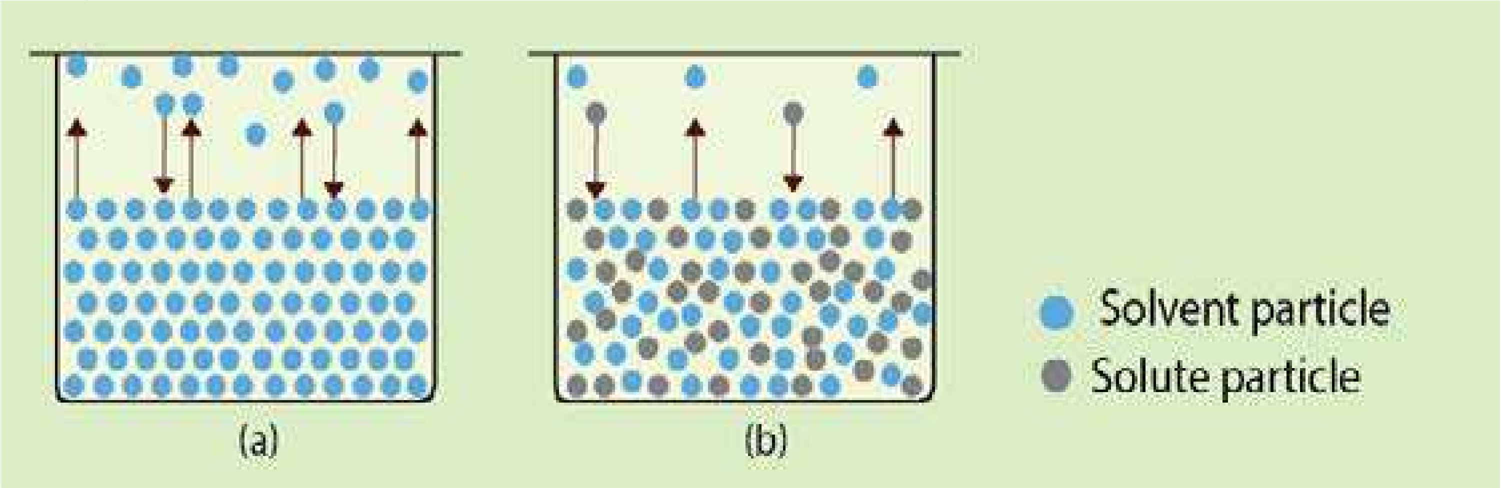


Fig (9.6) Lowering of vapour pressure

A quantitative relationship between the change of vapour pressure of a solvent due to addition of non-volatile and non-electrolyte solute and the mole fraction of solute has been given by Raoult.

According to equation (3), Raoult says that relative lowering of vapour pressure isequal to the mole fraction of solute.

$$\frac{\Delta p}{p^o}=x_2$$

If n_2 and n_1 are the number of moles of a solute and solvent respectively, then

$$x_2 = \frac{n_2}{n_1 + n_2}$$

So,
$$\frac{\Delta p}{p^o} = \frac{n_2}{n_1 + n_2}$$

For a dilute solution, n_2 can be ignored in denominator

Hence,
$$\frac{\Delta p}{p^o} = \frac{n_2}{n_1}$$

The number of moles of solute and solvent are obtained by dividing their masses in grams with their respective relative molecular masses. If W_1 and W_2 are the masses of solvent and solute while M_1 and M_2 are their relative molecular masses receptively, then

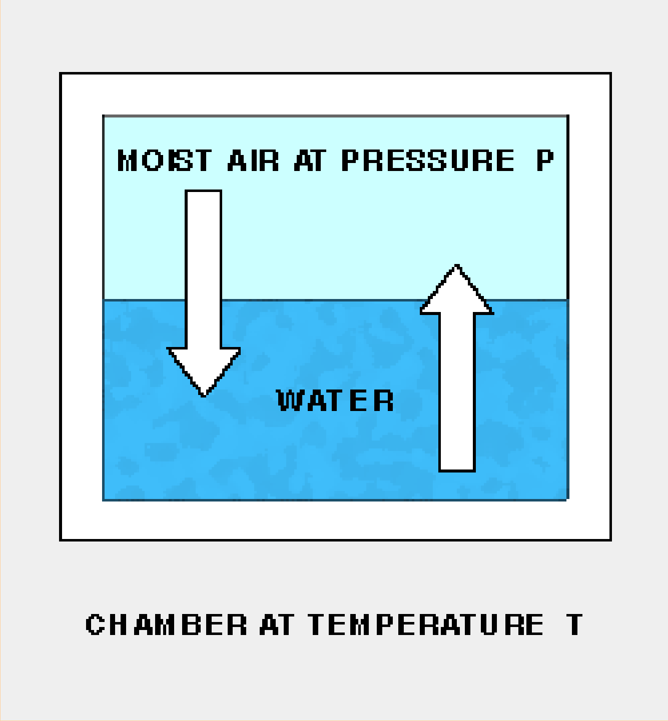
$$n_1 = \frac{W_1}{M_1} \quad \text{and} \quad n_2 = \frac{W_2}{M_2}$$

$$\frac{\Delta p}{p^o} = \frac{\frac{W_2}{M_2}}{\frac{W_1}{M_1}}$$

$$\frac{\Delta p}{p^o} = \frac{W_2}{M_2} \times \frac{M_1}{W_1} \qquad \text{............} \quad (5)$$

$$M_2 = \frac{p^o}{\Delta p} \times \frac{W_2 M_1}{W_1} \qquad \text{.............} \quad (6)$$

The molecular mass (M_2) of a non-volatile solute can be calculated from the equation (6).



Animation 9.19: Lowering of Vapour Pressure
Source & Credit: thunderscientific

Example 10:

Pure benzene has a vapour pressure of 122.0 torr at 32°C. When 20g of a non- volatile solute were dissolved in 300g of benzene, a vapour pressure of 120 torr was observed. Calculate the molecular mass of the solute. The molecular mass of benzene being 78.1.

Solution

Let the molecular mass of the solute be = M_2

Mass of solute dissolved (W_2) = 20 g

Vapour pressure of pure solvent (p°) = 122.0 torr

Vapour pressure of solution (p) = 120.0 torr

Lowering of vapour pressure (Δp) = 122.0 - 120.0 = 2.0 torr

Mass of solvent (W_1) = 300 g

Molar mass of solvent (M_1) = 78.1

Formula applied

$$\frac{\Delta p}{p^o} = \frac{W_2}{M_2} x \frac{M_1}{W_1}$$

$$M_2 = \frac{p^o}{\Delta p} x \frac{W_2 M_1}{W_1}$$

Putting the values

$$M_2 = \frac{122.0}{2.0} x \frac{20x78.1}{300} = \boxed{317.6 \text{ g mol}^{-1}} \text{ Answer}$$

9.6.3 Elevation of Boiling Point

The presence of a non-volatile non-electrolyte solute in the solution decreases the vapour pressure of the solvent. Greater, the concentration of solute, greater will be the lowering of vapour pressure. Therefore, the temperature at which a solvent in the solution state boils is increased. In order to understand it, determine the vapour pressures of a solvent at various temperatures. Plot a graph between temperatures on x-axis and vapour pressures on y-axis. A rising curve is obtained with the increase of temperature. The slope of the curve at high temperature is greater, which shows that at high temperature the vapour pressure increases more rapidly. Temperature T_1 on the curve AB which is for the pure solvent, corresponds to the boiling point of the solvent. The solvent boils when its vapour pressure becomes equal to the external pressure represented by p°.

When the solute is added in the solvent and vapour pressures are plotted vs temperatures, then a curve CD is obtained. This curve is lower than the curve AB because vapour pressures of solution are less than those of pure solvent. Solution will boil at higher temperature T_2 to equalize its pressure to p°. The difference of two boiling points gives the elevation of the boiling point ΔT_b.

The higher the concentration of solute, the greater will be the lowering in vapour pressure of solution and hence higher will be its boiling point. So, elevation of boiling point ΔT_b is directly proportional to the molality of solution.

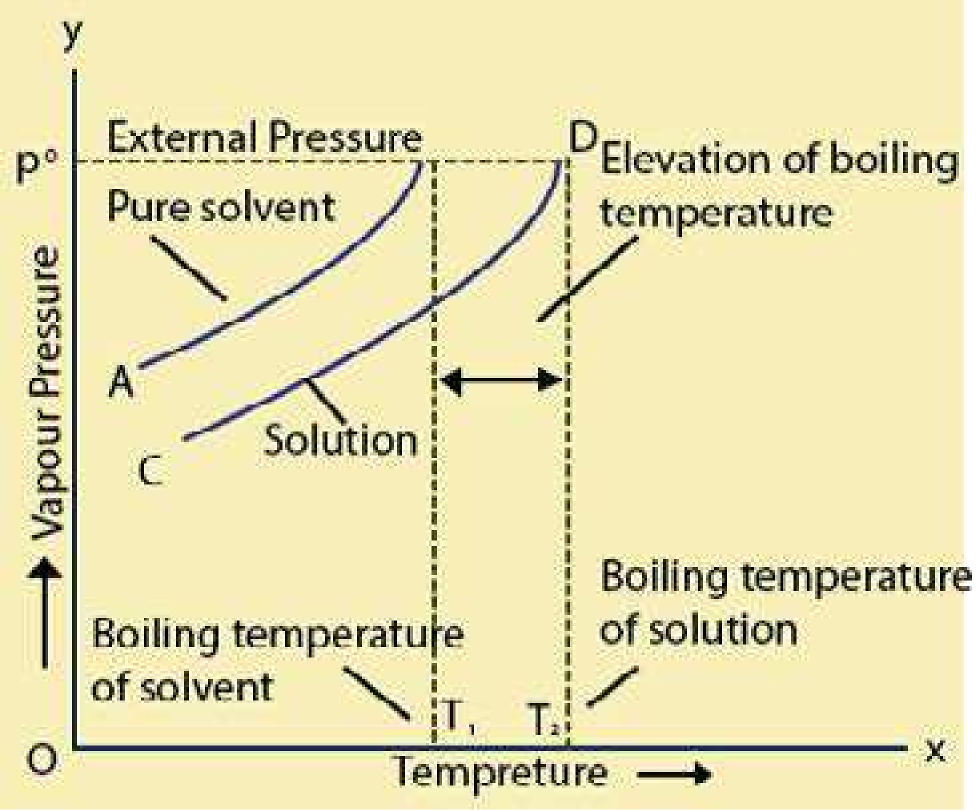


Fig (9.7) Elevation of boiling temperature curve

$$\Delta T_b = K_b m \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

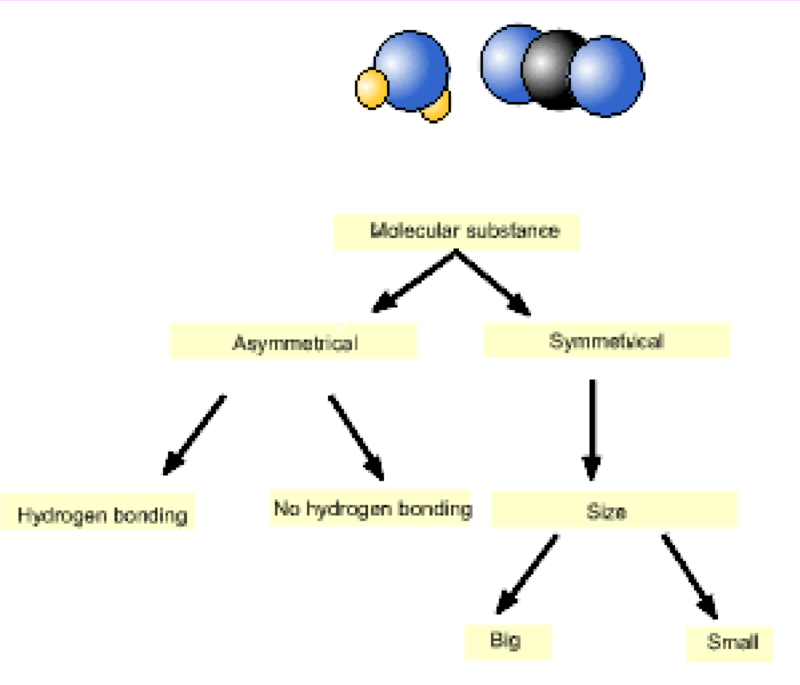
Where K_b is called the ebullioscopic constant or molal boiling point constant.

According to equation (8), molality of any solute determines the elevation of boiling point of a solvent. You may dissolve 6 g of urea in 500 g of H_2O or 18 g of glucose in 500 g of H_2O both give 0.2 molal solution and both have same elevation of boiling points i.e. 0.1 °C, which is 1/5th of 0.52°C. We say that ΔT_b (not T) is a colligative property. We know that

$$\text{Molality(m)} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \times \frac{1}{\text{Mass of solvent in kg}}$$

or

$$m = \frac{W_2}{M_2} \; \frac{1}{W_1/1000} = \frac{1000\,W_2}{M_2W_1} \qquad \text{..........} \quad (9)$$



Animation 9.20: Elevation of Boiling Point
Source & Credit: gif2fly

Putting the value of m from equation (9) into equation (8)

$$\Delta T_b = K_b \frac{1000\,W_2}{M_2W_1} \qquad \text{.........} \quad (10)$$

Rearranging equation (10)

$$\text{Molecular mass } (M_2) = \frac{K_b}{\Delta T_b} \times \frac{W_2}{W_1} \times 1000 \qquad \ldots\ldots\ldots\ldots \quad (11)$$

Equation (11) can be used to determine the molar mass of a non-volatile and nonelectrolyte solute in a volatile solvent.

9.6.4 Measurement of Boiling Point Elevation: Landsberger'S Method

This is one of the best methods for the measurement of boiling point elevation of a solution. The apparatus consists of four major parts.

(a) An inner tube with a hole in its side. This tube is graduated.

(b) A boiling flask which sends the solvent vapours into the graduated tube through a rosehead.

(c) An outer tube, which receives hot solvent vapours coming from the side hole of the inner tube.

(d) A thermometer which can read up to 0.01K.

The solvent is placed in the inner tube. Some solvent is also taken in a separate flask and its vapours are sent into this tube. These vapours cause the solvent in the tube to boil by its latent heat of condensation. This temperature is noted which is the boiling point of the pure solvent.

The supply of the vapours is temporarily cut off and a weighed pellet of the solute is dropped in the inner tube. The vapours of the solvent are again passed through it until the solution is boiled. This temperature is again noted. Fig (9.8).

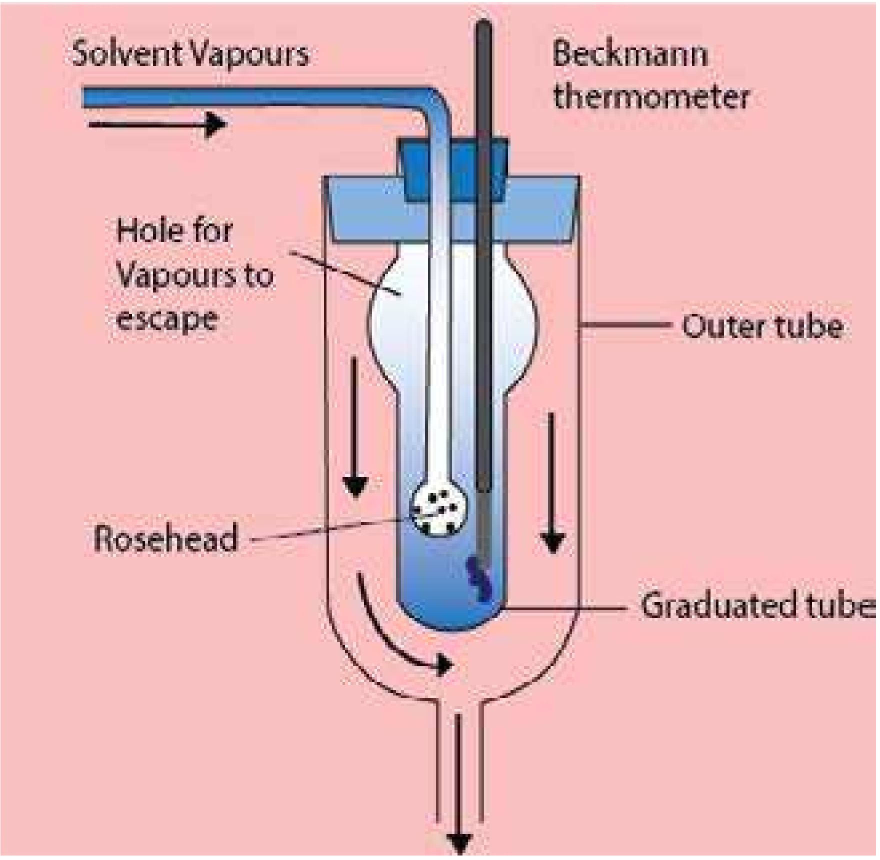


Fig (9.8) Landsberger method for measurement of elevation of boiling point

Now, the supply of the solvent vapours is cut off. The thermometer and the rosehead are removed and the volume of the solution is measured. The difference of the two boiling points gives the value of ΔT_b. The following formula is used to calculate the molecular mass of solute.

$$M_2 = \frac{K_b}{\Delta T_b} \frac{1000\ W_2}{W_1} \qquad \text{............} \quad (11)$$

Example 11:

The boiling point of water is 99.725 °C. To a sample of 600g of water are added 24.0 g of a solute having molecular mass of 58 g mol^{-1}, to form a solution. Calculate the boiling point of the solution.

Solution

Boiling point of pure H_2O =99.725°C

Mass of solvent (H_2O) W_1 =600 g

Mass of solute (W_2) =24.00 g

Molar mass of solute (M_2) =58 g mol^{-1}

The molal boiling point constant of H_2O (K_b) =0.52°C

Formula

$$\Delta T_b = K_b x \frac{1000\ W_2}{W_1\ x\ M_2}$$

$$= \frac{0.52\ x\ 1000\ x\ 24.00}{600\ x\ 58} = 0.358^{o}C$$

Boiling point of solution = boilingpoint of pure solvent + elevation of boiling point

$$=99.725 + 0.358 = \boxed{100.083^{o}C}\ \text{Answer}$$

9.6.5 Depression of the Freezing Point of a Solvent by a Solute

The freezing point of a substance is the temperature at which the solid and liquid phases of the substance co-exist. Freezing point is also defined as that temperature at which its solid and liquid phases have the same vapour pressures. When a non-volatile solute is added to a solvent, its vapour pressure is decreased. At the freezing point, there are two things in the vessel i.e. liquid solution and the solid solvent. The solution will freeze at that temperature at which the vapour pressures of both liquid solution and solid solvent are same. It means that a solution should freeze at lower temperature than pure solvent.

In order to understand it, plot a graph between vapour pressure temperature for pure solvent and that of solution. The curve ABC is for the pure solvent. The solvent freezes at temperature T_1 corresponding to the point B when the vapour pressure of freezing solvent is p°. The portion of the curve BC is for the solid solvent. This portion has a greater slop, showing that the change of vapour pressure with the change of temperature is more rapid Fig (9.9).

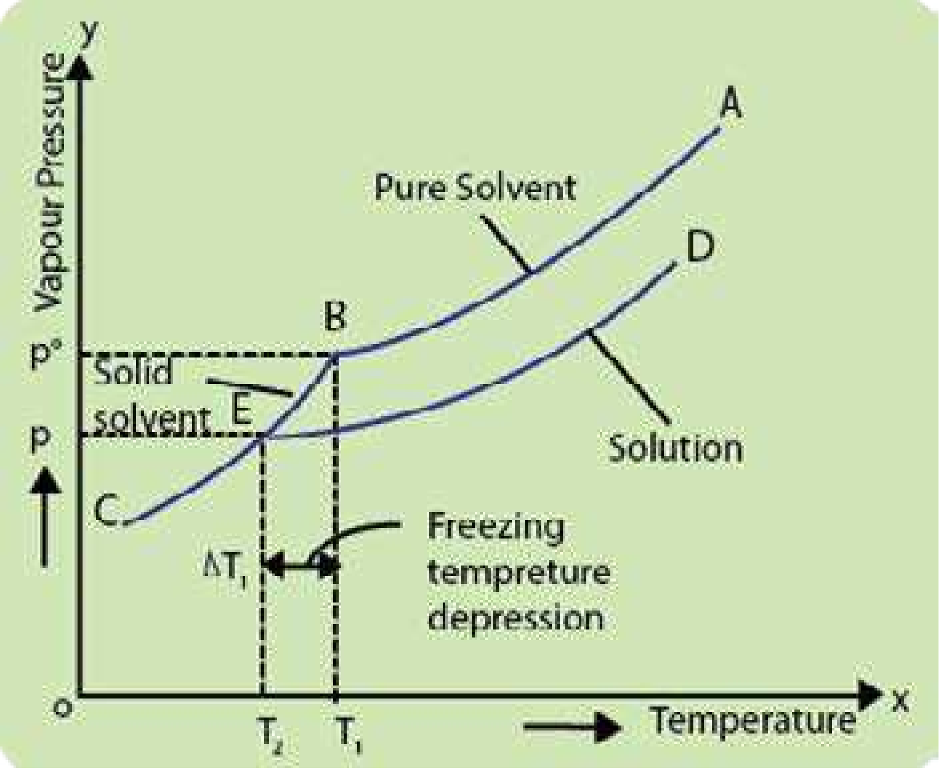


Fig (9.9) Depression of freezing point curve

The curve DEC for the solution will meet the curve BC at the point E. This is the freezing point of solution T_2, and corresponds to the vapour pressure p which is lower than p°. The reason is that vapour pressure of solution is less than the pure solvent.

Sensor Name	Units	Calib. Type	Calib. Date	Average	DAC setting	Interface
Auxiliary	Celsius	2pt Steinha...	—	Avg8	1000	LW II rev I
Color	%T	2pt linear	—	Avg1	1000	LW II rev I
Conductivity	mhos	2pt linear	—	Avg1	—	LW II rev I
Constant	—	none	—	Avg1	—	LW II rev I
Counter	—	none	—	Avg1	—	LW II rev I
DAC	mV	factory	—	Avg1	—	LW II rev I
DigitalOut	—	none	—	Avg1	—	LW II rev I
Diss Oxygen	—	2pt linear	—	Avg1	—	LW II rev I
I	uA	factory	—	Avg1	—	LW II rev I
IProbe	—	2pt linear	—	Avg1	1000	LW II rev I
Kelvin	—	2pt linear	—	Avg1	—	LW II rev I
Keyboard	—	none	—	Avg1	—	LW II rev I
Light	—	2pt linear	—	Avg1	1000	LW II rev I
Memory	—	none	—	Avg1	—	LW II rev I
mV	mV	factory	—	Avg1	—	LW II rev I
mVProbe	—	2pt linear	—	Avg1	—	LW II rev I

Animation 9.21: Depression of the Freezing Point of a Solvent by a Solute
Source & Credit: cod

Depression of freezing point = freezing point of pure solvent - freezing point of solution.

So, $\Delta T_f = T_1 - T_2$

This depression in freezing point ΔT_f is related to the molality (m) of the solution. The relationship is similar to that of elevation of the boiling point.

$$\Delta T_f \propto m$$

$$\Delta T_f = K_f m \qquad .... \qquad (12)$$

K_f is called the molal freezing point constant or the cryoscopic constant and m is the molality of the solution. To get the final expression, let us put the following expression (9) of molality into the equation (12) i.e.

$$m = \frac{1000\ W_2}{M_2 x W_1} \qquad .... \qquad (9)$$

We get $$\Delta T_f = K_f \frac{1000\ W_2}{M_2 x W_1} \qquad .... \qquad (13)$$

Where W_2= mass of solute and M_2= molar mass of the solute, W_1= mass of solvent in kg Rearranging equation (13)

$$\text{Molar mass of solute } (M_2) = \frac{K_f}{\Delta T_f} \frac{1000\ W_2}{W_1} \qquad .... \qquad (14)$$

9.6.6 Measurement of Freezing Point Depression Beckmann's Freezing Point Apparatus:

There are many methods but Beckmann's method is easy to perform The apparatus consists of three major parts. Fig.(9.10).

a. A freezing tube with a side arm. It contains solvent or solution and is fitted with a stirrer and a Beckmann's thermometer.

b. An outer larger tube into which the freezing tube is adjusted. The air jacket in between these tubes help to achieve a slower and more uniform rate of cooling.

c. A large jar containing a freezing mixture. Around 20 to 25g of the solvent is taken in the freezing tube. The bulb of the thermometer, is immersed in the solvent. First of all, approximate freezing point of the solvent is measured by directly cooling the freezing point tube in the freezing mixture.

The freezing tube is then put in the air jacket and cooled slowly. In this way, accurate freezing point of the solvent is determined. Now, the solvent is re-melted by removing the tube from the bath and weighed amount of 0.2 to 0.3 g of the solute is introduced in the side tube.

The freezing point of the solution is determined while stirring the solution. The difference of the two freezing points gives the value of ΔT_f and the following formula is used to calculate the molar mass of solute.

$$M_2 = \frac{K_f}{\Delta T_f} \frac{1000\ W_2}{W_1} \quad \ldots\ldots\ldots \quad (14)$$

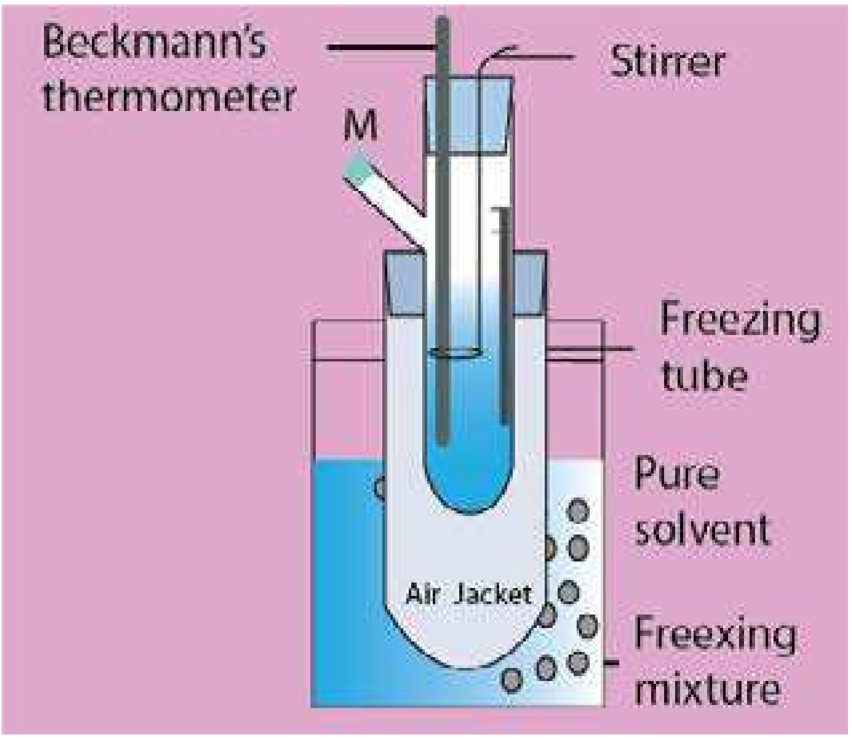


Fig (9.10) Beckmann's freezing point apparatus

Example 12:

The freezing point of pure camphor is 178.4°C. Find the freezing point of a solution containing 2.0 g of a non-volatile compound, having molecular mass 140, in 40g of camphor. The molal freezing point constant of camphor is 37.7 °C kg mol^{-1}.

Solution:

Freezing point of camphor = 178.4 °C
Mass of solute (W_2) =2.00g
Mass of solvent (W_1) = 40 g
Molar mass of solute (M_2) = 140
Molal freezing point constant of solvent = 37.7° C kg mol^{-1}.
Freezing point of solution = ?
Applying the equation

$$\Delta T_f = K_f \frac{1000\ W_2}{W_1\ x\ M_2}$$

We have to calculate, the freezing point of solution, so first we get the depression in freezig point ΔT_f then subtract it from freezing point of pure solvent.

$$\Delta T_f = \frac{37.7\ x\ 1000\ x\ 2}{40\ x\ 140} = 13.46^oC$$

Freezing point of solution $= 178.4 - 13.4 = \boxed{164.94^oC}$ Answer

9.6.7 Applications of Boiling Point Elevation and Freezing Point Depression Phenomena

Apart from the molecular mass determination, the presence of a solute increases the liquid range of the solution both by raising the boiling point and lowering the freezing point. The most important application of this phenomenon is the use of an antifreeze in the radiator of an'automobile. The solute is ethylene glycol, which is not only completely miscible with water but has a very low vapour pressure and non-volatile in character. When mixed with water, it lowers the freezing point as well as raises the boiling point.

During winter it protects a car by preventing the liquid in the radiator from freezing, as water alone, if it were used instead. In hot summer, the antifreeze solution also protects the radiator from boiling over.

Another, common application is the use of NaCl or KNO_3 to lower the melting point of ice. One can prepare a freezing mixture for use in an ice cream machine.

Animation 9.22: Applications of Boiling Point Elevation and Freezing Point Depression Phenomena
Source & Credit: lifestyle

9.7.0 ENERGETICS OF SOLUTION

In a solution, the distances between solute and solvent molecules or ions increase somewhat as compared with their pure states. This increase in the distance of solvent molecules requires energy to overcome the cohesive intermolecular forces. Hence, it is an endothermic process. Similarly, the separation of solute molecules also needs energy so it is also an endothermic process. The intermixing of solute with solvent molecules is to establish new intermolecular forces between unlike molecules. It releases energy and thus is an exothermic phenomenon. The strengths of the two type of forces will decide whether the process of dissolution will be endothermic or exothermic.

Thus, the process of dissolution occurs with either an absorption or release of energy. This is due to breakage and re-establishment of intermolecular forces of attraction between solute and solvent molecules.

When potassium nitrate is dissolved in water, the temperature of the solution decreases. It shows it to be an endothermic process. The solution of lithium chloride in water produces heat, showing that the process of dissolution is exothermic. The quantity of heat energy, that is absorbed or released when a substance forms solution, is termed as heat of solution.

So, the enthalpy or heat of solution of a substance is defined as the heat change when one mole of the substance is dissolved in a specified number of moles of solvent at a given temperature. It is given the symbol ΔH_{solu}. The ΔH_{solu} gives the difference between the energy possessed by the solution after its formation and the original energy of the components before their mixing i.e.

$$\Delta H_{solu} = H_{solution} - H_{components}$$

Here, ΔH_{solu} is the energy content of solution after its formation, while $H_{components}$ represents the energy contents of components before their mixing. However, both these factors can not actually be measured, only their difference i.e. the change ΔH_{solu} is practically measurable. If the value of ΔH_{solu} is negative, it would mean that the solution is having less energy than the components from which it was made, hence the dissolution process is an exothermic one. On the other hand, an endothermic process would have a positive ΔH_{solu} value. In Table (9.4) are given values of heats of solution of different ionic solids in water at infinite dilution.

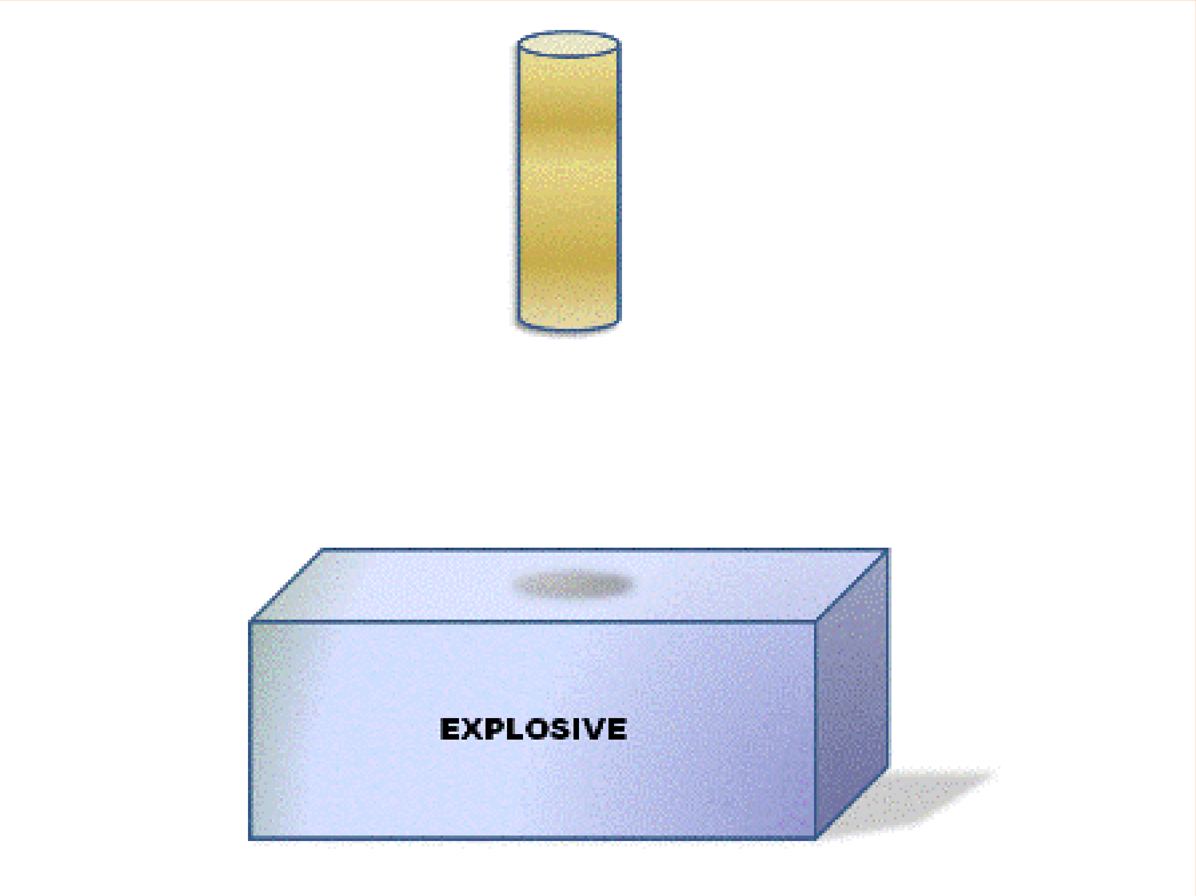
Table (9.4) Heats of solution of some ionic solids

Substance	Heats of solution (kJ mol^{-1})
NaCl	4.98
NH_4NO_3	26.0
KCl	17.8
KI	21.4
NH_4Cl	16.2
LiCl	-35.0
Li_2CO_3	-12.8

The magnitude of heat of solution gives information regarding the strength of intermolecular forces of attraction between components which mix to form a solution.

When one mole of sodium chloride (58.5g) is dissolved in 10 moles of water (180g), then 2.008 kJ of energy is absorbed.

$$NaCl + 10H_2O \rightarrow NaCl\,(10H_2O) \quad \Delta H = +2.008 kJ.$$



Animation 9.23: ENERGETICS OF SOLUTION
Source & Credit: ntu

9.7.1 Hydration Energy of Ions

When an ionic compound, say potassium iodide is dissolved in water, the first step, is the separation of K^+ and I ions from solid. In the second step, these separated ions are surrounded by solvent molecules. The first step breaks the lattice to separate the ions.

Since, energy is required to accomplish this step, so this step is endothermic. The amount of energy needed to separate a crystalline compound into isolated ions (or atoms) is known as lattice energy. The lattice energy of ionic solids is always higher than molecular solids.

Table (9.5) Hydration energies of common ions

Ion	ΔH^0 (ionmole^{-1})
H^+	-1075
Li^+	-499
Na^+	-390
Ag^+	-464
K^+	-305
Mg^{2+}	-1891
Cu^{2+}	-1562
NH_4^+	-281
F^-	-457
Cl^-	-384
Br^-	-351
OH^-	-460

In the second step, the ions are brought into water and get hydrated (solvated) Fig (9.11). A hydrated ion is attracted by the solvent dipoles and energy is released, so this step is exothermic. The energy given out by this step is known as the hydration energy (or solvation energy).

$$K^+ + I^- + xH_2O \rightarrow K^+(aq) + I^-(aq)$$

The final equation will be as follows:

$$KI(s) + xH_2O \rightarrow K^+(aq) + I^-(aq)$$

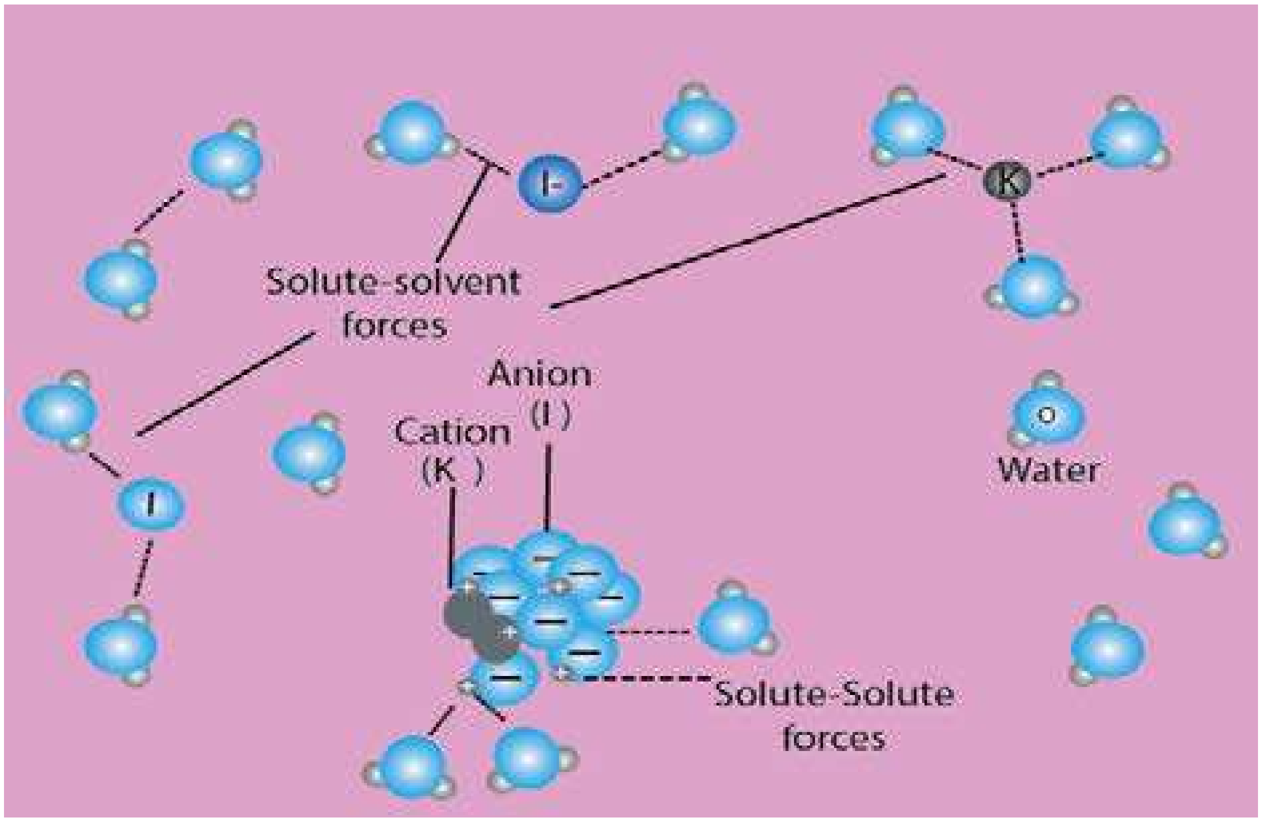
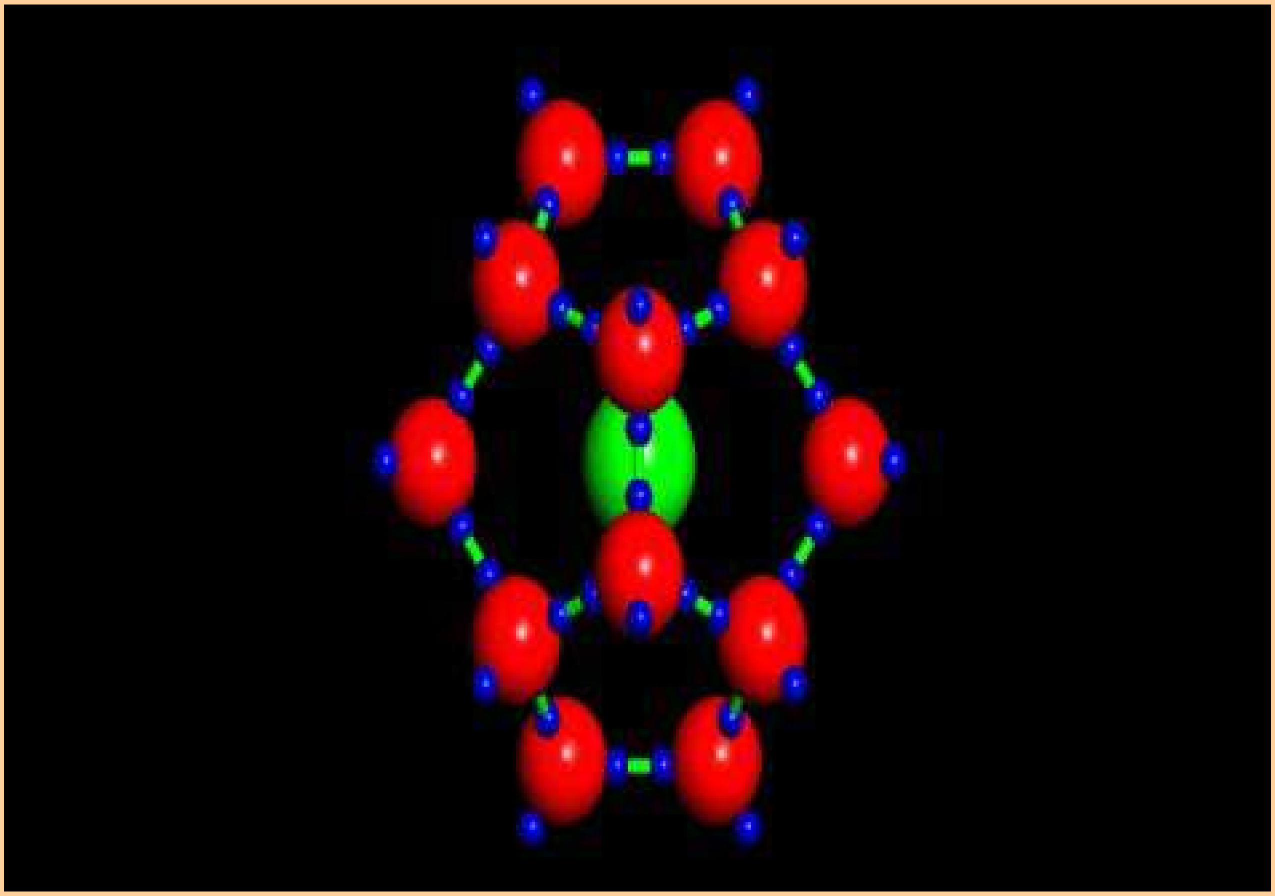


Fig (9.11) Interaction between water molecules and cations and anions provide the energy- necessary to overcome both the intermolecular forces between water molecules and the ionic bond in a potassium iodide

The values of hydration energies of individual ions, i.e. cations and anions are given in Table (9.5). It is interesting to compare these values with the ionic radii of the ions. Greater the size of monovalent cation, lesser is the heat of hydration. Divalent and trivalent cations have higher values due to high charge densities. Anions also show a definite trend of heat of hydration, depending upon their sizes.

On diluting a concentrated solution, there is a further heat change. This heat change depends on the amount of water used for dilution. The heat of dilution gradually decreases, so that eventually increasing the dilution produces no further heat change. This occurs when there are 800-1000 moles of water to one mole of solute. This stage is called infinite dilution and the heat of solution is expressed as:

$$\mathrm{NaCl(s)} + \mathrm{H_2O} \rightarrow \mathrm{NaCl(aq)} \square \quad \mathrm{Na^+(aq)} + \mathrm{Cl^-(aq)} \qquad \Delta H_{soln} = +\,4.98\,\mathrm{kJ\ mol^{-1}}$$



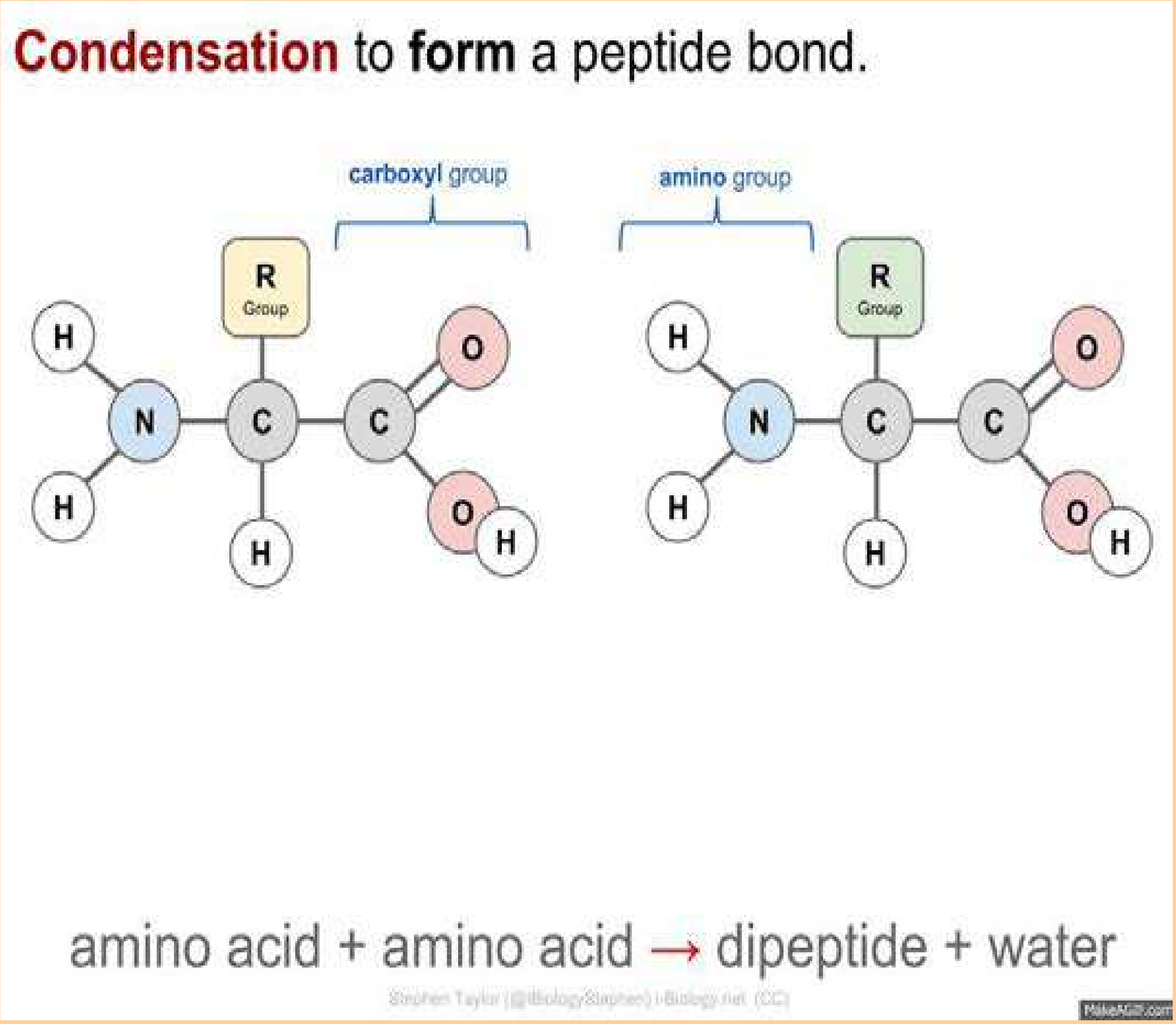
Animation 9.24: Hydration Energy of Ions
Source & Credit: arizona

9.8 HYDRATION AND HYDROLYSIS

9.8.1 Hydration

When ionic compounds are dissolved in water, they are dissociated into ions. Negative ions are surrounded by water molecules. The partial positively charged hydrogen atoms of water surround and attract the anions with electrostatic forces of attraction. Similarly positive ions of solute create attractions with partial negative oxygen atoms of water molecules. In this way, all the ions in the aqueous solution are hydrated.

The process in which water molecules surround and interact with solute ions or molecules is called hydration.

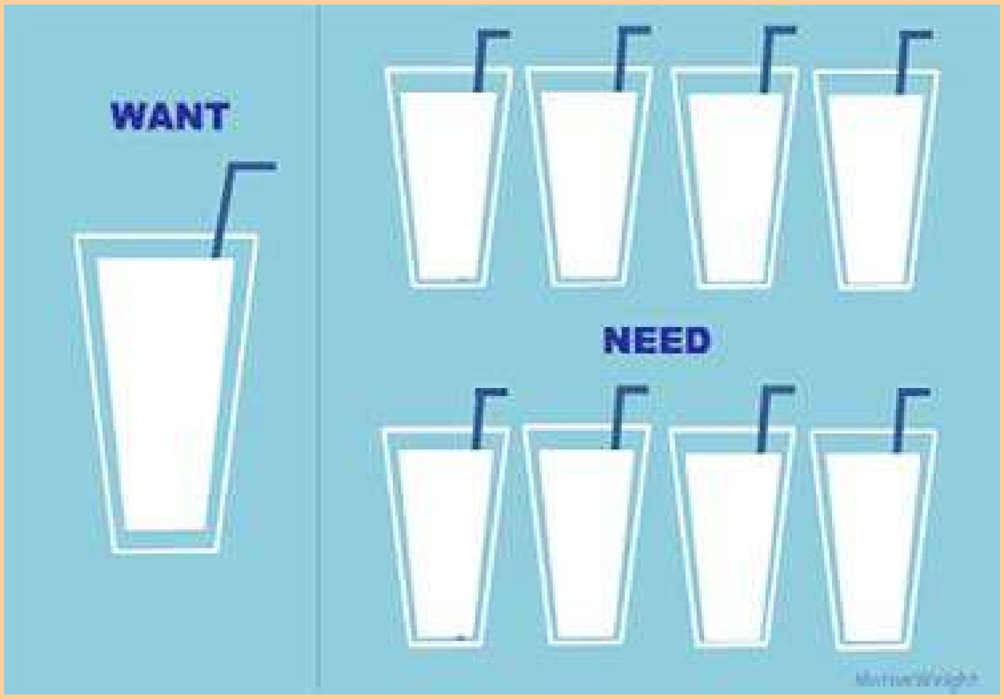


Condensation to **form** a peptide bond.

amino acid + amino acid → dipeptide + water

Animation 9.25: HYDRATION AND HYDROLYSIS
Source & Credit: i-biology.net

The ions, which are surrounded by water molecules, are called hydrated ions. The number of water molecules, which surround a given ion depends upon the size of the ions and the magnitude of its charge (charge/area). If the size of the ion is small and is highly charged positive ion, it has high charge density. Hence, greater number of water molecules will surround it.

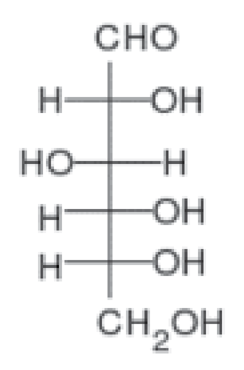


Animation 9.26: Hydration
Source & Credit: rebloggy

Negatively charged ions have low charge density, and have smaller number of water molecules surrounding them. Hence, the ion with high charge density has a greater ability to attract polar water molecules than ions with smaller charge density.

9.8.2 Hydrates

The crystalline substances, which contain chemically combined water in definite proportions is called a hydrate. Hydrates are mostly, produced when aqueous solution of soluble salt is evaporated. The formation of hydrates is not limited to salts but is common with acids, bases and elements. The water molecules are attached with cations in the hydrates. Anyhow, in $CuSO_4 .5H_20$, four water molecules, are attached with Cu^{2+} and one with SO_4^{2-}. The reason is that Cu^{2+} has a greater charge density. The size of Cu^{2+} is much smaller than SO_4^{2-}, which has same amount of charge.



Animation 9.27: Hydrates
Source & Credit: wikipedia

Water of Crystallization

Those water molecules, which combine with substances as they are crystallized from aqueous solutions, are called water of crystallization or water of hydration. Some familiar examples are as follows: $(COOH)_2.2H_2O$ (oxalic acid), $BaCl_2.2H_2O$, $Na_2CO_3.10H_2O$, $MgCl_2.6H_2O$, $Na_2B_4O_7.10H_2O$ (borax), $CaSO_4.2H_2O$ (gypsum), $MgSO_4.7H_2O$ (epsom salt) and $AlCl_3.6H_2O$.

9.8.3 Hydrolysis

When NaCl is dissolved in water, the resulting solution is neutral i.e. the concentration of each of H^+ and OH^- ions are equal to 10^{-7} M, as in pure water. But this balance between H^+ and OH^- ions can be disturbed with resulting change in the pH of solution when other salts are dissolved in water.

It is commonly, observed that different salts, upon dissolving in water, do not always form neutral solutions. For example, NH_4Cl, $AlCl_3$, $CuSO_4$ give acidic solutions in water. On the other hand, Na_2CO_3 and CH_3COONa form basic solutions in water. These interactions between salts and water are called hydrolytic reactions and the phenomenon is known as hydrolysis.It involves the reactions of the ions of different salts to give acidic or basic solutions. It is the decomposition of compounds with water, in which water itself is decomposed.

The hydrolysis of the salts mentioned above are shown as follows:

$$NH_4Cl + H_2O \rightleftharpoons NH_4OH + H^+ + Cl^-$$

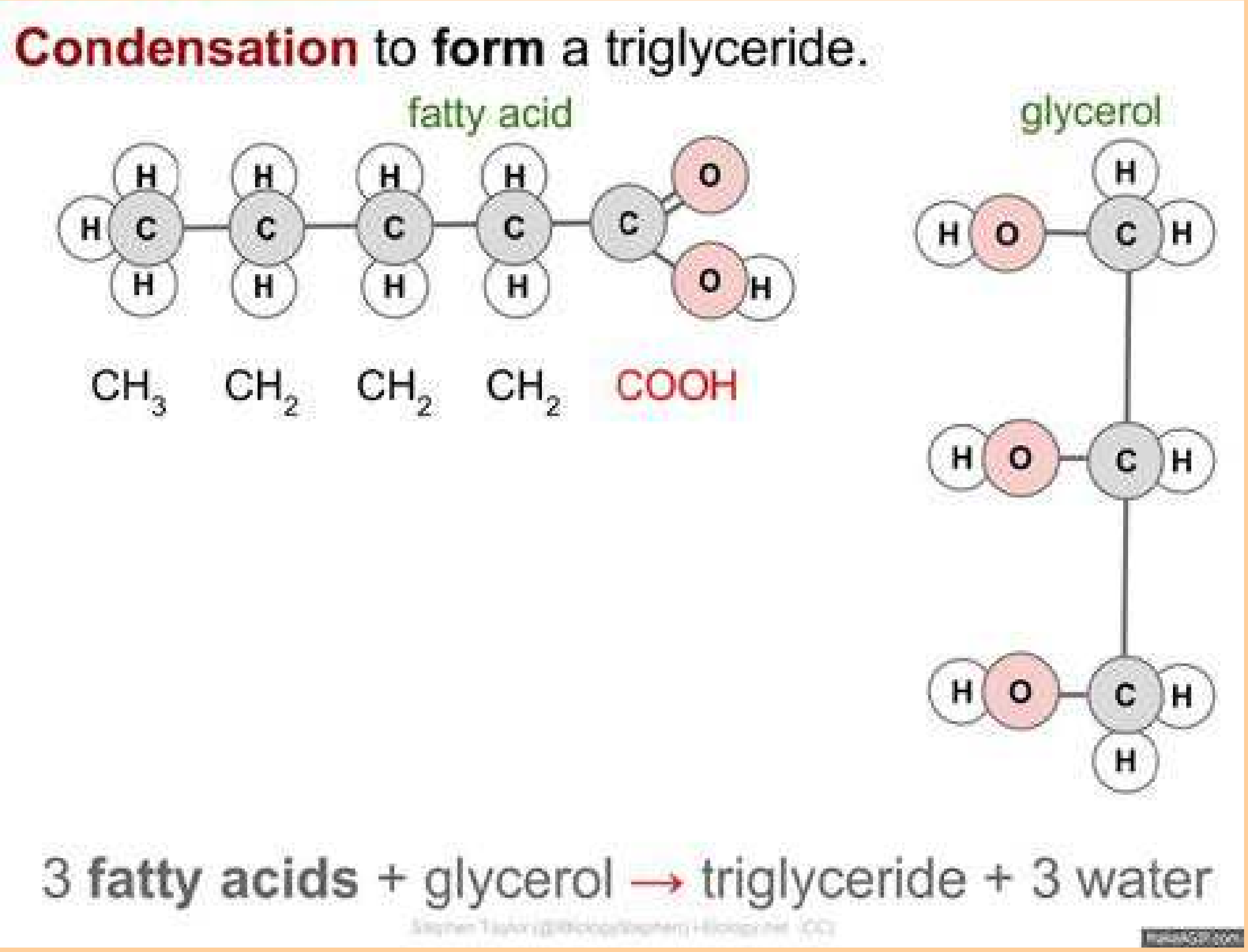
$$AlCl_3 + 3H_2O \rightleftharpoons Al(OH)_3 + 3H^+ + 3Cl^-$$

$$CuSO_4 + 2H_2O \rightleftharpoons Cu(OH)_2 + 2H^+ + SO_4^{2-}$$

These hydrolytic reactions, produce weak bases $Al(OH)_3$, NH_4OH and $Cu(OH)_2$. But, Cl^- and SO_4^{2-} are weak conjugate bases of HCl and H_2SO_4. They are not hydrolysed in water. H^+ ions remain free in solution and so their solution are acidic in character.

The K_a values of HCl and H_2SO_4 are very high as compared to K_b values of $Al(OH)_3$, NH_4OH and $Cu(OH)_2$. For CH_3COONa the reaction with water is

$$CH_3COONa + H_2O \rightleftharpoons CH_3COOH + Na^+ + OH^-$$



Animation 9.28: Hydrolysis
Source & Credit: i-biology.net

The acetate ion is hydrolyzed in water to give CH_3COOH and OH^- becomes free. Na^+ is not hydrolysed.

The result is that the solution becomes basic in nature. .Similarly, Na_3PO_4, Na_3AsO_4 etc give basic solutions in water due to the formation of a Na^+ ,OH^- and weak acids Na_3PO_4 and H_3AsO_4, which are least dissociated. The dissolution of KCl, Na_2SO_4, KBr, etc in water give neutral solutions. Because these salts are not hydrolysed in water. Their positive ions K^+, Na^+ are not hydrolysed by water. Similarly, their negative ions Cl^-, Br^-, SO_4^{2-} are also not hydrolysed. It means that the salts of strong bases and strong acids are not hydrolysed by water.

Anyhow, the salts derived from weak acids and weak bases may not give neutral solutions. It depends upon the pK_a and pK_b values of acid and base produced.

KEY POINTS

1. A solution, on average, is a homogeneous mixture of two or more kinds of different molecular or ionic substances. The substance, which is present in a large quantity is called a solvent and the other in small quantity is, called a solute.
2. Solutions containing relatively lower concentrations of solute are called dilute solutions, whereas those containing relatively higher concentrations of solutes are called concentrated solutions. Solubility is the concentration of a solute in a solution, when the solution is at equilibrium with the solute at a particular temperature.
3. The concentration of a solution may be expressed in a number of ways. i) percentage composition, ii) molarity, iii) molality, iv) mole fraction, v) parts per million.
4. Solutions may be ideal or non-ideal. Those solutions, which obey Raoult's law are ideal solutions. Raoult's law tells us that the lowering of vapour pressure of a solvent by a solute, at a constant temperature, is directly proportional to the concentration of solute.
5. Many solutions do not behave ideally, as they show deviations from Raoult's law. A solution may show positive or negative deviation from Raoult's law. Such liquid mixtures, which distill without change in composition, are called azeotropic mixtures.
6. Colligative properties of a solution are those properties, which depend on the number of solute and solvent molecules or ions and are independent of the nature of solute. Lowering of vapour pressure, elevation of boiling point and depression of freezing point and osmotic pressure are the important colligative properties of solutions.
7. Elevation of boiling point of a solvent in one molal solution is called molal boiling point constant or ebullioscopic constant. Depression of freezing point of a solvent in one molal solution is called molal freezing point constant or cryoscopic constant.
8. The enthalpy or heat of solution of a substance is the heat change when one mole of the substance is dissolved in a specified number of moles of solvent at a given temperature.
9. The process in which water molecules surround and interact with solute ions or molecules is called hydration. The crystalline substances, which contain molecules of water in their crystal lattices, are called hydrates. They are mostly produced, when aqueous solutions of soluble alts are evaporated.
10. Salts of weak acids with strong bases react with water to produce basic solutions, whereas salts of weak bases with strong acids react to give acidic solutions. Such reactions are called hydrolytic reactions, and the salts are said to be hydrolysed. Salts of strong acids and strong bases do not hydrolyse and give neutral solution.

EXERCISE

Q 1. Choose the correct answer for the given ones.

i) Molarity of pure water is

(a) 1 (b) 18 (c) 55.5 (d) 6

ii) 18 g glucose is dissolved in 90 g of water. The relative lowering of vapour pressure is equal to

(a) 1/5 (b) 5.1 (c) 1/51 (d) 6

iii) A solution of glucose is 10% w/v. The volume in which 1 g mole of it is dissolved will be

(a) 1dm^3 (b) 1.8dm^3 (c) 200cm^3 (d) 900cm^3

iv) An aqueous solution of ethanol in water may have vapour pressure

(a) equal to that of water (b) equal to that of ethanol

(c) more than that of water (d) less than that of water

v) An azeotropic mixture of two liquids boils at a lower temperature than either of them when:

(a) it is saturated

(b) it shows positive deviation from Raoult's law

(c) it shows negative deviation from Raoult's law

(d) it is metastabl

(vi) In azeotropic mixture showing positive deviation from Raoult's law, the volume of the mixture is

(a) slightly more than the total volume of the components

(b) slightly less than the total volume of the components

(c) equal to the total volume of the components

(d) none of these

(vii) Which of the following solutions has the highest boiling'point?

(a) 5.85 % solution of sodium chloride (b) 18.0 % solution of glucose

(c) 6.0 % solution of urea (d) All have the same boiling point

(viii) Two solutions of NaCl and KCl are prepared separately by dissolving same amount of the solute in water. Which of the following statements is true for these solutions?

(a) KCl solution will have higher boiling point than NaCl solution

(b) Both the solutions have different boiling points

(c) KCl and NaCl solutions possess same vapour pressure

(d) KCl solution possesses lower freezing point than NaCl solution

(ix) The molal boiling point constant is the ratio of the elevation in boiling point to

(a) molarity (b) molality

(c) mole fraction of solvent (d) mole fraction of solute

(x) Colligative properties are the properties of

(a) dilute solutions which behave as nearly ideal solutions

(b) concentrated solutions which behave as nearly non-ideal solutions

(c) both (i) and (ii)

d) neither (i) nor (ii)

Q 2. Fill in the blanks with suitable words

(i) Number of molecules of sugar in 1 dm^3 of 1M sugar solution is______ .

(ii) 100g of a 10% aqueous solution of NaOH contains 10g of NaOH in______ g of water.

(iii) When an azeotropic mixture is distilled, its ______ remains constant.

(iv) The molal freezing point constant is also known as____________ constant.

(v) The boiling point of an azeotropic solution of two liquids is lower than either of them because the solution shows___________ from Raoult's law.

(vi) Among equimolal aqueous solutions of NaCl, $BaCl_2$ and $FeCl_3$, the maximum depression in freezing point is shown by____________solution.

(vii) A solution of ethanol in water shows_________ deviations and gives azeotropic solution with________ boiling point than other components.

(viii) Colligative properties are used to calculate____________ of a compound.

(ix) The hydration energy of Br^- ion is__________ than that of F^- ion.

(x) The acqueous solution of NH_4Cl is______ while that of Na_2SO_4 is_____.

Q 3. Indicate True or False from the given statements

(i) At a definite temperature the amount of a solute in a given saturated solution is fixed.

(ii) Polar solvents readily dissolve non-polar covalent compounds.

(iii) The solubility of a substance decreases with increase in temperature, if the heat of a solution is negative.

(iv) The rate of evaporation of a liquid is inversely proportional to the intermolecular forces of attraction.

(v) The molecular mass of an electrolyte determined by lowering of vapour pressure is less than the theoretical molecular mass.

(vi) Boiling point elevation is directly proportional to the molality of the solution and inversely proportional to boiling point of solvent.

(vii) All solutions containing 1g of non-volatile non-electrolyte solutes in some solvent will have the same freezing point.

(viii) The freezing point of a 0.05 molal solution of a non-volatile non-electrolyte in water is -0.93 ^{0}C.

(ix) Hydration and hydrolysis are different process for Na_2SO_4.

(x) The hydration energy of an ion only depends upon its charge.

Q4. Define and explain the followings with one example in each case.

(a) A homogeneous phase
(b) A concentrated solution
(c) A solution of solid in a solid
(d) A consulate temperature
(e) A non-ideal solution
(f) Zeotropic solutions
(g) Heat of hydration
(h) Water of crystallization
(i) Azeotropic solution
(j) Conjugate solution

Q5. (a) What are the concentration units of solutions. Compare molar and molal solutions

(b) One has one molal solution of NaCl and one molal solution of glucose.
(i) Which solution has greater number of particles of solute?
(ii) Which solution has greater amount of the solvent?
(iii) How do we convert these concentrations into weight by weight percentage?

Q6. Explain the following with reasons

(i) The concentration in terms of molality is independent of temperature but molarity depends upon temperature.

(ii) The sum of mole fractions of all the components is always equal to unity for any solution.

iii) 100 g of 98 % H_2SO_4 has a volume of 54.34 cm^3 of H_2SO_4 .(Density = 1.84 g cm^{-3})

iv) Relative lowering of vapour pressure is independent of the temperature.

v) Colligative properties are obeyed when the solute is non-electrolyte, and also when the solutions are dilute.

vi) The total volume of the solution by mixing 100 cm^3 of water with 100 cm’^{3}of alcohol may not be equal to 200 cm^3. Justify it.

vii) One molal solution of urea, in water is dilute as compared to one molar solution of urea, but the number of particles of the solute is same. Justify it.

viii) Non-ideal solutions do not obey the Raoult’s law.

Q7. What are non ideal solutions? Discuss their types and give three example of each.

Q8.(a) Explain fractional distillation. Justify the two curves when composition is plotted against boiling point of solutions.

(b) The solutions showing positive and negative deviations cannot be fractionally distilled at their specific compositions. Explain it.

Q9(a) What are azeotropic mixtures? Explain them with the help of graphs?

(b) Explain the effect of temperature on phenol-water system.

Q10.(a) What are colligative properties? Why are they called so?

(b) What is the physical significance of K_b and K_f values of solvents?

Q 11. How do you explain that the lowering of vapour pressure is a colligative property? How do we measure the molar mass of a non volatile, non- electrolyte solute in a volatile solvent?

Q12. How do you justify that

(a) boiling points of the solvents increase due to the presence of solutes.

(b) freezing points are depressed due to the presence of solutes.

(c) the boiling point of one molal urea solution is 100.52 °C but the boiling point of two molal urea solution is less than 101.04°C.

(d) Beckmann's thermometer is used to note the depression in freezing point.

(e) in summer the antifreeze solutions protect the liquid of the radiator from boiling over.

(f) NaCl and KNO_3 are used to lower the melting point of ice.

Q13. What is Raoult's law. Give its three statements. How this law can help us to understand the ideality of a solution.

Q 14. Give graphical explanation for elevation of boiling point of a solution. Describe one method to determine the boiling point elevation of a solution.

Q 15. Freezing points of solutions are depressed when non-volatile solutes are present in volatile solvents. Justify it. Plot a graph to elaborate your answer. Also, give one method to record the depression of freezing point of a solution.

Q16. Discuss the energetics of solution. Justify the heats of solutions as exothermic and endothermic properties.

Q17.(a) Calculate the molarity of glucose solution when 9 g of it are dissolved in 250 cm^3 of solution.

(Ans: 0.2 mol dm^{-3})

(b) Calculate the mass of urea in 100 g of H_2O in 0.3 molal solution.

(Ans: 1.8g)

(c) Calculate the concentration of a solution in terms of molality, which is obtained by mixing 250 g of 20% solution of NaCl with 200 g of 40 % solution of NaCl.

(Ans: 6.94m)

Q18.(a) An aqueous solution of sucrose has been labeled as 1 molal. Find the mole fraction of the solute and the solvent.

(Ans: 0.0176, 0.9823)

(b) You are provided with 80% H_2SO_4 w/w having density 1.8 g cm^{-3} . How much volume of this H_2SO_4 sample is required to obtain one dm^3 o f 20% w/w H_2SO_4, which has a density o f 1.25 g cm^{-3}.

(Ans: 173.5cm1)

Q19. 250 cm^3 of 0.2 molar K_2SO_4 solution is mixed with 250 cm^3 of 0.2 molar KCl solution. Calculate the molar concentration of K^+ ions in the solution.

(Ans: 0.3 molar)

Q 20. 5g of NaCl are dissolved in 1000 g of water. The density of resulting solution is 0.997 g/cm^3. Calculate molality, molarity and mole fraction of this solution. Assume that the vol ume of the solution is equal to that of solvent.

(Ans: M = 0.08542, m = 0.0854, Mole fraction of NaCl= 0.00154, Mole fraction of H_2O =0.9984.)

Q 21. 4.675g of a compound with empirical formula C_3H_3O were dissolved in 212.5 g of pure benzene. The freezing point of solution, was found 1.02^{0}C less than that of pure benzene. The molal freezing point constant of benzene is 5.1^{0}C. Calculate (i) the relative molar mass and (ii) the molecular formula of the compound.

(Ans:110gmol^{-1}, $C_6H_6O_2$)

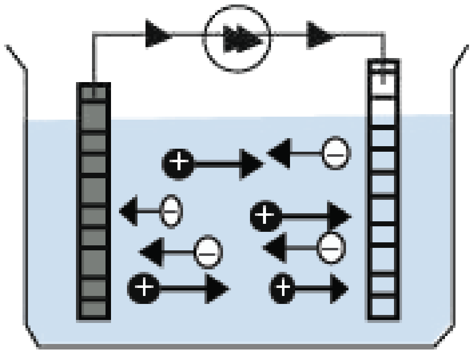
Q 22. The boiling point of a solution containing 0.2 g of a substance A in 20.0 g of ether (molar mass = 74) is 0.17 K higher than that of pure ether. Calculate the molar mass of A. Molal boiling point constant of ether is 2.16 K.

(Ans: 127gmol^{-1})

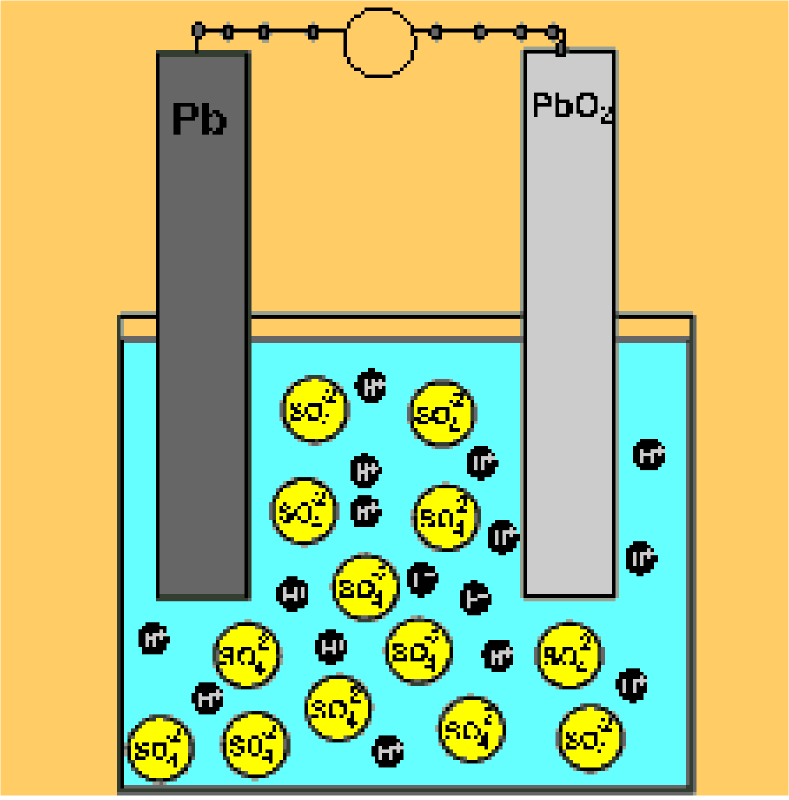
Q 23. 3 g of a non-volatile, non-electrolyte solute ‘X’ are dissolved in 50 g of ether (molar mass = 74) at 293 K. The vapour pressure of ether falls from 442 torr to 426 torr under these conditions. Calculate the molar mass of solute ‘X’.

(Ans: 122.6 g mol^{-1})

CHAPTER 10



ELECTROCHEMISTRY



Animation 10.1: ELECTROCHEMICAL CELLS
Source & Credit: dynamicscience

INTRODUCTION

Electrochemistry is concerned with the conversion of electrical energy into chemical energy in electrolytic cells as well as the conversion of chemical energy into electrical energy in galvanic or voltaic cells.

In an electrolytic cell, a process called electrolysis takes place. In this process electricity is passed through a solution or the fused state of electrolyte. The electricity provides sufficient energy to cause an otherwise non-spontaneous oxidation-reduction reaction to take place. A galvanic cell, on the other hand, provides a source of electricity. This source of electricity results from a spontaneous oxidation-reduction reaction taking place in the solution.

First of all, we should learn, the theoretical background of oxidation and reduction reaction and try to understand the balancing of equation.

Animation 10.2: ELECTROCHEMISTRY
Source & Credit : spiritsd

10.1 OXIDATION STATE AND BALANCING OF REDOX EQUATIONS

10.1.1 Oxidation Number or State

It is the apparent charge on an atom of an element in a molecule or an ion. It may be positive or negative or zero.

Rules for Assigning Oxidation Number

(i) The oxidation number of all elements in the free state is zero. This is often shown as a zero written on the symbol. For example, $\overset{o}{H}_2$, $\overset{o}{Na}$, $\overset{o}{Mg}$.

(ii) The oxidation number of an ion, consisting of a single element, is the same as the charge on the ion. For example, the oxidation number of K^+, Ca^{2+}, Al^{3+}, Br^-, S^{2-} are + 1, +2, +3, -1, -2, respectively.

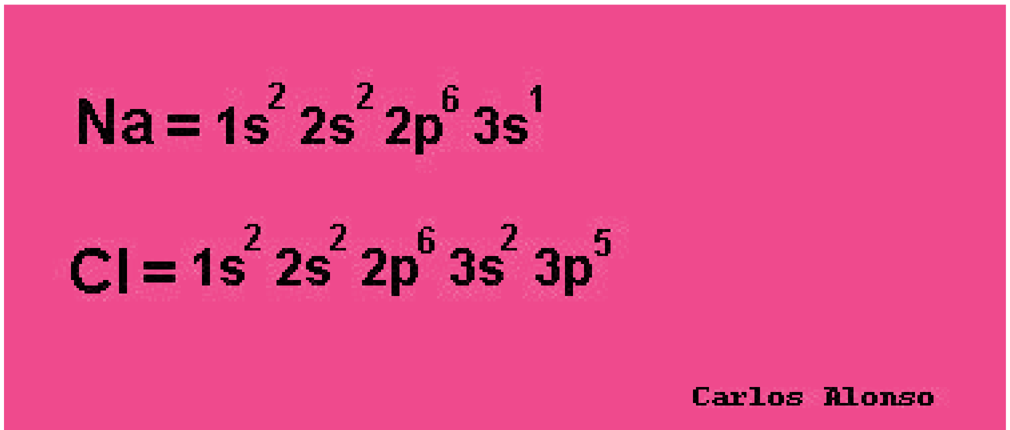
(iii) The oxidation number of hydrogen in all its compounds except metal hydrides is +1. In metal hydrides it is -1. (Na^+H^-, $Mg^{2+}H_2^{(-1)2}$)

(iv) The oxidation number of oxygen in all its compounds except in peroxides, OF_2 and in super oxides is -2. It is -1 in peroxides +2 in OF_2 and -1/2 in super oxides.

(v) In neutral molecules, the algebraic sum of the oxidation numbers of all the elements is zero.

(vi) In ions, the algebraic sum of oxidation number equals the charge on the ion.

(vii) In any substance the more electronegative atom has the negative oxidation number.



Animation 10.3: Oxidation Number
Source & Credit : alonsoformula

10.1.2 To Find Oxidation Number of an Element in a Compound or a Radical

The oxidation number or state of any atom of an element present in a compound or a radical can be determined by making use of the above said rules.

Example 1:

Calculate the oxidation number (O.N) of manganese in $KMnO_4$.

Solution

(Oxidation number of K) + (oxidation number of Mn)+4 (oxidation number of O) = 0

Where oxidation number of K = +1

oxidation number of O = -2

Let oxidation number of Mn = x

Putting these values in the above equation.

$$(+1) + x + 4(-2) = 0$$

or

$$x = +7$$

Thus the oxidation state of Mn in $KMnO_4$ is + 7.

Example 2:

Calculate the oxidation number (O.N) of sulphur in SO_4^{2-}.

Solution

$$
\begin{aligned}
[\text{oxidation number of S}] + 4[\text{oxidation number of O}] &= -2 \\
x + 4(-2) &= -2 \\
x &= +6
\end{aligned}
$$

Thus the oxidation number of sulphur in SO_4^{2-} is + 6 .

10.1.3 Balancing of Redox Equations by Oxidation Number Method

Carry out the following steps for balancing of redox equations by oxidation number method.

(i) Write down the skeleton equation of the redox reaction under consideration.

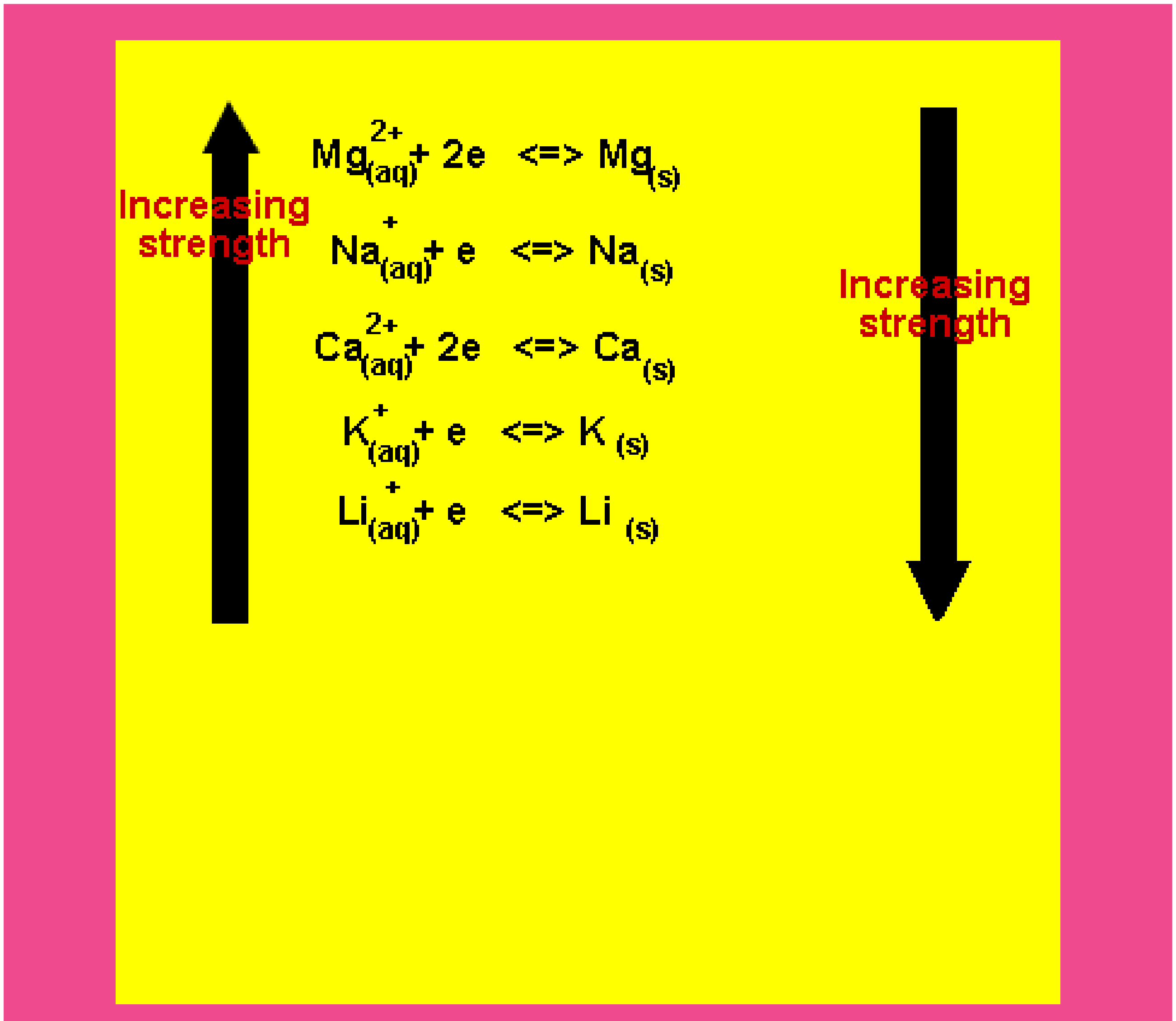
(ii) Identify the elements, which undergo a change in their oxidation number during the reaction.

(iii) Record the oxidation number above the symbols of the element, which have undergone a change in the oxidation number.

(iv) Indicate the change in oxidation number by arrows joining the atoms on both sides of the equation. It shows number of electrons gained or lost.

(v) Equate the increase or decrease in the oxidation number, i.e. electrons gained or lost by multiplying with a suitable digit.

(vi) Balance the rest of the equation by inspection method.



Animation 10.4: Redox reation
Source & Credit : dynamicscience

Example 3:

Balance the following equation by oxidation number method.

$$K_2Cr_2O_7 + HCl \rightarrow KCl + CrCl_3 + Cl_2 + H_2O$$

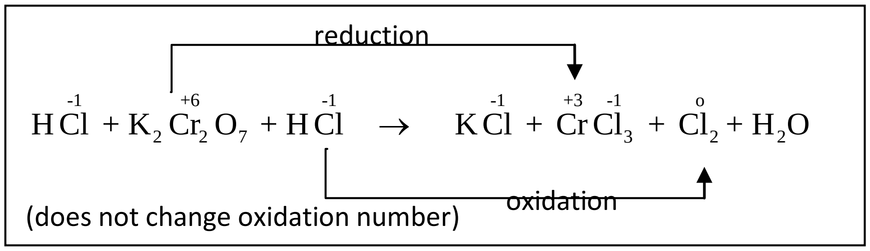
Solution

Let us balance the equation stepwise:

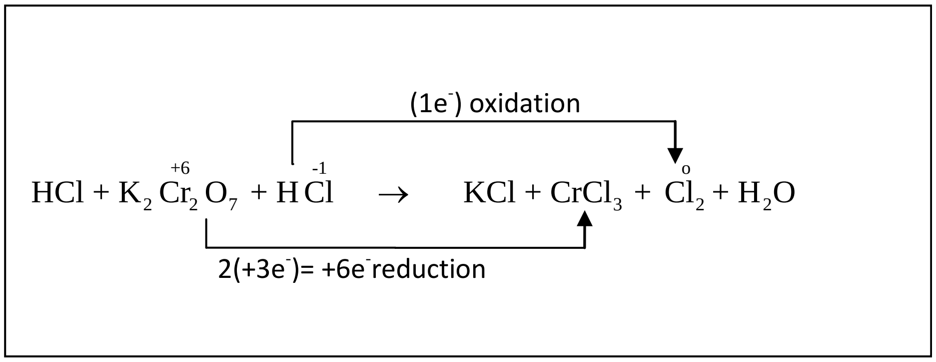
1. Write the equation with the oxidation number of each element

$$\overset{(+1)2}{K_2}\,\overset{(+6)2}{Cr_2}\,\overset{(-2)7}{O_7} + \overset{+1}{H}\,\overset{-1}{Cl} \rightarrow \overset{+1}{K}\,\overset{-1}{Cl} + \overset{+3}{Cr}\,\overset{(-1)3}{Cl_3} + Cl_2^{o} + \overset{(+1)2}{H_2}\,\overset{-2}{O}$$

2 . Identify, those elements whose oxidation numbers have changed. Equation shows that Cr goes from + 6 to +3 and it is reduced. Cl goes from -1 to zero and is oxidized. Moreover, the oxidation number of chlorine remains the same, i.e from -1 to -1 when KCl and $CrCl_3$ are produced. So, we should write HCl, twice on the left hand side. One of HCl on left side shows those Cl atoms which do not change their oxidation numbers Other HCl shows those Cl atoms which undergo a change in their oxidation numbers.



3. Draw the arrows between the same elements whose oxidation numbers have changed. Also, point out the change in oxidation number. Cr has changed its oxidation number from + 6 to + 3 and chlorine has changed from -1 to zero . It means 6 electrons have been gained by two Cr atoms and 1 electron has been lost by 1 chlorine atom.



4. In order to balance the number of electrons lost and gained multiply HCl with six. In this way, the 6 electrons lost by 6 Cl^- will be gained by $2Cr^{+6}$ to give $2Cr^{+3}$. But do not multiply other HCl molecules with anything at this moment.

$$HCl + K_2Cr_2O_7 + 6HCl \rightarrow KCl + CrCl_3 + Cl_2 + H_2O$$

5. Let us, balance Cr atoms by multiplying $CrCl_3$ by 2 . Balance Cl_2 on right hand side, whose oxidation number has changed by multiplying it with 3. In this way, the atoms which have been oxidized and reduced get balanced.

$$HCl + K_2Cr_2O_7 + 6HCl \rightarrow KCl + 2CrCl_3 + 3Cl_2 + H_2O$$

6 . To balance K atoms, multiply KCl by 2.

$$HCl + K_2Cr_2O_7 + 6HCl \rightarrow 2KCl + 2CrCl_3 + 3Cl_2 + H_2O$$

7. Now balance those atoms of chlorine which have not been oxidized or reduced. There are 8 such chlorine atoms on the right hand side with KC1 and $2CrCl_3$. So multiply HCl with eight. This HCl has produced KCl and $CrCl_3$.

$$8HCl + K_2Cr_2O_7 + 6HCl \rightarrow 2KCl + 2CrCl_3 + 3Cl_2 + H_2O$$

8 . Balance the rest of the equation by inspection method. To balance O atoms multiply H_2O with 7.

$$8HCl + K_2Cr_2O_7 + 6HCl \rightarrow 2KCl + 2CrCl_3 + 3Cl_2 + 7H_2O$$

or

$$K_2Cr_2O_7 + 14HCl \rightarrow 2KCl + 2CrCl_3 + 3Cl_2 + 7H_2O$$

This is the final balanced equation.

10.1.4 Balancing of Redox Equations by Ion-Electron Method

The balancing of redox equations by the loss and gain of electrons, usually involves quite a few ions, which do not undergo change in valence and which are not really necessary for the process of balancing. The ion-electron method eliminates all the unnecessary ions and retains only those, which are essential. Following, are the general rules for balancing the redox equations by ion-electron method.

1. Write a skeleton equation that shows only those substances that are actually involved in the reaction.
2. Split the equation into two half reactions, one showing oxidation half reaction and the other reduction half reaction.
3. The element should not be written as a free atom or ion unless it really exists as such. It should be written as a real molecular or ionic species.
4. Balance each partial equation as to the number of atoms of each element. In neutral or acidic solution, H_2O or H^+ ions may be added for balancing oxygen and hydrogen atoms. Oxygen atoms are balanced first. If the solution is alkaline, OH^- may be used for each excess oxygen on one side of the equation.
5. Balance each half reaction as to the number of charges by adding electrons to either the left or the right side of the equation.
6. Multiply each half reaction by a number chosen so that the total number of electrons lost by the reducing agent equals the number of electrons gained by the oxidizing agent
7. Add the two half reactions. Count the number of atoms of each element on each side of the equation and also check the net charge on each side, which should be equal on both sides.

Balancing of redox equations by ion-electron method, making use of the above rules. There are two types of such reactions Le. in acidic medium and basic medium. Now, let us discuss one example of each.

Example 4: (acidic medium)

Balance the equation for the reaction of HCl with $KMnO_4$ where Cl^- is oxidized to Cl_2 and MnO_4^- is reduced to Mn^{2+}. The skeleton equation which does not contain either H^+ or H_2O, is

Solution

$$Cl^- + MnO_4^- \rightarrow Cl_2 + Mn^{2+}$$

It is clear that Cl^- is oxidized to Cl_2 and MnO^{1-}_4 reduces to Mn^{2+}
Splitting the equation into half-reactions,
Oxidation half reaction

$$Cl^- \rightarrow Cl_2$$

Reduction half reaction

$$MnO_4^- \rightarrow Mn^{2+}$$

Balancing atoms on both sides of oxidation half reaction.

$$2Cl^- \rightarrow Cl_2 \qquad \text{.............} \qquad (1)$$

Now, balance the reduction half reaction. To balance O-atoms, add $4H_2O$ on R.H.S. and to balance H-atoms add $8H^+$ on L.H.S. The reason is that medium is acidic.

$$8H^+ + MnO_4^- \rightarrow Mn^{2+} + 4H_2O \qquad \text{.............} \qquad (2)$$

Balancing the charges by adding electrons in equation (1) and (2), we get (3) and (4).

$$2Cl^- \rightarrow Cl_2 + 2e^- \qquad \text{..............} \qquad (3)$$

$$8H^+ + MnO_4^- + 5e^- \rightarrow Mn^{2+} + 4H_2O \qquad \text{.........} \qquad (4)$$

For making the number of electrons lost in first equation equal to the number of electron gained in the second equation, multiply the first equation by 5 and second by 2. After adding both equations and cancelling the common species on both sides, balanced equation is obtained.

$$\begin{array}{ll} [2Cl^- & \rightarrow Cl_2 + 2e^-]x5 \\ [5e^- + 8H^+ + MnO_4^- & \rightarrow Mn^{2+} + 4H_2O]x2 \\ \hline 10Cl^- + 16H^+ + 2MnO_4^- & \rightarrow 5Cl_2 + 2Mn^{2+} + 8H_2O \end{array}$$

Example 5: (basic medium)

Balance the following equation in basic aqueous solution by ion-electron method.

$$MnO^{1-}_4(aq) + C_2O_4^{2-}(aq) + H_2O \rightarrow MnO_2(s) + CO_2(g) + OH^-(aq)$$

Solution

The following steps are involved in balancing of equation in basic aqueous solution by ion-electron method.

(i) Identify those elements, which undergo change in oxidation number by writing number above each element.

$$\overset{+7\;-8}{(MnO_4)^{1-}} + \overset{(+3)2\;-8}{(C_2O_4)^{2-}}\, \overset{+2\;-2}{H_2O} \rightarrow \overset{+4\;-4}{MnO_2} + \overset{+4\;-4}{CO_2} + \overset{-2\;+(1)}{(OH)^{1-}}$$

The elements undergoing a change in oxidation number are Mn and C.

(ii) Split the reaction into two half reactions, the oxidation and reduction half reactions.

$C_2O_4^{2-} \rightarrow CO_2$ (oxidation half reaction)

$MnO_4^{-1} \rightarrow MnO_2$ (reduction half reaction)

The elements undergoing a change in oxidation number are Mn and C.

(ii) Split the reaction into two half reactions, the oxidation and reduction half reactions.

$C_2O_4^{2-} \rightarrow CO_2$ (oxidation half reaction)

$MnO_4^{-1} \rightarrow MnO_2$ (reduction half reaction)

Balancing of Oxidation Half Reaction:

$$C_2O_4^{-2} \rightarrow CO_2$$

Balancing the C atoms in both sides of the half reaction.

$$C_2O_4^{-2} \rightarrow 2CO_2$$

Balancing the charges on both sides of the half reaction by adding the appropriate number of electrons to the more position side.

$$C_2O_4^{-2} \rightarrow 2CO_2 + 2e^- \quad .... \quad (1)$$

The oxidation half reaction is balanced.

Balancing of Reduction Half Reaction:

$$MnO_4^- \rightarrow MnO_2$$

Balance in O-atoms by adding OH^- ions on the side needing the oxygen. Add two OH^- ions for each oxygen atom needed. So, we have to add $4OH^-$ on R.H.S:

$$MnO_4^- \rightarrow MnO_2 + 4OH^-$$

Balance the hydrogen, by adding H_2O on the other side of the half reaction. Add one H_2O for each two OH^- ion. In this way, oxygen and hydrogen atoms are balanced.

$$2H_2O + MnO_4^- \rightarrow MnO_2 + 4OH^-$$

Balance the charges by adding three electrons to L.H.S. of equation

$$3e^- + 2H_2O + MnO_4^- \rightarrow MnO_2 + 4OH^- \quad .... \quad (2)$$

The reduction half reaction is balanced.

(iii) Multiply each half reaction by an appropriate number, so that the number of electrons on both the half reactions becomes equal. For this purpose, multiply the oxidation half reaction by 3 and the reduction half reaction by 2.

$$3C_2O_4^{-2} \rightarrow 6CO_2 + 6e^- \quad .... \quad (3)$$

$$2 \text{ x } [3e^- + 2H_2O + MnO_4^- \rightarrow MnO_2 + 4OH^-]$$

$$6e^- + 4H_2O + 2MnO_4^- \rightarrow 2MnO_2 + 8OH^- \quad .... \quad (4)$$

(iv) Add the two half-reactions to get the net ionic equation and cancel out anything appearing on both sides of the equation. For this purpose, add equation and equation (4).

$$\begin{array}{r} 3C_2O_4^{-2} \rightarrow 6CO_2 + 6e^- \\ 6e^- + 4H_2O + 2MnO_4^- \rightarrow 2MnO_2 + 8OH^- \\ \hline 3C_2O_4^{2-} + 4H_2O + 2MnO_4^- \rightarrow 6CO_2 + 2MnO_2 + 8OH^- \\ \hline \end{array}$$

Hence, the balance ionic equation is

$$2MnO_4^-{}_{(aq)} + 3C_2O_4^{2-} + 4H_2O \rightarrow 2MnO_{2(s)} + 6CO_{2(g)} + 8OH^-{}_{(aq)}$$

10.2.0 ELECTROLYTIC CONDUCTION

We know, that most metals are conductors of electricity because of the relatively free movement of their electrons throughout the metallic lattice. This electronic conduction is simply called metallic conduction.

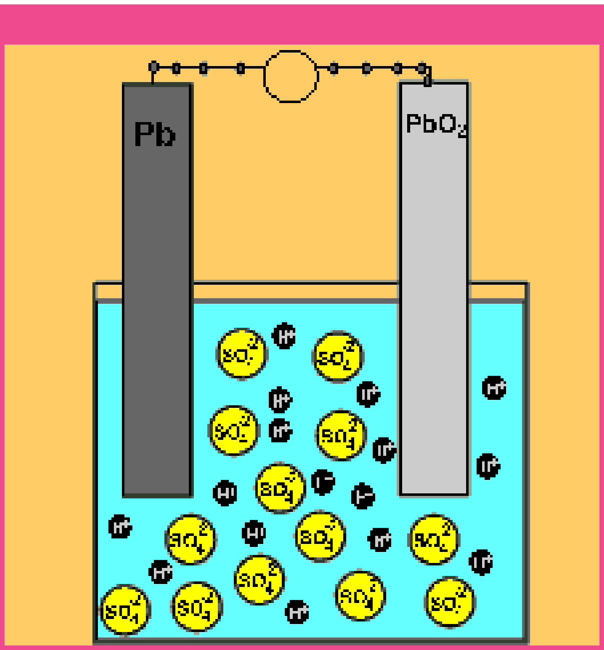
Electrolytes in the form of solution or in the fused state have the ability to conduct electricity. In this case, the current is not carried by free electrons through the solution or through the fused electrolyte. Here, the current is carried by ions having positive and negative charges. These ions are produced in the solution or in fused state due to ionization of the electrolyte. Ionization is the process in which ionic compounds when fused or dissolved in water split up into charged particles called ions.

$$PbBr_{2\,(s)} \xrightarrow{fused} Pb^{2+}{}_{(aq)} + Br^-{}_{(aq)}$$

$$NaCl_{(s)} \xrightarrow{H_2O} Na^+{}_{(aq)} + Cl^-{}_{(aq)}$$

Two electrodes are dipped in the solution of an electrolyte and electrolysis takes place. This forms an electrolytic cell An electrolytic cell is an electrochemical cell in which electric current is used to drive a non-spomaneous reaction. When a non-spontaneous reaction takes place at the expense of electrical energy, the process is called electrolysis. During this non-spontaneous reaction, the substances are deposited at respective electrodes and electrolyte is decomposed. Examples of electrolytic cells are Down's cell and Nelson's cell, etc.

10.2.1 Electrochemical Cells

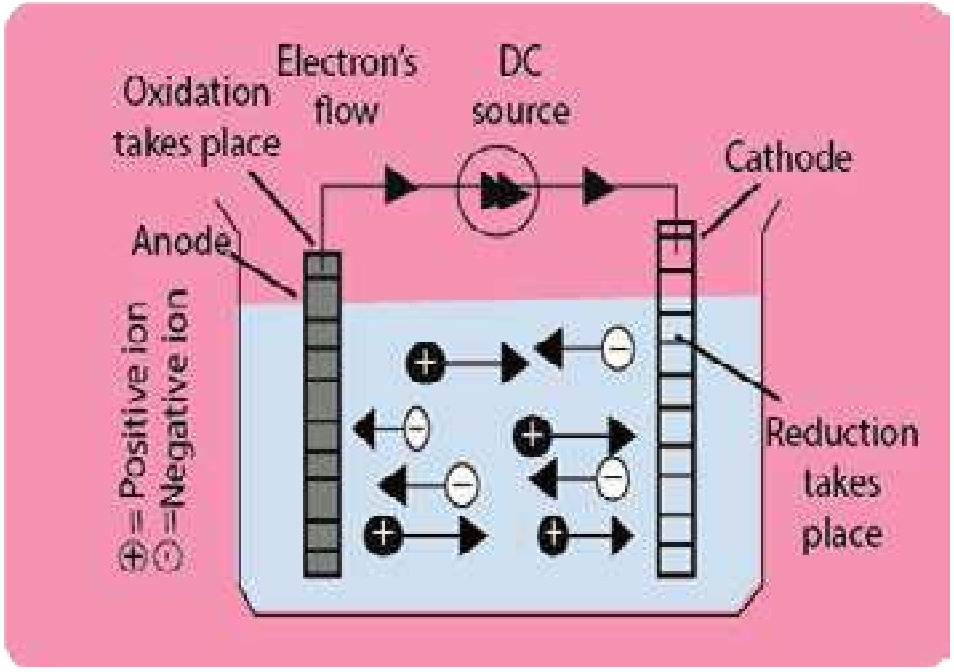


Animation 10.5: ELECTROCHEMICAL CELLS
Source & Credit : dynamicscience

10.2.2 Electrolytic Cells.

Look at the arrangement as shown in Fig. (10.1). It represents, an electrolytic cell, The electrolyte consists of positive and negative ions which are free to move in the solution. When a direct current (D.C) source is connected to the electrodes of the cell, each electrode acquires an electric charge.

Thus, on applying electric potential, the positive ions migrate towards the negative electrode, called cathode and the negative ions move towards the positive electrode, called the anode.



Ftg (10.1) The migration of ions in electrolytic cell

This movement of ionic charges through the liquid brought by the application of electricity is called electrolytic conduction and the apparatus used is known as electrolytic cell.

When electrolytic conduction occurs, electrochemical reactions takes place. The ions in the liquid come in contact with the electrodes. At the anode the negative ions give up electrons and are, therefore, oxidized. At the cathode the positive ions pick up electrons and are reduced. Thus during electrolytic conduction, oxidation takes place at the anode and the reduction takes place at the cathode. The liquid will continue to conduct electricity only as long as oxidation-reduction reactions, occurring at the electrodes, continue.

The electrochemical reactions that occur at the electrodes during the electrolytic conduction constitute the phenomenon of electrolysis.

Table (10.1a) Products of electrolysis

(using inert electrodes of platinum or graphite)

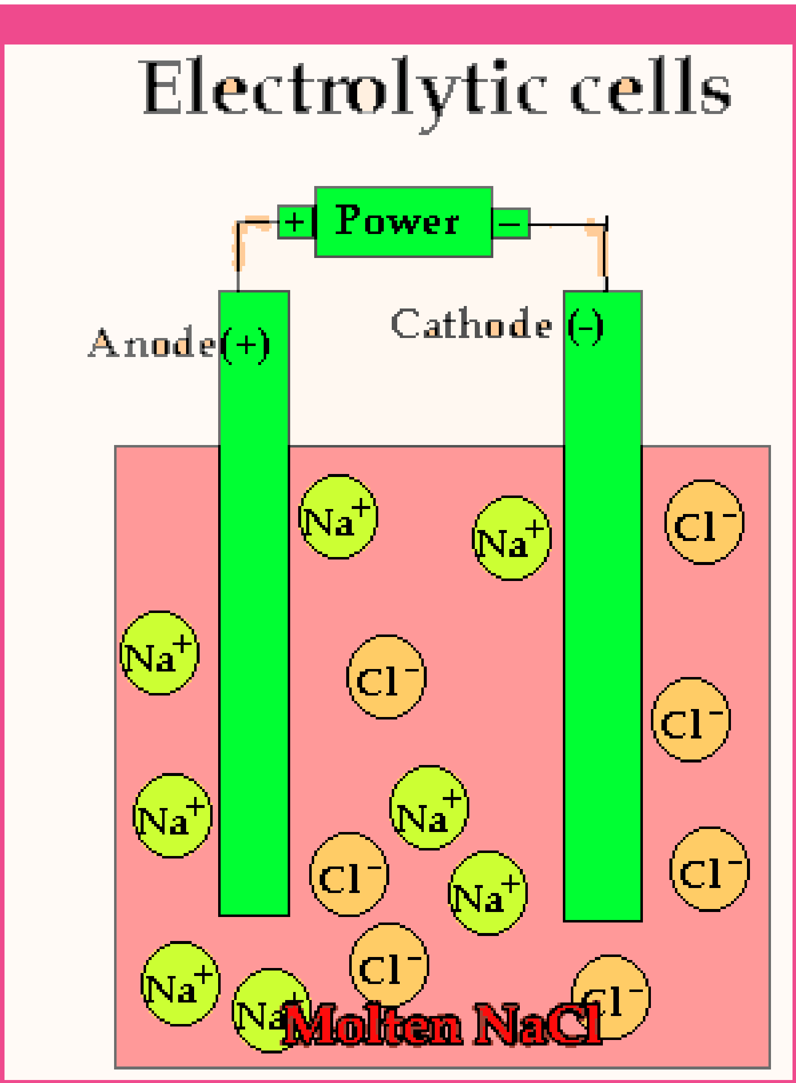
Electrolyte	Cathode	Anode
$PbBr_{2(molten)}$	Pb(s)	$Br_2(g)$
$NaCl_{(molten)}$	Na(s)	$Cl_2(g)$
NaCl(aq)	$H_2(g)$	$Cl_2(g)$
$CuCl_2(aq)$	Cu(s)	$Cl_2(g)$
$CuSO_4(aq)$	Cu(s)	$O_2(g)$
$KNO_3(aq)$	$H_2(g)$	$O_2(g)$
NaOH(aq)	$H_2(g)$	$O_2(g)$
$H_2SO_4(aq)$	$H_2(g)$	$O_2(g)$

When a molten salt is electrolyzed, the products are predictable. When an aqueous solution of a salt is electrolyzed, hydrogen and oxygen appear at the cathode and anode, respectively in certain cases. The products formed from a few electrolytes are shown in Table (10.1).

Table (10.1b) Products of electrolysis

(when electrodes take part in the reaction)

Electrolyte	Copper cathode	Copper anode
$CuSO_4$(aq)	Cu deposits	Cu (s) dissolves to form CU^{2-} ions
Electrolyte	Silver cathode	Silver anode
$AgNO_3$(aq) and HNO_3(aq)	Ag deposits	Ag (s) dissolves to form Ag$^+$ ions



Animation 10.6: Electrolytic Cells
Source & Credit : dynamicscience

10.2.3 Explanation of Electrolysis

(a) Fused Salts

When a fused salt is electrolyzed, the metal ions called cations arrive at the cathode which being negatively, charged supply electrons to them and thus discharge the cations. The anions move towards the anode, give up their electrons and are thus discharged. In the case of fused lead chloride, the equations for electrode processes are given as under.

At anode: $Pb^{2+}_{(\ell)} + 2e^- \rightarrow Pb_{(s)}$ (oxidation)

At cathode: $2Cl^-_{(\ell)} \rightarrow Cl_{2(g)} + 2e^-$ (reduction)

So, oxidation happens at anode and reduction at the cathode.

Similarly, for fused NaCl and fused $PbBr_2$ the electrolytes are decomposed during electrolysis. Fused Pb and Na are deposited at cathode and Cl_2(g) and Br_2 at anode.

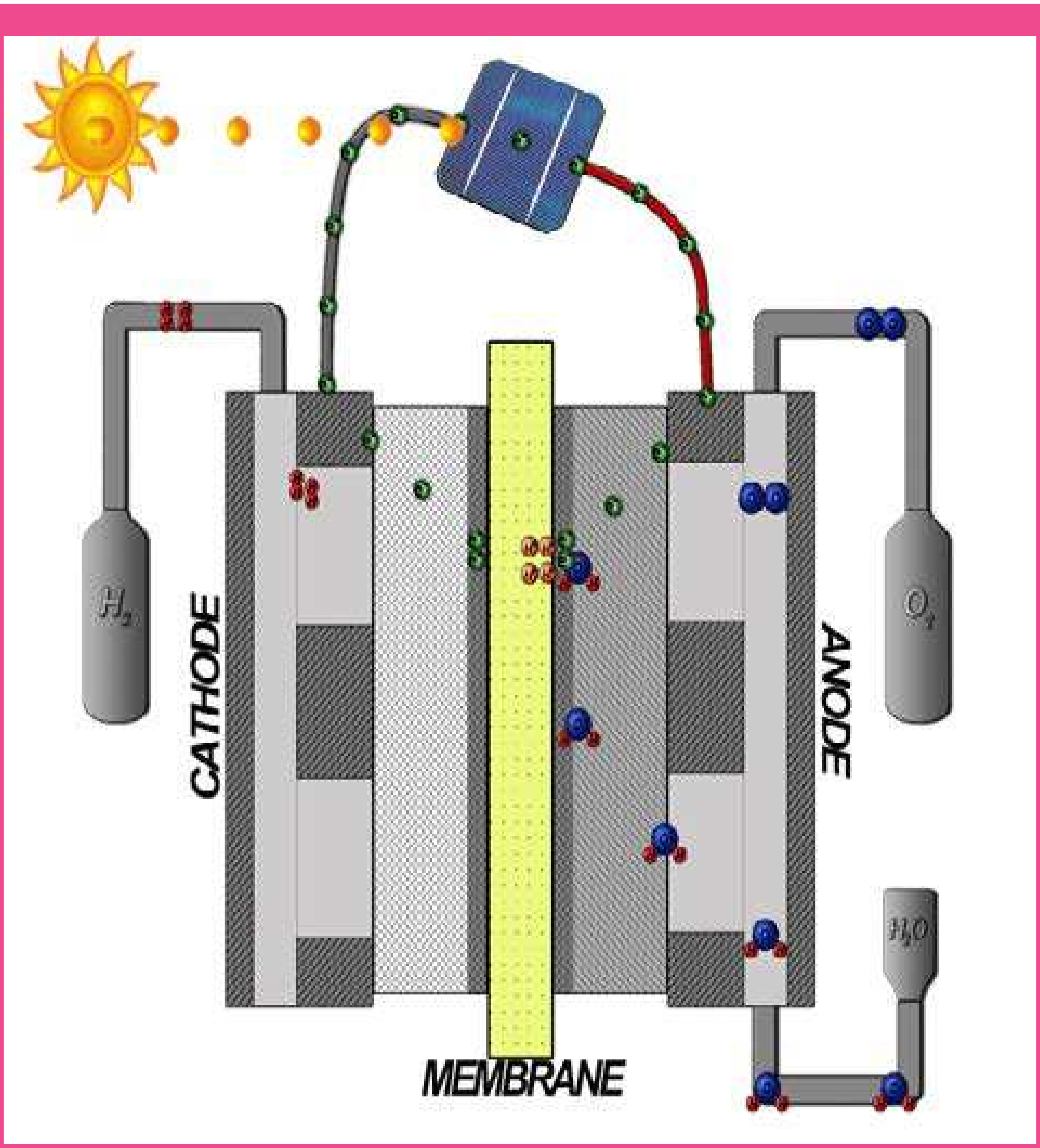
Electrons flow through the external circuit from anode to cathode. The electric current is conducted through the cell by the ions and through the external circuit by the electrons.

(b) Aqueous Solutions of Salts

The electrolysis of aqueous solutions is somewhat more complex. Its reason is the ability of water, to be oxidized as well as reduced. Hence, the products of electrolysis are not precisely predictable. Some, metal cations are not discharged from their aqueous solutions. While, electrolyzing aqueous sodium nitrate ($NaNO_3$) solution, sodium ions present are not discharged at the cathode. A small concentration of hydronium and hydroxyl ions arises from the dissociation of water:

$$NaNO_3 \rightarrow Na^+ + NO_3^-$$

$$2H_2O_{(\ell)} \rightarrow H_3O^+_{(aq)} + OH^-_{(aq)}$$



Animation 10.7: Electrolysis
Source & Credit : revolvy

Hydronium ions accept electrons from the cathode to form hydrogen atoms:

At cathode: $H_3O^+_{(aq)} + e^- \rightarrow H_{(g)} + H_2O_{(\ell)}$ (reduction)

Subsequently, hydrogen atoms combine rapidly to form hydrogen molecules at the cathode.

$$H_{(g)} + H_{(g)} \rightarrow H_{2(g)}$$

So, H_2 gas evolves at the cathode.

The concentration of hydronium ions is only 10^{-7} moles dm^{-3} in pure water. When these are discharged then more are formed by further dissociation of water molecules. This gives a continuous supply of such ions to be discharged. Sodium ions remain in solution, while hydrogen is evolved at the cathode. Thus, the reduction of the solute cations depends on the relative ease of the two competing reactions.

At the anode, both nitrate and hydroxide ions are present. Hydroxide ions are easier to discharge than nitrate ions. Nitrate ions remain in solution while the electrode reaction is:

At anode: $OH^{-}_{(aq)} \rightarrow OH_{(aq)} + e^{-}$ (oxidation)

The OH groups combine to give O_2 gas as follows.

$$4OH \rightarrow O_{2(g)} + 2H_2O_{(\ell)} \text{ (anode)}$$

So, O_2 gas evolves at the anode.

But, remember that the expected order of the discharge of ions may also depend upon their concentrations.

10.2.4 Electrolytic Processes of Industrial Importance

Various types of electrolytic cels are employed on industrial scale. Some of the important ones are given here.

(i) Extraction of sodium by the electrolysis of fused sodium chloride is carried out in Down's cell. In this case, molten sodium chloride is electrolyzed between iron cathode and graphite anode. The cell is planted to get sodium metal commercially chlorine is obtained as a by product.

$$NaCl_{(s)} \rightarrow Na^{+}_{(\ell)} + Cl^{-}_{(\ell)}$$

At anode

$$2Cl^{-}_{(\ell)} \rightarrow 2Cl_{(g)} + 2e^{-} \text{ (oxidation)}$$

$$Cl_{(g)} + Cl_{(g)} \rightarrow Cl_{2(g)}$$

At cathode

$$2Na^{+}_{(\ell)} + 2e^{-} \rightarrow 2Na_{(s)} \text{ (reduction)}$$

By adding the two reactions at anode and cathode, the overall reaction is

$$2Na^{+}_{(\ell)} + 2Cl^{-}_{(\ell)} \rightarrow 2Na^{\circ}_{(s)} + Cl^{\circ}_{(g)}$$

(ii) Caustic soda is obtained on industrial scale by the electrolysis of concentrated aqueous solution of sodium chloride using titanium anode and mercury or steel cathode This electrolysis is carried out in Nelson cell and Castner- Kellner cell or Hg- cell.

$$NaCl_{(s)} \quad \square \quad Na_{(aq)}^{+} + Cl^{-}_{(aq)}$$

At anode $\quad 2Cl^{-}_{(g)} \rightarrow Cl_{2(g)} + 2e^{-}$ (oxidation)

At cathode $\quad 2H_2O_{(\ell)} + 2e^{-} \rightarrow H_{2(g)} + 2OH^{-}_{(aq)}$ (reduction)

By combining, the electrode reactions and including Na^{+} ions, the overall reaction is

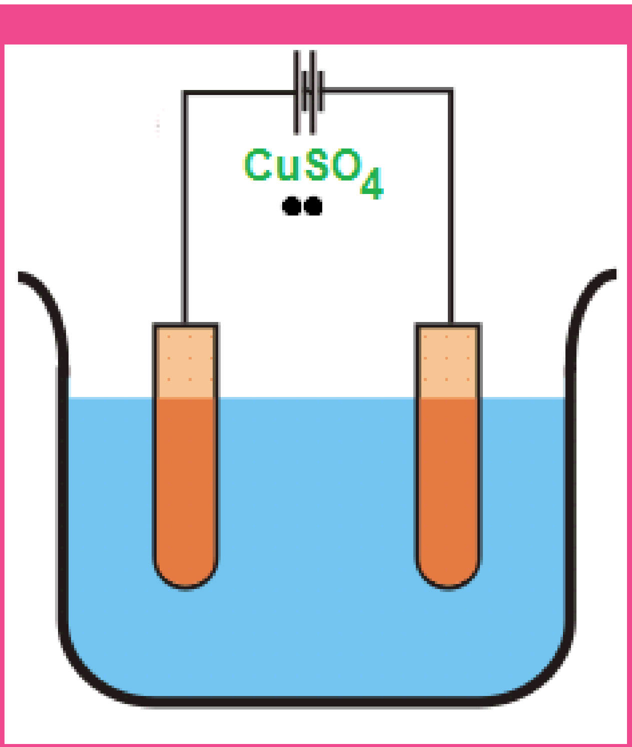
$$2Na^{+}_{(aq)} + 2Cl^{-}_{(aq)} + 2H_2O_{(l)} \rightarrow Cl_{2(g)} + H_{2(g)} + 2Na^{+}_{(aq)} + 2OH^{-}_{(aq)}$$

Here, chlorine and hydrogen are obtained as by products, and Na^{+} is not discharged at cathode.

(iii) Magnesium and calcium metals are extracted by the electrolysis of their fused chlorides. Mg and Ca are collected at cathodes while Cl_2 at anodes

(iv) Aluminium is extracted by electrolyzing fused bauxite, $Al_2O_32H_2O$ in the presence of fused cryolite, Na_3AlF_6. This process is called Hall-Beroult process.

(v) Anodized aluminium is prepared by making it an anode in an electrolytic cell containing sulphuric acid or chromic acid, which coats a thin layer of oxide on- it. The aluminium oxide layer resists attack for corrosive agents. The freshly anodized aluminium is hydrated and can absorb dyes.



Animation 10.8: Application of Electrolysis
Source & Credit : electrical4u

(vi) Electrolyticcell can also be used for the purification of copper. Impure copper is made the anode and a thin sheet of pure copper is made the cathode. Copper sulphate solution is used as an electrolyte. The atoms of Cu from impure Cu^- anode are converted to Cu^{2+}ions and migrate to cathode which is made up of pure Cu. In this way Cu anode is purified. Impurities are left at anode.

(vii) Copper, silver, nickel and chromium plating is done by various types of electrolytic cells. One metal is deposited at the surface of another metal.

10.2.5 Voltaic or Galvanic Cell

A voltaic or a galvanic cell consists of two half-cells that are electrically connected. Each half cell is a portion of the total cell in which a half reaction takes place. Fig. (10.2) shows such a galvanic cell. The left half cell consists of a strip of zinc metal dipped in 1.0 M solution of zinc sulphate giving the following equilibrium:

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$$

.

The right half-cell is a copper metal strip that dips into 1.0 M copper sulphate solution and the equilibrium here is represented as follows:

$$Cu(s) \rightarrow Cu^{2+} + 2e^{-}$$

These half-cells in Fig (10.2) are connected electrically by a salt bridge. If the solutions were to mix, direct chemical reactions would take place, destroying the half-cells. The salt bridge contains an aqueous solution of potassium chloride in a gel. Zinc tends to lose electrons more readily than copper.

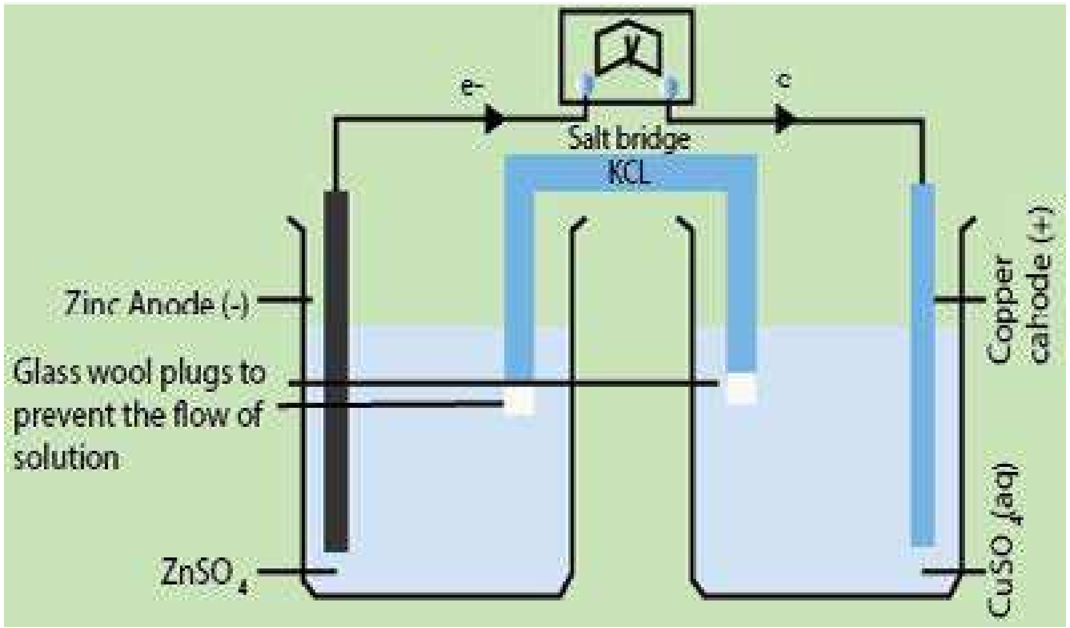


Fig (10.2) A Galvanic cell consisting of Zn and Cu electrodes at 25°C and unit concentration of electrolytic solutions.

Zn electrode takes on a negative charge relative to the copper electrode. If the external circuit is closed by connecting the two electrodes as shown in the figure, electrons flow from the zinc through the external circuit to copper electrode. The following half-cell reactions occur at two electrodes and cell potential at standard conditions is 1.1volts . It is denoted by E°.

At anode $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^{-}$ (oxidation)

At cathode $Cu^{2+}_{(aq)} + 2e^{-} \rightarrow Cu_{(s)}$ (reduction)

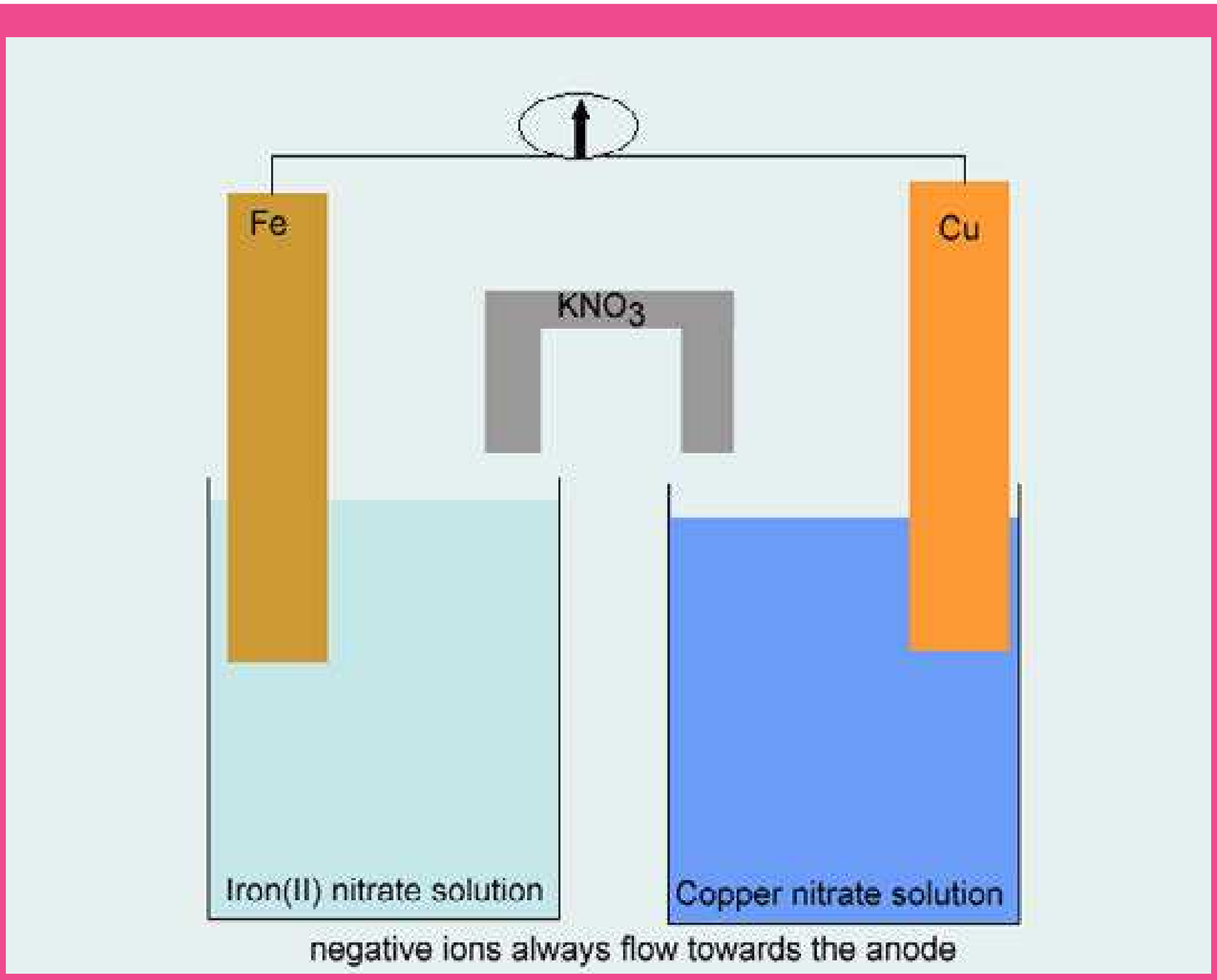
The overall voltaic cell reaction is the sum of these two half cell reactions.

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)} \qquad E^{o}=1.1V$$

This voltaic cell can be represented as follows;

$$Zn_{(s)}/Zn^{2+}_{(aq)}1M \square Cu^{2+}_{(aq)}+1M/Cu_{(s)} \qquad E^{o}=1.1V$$

Note that reduction occurs at the copper electrode and oxidation occurs at the zinc electrode. Sign □ shows the presence of salt bridge.



Animation 10.9: Galvanic Cell
Source & Credit : dynamicscience

Function of Salt Bridge

Let us, examine the purpose of the salt bridge. Since, zinc ions are produced as electrons leave the anode, we have a process which tends to produce a net positive charge in the left beaker. Actually, the concentration of Zn^{2+} ions increase in the left compartment. Similarly, the arrival of the electrons at the copper cathode and their reaction with copper ions tend to produce a net negative charge in the right beaker.

The purpose of the salt bridge is to prevent any net charge accumulation in either beaker by allowing negative ions to leave the right beaker, diffuse through the bridge and enter the left beaker. If this diffusional exchange of ions does not occur, the net charge accumulating in the beakers would immediately stop the flow of electrons through the external circuit and the oxidation-reduction reaction would stop.

Many other oxidation - reduction reactions can be carried out successfully in galvanic cells using different electrodes. It is natural to think of these cell processes as separated into two half-reactions which occur at the two electrodes. In a voltaic cell the electric current in the external circuit can be used to light a bulb, drive a motor and so on.

Voltaic Cell is Reversible Cell

On the other hand, if the external circuit is replaced by a source of electricity that opposes the voltaic cell, the electrode reactions can be reversed. Now, the external source pushes the electrons in the opposite direction and supplies energy or work to the cell so that the reverse non-spontaneous reaction occurs. Such, a cell is called a reversible cell.

For the zinc-copper cell, the half cell reactions are reversed to give.

$$Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)} \qquad \text{(reduction)}$$

$$Cu_{(s)} \rightarrow Cu^{2+} + 2e^- \qquad \text{(oxidation)}$$

and the overall reaction being reversed, becomes

$$Zn^{2+}_{(aq)} + Cu_{(s)} \rightarrow Zn_{(s)} + Cu^{2+}_{(aq)}$$

Oxidation occurs at the copper electrode and reduction takes place at the zinc electrode and the cell operates as an electrolytic cell in which energy from an external source drives a non-spontaneous reaction.

When a cell operates as a voltaic the electrode at which reduction occurs is called the cathode while the electrode at which oxidation takes place is called the anode. Hence in voltaic cell, Zn acts as an anode and Cu acts as a cathode.

10.3.0 ELECTRODE POTENTIAL

When a metal strip is placed in a solution of its own ions, there are two tendencies. The metal atoms may dissolve as positive ions. In this way, the electrons are deposited on the metal electrode. On the other hand, the metal ions present in solution may take up electrons from the metal and get discharged as atoms.

It imparts a positive charge to the metal. In either case, a potential difference is set up between the metal and the solution, which is called single electrode potential.

The potential set up when an electrode is in contact with one molar solution of its own ions at 298 K is known as standard electrode potential or standard reduction potential of the element. It is represented as E°.

Standard electrode potential of hydrogen has arbitrarily been chosen as zero, while the standard electrode potentials of other elements can be found by comparing them with standard hydrogen electrode potential. The electrode potential, set up when a metal piece is placed in a solution containing its own ions, can be explained in terms of equilibrium between the atoms of the metal and its ions in solution. It is believed that when a metal is placed in a solution, some of its atoms tend to give electrons to the piece of metal and pass into the solution as positively charged ions.

At the same time the metallic ions already present in solution tend to take up electrons from the piece of metal and deposit themselves as neutral atoms. Whichever tendency is greater in a given case determines w hether the metal becomes negatively or positively charged, compared with the solution. When equilibrium is eventually attained, the two opposing processes continue at the same rate and there is no further change in the potential difference.

A rod of zinc , for example, will bear an accumulation of negative charges. This is due to the net ionization of some of its atoms. The negative charge on the Zn-rod will attract an atmosphere of positively charged zinc ions around the rod to form an electrical double layer as shown in Fig. (10.3). The equilibrium can, therefore, be represented as:

$$Zn_{(s)} \rightleftharpoons Zn^{2+}_{(aq)} + 2e^{-}$$

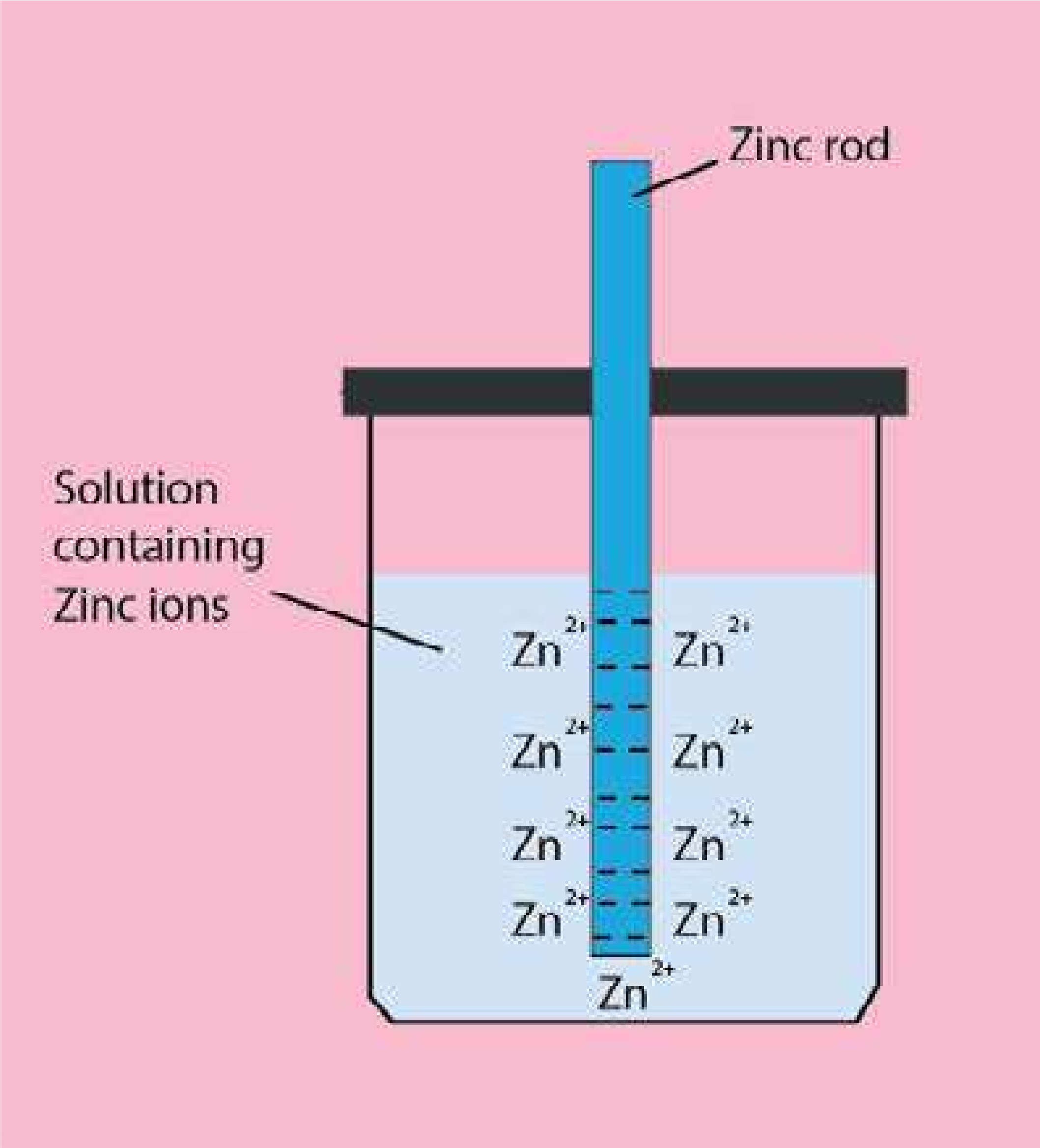
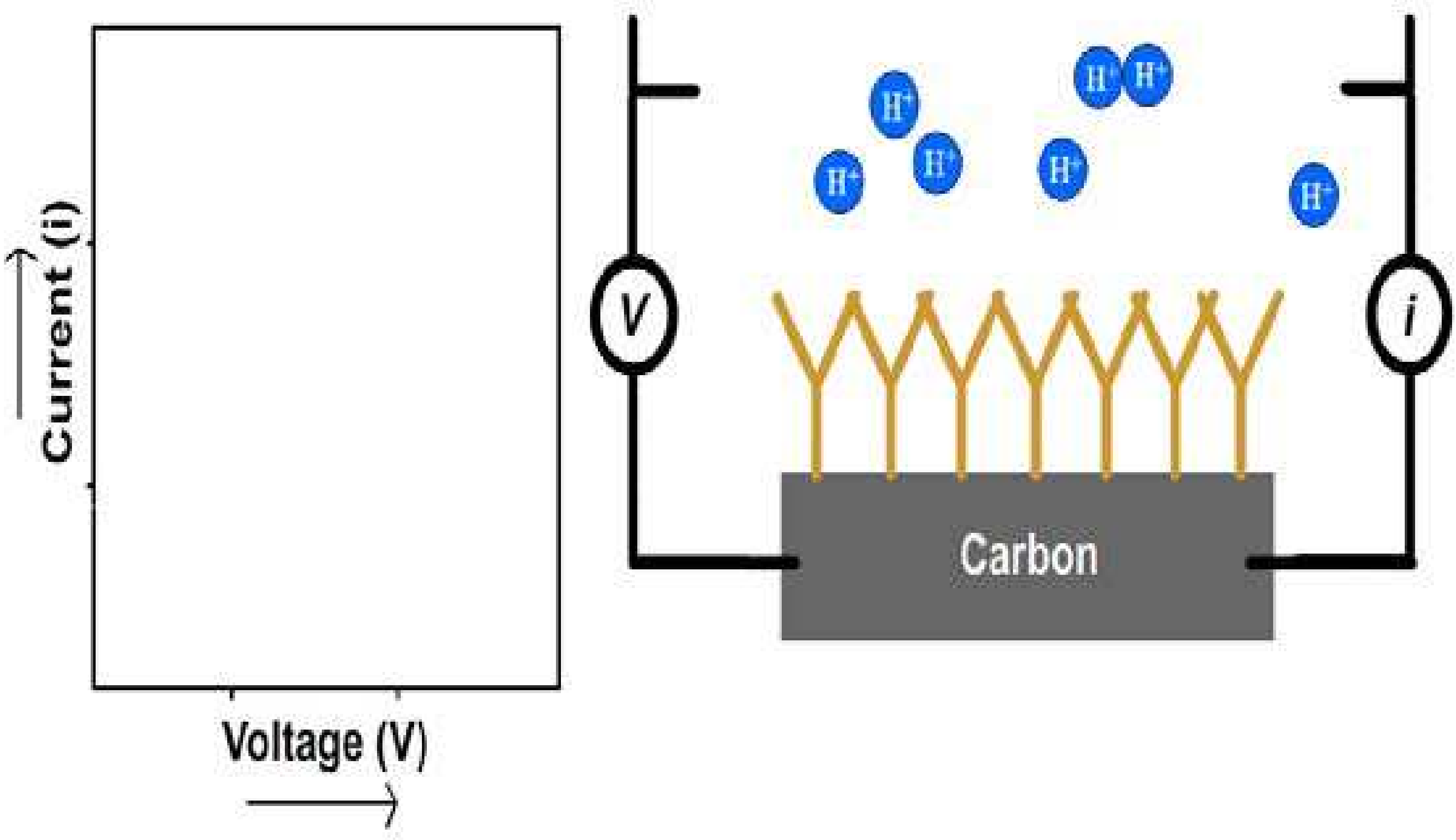


Fig. (10.3) Equilibrium between zinc and its ions in solution



Animation 10.10: ELECTRODE
Source & Credit : senovasystems

10.3.1 Standard Hydrogen Electrode (SHE)

A standard hydrogen electrode which is used as a standard is shown in Fig. (10.4). It consists of a piece of platinum foil, which is coated electrolytically with finely divided platinum black, to give it a large surface area and suspended in one molar solution of HCl.

Pure hydrogen gas at one atmosphere pressure is continuously bubbled into 1M HCl solution. The platinum acts as an electrical conductor and also facilitates the attainment of equilibrium between the gas and its ions in solution. The potential of this electrode is arbitrarily taken as zero.

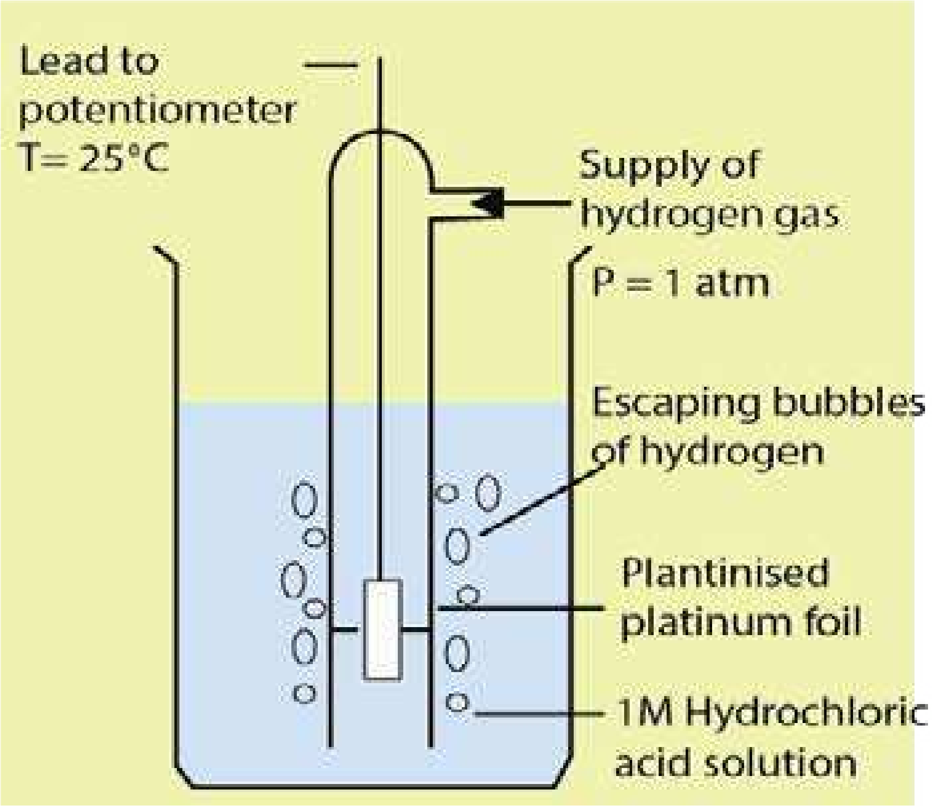


Fig.(10.4)Standard hydrogen electrode(S.H.E)

10.3.2 Measurement of Electrode Potential

In any measurement of electrode potential, the concerned electrode is joined electrolytically with the standard hydrogen electrode (SHE) and a galvanic cell is established. The two solutions are separated by a porous partition or a salt bridge containing a concentrated solution of potassium chloride. The salt bridge is used to provide a highly conducting path between the two electrolytic solutions. The potential difference is measured by a voltmeter which gives the potential of the electrode, as the potential of SHE is zero. An oxidation or reduction may take place at SHE depending upon the nature of the electrode which is coupled with it.

To measure the electrode potential of zinc, a galvanic cell is established between zinc electrode dipped in 1 M solution of its ions and standard hydrogen electrode at 25 °C as shown in Fig (10.5). Under the standard conditions, the voltmeter reads 0.76 volts and the deflection is in such a direction as to indicate that zinc has a greater tendency to give off electrons than hydrogen has. In other words, the half reaction $Zn_{(s)} \rightarrow Zn^{2+} + 2e^-$ has greater tendency to occur than $H_{2(g)} \rightarrow 2H^+ + 2e^-$ by 0.76 volts. The standard electrode potential of zinc is, therefore, 0.76 volts. It is called oxidation potential of Zn and is given the positive sign.

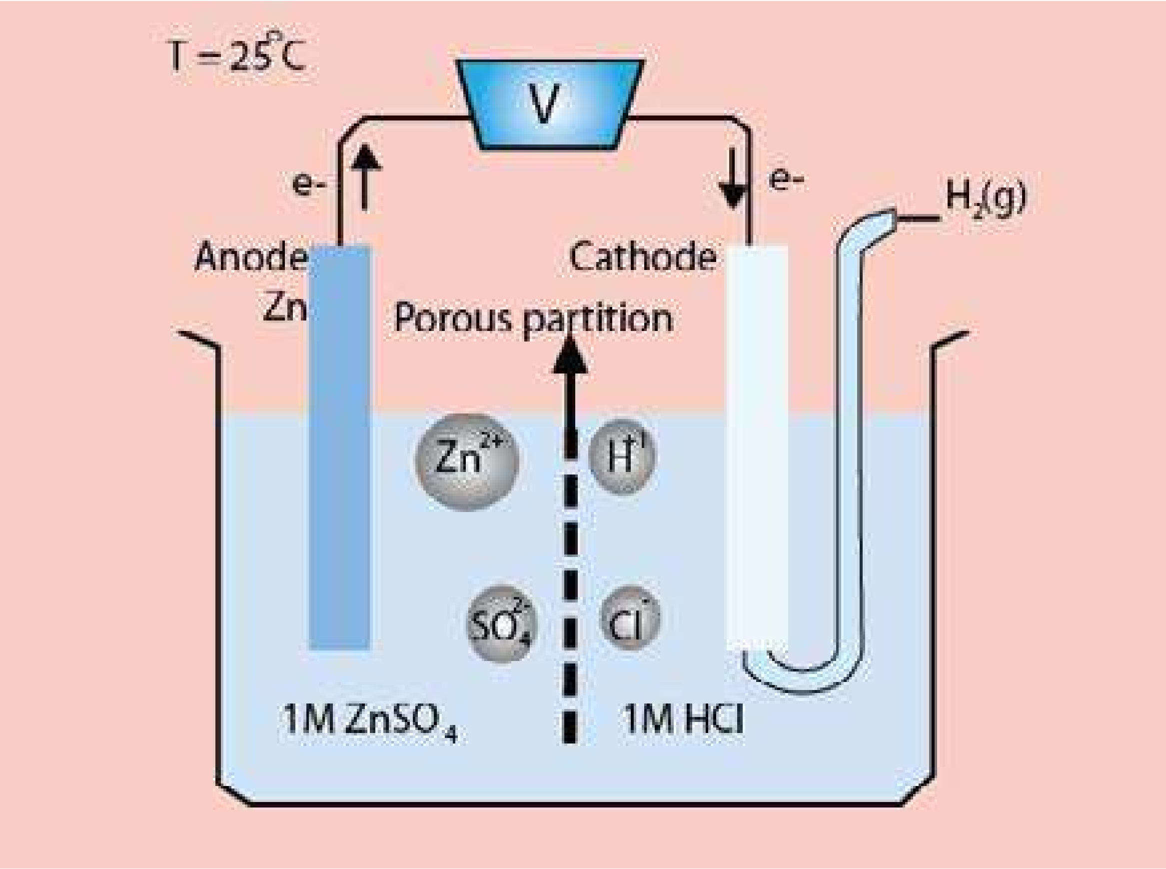


Fig (10.5) Electrode potential of zinc.

The reduction potential Zn-electrode is -0.76 volt. The electrode reactions will be shown as follows.

At anode $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$ (oxidation)

At cathode $2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$ (reduction)

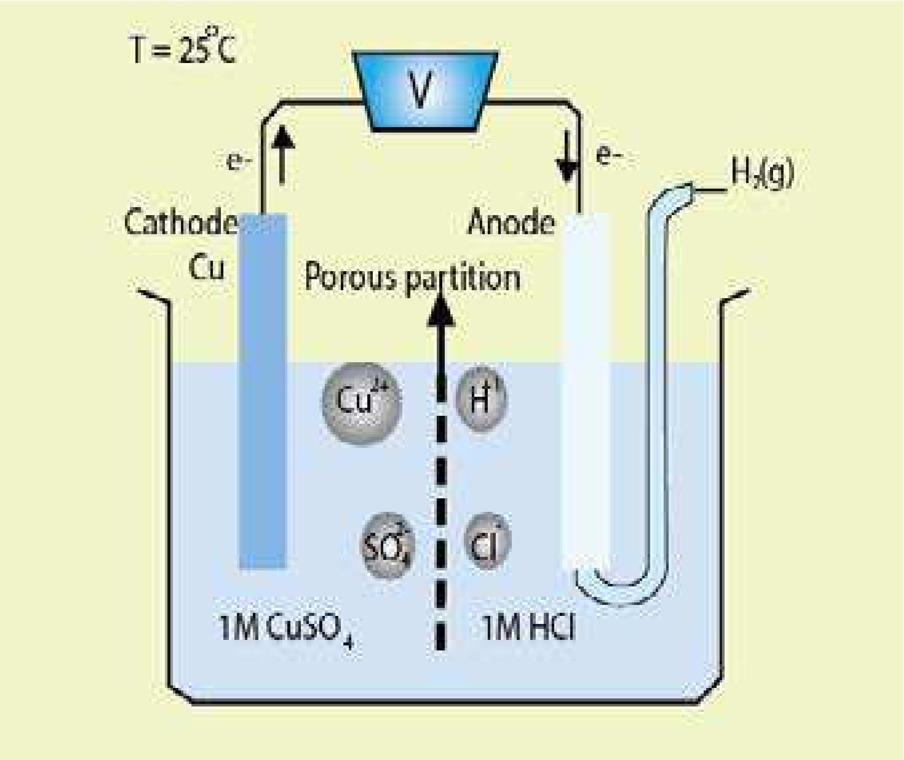


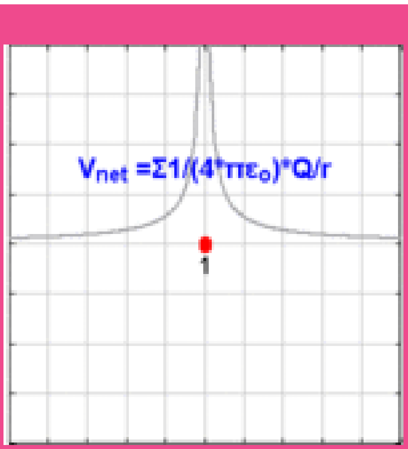
Fig (10.6) Electrode potential of copper

The electrode potential of copper can also be measured using the same type of galvanic cell in which copper is an electrode dipped in 1 M solution of its ions and connected with .SHE Fig (10.6). Under standard conditions, the voltmeter reads 0.34 volts and the deflection is in such a direction, as to indicate that hydrogen has a greater tendency to give off electrons than copper has.

In other words, the half reaction $H_{2(g)} \rightarrow 2H^+ + 2e^-$ has a greater tendency to occur than $Cu_{(s)} \rightarrow Cu^{2+} + 2e^-$ by 0.34 volt. So the standard electrode potential of Cu is 0.34 volts. It is called reduction potential of Cu. When the sign is reversed, then the -0.34 V is called oxidation potential of Cu electrode. The reactions taking place at two electrodes will be shown as follows.

At anode $H_{2(g)} \rightarrow 2H^+ + 2e^-$

At cathode $Cu^{2+} + 2e^- \rightarrow Cu_{(s)}$

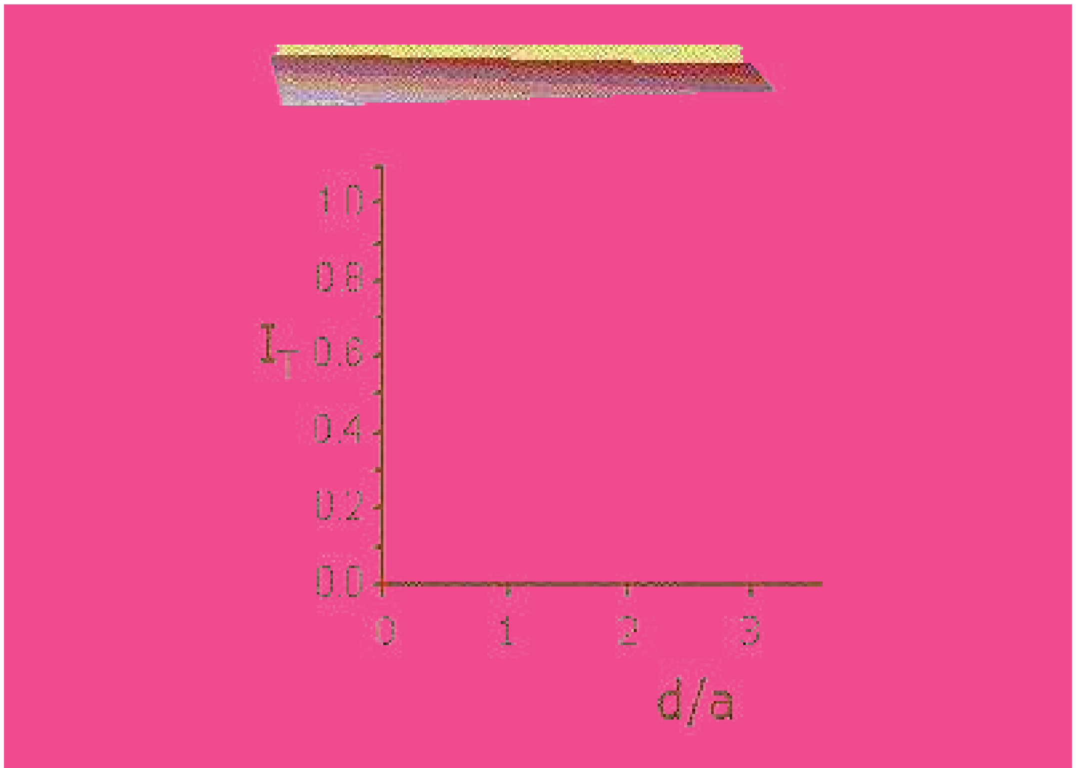


Animation 10.11: Electric potential
Source & Credit : wikipedia

10.4 THE ELECTROCHEMICAL SERIES

When elements are arranged in the order of their standard, electrode potentials on the hydrogen scale, the resulting list is known as electrochemical series.

Such a series of elements is shown in Table (10.2). The electrode potentials have been given in the reduction mode as recommended by the International Union of Pure and Applied Chemists (IUPAC). In some textbooks, half reactions are written in the oxidation mode and the corresponding potentials are oxidation potentials. The magnitude of the potential is not affected by the change in mode but the signs are reversed. Therefore, before using standard electrode potential data, it is necessary to ascertain which mode is being used. An important point to remember in using reduction potential values is that they relate only to standard conditions i.e. 1 M solution of ions, 25°C and one atmospheric pressure. Changes in temperature, concentration and pressure will affect the values of reduction potential.



Animation 10.12: ELECTROCHEMICAL
Source & Credit : skleac

Table (10.2) Standard reduction potentials (E°) of substances at 298 K

Element	Electrode	Standard Reduction Potential (E^0)
Li	$Li^{+}+e^{-} \rightarrow Li$	-3.045
K	$K^{+}+e^{-} \rightarrow K$	-2.925
Ca	$Ca^{2+}+2e^{-} \rightarrow Ca$	-2.87
Na	$Na^{+}+e^{-} \rightarrow Na$	-2.714
Mg	$Mg^{2+}+2e^{-} \rightarrow Mg$	-2.37
Al	$Al^{3+}+3e^{-} \rightarrow Al$	-1.66
Zn	$Zn^{2+}+2e^{-} \rightarrow Zn$	-0.76
Cr	$Cr^{3+}+3e^{-} \rightarrow Cr$	-0.74
Fe	$Fe^{2+}+2e^{-} \rightarrow Fe$	-0.44
Cd	$Cd^{2+}+2e^{-} \rightarrow Cd$	-0.403
Ni	$Ni^{2+}+2e^{-} \rightarrow Ni$	-0.25
Sn	$Sn^{2+}+2e^{-} \rightarrow Sn$	-0.14
Pb	$Pb^{2+}+2e^{-} \rightarrow Pb$	-0.126
H_2	$2H^{+}+2e^{-} \rightarrow H_2$	(Reference Electrode) 0.000
Cu	$Cu^{2+}+2e^{-} \rightarrow Cu$	+0.34
Cu	$Cu^{+}+e^{-} \rightarrow Cu$	+0.521
I_2	$I_2+2e^{-} \rightarrow 2I^{-}$	+0.535
Fe	$Fe^{3+}+3e^{-} \rightarrow Fe$	+0.771
Ag	$Ag^{+}+e^{-} \rightarrow Ag$	+0.7994
Hg	$Hg^{2+}+2e^{-} \rightarrow Hg$	+0.885
Br_2	$Br_2+2e^{-} \rightarrow 2Br^{-}$	+1.08
Cl_2	$Cl_2+2e^{-} \rightarrow 2Cl^{-}$	+1.360
Au	$Au^{3+}+3e^{-} \rightarrow Au$	+1.50
F_2	$F_2+2e^{-} \rightarrow 2F^{-}$	+2.87

Increasing reduction potentials ↓

Increasing strength as an oxidizing agent

Decreasing reduction potentials ↑

Increasing strength as a reducing agent

10.4.1 Applications of Electrochemical Series

(i) Prediction of the feasibility of a Chemical Reaction

When we look at the electrochemical series, it is easy to predict whether a particular reaction will take place or not. For example, Cu^{2+} (aq) can oxidize solid zinc but Zn^{2+} (aq) cannot oxidize solid copper. Standard reduction potential values of copper and zinc can explain this

$$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)} \qquad E^o = +0.34 volt$$

$$Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)} \qquad E^o = -0.76 volts$$

Since zinc is being oxidized so the reverse reaction will be considered.

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^- \qquad E^o = -0.76 \text{ volts (oxidation)}$$

The overall reaction will thus be

$$Cu^{2+}_{(aq)} + Zn_{(s)} \rightarrow Cu_{(s)} + Zn^{2+}_{(aq)} \qquad E^o_{cell} = 1.10 \text{ volts}$$

The overall positive value for the reaction potential suggests that the process is energetically feasible. If the sum of E° values of the two half cell reactions is negative, then the reaction will not be feasible.

(ii) Calculation of the Voltage or Electromotive Force (emf) of Cells:

In a galvanic cell, the electrode occupying a higher position in the electrochemical series, will act as anode and oxidation takes place on it. Similarly, the electrode occupying the lower position in the series will act as a cathode and reduction will take place on it. Let us find out a cell potential or the emf of the cell already discussed as above. The half cell reactions are:

$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$ (oxidation half reaction)

$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$ (reduction half reaction)

$Cu^{2+}_{(aq)} + Zn_{(s)} \rightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$ (complete cell reaction)

The oxidation potential of Zn is positive. The reduction potential of Cu^{2+} is also positive. The cell voltage or emf of the cell is given by

$$E^o_{cell} = E^o_{oxi} + E^o_{red}$$

$$E^o_{cell} = 0.76 + 0.34 = 1.10 \text{ volts}$$

The cell voltage or emf measures the force with which electrons move in the external circuit and therefore measures the tendency of the cell reaction to takes place. Galvanic cells, thus, give quantitative measure of the relative tendency of the various reactions to occur.

(iii) Comparison of Relative Tendency of Metals and Nonmetals to Get Oxidized or Reduced

The value of the reduction potential of a metal or a nonmetal tells us the tendency to lose electrons and act as a reducing agent. It also gives the information about the tendency of a species to gain electrons and act as an oxidizing agent. Greater the value of standard reduction potential of a given species, greater is its tendency to accept electrons to undergo reduction and hence to act as an oxidizing agent. For example, ions like Au^{3+}, Pt^{2+}, Hg^{2+}, Ag^+, Cu^{2+} and the nonmetals elements like F_2, Cl_2, Br_2 and I_2 which lie below the SHE, have a strong tendency to gain electrons and undergo reduction.

The series tell us that strong oxidizing agents like F_2, Cl_2, Br_2, etc. have a large positive value of standard reduction potentials, while strong reducing agents have large negative values like Li, K, Ca, Na,etc. which lie above SHE.

(iv) Relative Chemical Reactivity of Metals

Greater the value of standard reduction potential of a metal, smaller is its tendency to lose electrons to change into a positive ion and hence lower will be its reactivity. For example, metals like Li, Na, K and Rb are highly reactive. Coinage metals, Cu, Ag, and Au are the least reactive because they have positive reduction potentials.

Similarly, metals like Pb, Sn, Ni, Co and Cd which are very close to SHE react very slowly with steam to liberate hydrogen gas, while the metals like Fe, Cr, Zn, Mn, Al and Mg which have more negative reduction potentials react with steam to produce the metallic oxides and hydrogen gas.

(v) Reaction of Matels with Dilute Acids

Greater the value of standard reduction potential of a metal, lesser is its tendency to lose electrons to form metal ions and so weaker is its tendency to displace H^+ ions from acids as H_2 gas. For example, metals like Au, Pt, Ag and Cu which have sufficiently high positive values of reduction potentials, do not liberate hydrogen gas from acids. While, metals like Zn, Mg and Ca which are close to the top of the series and have very low reduction potentials, liberate hydrogen gas, when they react with acids.

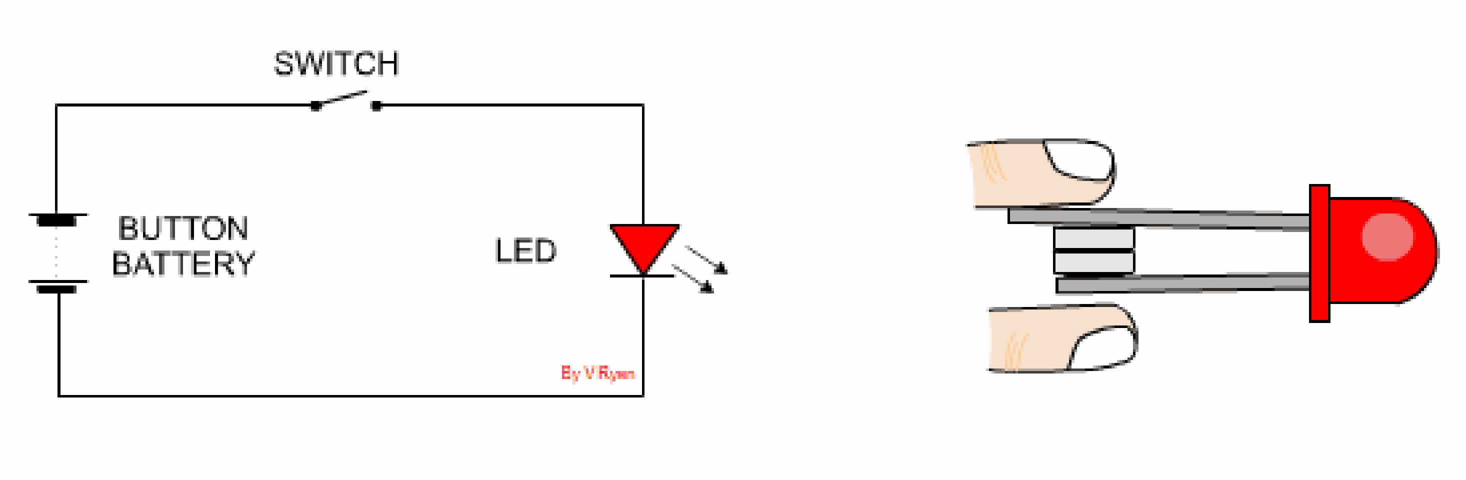
(vi) Displacement of One Metal by Another from its Solution

One metal will displace another metal from the aqueous solution of its salt if it lies above in the electrochemical series. For example, Fe can displace Cu from $CuSO_4$, Zn does not displace Mg from solution of $MgSO_4$.

10.5 MODERN BATTERIES AND FUEL CELLS

Those cells which cannot be recharged are called primary cells. Examples are dry cell, alkaline battery, mercury and silver battery. Those ones which can be recharged are called secondary cells.

Examples are lead-acid battery, Ni-Cd-battery and fuel cells. A few examples of some modern batteries and fuel cell are described in this section.



Animation 10.13: MODERN BATTERIES
Source & Credit : technologystudent

10.5.1 Lead Accumulator or Lead-Acid Battery (Rechargeable)

It is commonly used as a car battery. It is secondary or a storage cell. Passing a direct current through it must charge it. The charged cell can then produce electric current when required. The cathode of a fully charged lead accumulator is lead oxide, PbO_2 and its anode is metallic lead. The electrolyte is 30% sulphuric acid solution (density 1.25 g cm^{-3}). When the two electrodes are connected through an external circuit, it produces electricity by discharge Fig (10.7). A single cell provides around 2 volts. For 12 volts, 6 cells are connected in series.

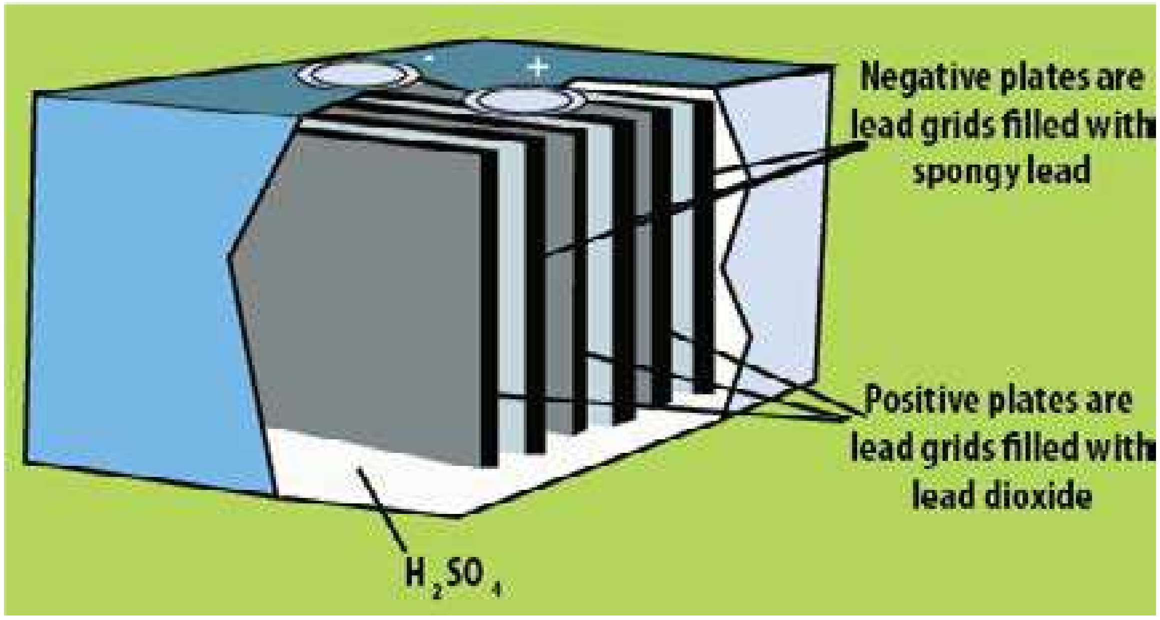
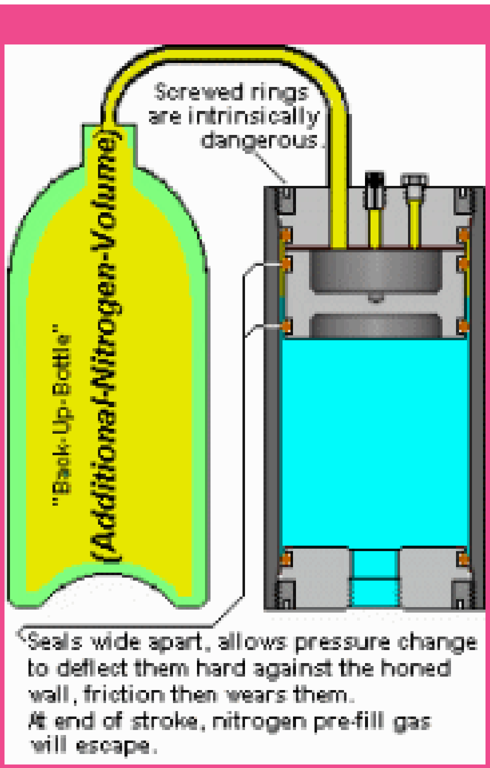


Fig (10.7) Lead accumulator



Animation 10.14: Hydraulic Accumulators
Source & Credit : hydraulic

Discharging

At the anode the lead atoms release two electrons each to be oxidized to Pb^{2+} ions, which combine with SO_4^{2-} ions present in the electrolyte and get deposited on the anode as $PbSO_4$.

At the cathode

$$PbO_{2(s)} + 4H^+_{(aq)} + SO_4{}^{2-}{}_{(aq)} + 2e \rightarrow PbSO_{4(s)} + 2H_2O_{(\ell)} \qquad \text{(reduction)}$$

At the anode

$$Pb_{(s)} + SO_4{}^{2-}{}_{(aq)} \rightarrow PbSO_{4(s)} + 2e^- \qquad \text{(oxidation)}$$

The electrons released pass round an external circuit as an electric current to be used for starting the engine of a vehicle, for lighting up of car lights and so on.

At the cathode the electrons from the anode are accepted by PbO_2 and hydrogen ions from the electrolyte then undergo a redox reaction to produce lead ions and water as follows:

The Pb^2 ions then combine with the SO_4^2 ions and they both deposit at the cathode as $PbSO_4$. When both electrodes are completely covered with $PbSO_4$ deposits, the cell will cease to discharge any more current until it is recharged. The overall reaction is

$$Pb_{(s)} + PbO_{2(s)} + 4H^+_{(aq)} + 2SO_4{}^{2-}{}_{(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(\ell)}$$

A typical 12-V car battery has six cells connected in series. Each delivers 2V Each cell contains two lead grids packed with the electrode materials. The anode is spongy lead , and cathode is powered PbO_4. The grid is immersed in an electrolytic solution of $\approx 3.2M$ H_2SO_4 (30%). Fibre glass sheets between the grids prevent shorting by accidental physic al contact. When the cell is discharged, it generates electrical energy as a voltaic cell.

Recharging

During the process of recharging, the anode and the cathode of the external electrical source are connected to the anode and the cathode of the cell respectively. The redox reactions at the respective electrodes are then reversed. These reactions are summarized as follows:

At anode $PbSO_{4(s)} + 2e \rightarrow Pb_{(s)} + SO_4{}^{2-}{}_{(aq)}$ (reduction)

At cathode $PbSO_{4(s)} + 2H_2O \rightarrow PbO_{2(s)} + 4H^+{}_{(aq)} + SO_4{}^{2-}{}_{(aq)} 2e^-$ (oxidation)

The overall reaction is

$$2PbSO_{4(s)} + 2H_2O \rightarrow Pb_{(s)} + PbO_{2(s)} + 4H^+{}_{(aq)} + SO_4{}^{2-}{}_{(aq)}$$

During the process of discharging, the concentration of the acid falls decreasing its density to 1.15g cm^3. After recharging, the acid is concentrated again bringing its density to its initial value of 1.25g cm^3. At the same time the voltage of the battery, which has dropped during discharging, return to around 12 volts.

10.5.2 Alkaline Battery (non-rechargeable)

It is a dry alkaline cell, which uses zinc and manganese dioxide as reactants. Zinc rod serves as the anode and manganese dioxide functions as the cathode. The electrolyte, however, contains potassium hydroxide and is therefore basic (alkaline).

The battery is enclosed in a steel container. The zinc anode is also slightly porous giving it a larger effective area. This allows the cell to deliver more current than the common dry cell. It has also longer life. The reactions in the alkaline battery.are shown as follows:

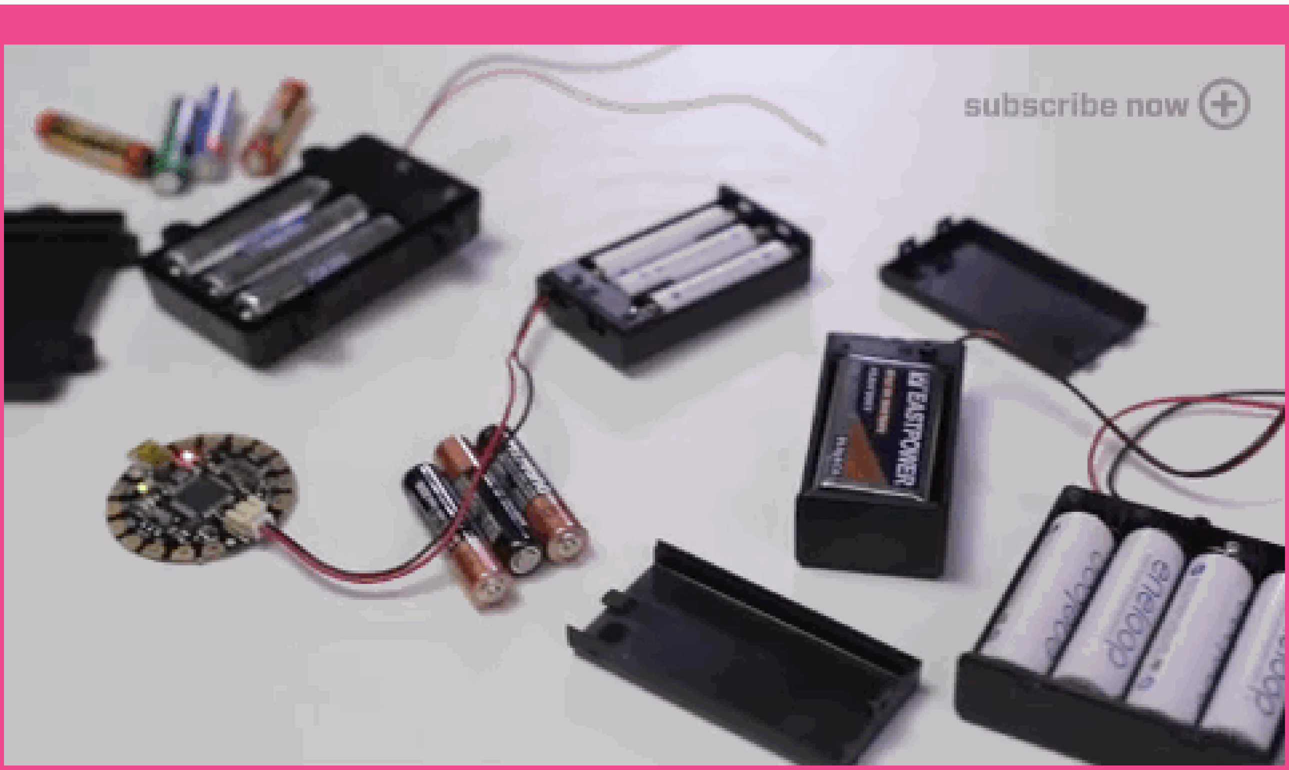
$Zn_{(s)} + 2OH^-{}_{(aq)} \rightarrow Zn(OH)_{2(s)} + 2e^-$ (anode)

$2MnO_{2(s)} + H_2O_{(\ell)} + 2e^- \rightarrow Mn_2O_{3(s)} + 2OH^-{}_{(aq)}$ (cathode)

The overall reaction is

$$Zn_{(s)} + 2MnO_{2(s)} + H_2O_{(l)} \rightarrow Zn(OH)_{(s)} + Mn_2O_{3(s)}$$

The voltage of the cell is 1.5 V



Animation 10.15: Alkaline Battery
Source & Credit : adafruit

10.5.3 Silver Oxide Battery

These tiny and rather expensive batteries Fig. 10.8 have become popular as power sources in electronic watches, auto exposure cameras and electronic calculators. The cathode is of silver oxide, Ag,0, and the anode is of zinc metal. The following reactions occur in a basic electrolyte.

At the anode

$$Zn_{(s)} + 2OH^-_{(aq)} \rightarrow Zn(OH)_{2(s)} + 2e^- \qquad \text{(oxidation)}$$

At the cathode

$$Ag_2O_{(s)} + H_2O_{(\ell)} + 2e^- \rightarrow 2Ag_{(s)} + 2OH^-_{(aq)} \quad \text{(reduction).}$$

The overall reaction is

$$Zn_{(s)} + Ag_2O_{(s)} + H_2O_{(l)} \rightarrow Zn(OH)_2 + 2Ag_{(s)}$$

The voltage of silver oxide battery is about 1.5 V

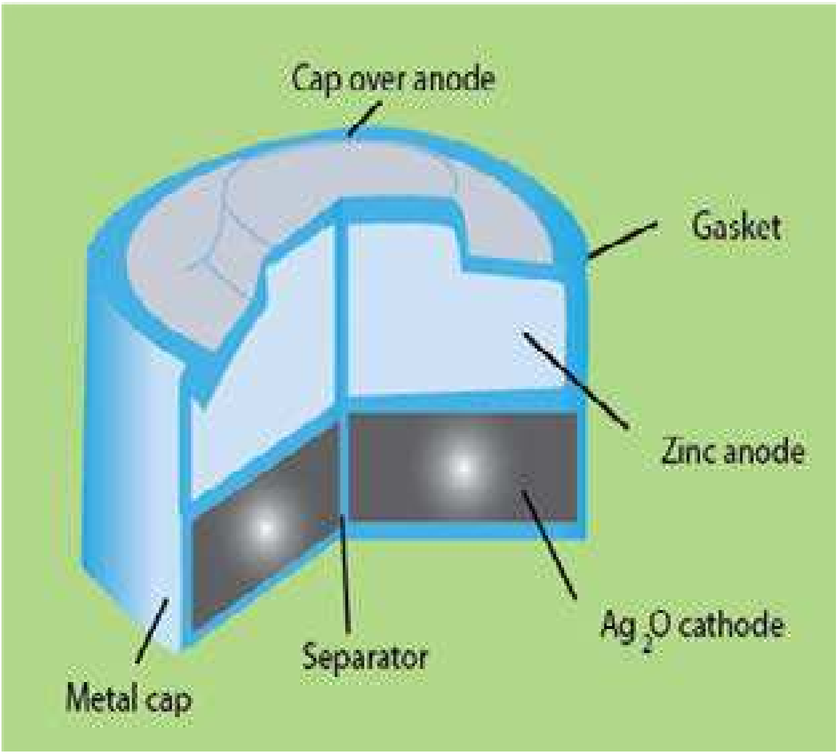


Fig (10.8) A silver oxide battery

10.5.4 Nickel Cadmium Cell (Rechargeable)

A strong cell that has acquired wide spread use in recent years is the NICAD or nickel cadmium battery. It is a rechargeable cell. The anode is composed of cadmium, which undergoes oxidation in an alkaline electrolyte.

At the anode

$$Cd_{(s)} + 2OH^{-}_{(aq)} \rightarrow Cd(OH)_{2(s)} + 2e^{-} \qquad \text{(oxidation)}$$

The cathode is composed of NiO_2 which undergoes reduction.

At the cathode

$$NiO_2 + 2H_2O_{(\ell)} + 2e^- \rightarrow Ni(OH)_{2(s)} + 2OH^-_{(aq)} \qquad \text{(reduction)}$$

The net cell reaction during the discharge is :

$$Cd_{(s)} + NiO_{2(s)} + 2H_2O_{(\ell)} \rightarrow Cd(OH)_{2(s)} + Ni(OH)_{2(s)}$$

Just like lead storage cell, the solid reaction products adhere to the electrodes. For this reason, the reaction is easily reversed during recharging. Because no gases are produced during either charging or discharging, the battery can be sealed. It is used in battery operated tools and portable computers. It also finds its application in cordless razors, photoflash units. It is light weight. Voltage of the cell is 1.4 V.

10.5.5 Fuel Cells (rechargeable)

Fuel cells are other means by which chemical energy may be converted into electrical energy. When gaseous fuels, such as hydrogen and oxygen are allowed to undergo a reaction, electrical energy can be obtained.

This cell finds importance in space vehicles. The cell is illustrated in Fig. (10.10). The electrodes are hollow tubes made of porous compressed carbon impregnated with platinum, which acts as a catalyst. The electrolyte is KOH. At the electrodes, hydrogen is oxidized to water and oxygen is reduced to hydroxide ions.

$$[H_{2(g)} + 2OH^-_{(aq)} \rightarrow 2H_2O_{(\ell)} + 2e^-] \text{ x } 2 \qquad \text{(anode)}$$

$$O_{2(g)} + 2H_2O_{(\ell)} + 4e^- \rightarrow 4OH^-_{(aq)} \qquad \text{(cathode)}$$

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(\ell)} \qquad \text{(overall reaction)}$$

Such a cell runs continuously as long as reactants are supplied.

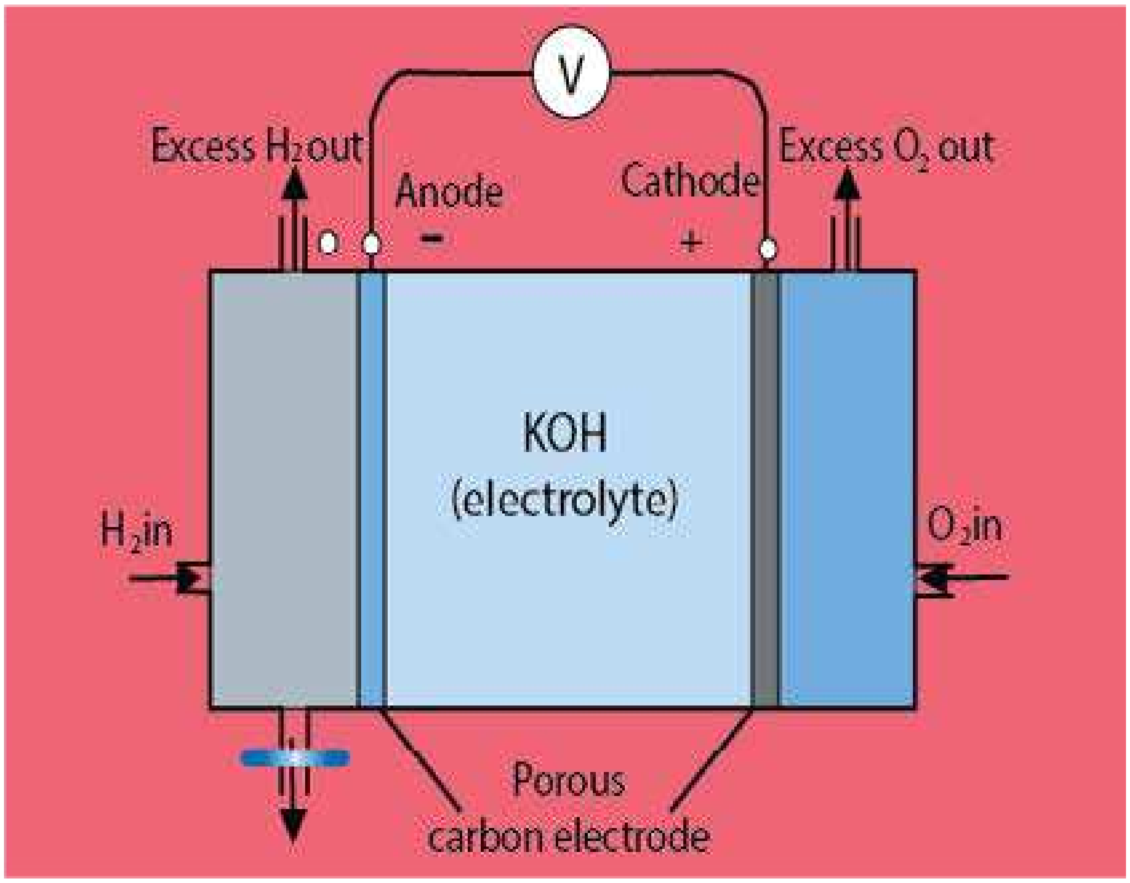
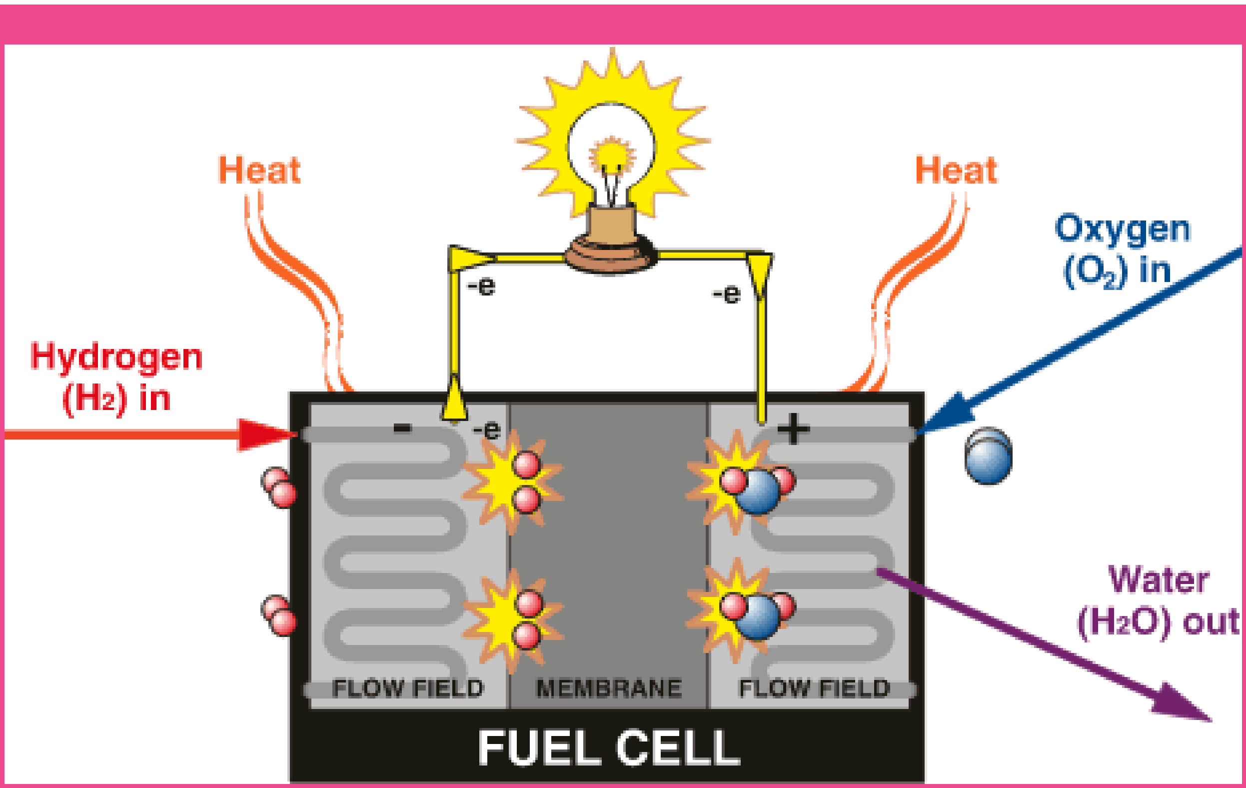


Fig (10.10) Hydrogen - Oxygen Fuel cell



Animation 10.16: Fuel Cells
Source & Credit : solaren

This fuel cell is operated at a high temperature so that the water formed as a product of the cell reaction evaporates and may be condensed and used as drinking water for an astronaut. A number of these cells are usually connected together so that several kilowatts of power can be generated.

The fuel cell produce electricity and pure water during space flights. Fuel cell are light, portable and sources of electricity. Many fuel cells do not produce pollutants. Some other cell reactions in fuel cell are :

(i) $2NH_3 + 3/2\ O_2 \rightarrow N_2 + 3H_2O_{(\ell)}$

(ii) $N_4H_4 + O_2 \rightarrow N_2 + 2H_2O_{(\ell)}$

(iii) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O_{(\ell)}$

Fuel cells are very efficient. They convert about 75% of fuels bond energy into electricity.

KEY POINTS

1. Electrochemistry is the branch of science which deals with the conversion of electrical energy to chemical energy and vice versa.
2. Electrolytic conduction is carried out by the ions produced when an ionic compound is in fused state or dissolved in water. Electrolysis is the process in which a chemical reaction takes place at the expense of electrical energy. Electrolysis is used for the extraction of elements and for the commercial preparation of several compounds. It is also used for electroplating.
3. A Galvanic or a voltaic cell produces electrical energy at the expense of chemical energy. Electrode potential is developed when a metal is dipped into a solution of its own ions.
4. The potential of standard hydrogen electrode is arbitrarily fixed as 0.00 volts. Electrode potential of an element is measured when it is coupled with standard hydrogen electrode. When elements are arranged in order of their standard electrode potentials on the hydrogen scale, the resulting list is known as electrochemical series. Electrochemical series is used to predict the feasibility of a redox chemical reaction.
5. Modern batteries and fuel cell include lead accumulator, alkaline battery, silver oxide battery, nickel cadmium cell and hydrogen oxygen fuel cell.
6. The oxidation number is the apparent charge which an atom has in a molecule. Redox chemical equations can be balanced using oxidation number method and ion electron method.

EXERCISE

Q.1 Multiple choice questions. For each question there are four possible answers a, b, c and d. Choose the one you consider correct.

(i) The cathodic reaction in the electrolysis of dil. H_2SO_4 with Pt electrodes is:-

(a) Reduction (b) Oxidation

(c) Both oxidation and reduction (d) Neither oxidation or reduction

(ii) Which of the following statements is not correct about galvanic cell?

(a) Anode is negatively charged (b) Reduction occurs at anode

(c) Cathode is positively charged (d) Reduction occurs at cathode

(iii) Stronger the oxidizing agent, greater is the:

(a) oxidation potential (b) reduction potential

(c) redox potential (d) E.M.F of cell

(iv) If the salt bridge is not used between two half cells, then the voltage.

(a) Decrease rapidly (b) Decrease slowly

(c) Does not change (d) Drops to zero

(v) If a strip of Cu metal is placed in a solution of $FeSO_4$:

(a) Cu will be deposited (b) Fe is precipitated out

(c) Cu and Fe both dissolve (d) No reaction take place

Q.2 Fill in the blank.

(i) The oxidation number of O-atom is __________ in OF_2 and is __________ in H_2O_2.

(ii) Conductivity of metallic conductors is due to the flow of _______while that of electrolytes is due to flow of________ .

(iii) Reaction taking place at the _______is termed as oxidation and at the ________ is called as reduction.

(iv) ________ is set up when a metal is dipped in its own ions.

(v) Cu metal_________ the Cu-cathode when electrolysis is performed for $CuSO_4$ solution with Cu- cathodes.

(vi) The reduction potential of Zn is _________ volts and its oxidation potential is _________ volts.

(vii) In a fuel cell,__________react together in the presence of_____ .

Q.3 Mark the following statements true or false.

(i) In electrolytic conduction, electrons flow through the electrolyte.

(ii) In the process of electrolysis, the electrons in the external circuit flow from cathode to anode.

(iii) Sugar is a non-electrolyte in solid form and when dissolved in water will allow the passage of an electric current.

(iv) A metal will only allow the passage of an electric current when it is in cold state.

(v) The electrolytic products of aqueous copper (II) chloride solution are copper and chlorine.

(vi) Zinc can displace iron form its solution.

(vii) S.H.E. acts as cathode when connected with Cu-electrode.

(viii) A voltaic cell produces electrical energy at the expense of chemical energy.

(ix) Lead storage battery is not a reversible cell.

(x) Cr changes its oxidation number when $K_2Cr_2O_7$ reacts with HCl.

Q.4 (a) Explain the term oxidation number with examples.

(b) Describe the rules used for the calculation of oxidation number of an element in molecules and ions giving examples.

(c) Calculate the oxidation number of chromium in the following compounds.

(i) $CrCl_3$ (ii) $Cr_2(SO_4)_3$ (iii) K_2CrO_4 (iv) $K_2Cr_2O_7$

(v) CrO_3 (vi) Cr_2O_3 (vii) $Cr_2O_7^{2-}$

(Ans: (i)+3,(ii)+3,(iii)+6,(iv)+6,(v) + 6(vi)+3)

(d) Calculate the oxidation numbers of the elements underlined in the following compounds.

(i) $Ca(\underline{Cl}O_3)_2$ (ii) $Na_2\underline{C}O_3$ (iii) $Na_2\underline{P}O_4$ (iv) $H\underline{N}O_3$

(v) $Cr_2(\underline{S}O_4)_3$ (vi) $H\underline{P}O_3$ (vii) $K_2\underline{Mn}O_4$

(Ans : (i) +5, (ii) +4, (iii) +5, (iv) +5, (v) +6 , (vi)+5 (vii) + 6)

Q.5 (a) Describe the general rules for balancing a redox equation by oxidation number method.

(b) Balance the following equations by oxidation number method

(i) $Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO_2 + H_2O$

(ii) $Zn + HNO_3 \rightarrow Zn(NO_3)_2 + NO + H_2O$

(iii) $Br_2 + NaOH \rightarrow NaBr + NaBrO_3 + H_2O$

(iv) $MnO_2 + HCl \rightarrow MnCl_2 + H_2O + Cl_2$

(v) $FeSO_4 + K_2Cr_2O_7 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + H_2O$

(vi) $HNO_3 + HI \rightarrow NO + H_2O + I_2$

(vii) $Cu + H_2SO_4 \rightarrow CuSO_4 + SO_2 + H_2O$

(viii) $HI + H_2SO_4 \rightarrow I_2 + SO_2 + H_2O$

(ix) $NaCl + H_2SO_4 + MnO_2 \rightarrow Na_2SO_4 + MnSO_4 + H_2O + Cl_2$

Q.6 (a) Describe the general rules for balancing a redox equation by ion-electron method.

(b) Balance the following ionic equations by ion-electron method.

(i) $Fe^{3+} + Sn^{2+} \rightarrow Fe^{2+} + Sn^{4+}$

(ii) $MnO_4{}^{1-}{}_{(aq)} + C_2O_4{}^{2-}{}_{(aq)} \rightarrow Mn^{2+}{}_{(aq)} + CO_{2(g)}$

(iii) $Cr_2O_7{}^{2-} + Cl^{-} \rightarrow 2Cr^{3+} + 3Cl_2$

(iv) $Cu + NO_3{}^{1-} \rightarrow Cu^{2+} + 2NO_2$

(v) $Cr_2O_7{}^{2-} + Fe^{2+} \rightarrow Cr^{3+} + Fe^{3+}$ (acidic media)

(vi) $S_2O_3{}^{2-} + OCl^{1-} \rightarrow Cl^{-} + S_4O_6{}^{2-}$ (acidic media)

(vii) $IO_3{}^{1-} + AsO_3{}^{3-} \rightarrow I^{-} + AsO_4{}^{3-}$ (acidic media)

(viii) $Cr^{3+} + BiO_3{}^{1-} \rightarrow Cr_2O_7{}^{2-} + 3Bi^{3+}$ (acidic media)

(ix) $H_3AsO_3 + Cr_2O_7{}^{2-} \rightarrow 3H_3AsO_4 + 2Cr^{3+}$ (acidic media)

(x) $CN^{-} + MnO_4{}^{1-} \rightarrow CNO^{-} + MnO_{2(s)}$ (basic media)

Q.7 Describe the electrolysis of molten sodium chloride, and a concentrated solution of sodium chloride.

Q.8 What is the difference between single electrode potential and standard electrode potential? How can it be measured? Give its importance.

Q.9 Outline the important applications of electrolysis. Write the electrochemical reactions involved therein.Discuss the electrolysis of $CuSO_4$ using Cu-electrodes and $AgNO_3$ solution using Ag electrode.

Q.10 Describe the construction and working of standard hydrogen electrode.

Q.11 Is the reaction $Fe^{3+} + Ag \rightarrow Fe^{2+} + Ag^{+}$ spontaneous? If not, write spontaneous reaction involving these species.

Q.12 Explain the difference between

(a) Ionization and electrolysis. (b) Electrolytic cell and voltaic cell

(c) Conduction through metals and molten electrolytes.

Q.13 Describe a galvanic cell explaining the functions of electrodes and the salt bridge.

Q.14 Write comprehensive notes on:

(a) Spontaneity of oxidation reduction reactions.

(b) Electrolytic conduction.

(c) Alkaline, silver oxide and nickel-cadmium batteries, fuel cell.

(d) Lead accumulator, its desirable and undesirable features.

Q.15 Will the reaction be spontaneous for the following set of half reactions. What will be the value of E_{cell}?

(i) $Cr^{3+}_{(aq)} + 3e^- \rightarrow Cr_{(s)}$

(ii) $MnO_{2(s)} + 4H^+ + 2e^- \rightarrow Mn^{2+}_{(aq)} + 2H_2O_{(\ell)}$

(Standard reduction potential for reaction (i) = -0.74V and for the reaction (ii) = + 1.28V).

Q16. Explain the following with reasons.

(a) A porous plate or a salt bridge is not required in lead storage cell.

(b) The standard oxidation potential of Zn is 0.76 V and its reduction potential is -0.76 V

(c) Na and K can displace hydrogen from acids but Pt, Pd and Cu can not.

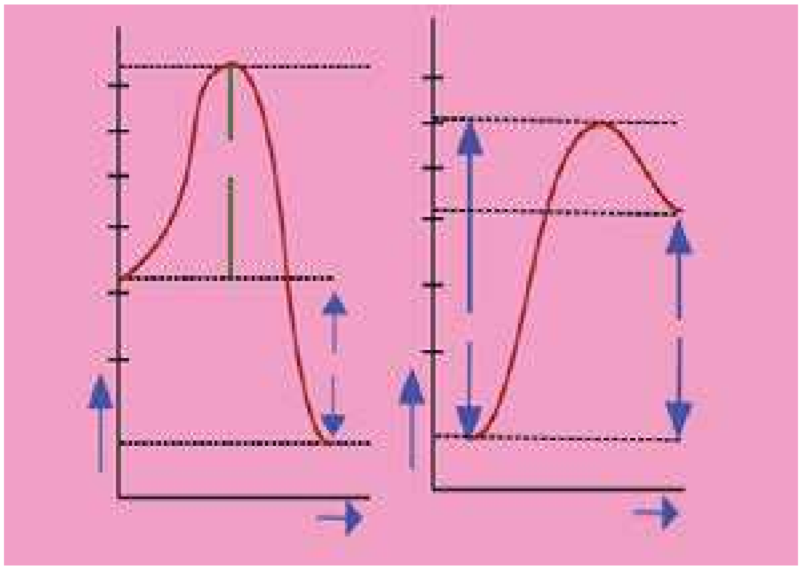
(d) The equilibrium is set up between metal atoms of electrode and ions of metal in a cell.

(e) A salt bridge maintains the electrical neutrality in the cell.

(f) Lead accumulator is a chargeable battery.

(g) Impure Cu can be purified by electrolytic process.

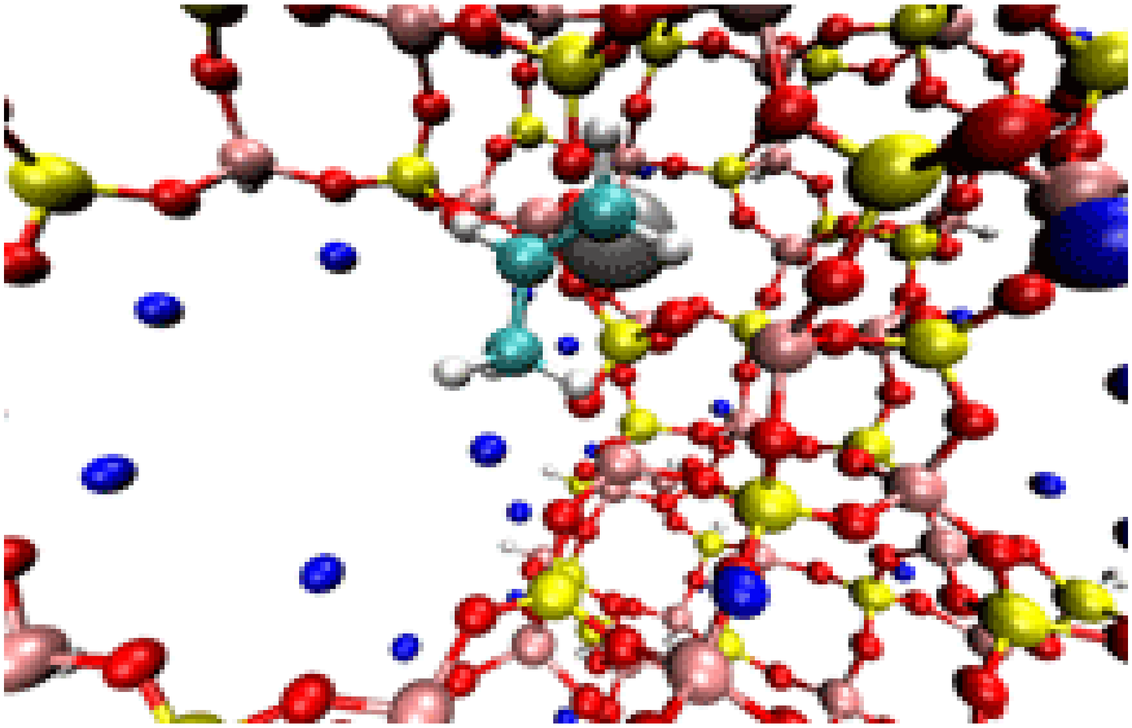
(h) SHE acts as anode when connected with Cu electrode but as cathode with Zn electrode.



CHAPTER

11

REACTION KINETICS

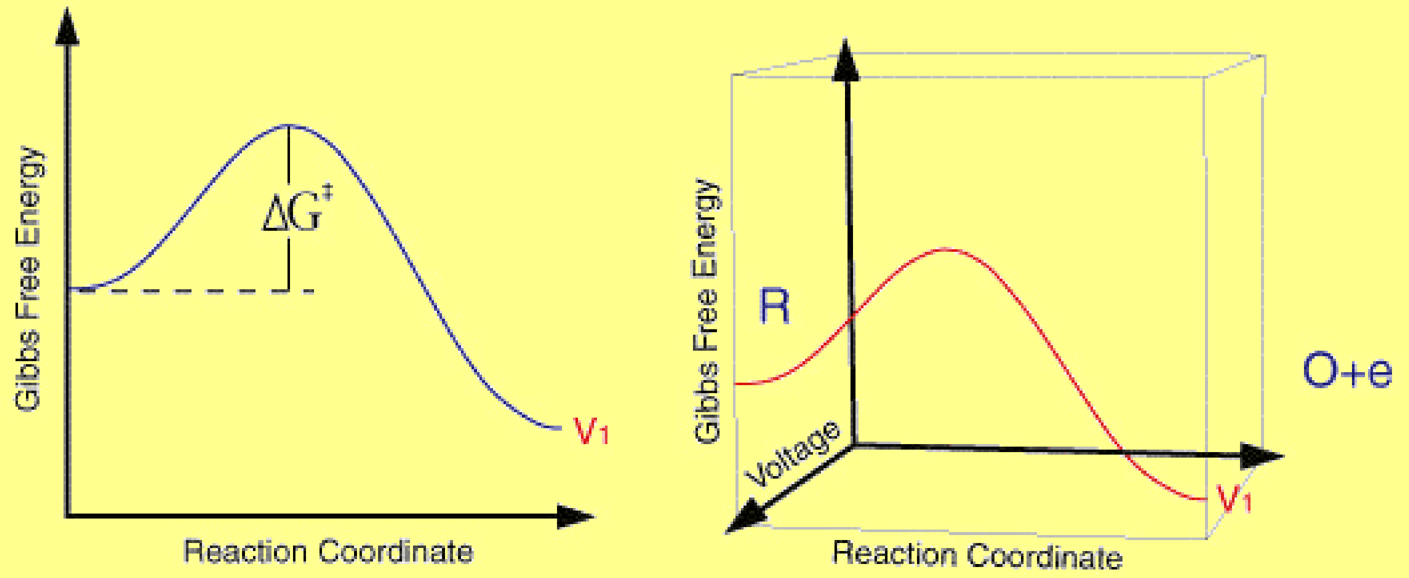


Animation 11.1: Spectrometer
Source & Credit: eLearn

11.0.0 INTRODUCTION

It is a common observation that rates of chemical reactions differ greatly. Many reactions, in aqueous solutions, are so rapid that they seem to occur instantaneously. For example, a white precipitate of silver chloride is formed immediately on addition of silver nitrate solution to sodium chloride solution. Some reactions proceed at a moderate rate e.g. hydrolysis of an ester. Still other reactions take a much longer time, for example,the rusting of iron, the chemical weathering of stone work of buildings by acidic gases in the atmosphere and the fermentation of sugars.

The studies concerned with rates of chemical reactions and the factors that affect the rates of chemical reactions constitute the subject matter of reaction kinetics. These studies also throw light on the mechanisms of reactions. All reactions occur in single or a series of steps. If a reaction consists of several steps, one of the steps will be the slowest than all other steps. The slowest step is called the rate determining step. The other steps will not affect the rate. The rates of reactions and their control are often important in industry. They might be the deciding factors that determine whether a certain chemical reaction may be used economically or not. Many factors influence the rate of a chemical reaction. It is important to discover the conditions under which the reaction will proceed most economically.

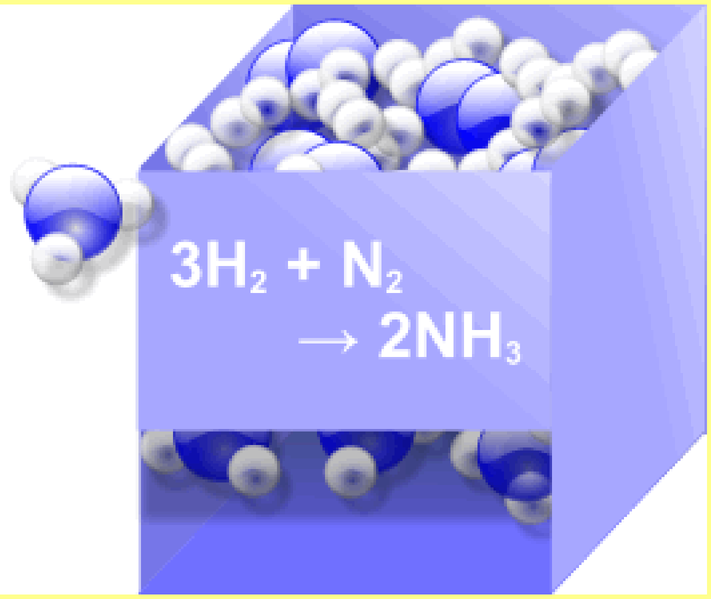


Animation 11.2: Kinetics
Source & Credit : ceb.cam

11.1.0 RATE OF REACTION

During a chemical reaction, reactants are converted into products. So the concentration of the products

increases with the corresponding decrease in the concentration of the reactants as they are being consumed.



Animation 11.3: RATE OF REACTION
Source & Credit : blobs

The situation is explained graphically in Fig.(11.1) for the reactant A which is changing irreversibly to the product B.

The slope of the graph for the reactant or the product is the steepest at the beginning. This shows a rapid decrease in the concentration of the reactant and consequently, a rapid increase in the concentration of the product. As the reaction proceeds, the slope becomes less steep indicating that the reaction is slowing down with time. It means that the rate of a reaction is changing every moment. The following curve for reactants should touch the time axis in the long run. This is the stage of completion of reaction. The rate of a reaction is defined as the change in concentration of a reactant or a product divided by the time taken for the change.

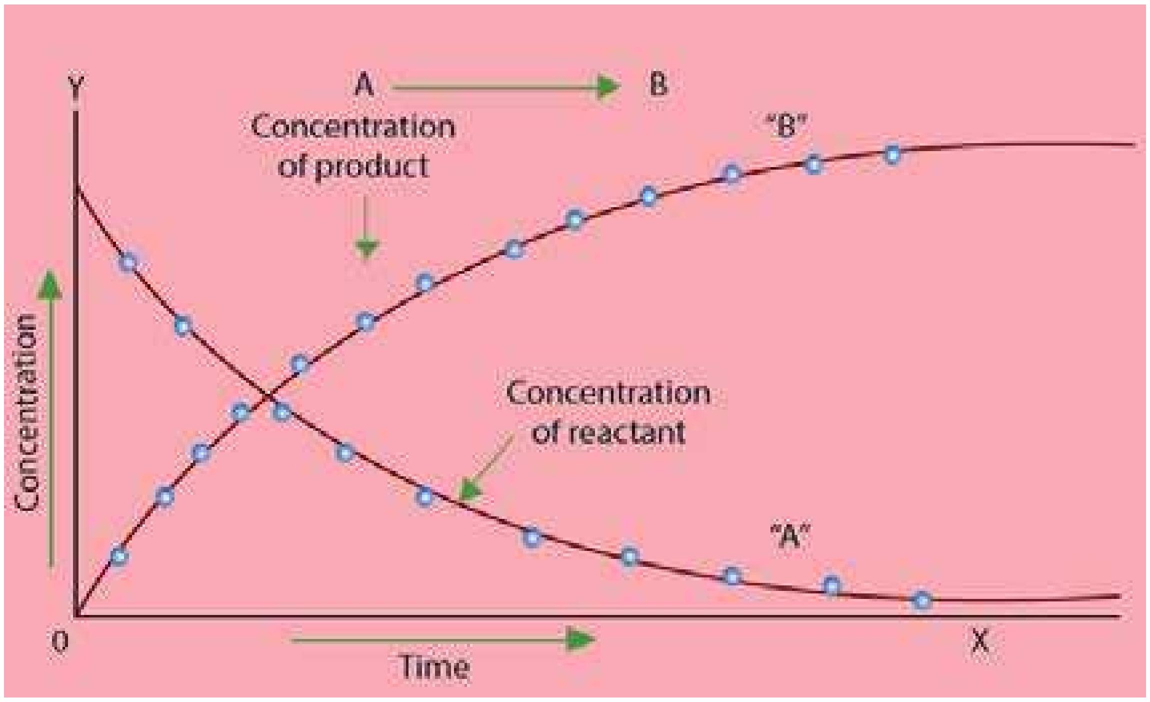


Fig. (11.1) Change in the concentration of reactants and products with time for the reaction

$A \rightarrow B$

The rate of reaction has the units of concentration divided by time. Usually the concentration is expressed in mol dm^{-3} and the time in second, thus the units for the reaction rate are mol $dm^{-3}s^{-1}$.

$$\text{Rate of reaction} = \frac{\text{change in concentration of the substance}}{\text{time taken for the change}}$$

For a gas phase reaction, units of pressure are used in place of molar concentrations. It follows from the above graph that the change in concentration of the reactant A or the product B is much more at the start of reaction and then it decreases gradually.

So the reaction rate decreases with time. It never remains uniform during different time periods. It decreases continuously till the reaction ceases.

$$\text{Rate of reaction} = \frac{\text{mol dm}^{-3}}{\text{seconds}} = \text{mol dm}^{-3}\ \text{s}^{-1}$$

11.1.1 Instantaneous and Average Rate

The rate at any one instant during the interval is called the instantaneous rate. The rate of reaction between two specific time intervals is called the average rate of reaction.

The average rate and instantaneous rate are equal for only one instant in any time interval. At first, the instantaneous rate is higher than the average rate. At the end of the interval the instantaneous rate becomes lower than the average rate. As the time interval becomes smaller, the average rate becomes closer to the instantaneous rate.

The average rate will be equal to the instantaneous rate when the time interval approaches zero. Thus the rate of reaction is instantaneous change in the concentration of a reactant or a product at a given moment of time.

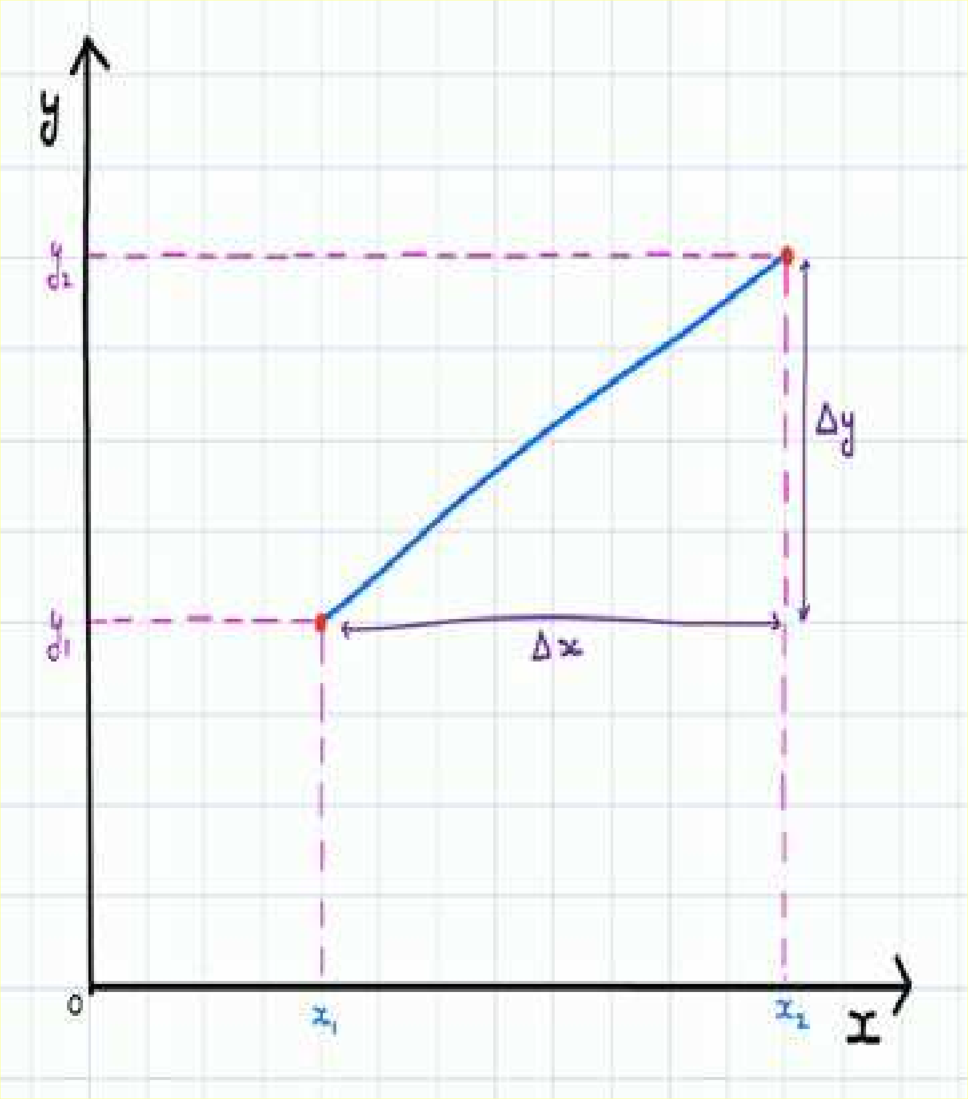
$$\text{Rate of reaction} = \frac{dx}{dt}$$

Where dx is a very small change in the concentration of a product in a very small time interval dt. Hence, dx/dt is also called rate of change of concentration with respect to time.

The rate of a general reaction, $A \rightarrow B$, can be expressed in terms of rate of disappearance of the reactant A or jthe rate of appearance of the product B. Mathematically,

$$\text{Rate of reaction} = \frac{-d[A]}{dt} = +\frac{d[B]}{dt}$$

Where d[A] and d[B] are the changes in the concentrations of A and B, respectively. The negative sign in the term indicates a decrease in the concentration of the reactant A. Since the concentration of product increases with time, the sign in rate expression involving the change of concentration of product is positive.



Animation 11.4: Average and Instantaneous Rate of Change
Source & Credit : brilliant

11.1.2 Specific Rate Constant or Velocity Constant

The relationship between the rate of a chemical reaction and the active masses, expressed as concentrations, of the reacting substances is summarized in the law of mass action. It states that the rate of reaction is proportional to the active mass of the reactant or to the product of active masses if more than one reactants are involved in a chemical reaction.

For dilute solutions, active mass is considered as equal to concentration. By applying the law of mass action to a general reaction.

$$aA + bB \rightarrow cC + dD$$

Rate of reaction $= k\,[A]^a\ [B]^b$

This expression is called rate equation. The brackets [ ] represent the concentrations and the proportionality constant k is called rate constant or velocity constant for the reaction.

If $[A] = 1\ \text{mol dm}^{-3}$ and $[B] = 1\ \text{mol dm}^{-3}$

$$\text{Rate of reaction} = k \times 1^a \times 1^b = k$$

Hence the specific rate constant of a chemical reaction is the rate of reaction when the concentrations of the reactants are unity. Under the given conditions, k remains constant, but it changes with temperature.

Animation 11.5: Velocity Constant
Source & Credit : wikia

11.1.3 Order of Reaction

For a general reaction between A and B where ‘a’ moles of A and ‘b’ moles of B react to form ’c’ moles of C and ’d’ moles of D.

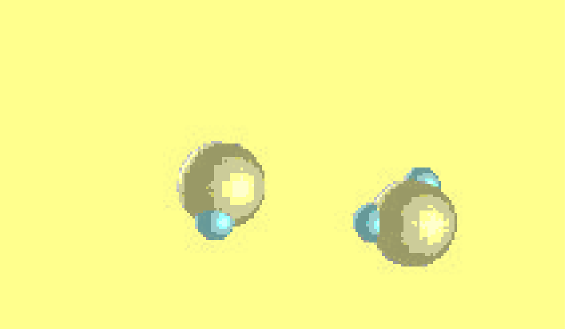
$$aA + bB \rightarrow cC + dD$$

We can write the rate equation as:

$$R = k\,[A]^a\ [B]^b$$

The exponent ’a’ or ‘b’ gives the order of reaction with respect to the individual reactant. Thus the reaction is of order ‘a’ with respect to A and of order b with respect to B. The overall order of reaction is (a+b). The order of reaction is given by the sum of all the exponents to which the concentrations in the rate equation are raised. The order of reaction may also be defined as the number of reacting molecules, whose concentrations alter as a result of the chemical change.

It is important to note that the order of a reaction is an experimentally determined quantity and can not be inferred simply by looking at the reaction equation. The sum of the exponents in the rate equation may or may not be the same as in a balanced chemical equation. The chemical reactions are classified as zero, first, second and third order reactions. The order of reaction provides valuable information about the mechanism of a reaction.



Animation 11.6: Rate and Order of Reaction
Source & Credit : science.uwaterloo

Examples of Reactions Showing Different Orders

1. Decomposition of nitrogen pentoxide involves the following equation.

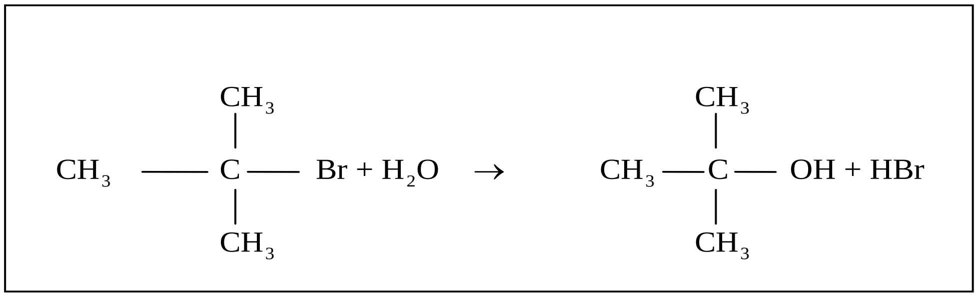
$$2N_2O_5(g) \rightarrow 2N_2O_4(g) + O_2(g)$$

The experimentally determined rate equation for this reaction is as follows:

$$\text{Rate} = k[N_2O_5]$$

This equation suggests that the reaction is first order with respect to the concentration of N_2O_5.

2. Hydrolysis of tertiary butyl bromide



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br + H_2O \rightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH + HBr$$

The rate equation determined experimentally for this reaction is

$$\text{Rate} = k[(CH_3)_3CBr]$$

The rate of reaction remains effectively independent of the concentration of water because, being a solvent, it is present in very large excess. Such type of reactions have been named as pseudo first order reactions.

3. Oxidation of nitric oxide with ozone has been shown to be first order with respect to NO and first order with respect to O_3. The sum of the individual orders gives the overall order of reaction as two.

$$NO(g)+O_3(g) \rightarrow NO_2(g)+O_2(g)$$

$$\text{Rate} = k[NO][O_3]$$

4. Consider the following reaction

$$2FeCl_3(aq) + 6KI(aq) \rightarrow 2FeI_2(aq) + 6KCI(aq) + I_2$$

This reaction involves eight reactant molecules but experimentally it has been found to be a third order reaction.

$$\text{Rate} = k[FeCl_3][KI]^2$$

This rate equation suggests that the reaction is, in fact, taking place in more than one steps. The possible steps of the reaction are shown below.

$$FeCl_3(aq) + 2KI(aq) \xrightarrow{\text{slow}} FeI_2(aq) + 2KCl(aq) + Cl^-(aq)$$

$$2KI(aq) + 2Cl^-(aq) \xrightarrow{\text{fast}} 2KCl(aq) + I_2(s)$$

5. The order of a reaction is usually positive integer or a zero, but it can also be in fraction or can have a negative value. Consider the formation of carbon tetrachloride from chloroform.

$$CHCl_3(\ell) + Cl_2(g) \rightarrow CCl_4(\ell) + HCl(g)$$

$$\text{Rate} = k[CHCl_3][Cl_2]^{1/2}$$

The sum of exponents will be 1 + 1/2= 1.5, so the order of this reaction is 1.5.

From the above examples, it is clear that order of reaction is not necessarily depending upon the coeffients of balanced equation. The rate equation is an experimental expression. A reaction is said to be zero order if it is entirely independent of the concentration of reactant molecules. Photochemical reactions are usually zero order.

11.1.4 Half Life Period

Half life period of a reaction is the time required to convert 50% of the reactants into products. For example, the half life period for the decomposition of N_2O_5 at 45°C is 24 minutes.

It means that if we decompose 0.10 mole dm^{-3} of N_2O_5 at 45 °C, then after 24 minutes 0.05 mole dm^{-3} of N_2O_5 will be left behind. Similarly after 48 minutes 0.025(25%) mole dm^{-3} of N_2O_5 will remain unreacted and after 72 minutes (3 half times) 0.0125 (12.5%) mole dm^{-3} of N_2O_5, will remain unreacted.

Decomposition of N_2O_5 is a first order reaction and the above experiment proves that the half-life period of this reaction is independent of the initial concentration of N_2O_5. This is true for all first order reactions. The disintegration of radioactive $^{235}_{92}U$ has a half-life of 7.1×10^8 or 710 million years. If one kilogram sample disintegrates, then 0.5 kg of it is converted to daughter elements in 710 million years. Out of 0.5 kg of $^{235}_{92}U$, 0.25kg disintegrates in the next 710 million years. So, the half-life period for the disintegration of a radioactive substance is independent of the amount of that substance.

What is true for the half-life period of first order reactions does not remain true for the reactions having higher orders. In the case of second order reaction, the half-life period is inversely proportional to the initial concentration of the reactant. For a third order reaction, half life is inversely proportional to the square of initial concentration of reactants. Briefly we can say that

$$[t_{1/2}]_1 \propto \frac{1}{a^o}, \quad \text{scince}[t_{1/2}]_1 = \frac{0.693}{k}$$

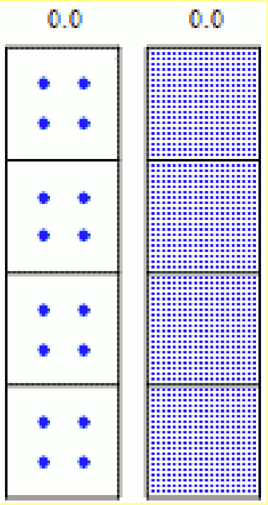
$$[t_{1/2}]_2 \propto \frac{1}{a^1}, \quad \text{scince}[t_{1/2}]_2 = \frac{1}{k_a}$$

$$[t_{1/2}]_3 \propto \frac{1}{a^2}, \quad \text{scince}[t_{1/2}]_3 = \frac{1.5}{ka^2}$$

Where $[t_{1/2}]_1$, $[t_{1/2}]_2$, and $[t_{1/2}]_3$ are the half-life periods for 1st, 2nd and 3rd order reactions respectively and 'a' is the initial concentration of reactants. In general for the reaction of nth order:

$$[t_{1/2}]_n \propto \frac{1}{a^{n-1}}$$

The half-life period of any order reaction is, thus, inversely proportional to the initial concentration raised to the power one less than the order of that reaction. So, if one knows the initial concentration and half-life period of a reaction, then order of that reaction can be determined.



Animation 11.7: Half Life
Source & Credit : askiitians

Example 1:

Calculate the half-life period of the following reaction when the initial concentration of HI is 0.05 M.

$$2HI(g) \rightarrow H_2(g) + I_2(g)$$

The value of rate constant k = 0.079 $dm^3\ mol^{-1}\ s^{-1}$ at 508 °C and rate expression is

$$\text{Rate} = k[HI]^2$$

Solution:

According to the rate expression it is a second order reaction. The half life paired of a second order reaction is

$$\left[t_{\frac{1}{2}}\right]_2 = \frac{1}{ka^{2-1}} = \frac{1}{ka}$$

Putting the values of k and a.

So, $$\left[t_{\frac{1}{2}}\right]_2 = \frac{1}{k \text{ x } a} = \frac{1}{(0.079dm^3mol^{-1}s^{-1})(0.050moldm^{-3})} = \frac{1}{0.079 \text{ x } 0.05}\text{sec.}$$

$$\left[t_{\frac{1}{2}}\right]_2 = \boxed{253\text{sec}}\text{Answer}$$

So, in 253 seconds, the half of HI i.e., 0.05/2=0.025 moles is decomposed.

11.1.5 Rate Determining Step

Finding out the rate equation of a reaction experimentally is very useful. Actually it gives us an opportunity to look into the details of reaction. Rate equation of example (4) in article 11.1.3 showed clearly that the reaction is taking place in more than one steps. There are many such reactions in chemistry which occur in a series of steps.

If a reaction occurs in several steps, one of the steps is the slowest. The rate of this step determines the overall rate of reaction. This slowest step is called the rate determining or rate limiting step. The total number of molecules of reacting species taking part in the rate determining step appear in the rate equation of the reaction.

Let us consider the following reaction

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

The rate equation of the reaction is found to be

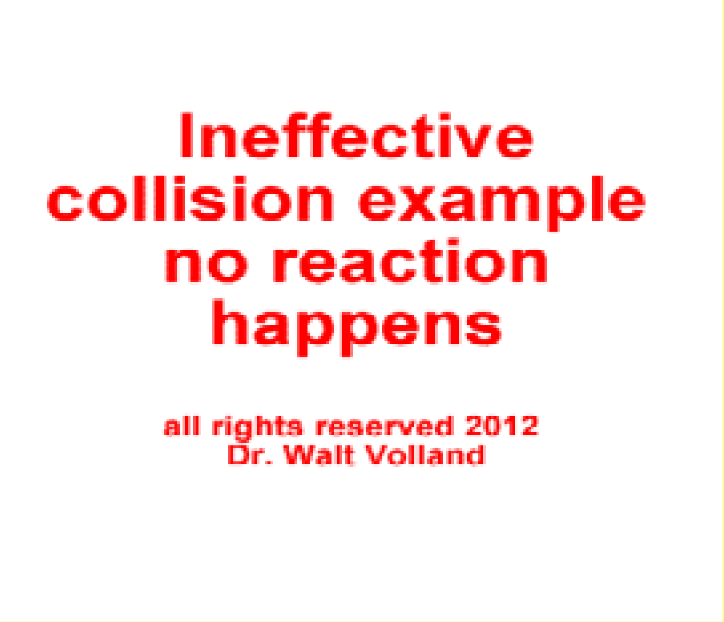
$$\text{Rate} = k[NO_2]^2$$

This equation shows that the rate of reaction is independent of the concentration of carbon monoxide. In other words the equation tells us that reaction involves more than one steps and two molecules of NO_2 are involved in the rate determining step. The proposed mechanism for this reaction is as follows.

$$NO_2(g) + NO_2(g) \xrightarrow{\text{slow}} NO_3(g) + NO(g) \quad \text{(rate determining step)}$$

$$NO_3(g) + CO(g) \xrightarrow{\text{fast}} NO_2(g) + CO_2(g)$$

The first step is the rate determining step and NO_3 which does not appear in the final balanced equation, is called the reaction intermediate. The reaction intermediate has a temporary existence and it is unstable relative to the reactants and the products. This is a species with normal bonds and may be stable enough to be isolated under special conditions. This reaction is a clear example of the fact that a balanced chemical equation may not give any information about the way the reaction actually takes place.



Ineffective collision example no reaction happens

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Dr. Walt Volland

Animation 11.8: Rate Determining Step
Source & Credit : 800mainstreet

11.2.0 DETERMINATION OF THE RATE OF A CHEMICAL REACTION

Determination of the rate of a chemical reaction involves the measurement of the concentration of reactants or products at regular time intervals as the reaction progresses. When the reaction goes on, the concentrations of reactants decrease and those of products increase. The rate of a reaction, therefore, is expressed in terms of the rates at which the concentrations change.

$$\text{Rate of reaction} = \frac{\Delta C}{\Delta t} = \frac{\text{mol dm}^{-3}}{\text{seconds}}$$

$$= \text{mol dm}^{-3}\text{s}^{-1}$$

Suppose, the concentration of a reactant of any chemical reaction changes by 0.01 mol dm^{-3} in one second, then rate of reaction is, 0 .01 mole dm^{-3} s^{-1}.

Rate of a chemical reaction always decreases with the passage of time during the progress of reaction. To determine the rate of reaction for a given length of time, a graph is plotted between time on x-axis and concentration of reactant on y-axis whereby a curve is obtained.

To illustrate it, let us investigate the decomposition of HI to H_2 and I_2 at 508°C. Table(11.1) tells us that the change in concentration of HI for first 50 seconds is 0.0284 mol dm^{-3} but between 300 to 350 sec, the decrease is 0.0031 mol dm^3. By using the data, a graph is plotted as shown in Fig (11.2). The graph is between time on x-axis and concentration of HI in mol dm^{-3} on y-axis. Since HI is a reactant, so it is a falling curve. The steepness of the concentration-time curve reflects the progress of reaction. Greater the slope of curve near the start of reaction, greater is the rate of reaction.

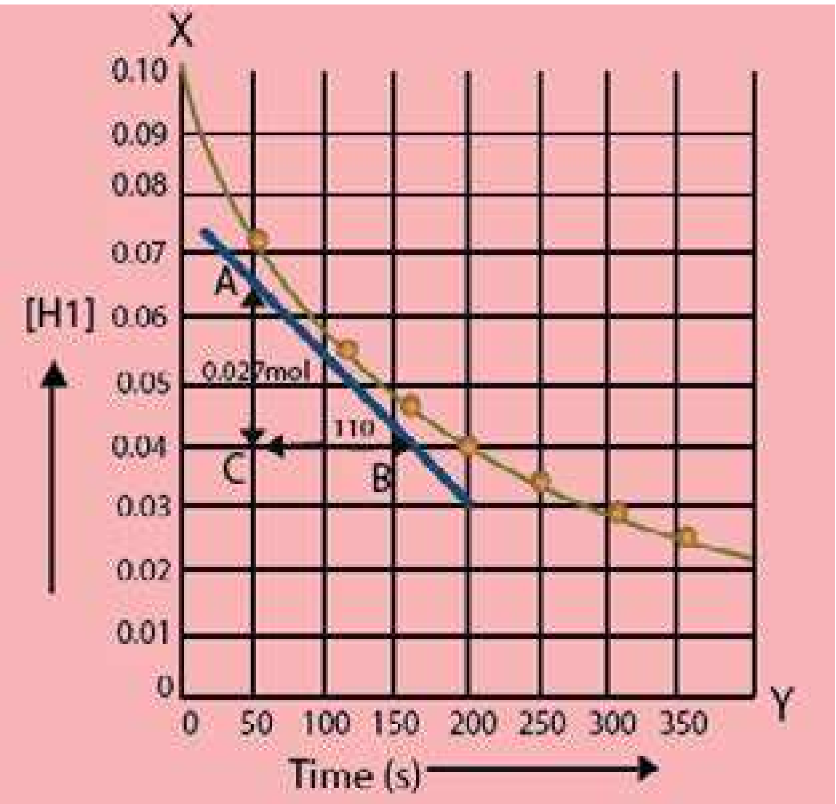


Fig.(11.2) T he change in the HI concentration with time for the reaction $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ at 508°C.

Table (11.1) Change in concentration of HI with regular intervals $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

Concentration of HI (mol dm^{-3})	Time (s)
0.100	0
0.0716	50
0.0558	100
0.0457	150
0.0387	200
0.0336	250
0.0296	300
0.0265	350

In order to measure the rate of reaction, draw a tangent say, at 100 seconds, on the curve and measure the slope of that tangent. The slope of the tangent is the rate of reaction at that point i.e., after 100 seconds. A right angled triangle ABC is completed with a tangent as hypotenuse. Fig. (11.2) shows that in 110 sec, the change in concentration is 0.027 mole dm^{-3}, and hence the

$$\text{Slope or rate} = \frac{0.027\text{mol dm}^{-3}}{110\text{ sec}}$$

$$=2.5\text{x}10^{-4}\ \text{mol dm}^{-3}\text{s}^{-1}$$

Animation 11.9: Chemical Reaction Rates
Source & Credit : crescentok

This value of rate means that in a period of one sec in 1 dm^3 solution, the concentration of HI disappears by 2.5 x 10^{-4} moles, changing into the products.

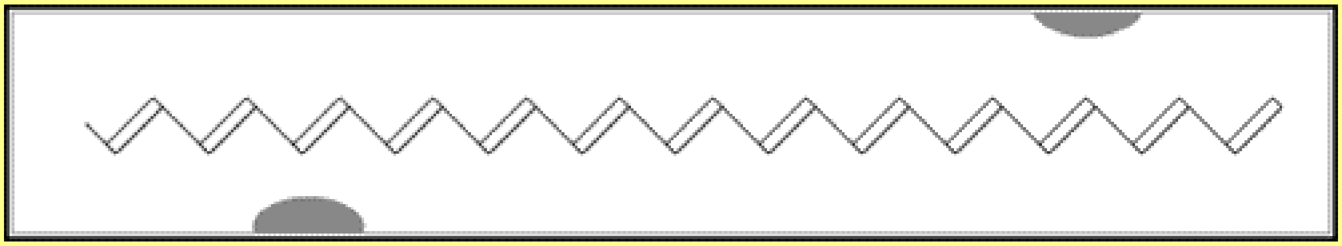
The right angled triangle ABC can be of any size, but the results for the rate of reaction will be the same.

If we plot a graph between time on x-axis and concentration of any of the products i.e H_2 or I_2, then a rising curve is obtained. The value of the tangent at 100 seconds will give the same value of rate of reaction as 2.5 x 10^{-4} mol $dm^{-3}S^{-1}$.

The change in concentrations of reactants or products can be determined by both physical and chemical methods depending upon the type of reactants or products involved.

11.2.1 Physical Methods

Some of the methods used for this purpose cure the following: In these methods, a curve has to be plotted as mentioned in 11.2.0. The nature of the curve may be rising for products and falling for reactants. Anyhow, the results will be same for the same reaction under the similiar conditions.



Animation 11.10: Electrical Conductivity of materials focused on polymer
Source & Credit : wikidot

(i) Spectrometry

This method is applicable if a reactant or a product absorbs ultraviolet, visible or infrared radiation. The rate of reaction can be measured by measuring the amount of radiation absorbed.

(ii) Electrical Conductivity Method

The rate of a reaction involving ions can be studied by electrical conductivity method. The conductivity of such a solution depends upon the rate of change of concentration of the reacting ions or the ions formed during the reaction. The conductivity will be proportional to the rate of change in the concentration of such ions.

(iii) Dilatometric Method

This method is useful for those reactions, which involve small volume changes in solutions. The volume change is directly proportional to the extent of reaction.

(iv) Refractrometric Method

This method is applicable to reactions in solutions, where there are changes in refractive indices of the substances taking part in the chemical reactions.

(v) Optical Rotation Method

In this method, the angle through which plane polarized light is rotated by the reacting mixture is measured by a polarimeter. The extent of rotation determ ines the concentration of optically active substance. If any of the species in the reaction mixture is optically active, then this method can be followed to find out the rate of reaction.

11.2.2 Chemical Method

This is particularly suitable for reactions in solution. In this method, we do the chemical analysis of a reactant or a product.

The acid hydrolysis of an ester (ethyl acetate) in the presence of a small amount of an acid is one of the best examples.

$$CH_3COOC_2H_5(\ell) + H_2O(\ell) \xrightarrow{H^+\text{(catalyst)}} CH_3COOH(\ell) + C_2H_5OH(\ell)$$

In case of hydrolysis of an ester, the solution of ester in water and the acid acting as a catalyst are allowed to react. After some time, a sample of reaction mixture is withdrawn by a pipette and run into about four times its volume of ice cold water. The dilution and chilling stops the reaction. The acid formed is titrated against a standard alkali, say NaOH, using phenolphthalein as an indicator.

The analysis is repeated at various time intervals after the start of reaction. This would provide an information about the change in concentration of acetic acid formed during the reaction at different time intervals. The different concentrations of acetic acid are plotted against the time whereby a rising curve is obtained as shown in Fig (11.3).

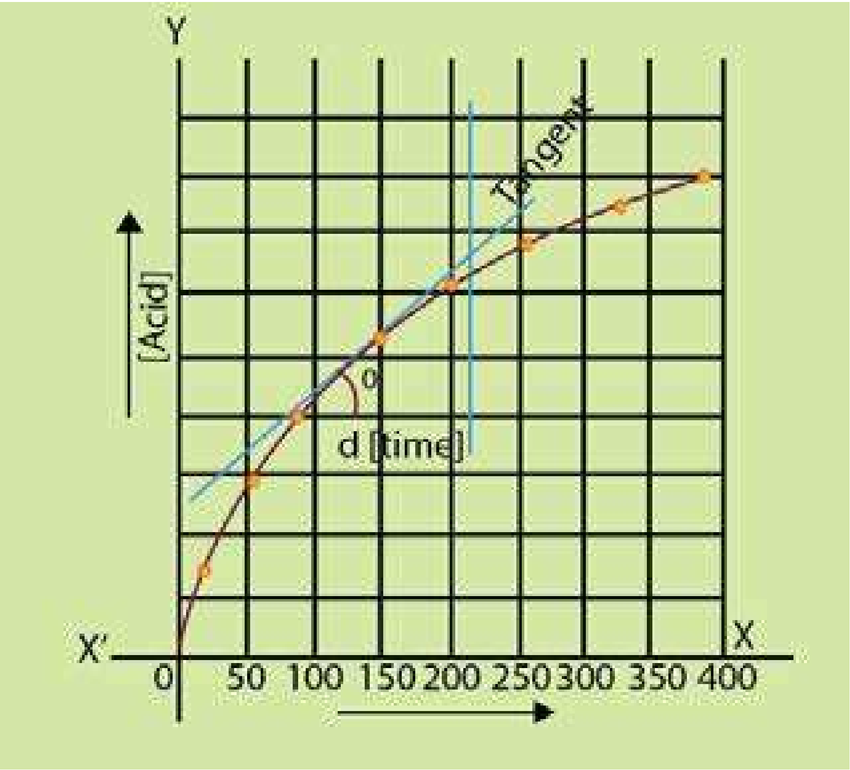


Fig. (11.3) Measurement of rate of ester hydrolysis

The slope of the curve at any point will give the rate of reaction. Initially, the rate of reaction is high but it decreases with the passage of time. When the curve becomes horizontal, the rate becomes zero.

If we plot the graph for decreasing concentrations of $CH_3COOC_2H_5$, then falling curves are obtained as shown in Fig.(11.2) If we have any laboratory technique to record the changing concentration of ester or alcohol, we can measure the rate of the reaction. This is a pseudo first order reaction. Actually water being in large excess in comparison to ester does not affect the rate and we think that water is not taking part in the reaction.

Animation 11.11: Chemical Method
Source & Credit : fg-a

11.3. ENERGY OF ACTIVATION

For a chemical reaction to take place, the particles atoms, ions or molecules of reactants must form a homogeneous mixture and collide with one another. These collisions may be effective or ineffective depending upon the energy of the colliding particles. When these collisions are effective they give rise to the products otherwise the colliding particles just bounce back. The effective collisions can take place only when the colliding particles will possess certain amount of energy and they approach each other with the proper orientation. The idea of proper orientation means that at the time of collision, the atoms which are required to make new bonds should collide with each other. The minimum amount of energy, required for an effective collision is called activation energy.

If all the collisions among the reacting species at a given temperature are effective in forming the products, the reaction is completed in a very short time. Most of the reactions, are, however, slow showing that all the collisions are not equally effective.

Let us study a reaction between molecules A_2 and B_2 to form a new molecule AB. If these molecules will have energy equal to or more than the activation energy, then upon collisions their bonds will break and new bonds will be formed. The phenomenon is shown in Fig. (11.4)

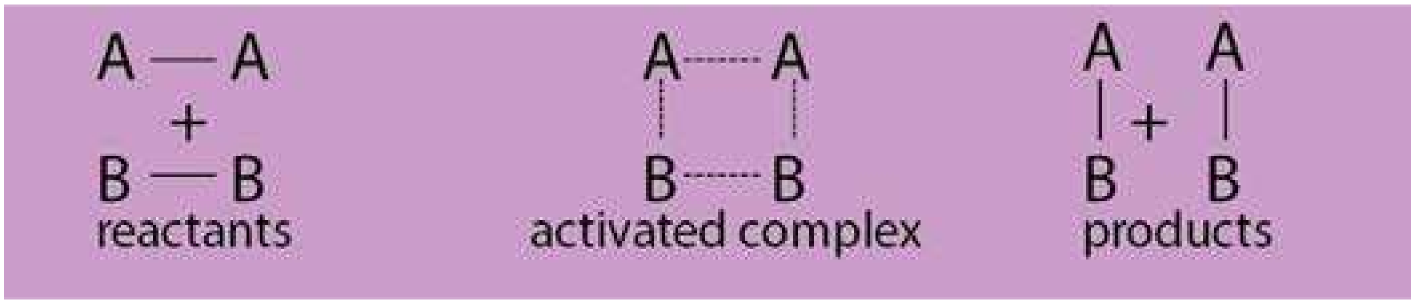


Fig. (11.4) Collisions of molecules, formation of activated complex and formation of products

Activated complex is an unstable combination of all the atoms involved in the reaction for which the energy is maximum. It is a short lived species and decomposes into the products immediately. It has a transient existence, that is why it is also called a transition state.

When the colliding molecules come close to each other at the time of collision, they slow down, collide and then fly apart. If the collision is effective then the molecules flying apart are chemically different otherwise the same molecules just bounce back.

When the molecules slow down just before the collision, their kinetic energy decreases and this results in the corresponding increase in their potential energy. The process can be understood with the help of a graph between the path of reaction and the potential energy of the reacting molecules. Fig. (11.5a,b)

The reactants reach the peak of the curve to form the activated complex. E_a is the energy of activation and it appears as a potential energy hill between the reactants and the products. Only, the colliding molecules with proper activation energy, will be able to climb up the hill and give the products. If the combined initial kinetic energy of the reactants is less than E_a, they will be unable to reach the top of the hill and fall back chemically unchanged.

This potential energy diagram can also be used to study the heat evolved or absorbed during the reaction. The heat of reaction is equal to the difference in potential energy of the reactants and the products. For exothermic reactions, the products are at a lower energy level than the reactants and the decrease in potential energy appears as increase in kinetic energy of the products Fig. (11.5a). For endothermic reactions, the products are at higher energy level than the reactants and for such reactions a continuous source of energy is needed to complete the reaction Fig. (11.5b).

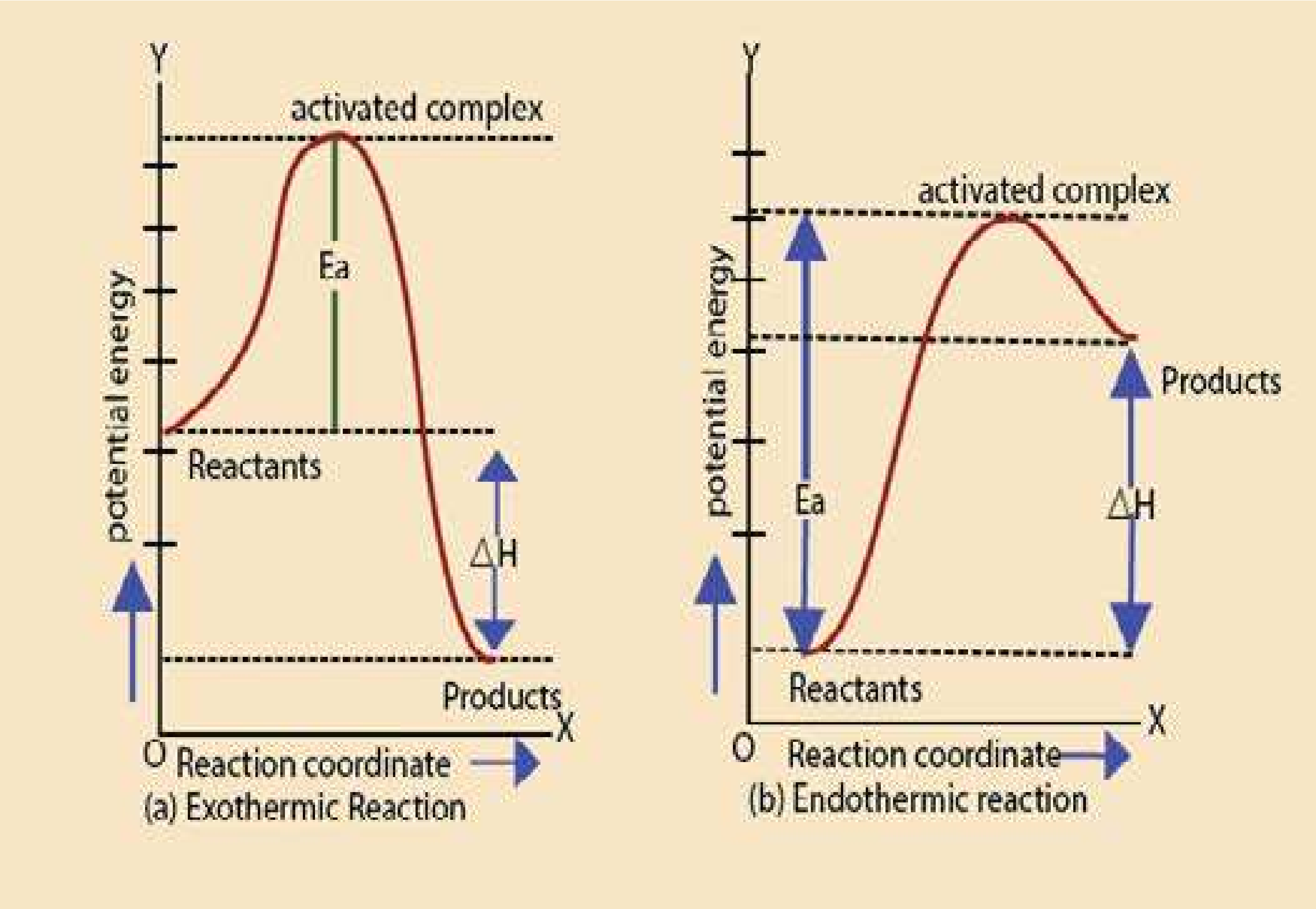
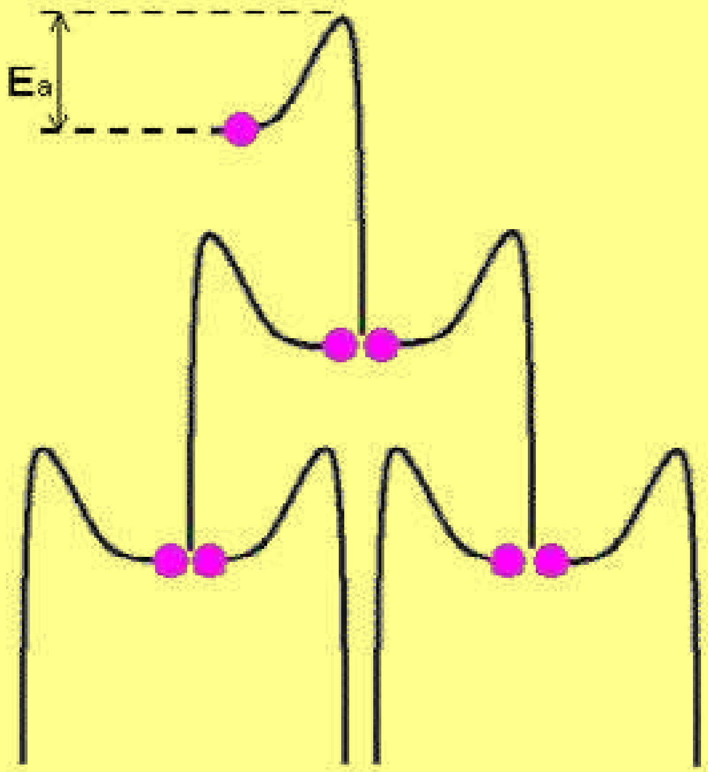


Fig. (11.5) A graph between path of reaction and the potential energy of the reaction

The energy of activation of forward and backward reactions are different for all the reactions. For exothermic reactions the energy of activation of forward reaction is less than that of backward reaction, while reverse is true for endothermic reactions. Energy of activation of a reaction provides a valuable information about the way a reaction takes place and thus helps to understand the reaction.



Animation 11.12: Activation Energy and Spontaneous reactions
Source & Credit : thompsona

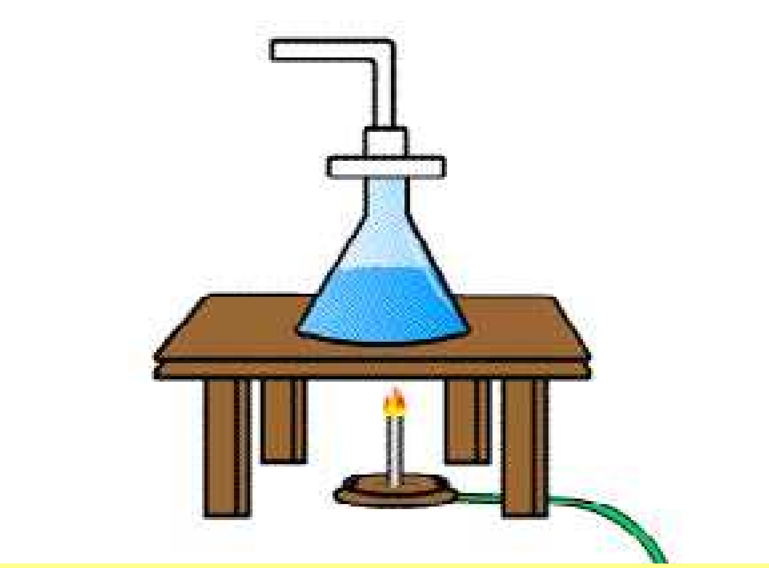
11.4 FINDING THE ORDER OF REACTION

The order of a reaction is the sum of exponents of the concentration terms in the rate expression of that reaction.

It can be determined by the following methods.

(i) Method of hit and trial
(ii) Graphical method
(iii) Differential method
(iv) Half life method
(v) Method of large excess

Here we will only discuss half-life method and the method of large excess.



Animation 11.13: Determination of Order of a Reaction
Source & Credit : askiitians

11.4.1 Half Life Method

As mentioned earlier, half life of a reaction is inversely proportional to the initial concentration of reactants raised to the power one less than the order of reaction.

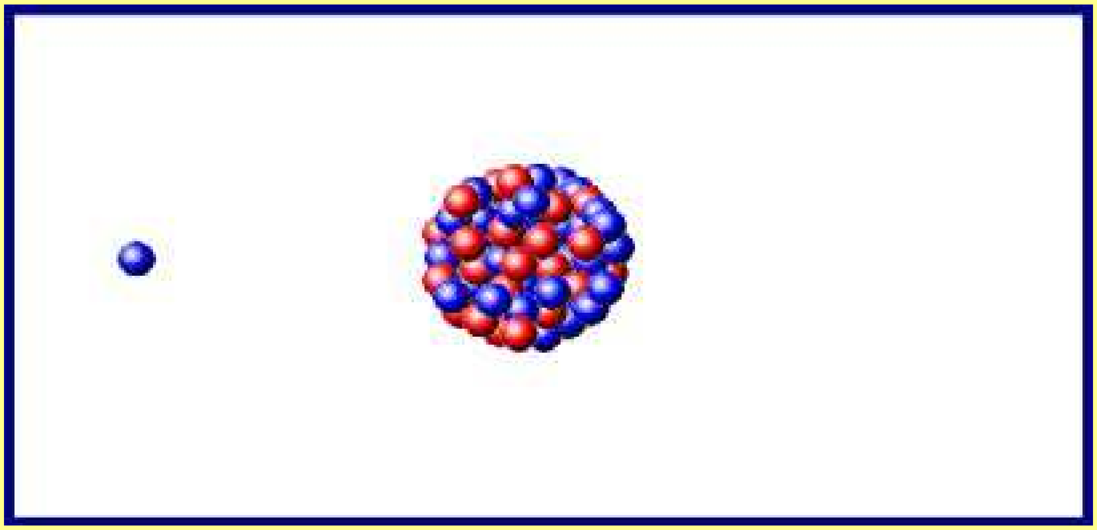
Therefore, $$(t_{1/2})_n \propto \frac{1}{a^{n-1}}$$

Let us perform a reaction twice by taking two different initial concentrations 'a_1' and 'a_2' and their half-life periods are found to be t_1 and t_2 respectively.

$$t_1 \propto \frac{1}{a_1^{\ n-1}} \qquad \text{and} \qquad t_2 \propto \frac{1}{a_2^{\ n-1}}$$

Dividing the two relations: $$\frac{t_1}{t_2} = \left[\frac{a_2}{a_1}\right]^{n-1}$$

Taking log on both sides: $$\log\frac{t_1}{t_2} = (n-1)\log\left[\frac{a_2}{a_1}\right]$$



Animation 11.14: Half Life
Source & Credit : wikipedia

$$n-1=\frac{\log\left[\frac{t_1}{t_2}\right]}{\log\left[\frac{a_2}{a_1}\right]}$$

Rearranging

$$n=1+\frac{\log\left[\frac{t_1}{t_2}\right]}{\log\left[\frac{a_2}{a_1}\right]}$$

So, if we know the two initial concentrations and two half life values we can calculate the order of reaction (n).

Example 2:

In the thermal decomposition of N_2O at 760 °C, the time required to decompose half of the reactant was 255 seconds at the initial pressure of 290 mm Hg and 212 seconds at the initial pressure of 360 mmHg. Find the order of this reaction.

Solution:

The initial pressures of $N_2O(g)$ are the initial concentrations.

Data $a_1 = 290\text{mm Hg}$ $t_1 = 255\text{ seconds}$

$a_2 = 360\text{mm Hg}$ $t_2 = 212\text{ seconds}$

Formula used

$$n = 1 + \frac{\log\left[\frac{t_1}{t_2}\right]}{\log\left[\frac{a_2}{a_1}\right]}$$

Putting the values in the above equation

$$n = 1 + \frac{\log\left[\frac{255}{212}\right]}{\log\left[\frac{360}{290}\right]}$$

$$n = 1 + \frac{0.0802}{0.0940}$$

$$n = 1 + 0.85 = 1.85 \approx 2$$

1.85 is close to 2, hence the reaction is of second order.

11.4.2 Method of Large Excess

In this method, one of the reactants is taken in a very small amount as compared to the rest of the reactants. The active masses of the substances in large excess remain constant throughout. That substance taken in small amount controls the rate and the order is noted with respect to that.

The reason is that a small change in concentration of a substance taken in very small amount affects the value of rate more appreciably. The hydrolysis of ethyl acetate as mentioned earlier shows that water being in large excess does not determine the order.

In this way, the reaction is repeated by taking rest of the substances in small amounts one by one and overall order is calculated. The method will be further elaborated in article 11.5.2.

11.5. FACTORS AFFECTING RATES OF REACTIONS

All those factors which change the number of effective collisions per second, affect the rate of a chemical reaction. Some of the important factors are as follows.

Animation 11.15: FACTORS AFFECTING RATES OF REACTIONS
Source & Credit : askiitians

11.5.1 Nature of Reactants

The rate of reaction depends upon the nature of reacting substances. The chemical reactivity of the substances is controlled by the electronic arrangements in their outermost orbitals. The elements of I-A group have one ejectron in their outermost s-orbital. They react with water more swiftly than those of II-A group elements having two electrons in their outermost s-orbital. Similarly, the neutralization and double decomposition reactions are very fast as compared to those reactions in which bonds are rearranged. Oxidation-reduction reactions involve the transfer of electrons and are slower than ionic reactions.

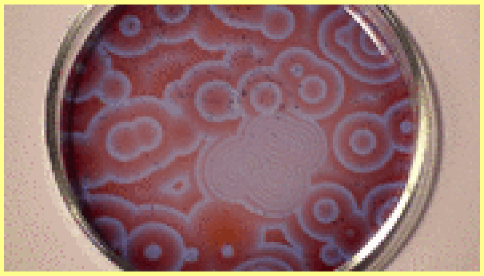
11.5.2 Concentration of Reactants

The reactions are due to collisions of reactant molecules. The frequency with which the molecules collide depends upon their concentrations. The more crowded the molecules are, the more likely they are to collide and react with one another. Thus, an increase in the concentrations of the reactants will result in the corresponding increase in the reaction rate, while a decrease in the concentrations will have a reverse effect. For example, combustion that occurs slowly in air (21 % oxygen) will occur more rapidly in pure oxygen.

Similarly, limestone reacts with different concentrations of hydrochloric acid at different rates. In the case of a gaseous reactant, its concentration can be increased by increasing its pressure. Therefore, a mixture of H_2 and Cl_2 will react twice as fast if the partial pressure of H_2 or Cl_2 is increased from 0.5 to 1.0 atmosphere in the presence of excess of the other component.

The effect of change in concentration on the rate of a chemical reaction can be nicely understood from the following gaseous reaction.

$$2NO(g) + 2H_2(g) \rightarrow 2H_2O(g) + N_2(g)$$



Animation 11.16: Reactants
Source & Credit : giphy

In this reaction, four moles of the reactants form three moles of the products, so the pressure drop takes place during the progress of reaction. The rates of reaction between NO and H_2 at 800°C are studied by noting the change in pressure. The following Table (11.2) has been obtained experimentally for the above reaction.

Table (11.2) Effect of change in concentrations of reactants on the rate of reaction

[NO] in (mol dm^{-3})	[H_2] in (mol dm^{-3})	Initial rate (atm min^{-1})
0.006	0.001	0.025
0.006	0.002	0.050
0.006	0.003	0.075
0.001	0.009	0.0063
0.002	0.009	0.025
0.003	0.009	0.056

Table (11.2)shows the results of six experiments. In the first three experiments the concentration of H_2 is increased by keeping the concentration of NO constant. By doubling the concentration of H_2, the rate is doubled and by tripling the concentration of H_2, the rate is tripled. So, the rate of reaction is directly proportional to the first power of concentration of H_2.

$$\text{Rate} \propto [H_2]$$

In the next three experiments, the concentration of H_2 is kept constant. By doubling the concentration of NO, the rate increases four times and by tripling the concentration of NO the rate is increased nine times. So, the rate is proportional to the square of concentration of NO.

$$\text{Rate} \propto [NO]^2$$

The overall rate equation of reaction is,

$$\text{Rate} \propto [H_2][NO]^2$$

or $$\text{Rate} = k[H_2]^1[NO]^2$$

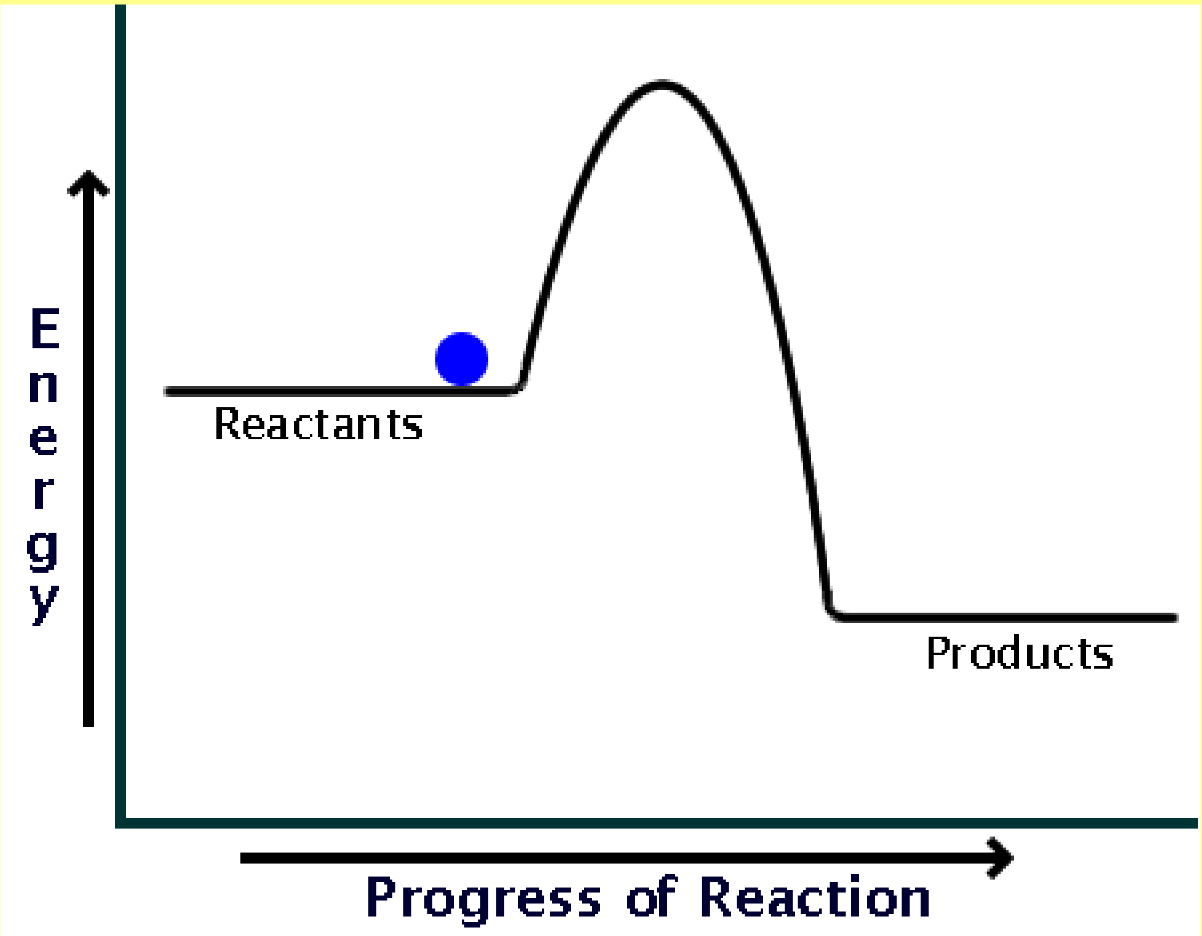
Hence, the reaction is a third order one. This final equation is the rate law for this reaction. It should be kept in mind that rate law cannot be predicted from the balanced chemical equation. This set of experiments helps us to determine the order of reaction as well.

The possible mechanism consisting of two steps for the reaction is as follows:

(i) $2NO(g) + H_2(g) \xrightarrow{slow} N_2(g) + H_2O_2(g)$ (rate determining)

(ii) $H_2O_2(g) + H_2(g) \xrightarrow{fast} 2H_2O(g)$

The step (i) is slow and rate determining.



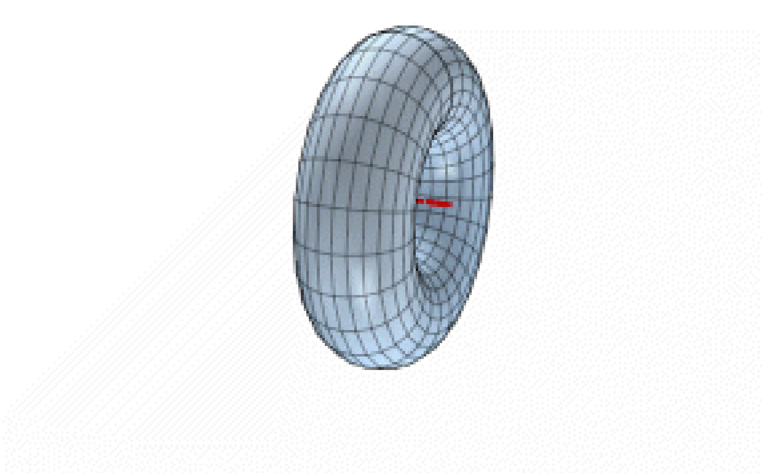
Animation 11.17: Concentration of Reactants
Source & Credit : socratic

11.5.3 Surface Area

The increased surface area of reactants, increases the possibilities of atoms and molecules of reactants to come in contact with each other and the rates enhance. For example, Al foil reacts with NaOH moderately when warmed, but powdered Al reacts rapidly with cold NaOH and H_2 is evolved with frothing.

$$2AI + 2NaOH + 6H_2O \rightarrow 2NaAI(OH)_4 + 3H_2$$

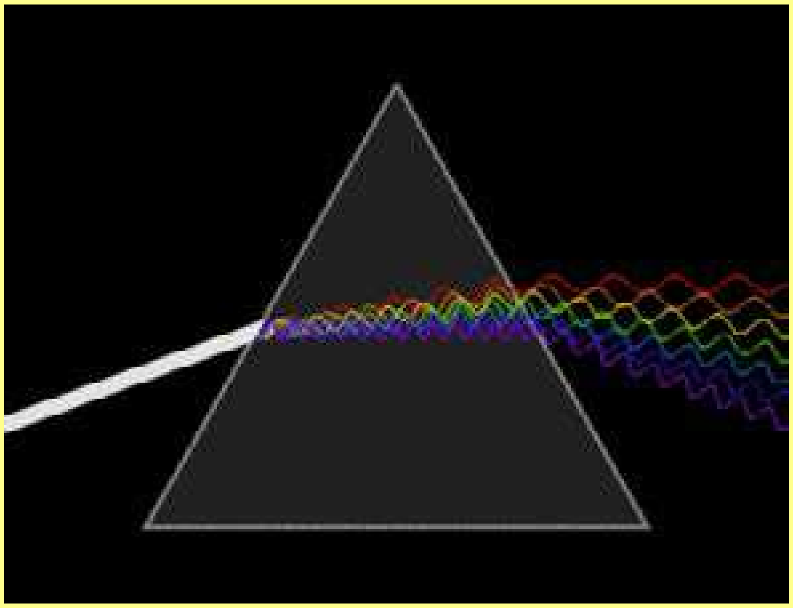
Similarly, $CaCO_3$ in the powder form reacts with dilute H_2SO_4 more efficiently than its big pieces.



Animation 11.18: Surface Area
Source & Credit : darelhardy

11.5.4 Light

Light consists of photons having definite amount of energies depending upon their frequencies. When the reactants are irradiated, this energy becomes available to them and rates of reactions are enhanced. The reaction of CH_4 and Cl_2 requires light. The reaction between H_2 and Cl_2 at ordinary pressure is negligible in darkness, slow in daylight, but explosive in sunlight. Similarly, light is vital in photosynthesis, and the rate is influenced by light.



Animation 11.19: Light
Source & Credit : wikipedia

11.5.5 Effect of Temperature on Rate of Reaction

The collision theory of reaction rates convinces us that the rate of a reaction is proportional to the number of collisions among the reactant molecules. Anything, that can increase the frequency of collisions should increase the rate. We also know, that every collision does not lead to a reaction. For a collision, to be effective the molecules must possess the activation energy and they must also be properly oriented. For nearly all chemical reactions, the activation energy is quite large and at ordinary temperature very few molecules are moving fast enough to have this minimum energy.

All the molecules of a reactant do not possess the same energy at a particular temperature. Most of the molecules will possess average energy. A fraction of total molecules will have energy more than the average energy. This fraction of molecules is indicated as shaded area in Fig.(11.6).

As the temperature increases, the number of molecules in this fraction also increases. There happens a wider distribution of velocities. The curve at higher temperature T_2 has flattened. It shows that molecules having higher energies have increased and those with less energies have deceased. So, the number of effective collisions increases and hence the rate increases. When the temperature of the reacting gases is raised by 10K, the fraction of molecule with energy more than E_a roughly doubles and so the reaction rate also doubles. Arrheinus has studied the quantitative relationship between temperature, energy of activation and rate constant of a reaction.

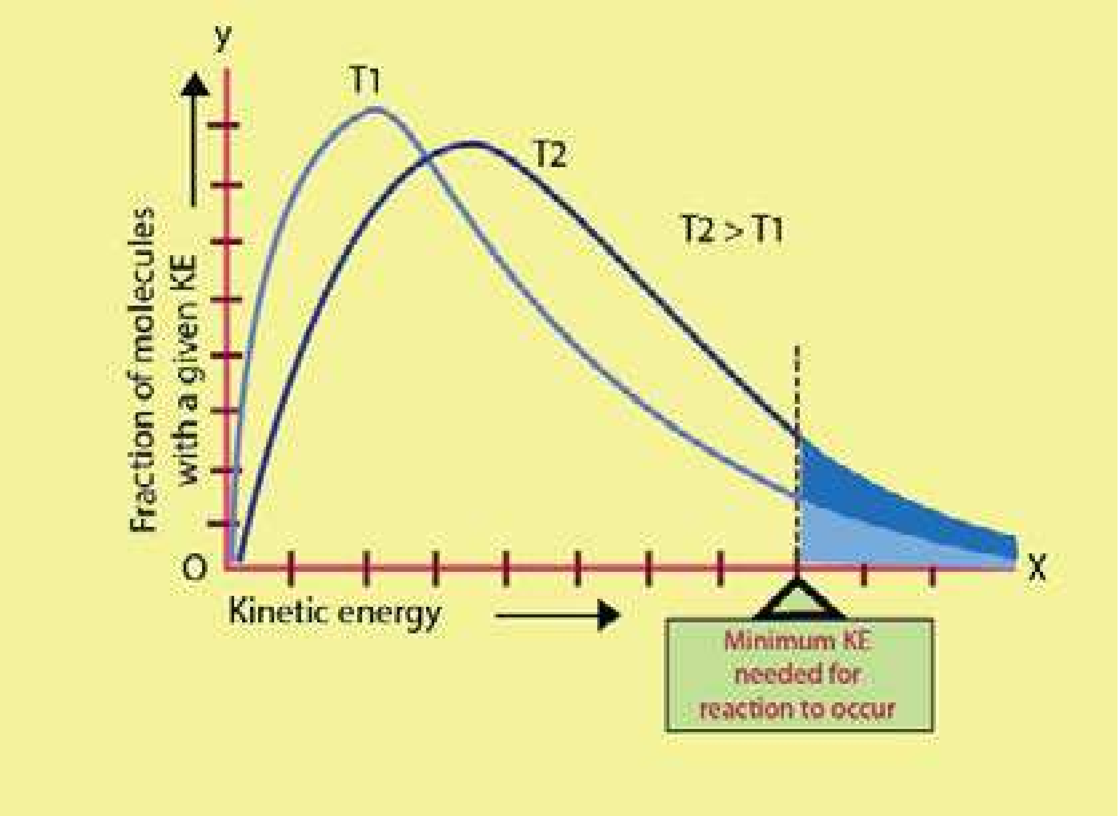
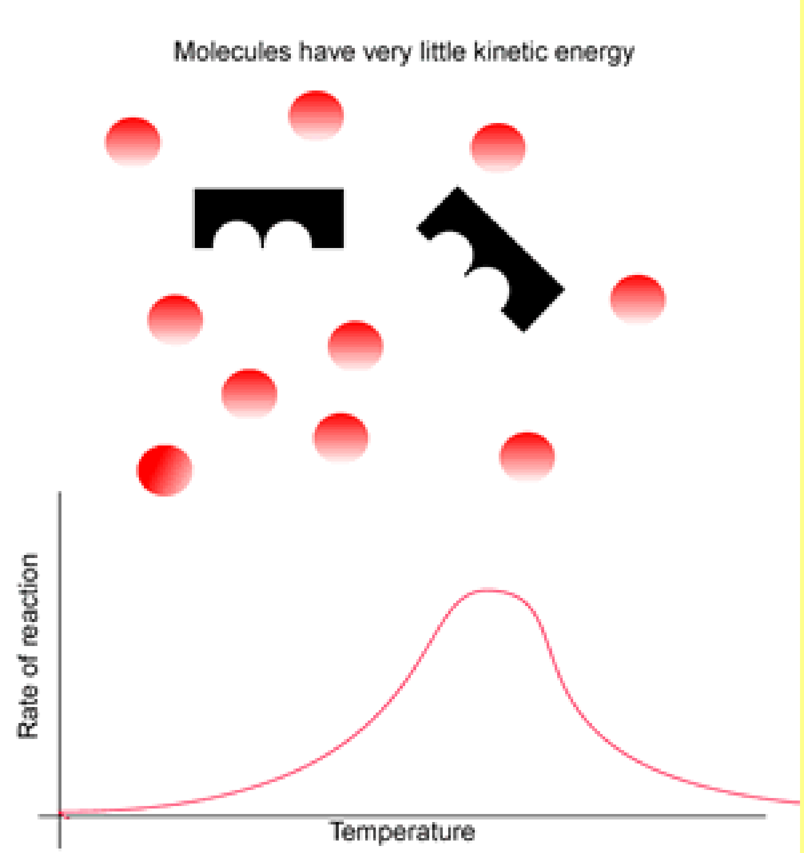


Fig. (11.6) Kinetic energy distributions for a reaction mixture at two different temperatures. The size of the shaded areas under the curves are proportional to the total fraction of the molecules that possess the minimum activation energy.



Animation 11.20: Effect of Temperature on Rate of Reaction
Source & Credit : dynamicscience

11.5.6 Arrhenius Equation

Arrhenius equation explains the effect of temperature on the rate constant of a reaction. The rate constant 'k' for many simple reactions is found to vary with temperature.
According to Arrhenius:

$$k=Ae^{-Ea/RT} \qquad \text{........ (1)}$$

So, 'k' is exponentially related to activation energy (E_a) and temperature (T). R is general gas constant and e is the base of natural logarithm. The equation shows that the increase in temperature, increases the rate constant and the reactions of high activation energy have low 'k' values.

The factor 'A' is called Arrhenius constant and it depends upon the collision frequency of the reacting substances. This equation helps us to determine the energy of activation of the reaction as well. For this purpose, we take natural log of Arrhenius equation, which is expressed as ℓn. The base of natural log is e and its value is 2.718281.

Now, take natural log on both sides

$$\ell nk = \ell n(Ae^{-Ea/RT})$$

or $$\ell nk = \ell nA + \ell ne^{-Ea/RT}$$

or $$\ell nk = \ell nA + \frac{-E}{RT}\ell ne$$

Since $\ell ne = 1$ (log of a quantity with same base is unity)

Therefore $$\ell nk = \frac{-E_a}{RT} + \ell nA \qquad \text{.......... (2)}$$

The equation (1) is the equation of straight line, and from the slope of straight line E_a can be calculated. In order to convert this natural log into common log of base 10, we multiply the ℓn term with 2.303.

$$2.303 \log k = \frac{-E_a}{RT} + 2.303 \log A$$ (The base of common log is 10)

Dividing the whole equation by 2.303

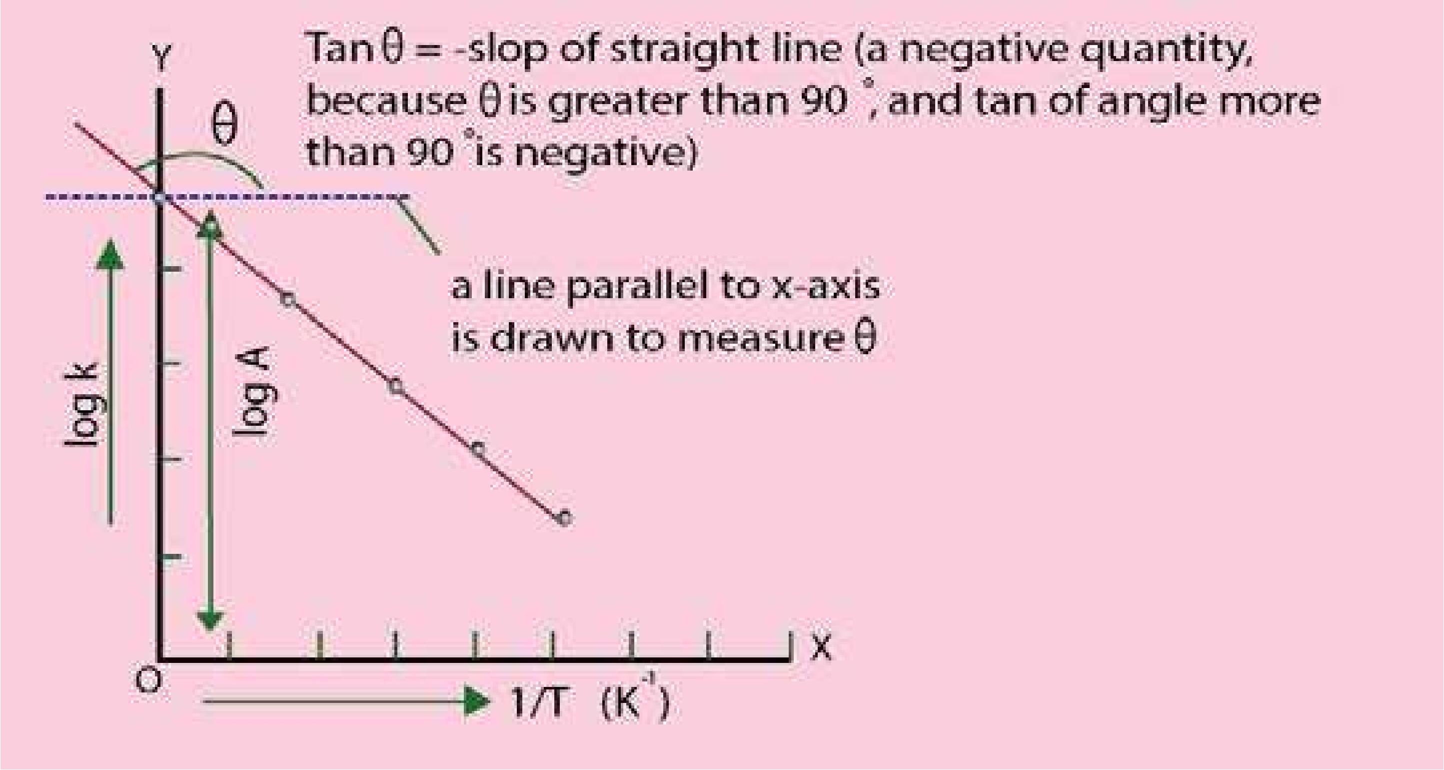
$$\log k = \frac{-E_a}{2.303RT} + \log A \qquad \text{.......... (3)}$$

This equation (3) is again the equation of straight line resembling.

$$y = -mx + c$$

Where 'm' is slope of straight line and 'c' is the intercept of straight line. Temperature is independent variable in this equation while rate constant k is dependent variable. The other factors like E_a, R and A are constants for a given reaction.

When a graph is plotted between $\frac{1}{T}$ on x-axis and log k on y-axis, a straight line is obtained with a negative slope. Actually, $\frac{E_a}{RT}$ has negative sign so the straight line has two ends in second and fourth quadrants, Fig. (11.7).



Tan θ = -slop of straight line (a negative quantity, because θ is greater than 90°, and tan of angle more than 90° is negative)

a line parallel to x-axis is drawn to measure θ

Fig. (11.7) Arrhenuis plot to calculate the energy of activation

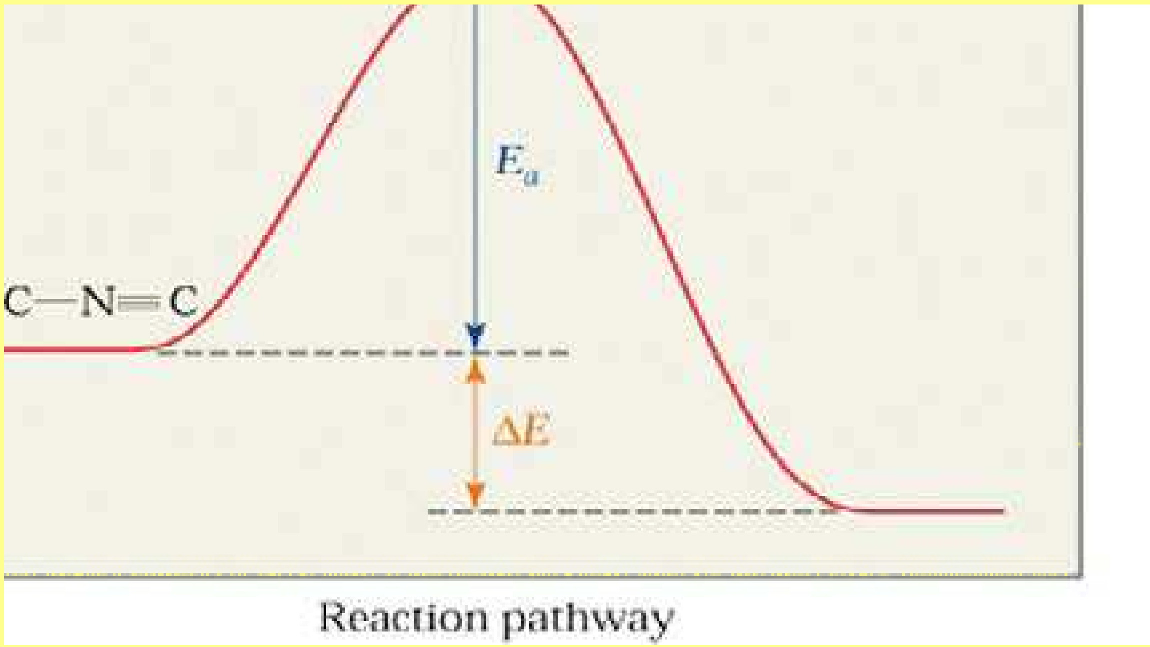
The slope of the straight line is measured by taking the tangent of that angle θ which this straight line makes with the x-axis. To measure the slope, draw a line parallel to x-axis and measure angle θ . Take tan θ which is slope. This slope is equal to $\frac{-E_a}{2.303R}$.

$$\text{Slop} = \frac{-E_a}{2.303\ R}$$

Therefore $$E_a = -\text{Slop} \times 2.303\ R \qquad \text{..........(4)}$$

The straight lines of different reactions will have different slopes and different 'E_a' values. The units of slope are in kelvins (K).

Since $$\text{Slop} = \frac{\text{J mol}^{-1}}{2.303\ \text{JK}^{-1}\text{mol}^{-1}} = \text{K}$$



Animation 11.21: Arrhenius Equation
Source & Credit : wps

Example 3:

A plot of Arrhenius equation Fig (11.8) for the thermal decompositions of N_2O_5 is shown in the following figure. The slope is found to be -5400 K. Calculate the energy of activation of this reaction.

Solution:

(i) The reaction is

$$N_2O_5 \rightarrow 2NO_2 + 1/2O_2$$

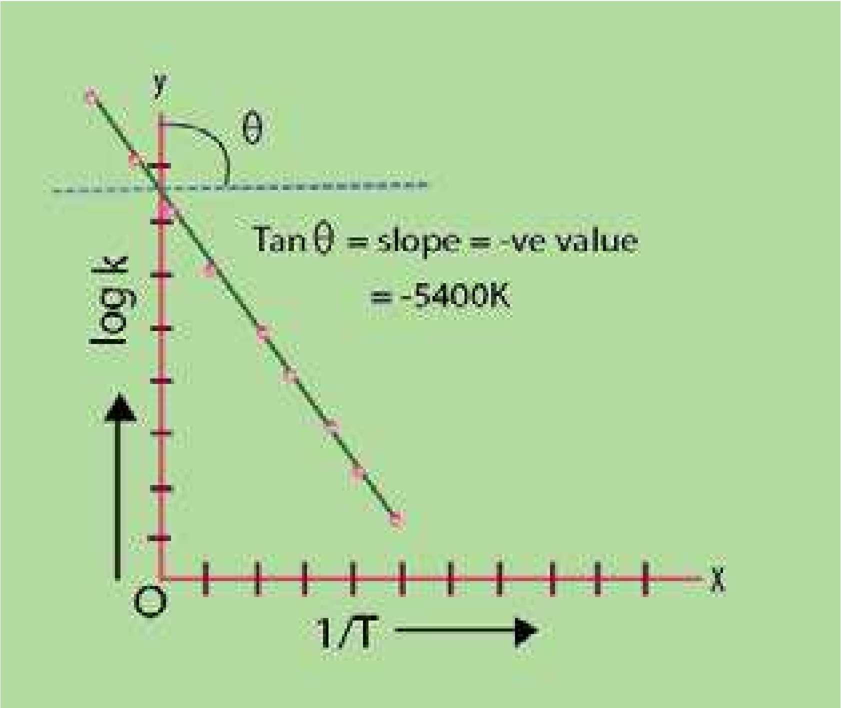


Fig. (11.8) Arrhenius plot for decomposition of N_2O_5

Slope of the straight line = -5400 K

Equation used, E_a = -slope x 2.303 R

R = $8.3143 JK^{-1}mol^{-1}$

Putting the values,

E_a =-(-5400K)x 2.303 x $8.3143JK^{-1}mol^{-1}$

E_a= +103410 J mol^{-1}

E_a = 103.410 kJ mol^{-1}

Hence, the decomposition of N_2O needs $103.4kJmol^{-1}$ energy more than the average energy to cross the energy barrier Fig.(11.9)

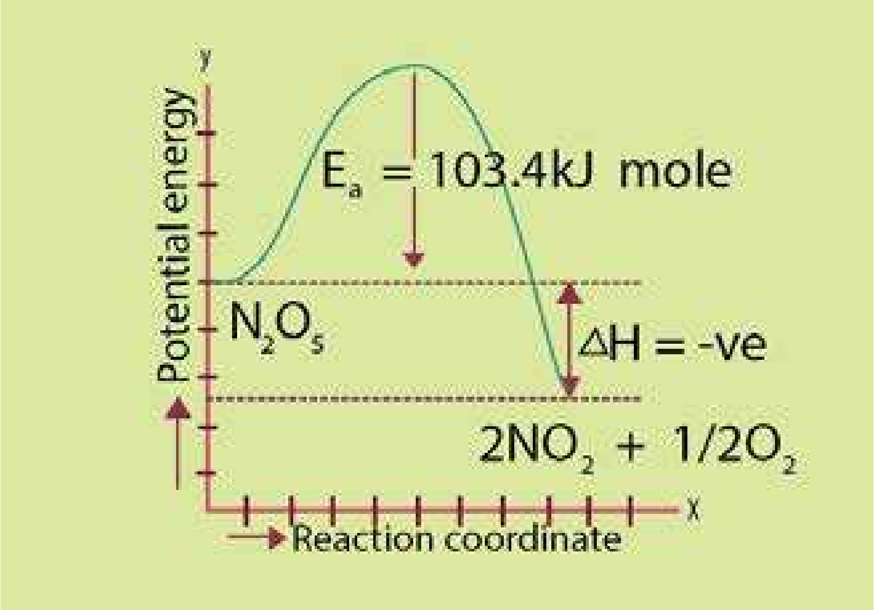


Fig. (11.9) Potential energy diagram of N_2O_5 decomposition

11.6 CATALYSIS

A catalyst is defined as a substance which alters the rate of a chemical reaction, but remains chemically unchanged at the end of the reaction. A catalyst is often present in a very small proportion. For example, the reaction between H_2 and O_2 to form water is very slow at ordinary temperature, but proceeds more rapidly in the presence of platinum. Platinum acts as a catalyst. Similarly, $KClO_3$ decomposes much more rapidly in the presence of a small amount of MnO_2. HCl is oxidised to Cl_2 in the presence of $CuCl_2$.

$$4HCl+O_2 \xrightarrow{CuCl_2} 2H_2O+2Cl_2$$

The process, which takes place in the presence of a catalyst, is called catalysis. A catalyst provides a new reaction path with a low activation energy barrier, Fig.(11.10). A greater number of molecules are now able to get over the new energy barrier and reaction rate increases.

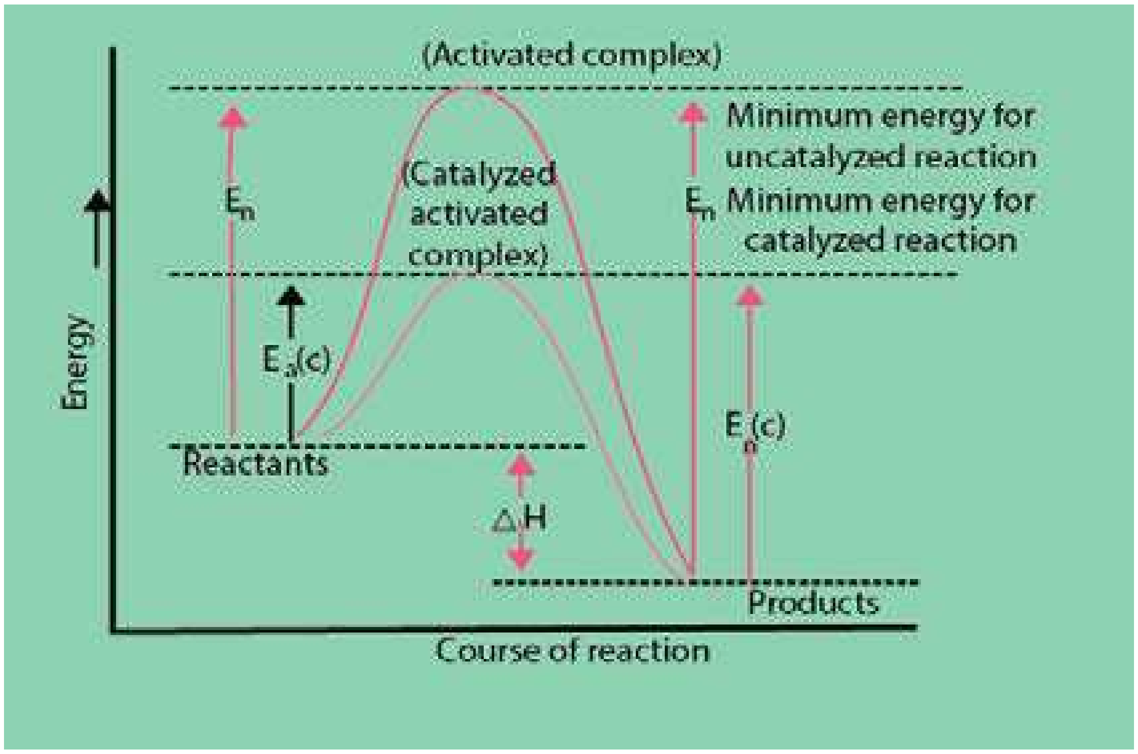
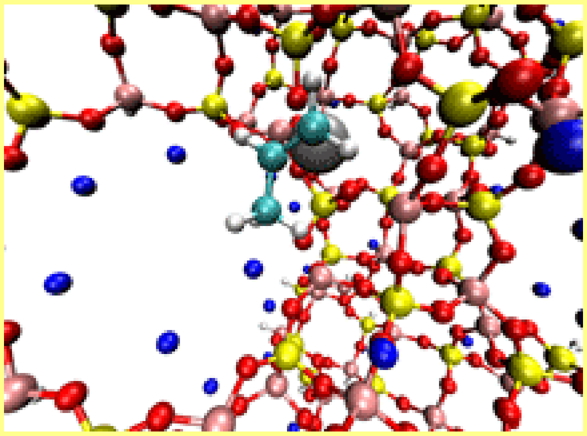


Fig. (11.10) Catalyzed and uncatalyzed reactions.



Animation 11.22: CATALYSIS
Source & Credit : lsa.umich

Types of Catalysis

(a) Homogeneous Catalysis
(b) Heterogeneous Catalysis

(a) Homogeneous Catalysis

In this process, the catalyst and the reactants are in the same phase and the reacting system is homogeneous throughout. The catalyst is distributed uniformly throughout the system. For example:

(i). The formation of SO_3 (g) from SO_2 (g) and O_2 (g) in the lead chamber process for the manufacture of sulphuric acid, needs NO (g) as a catalyst. Both the reactants and the catalyst are gases.

$$2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$$

(ii). Esters are hydrolysed in the presence of H_2SO_4. Both the reactants and the catalyst are in the solution state.

$$CH_3COOC_2H_5(aq) + H_2O(\ell) \xrightarrow[H_2SO_4]{H_3O^+} CH_3COOH(aq) + C_2H_5OH(aq)$$

(b) Heterogeneous Catalysis

In such systems, the catalyst and the reactants are in different phases. Mostly, the catalysts are in the solid phase, while the reactants are in the gaseous or liquid phasse. For example:

(i). Oxidation of ammonia to NO in the presence of platinum gauze helps us to manufacture HNO_3.

$$4NH_3(g) + 5O_2(g) \xrightarrow{Pt(s)} 4NO(g) + 6H_2O(g)$$

(ii) Hydrogenation of unsaturated organic compounds are catalysed by finely divided Ni, Pd or Pt.

$$CH_2 = CH_2(g) + H_2(g) \xrightarrow{Ni(s)} CH_3 - CH_3(g)$$

11.6.1 Characteristics of a Catalyst

There are many types of catalysts with varying chemical compositions, but the following features are common to most of them.

1. A catalyst remains unchanged in mass and chemical composition at the end of reaction. It may not remain in the same physical state. MnO_2 is added as a catalyst for the decomposition of $KClO_3$ in the form of granules. It is converted to fine powder at the end of reaction. It has been found in many cases that the shining surfaces of the solid catalyst become dull.
2. Sometimes, we need a trace of a metal catalyst to affect very large amount of reactants. For example, 1 mg of fine platinum powder can convert 2.5 dm^3 of H_2 and 1.25 dm^3 of O_2 to water. Dry HCl and NH_3 don't combine, but in the presence of trace of moisture, they give dense white fumes of NH_4Cl. Thousands of dm^3 of H_2O_2, can be decomposed in the presence of 1 g of colloidal platinum.
3. A catalyst is more affective, when it is present in a finely divided form. For example, a lump of platinum will have much less catalytic activity than colloidal platinum. In the hydrogenation of vegetable oils finely divided nickel is used.
4. A catalyst cannot affect the equilibrium constant of a reaction but it helps the equilibrium to be established earlier. The rates of forward and backward steps are increased equally.
5. A catalyst cannot start a reaction, which is not thermodynamically feasible. It is now considered that a catalyst can initiate a reaction. The mechanism of a catalysed reaction is different from that of an uncatalysed reaction.

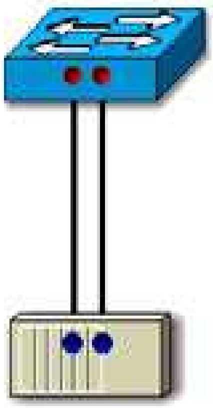
For example:

(i) The presence of CO as an impurity with hydrogen decreases the catalytic activity of catalyst in the Haber's process for the manufacture of NH_3.
(ii) The manufacture of H_2SO_4 in the contact process needs platinum as a catalyst. The traces of arsenic present as impurities in the reacting gases makes platinum ineffective. That's why arsenic purifier is employed in the contact process.

11.6.2 Activation of Catalyst

Such a substance which promotes the activity of a catalyst is called a promotor or activator. It is also called “catalyst for a catalyst”. For example :

(i) Hydrogenation of vegetable oils is accelerated by nickel. The catalytic activity of nickel can be increased by using copper and tellurium.



Animation 11.23: Characteristics of a Catalyst
Source & Credit : logilent

(ii) In Haber’s process for the manufacture of ammonia, iron is used as a catalyst. If small amounts of some high melting oxides like aluminum oxide, chromium oxide or rare earth oxides are added, they increase the efficiency of iron.

Negative Catalysis

When the rate of reaction is retarded by adding a substance, then it is said to be a negative catalyst or inhibitor. For example, tetraethyl lead is added to petrol, because it saves the petrol from pre-ignition.

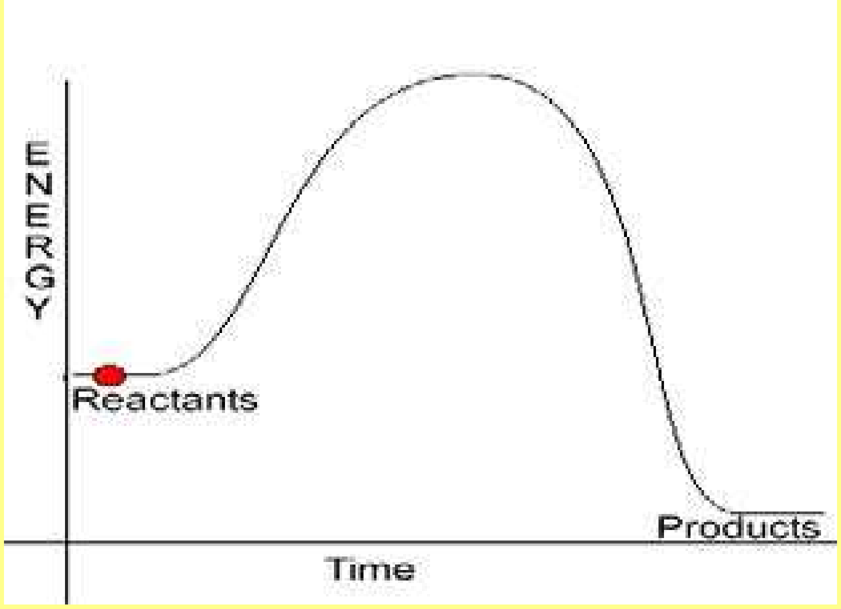
Autocatalyst

In some of the reactions, a product formed acts as a catalyst. This phenomenon is called auto-catalysis. For example:

(i) When copper is allowed to react with nitric acid, the reaction is slow in the beginning. It gains the speed gradually and finally becomes very fast. This is due to the formation of nitrous acid during the reaction, which accelerates the process.

(ii) The reaction of oxalic acid with acidified $KMnO_4$ is slow at the beginning, but after sometimes, $MnSO_4$ produced in the reaction makes it faster.

$$2KMnO_4 + 3H_2SO_4 + 5(COOH)_2 \xrightarrow{Mn^{2+}} K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

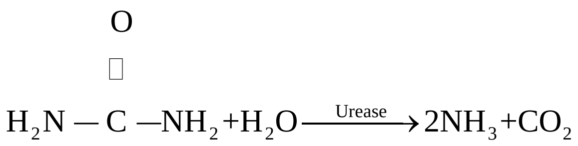


Animation 11.24: Activation of Catalyst
Source & Credit : dynamicscience

11.6.3. Enzyme catalysis

Enzymes are the complex protein molecules and catalyze the organic reactions in the living cells. Many enzymes have been identified and obtained in the pure crystalline state. However, the first enzyme was prepared in the laboratory in 1969. For example:

(i) Urea undergoes hydrolysis into NH_3 and CO_2 in the presence of enzyme urease present in soyabean.



$$H_2N-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2+H_2O\xrightarrow{\text{Urease}}2NH_3+CO_2$$

(ii) Concentrated sugar solution undergoes hydrolysis into glucose and fructose by an enzyme called invertase, present in the yeast.

$$C_{12}H_{22}O_{11}+H_2O\xrightarrow{\text{Inertase}}C_6H_{12}O_6+C_6H_{12}O_6$$

(iii) Glucose is converted into ethanol by the enzyme zymase present in the yeast.

$$C_6H_{12}O_6\xrightarrow{\text{Zymase}}2C_2H_5OH+2CO_2$$

Enzymes have active centres on their surfaces. The molecules of a substrate fit into-their cavities just as a key fits into a lock Fig. (11.11). The substrate molecules enter the cavities, form the complex, reactants and the products get out of the cavity immediately. Michaulis and Menter(1913) proposed the following mechanism for enzyme catalysis

$$E+S\rightleftharpoons ES\rightarrow P+E$$

Where

E = enzyme, S = substrate (reactant)

ES = activated complex, P = product

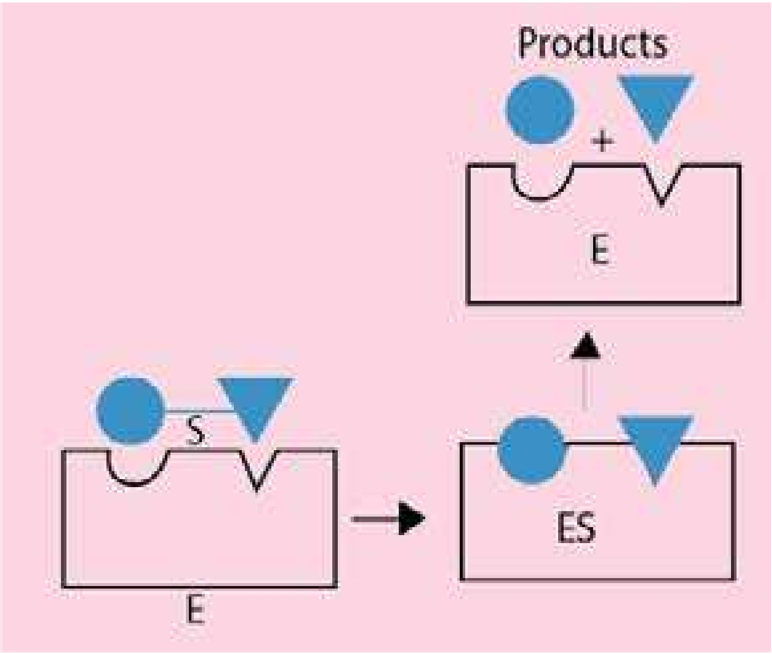
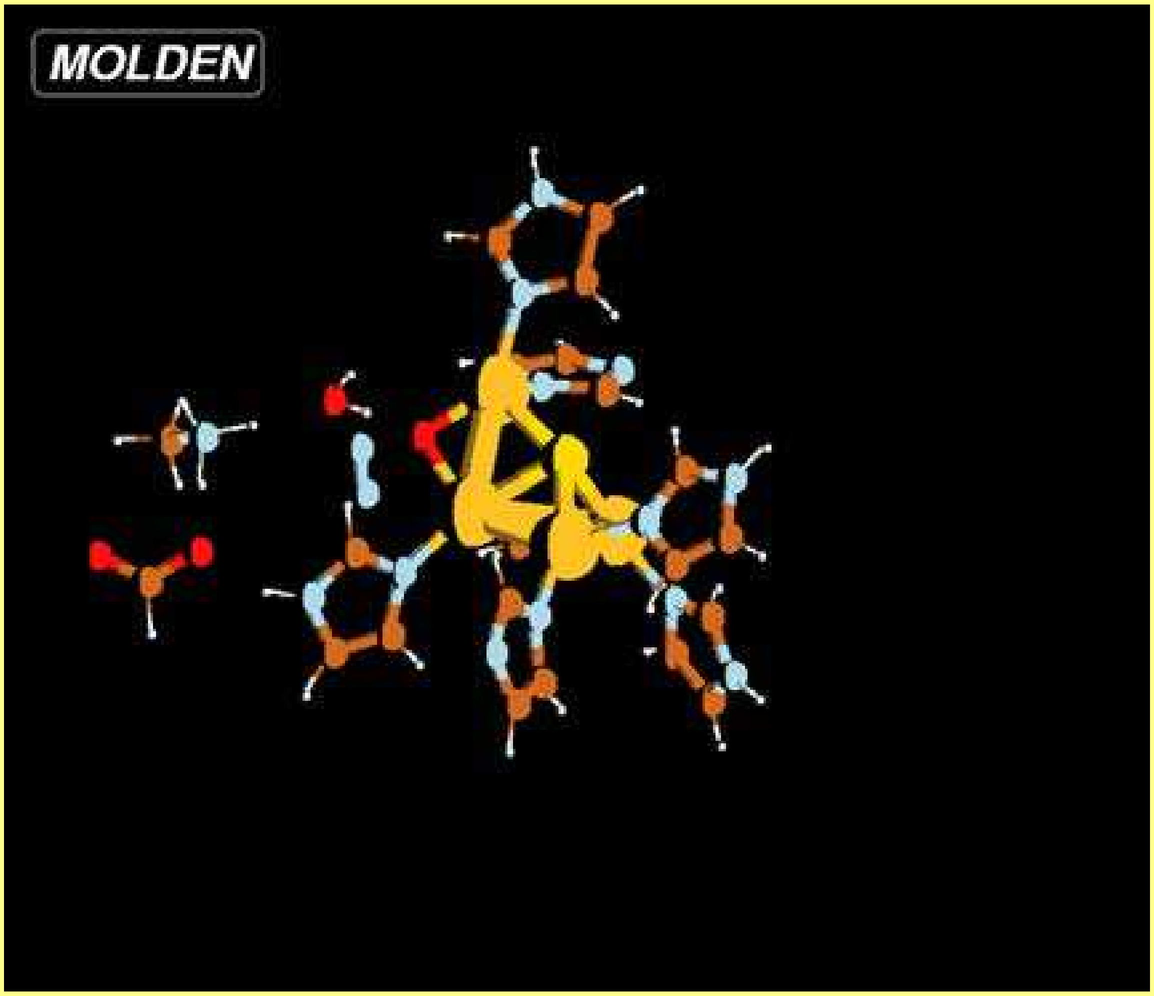


Fig. (11.11) Lock and key model of enzyme catalysis



Animation 11.25: Enzyme catalysis
Source & Credit : kth

11.6.4 Characteristics of Enzyme Catalysis

The role of enzyme as catalysts is like inorganic heterogeneous catalysts. They are unique in their efficiency and have a high degree of specificity. For example:

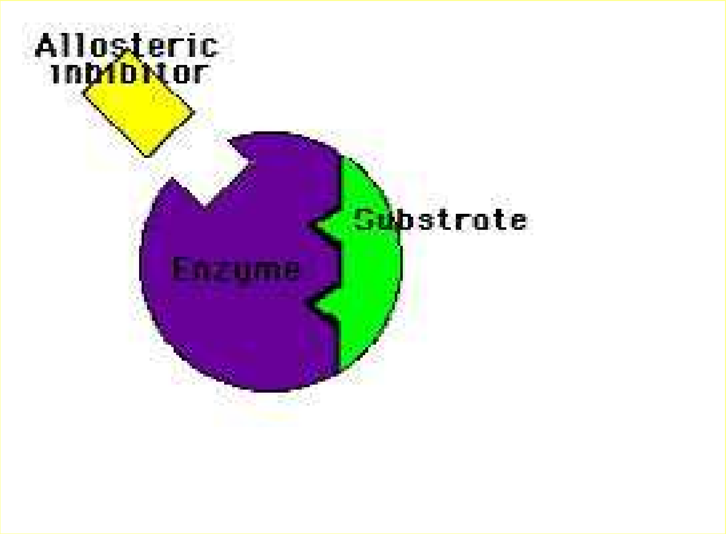
(i) Enzymes are the most efficient catalysts known and they lower the energy of activation of a reaction.

(ii) Enzymes catalysis is highly specific, for example, urease catalyses the hydrolysis of urea only and it cannot hydrolyse any other amide even methyl urea.

(iii) Enzyme catalytic reactions have the maximum rates at an optimum temperature.

(iv) The pH of the system also controls the rates of the enzyme catalysed reaction and the rate passes through a maximum at a particular pH, known as an optimum pH. The activity of enzyme catalyst is inhibited by a poison.

(v) The catalytic activity of enzymes is greatly enhanced by the presence of a co-enzyme or activator.



Animation 11.26: Characteristic of Enzyme
Source & Credit : tdmu

KEY POINTS

1. The studies concerned with rates of chemical reactions and factors that affect the rates of chemical reactions and the mechanism of reactions constitute the subject matter of reaction kinetics.
2. The rate of a reaction is the change in the concentration of a reactant or a product divided by the time taken for the reaction. The rate of reaction between two specific time intervals is called the average rate of reaction. While the rate at any one instant during the interval is called the instantaneous rate. Rate constant of a chemical reaction is rate of reaction when the concentrations of reactants are unity.
3. Order of reaction is the sum of exponents of the concentation terms in the rate expression of a chemical reaction.The exponents in the expression may or may not be different from the coefficients of the chemical equation. Order of a reaction may be zero, whole number or fractional.
4. Half life period of a reaction is the time required to convert 50% of the reactants into products. Half-life period of any reaction is inversely proportional to the initial concentration raised to the power one less than the order of that reaction.
5. The step which limits how fast the overall reaction can proceed, is known as the rate determining step.
6. Determination of the rate of a chemical reaction involves the measurement of the concentration of reactants or products at regular time intervals during the progress of reaction. The change in concentration of reactants and products can be determined by both physical and chemical methods.
7. The effective collisions between the colliding species will take place only when the reactant molecules possess minimum amount of energy, which is called the energy of activation. Moreover, proper orientation is also necessary.
8. All those factors, which change the number of effective collisions per second, affect the rate of chemical reaction. Some of the important factors are, nature and concentration of reactants, surface area, light, and temperature and catalyst.
9. A catalyst is a substance, which alters the rate of a chemical reaction, but itself remains chemically unchanged at the end of reaction. The process when the catalyst and the reactants are in the same phase is said to be a homogenous catalysis. In case of heterogeneous catalysis, the catalyst and the reactants are in different phases. A substance, which promotes the activity of a catalyst, is called promoter or activator. In certain reactions, a product formed acts as a catalyst, the phenomenon is called auto-catalysis.
10. Enzymes are the complex protein molecules, which catalyze the reactions in the living cells.

EXERCISE

Q.1 Multiple choice questions.

(i) In zero order reaction, the rate is independent of

a) temperature of reaction. (b) concentration of reactants,

c) concentration of products (d) none of these

(ii) If the rate equation of a reaction $2A + B \rightarrow$ products is, rate =k$[A]^2$ [B], and A is present in large excess, then order of reaction is

a) 1 (b) 2 (c) 3 (d) none of these

(iii) The rate of reaction

a) increases as the reaction proceeds.

b) decreases as the reaction proceeds.

c) remains the same as the reaction proceeds.

d) may decrease or increase as the reaction proceeds.

(iv) With increase of 10°C temperature the rate of reaction doubles. This increase in ate of reaction is due to:

a) decrease in activation energy of reaction.

b) decrease in the number of collisions between reactant molecules.

c) increase in activation energy of reactants.

d) increase in number of effective collisions.

(v) The unit of the rate constant is the same as that of the rate of reaction in

(a) first order reaction. (b) second order reaction.

(c) zero order reaction. (d) third order reaction.

Q.2 Fill in the blanks with suitable words.

(i) The rate of an endothermic reaction_______ with the increase in temperature.

(ii) All radioactive disintegration nuclear reactions are of________ order

(iii) For a fast reaction the rate constant is relatively and half - life is ______ .

(iv) The second order reaction becomes______ if one of the reactants is in large excess.

(v) Arrhenius equation can be used to find out________of a reaction.

Q.3 Indicate true or false as the case may be.

(i) The half life of a first order reaction increases with temperature.
(ii) The reactions having zero activation energies are instantaneous.
(iii) A catalyst makes a reaction more exothermic.
(iv) There is difference between rate law and the law of mass action.
(v) The order of reaction is strictly determined by the stoichiometry of the bdanced equation.

Q4. What is chemical kinetics? How do you compare chemical kinetics with clemical equilibrium and thermodynamics.

Q5. The rate of a chemical reaction with respect to products is written with positive sign, but with respect to reactants is written with a negative sign. Explain it with reference to the following hypothetical reaction.

$$aA + bB \rightarrow cC + dD$$

Q6 . What are instantaneous and average rates? Is it true that the instantaneousrate of a reaction at the beginning of the reaction is greater than average rate and beomes far less than the average rate near the completion of reaction?

Q7. Differentiate between

(i) Rate and rate constant of a reaction
(ii) Homogeneous and heterogeneous catalyses
(iii) Fast step and the rate determining step
(iv) Enthalpy change of reaction and energy of activation of reaction

Q8. Justify the following statements

(i) Rate of chemical reaction is an ever changing parameter uner the given conditions.
(ii) The reaction rate decreases every moment but rate constant 'k' of the reation is a constant quantity, under the given conditions.
(iii) 50% of a hypothetical first order reaction completes in one hour. The renaming 50% needs more than one hour to complete.
(v) The radioactive decay is always a first order reaction.

(iv) The unit of rate constant of a second order reaction is $dm^3\ mol^{-1}s^{-1}$, but the uit of rate of reaction is mol $dm^{-3}s^{-1S}$.

(vi) The sum of the coefficients of a balanced chemical equation is not neessarily important to give the order of a reaction.

(vii) The order of a reaction is obtained from the rate expression of a reaction anthe rate expression is obtained from the experiment.

Q9. Explain that half life method for measurement of the order of a reaction can help us to measure the order of even those reactions which have a fractional order.

Q10. A curve is obtained when a graph is plotted between time on x-axis and concentration on y-axis. The measurement of the slopes of various points give us the instantaneous rates of reaction. Explain with suitable examples.

Q11. The rate determining step of a reaction is found out from the mechanism of that reaction. Explain it with few examples.

Q12. Discuss the factors which influence the rates of chemical reactions.

Q.13. Explain the following facts about the reaction.

$$2NO(g) + 2H_2(g) \rightarrow 2H_2O(g) + N_2(g)$$

(i) The changing concentrations of reactants, change the rates of this reaction.

(ii) Individual orders with respect to NO and H_2 can be measured.

(iii) The overall order can be evaluated by keeping the concentration of one of the substances constant.

Q14. The collision frequency and the orientation of molecules are necessary conditions for determining the proper rate of reaction. Justify the statement.

Q.15. How does Arrhenius equation help us to calculate the energy of activation of a reaction?

Q16. Define the following terms and give examples

(i) Homogeneous catalysis
(ii) Heterogeneous catalysis
(iii) Activation of a catalyst
(iv) Auto-catalysis
(v) Catalytic poisoning
(vi) Enzyme catalysis

Q17. Briefly describe the following with examples

(i) Change of physical state of a catalyst at the end of reaction.
(ii) A very small amount of a catalyst may prove sufficient to carry out a reaction.
(iii) A finely divided catalyst may prove more effective.
(iv) Equilibrium constant of a reversible reaction is not changed in the presence of a catalyst.
(v) A catalyst is specific in its action.

Q18. What are enzymes? Give examples in which they act as catalyst. Mention the characteristics of enzyme catalysis.

Q19. In the reaction of NO and H_2, it was observed that equimolecular mixture of gases at 340.5 mm Hg pressure was half changed in 102 seconds. In another experiment with an initial pressure of 288 mm of Hg, the reaction was half completed in 140 seconds. Calculate the order of reaction.

(Ans:2.88)

Q20. A study of chemical kinetics of a reaction

$$A + B \rightarrow \text{Products}$$

gave the following data at 25 °C. Calculate the rate law.

[A]	[B]	Rate
1.00	0.15	4.2×10^{-6}
2.00	0.15	8.4×10^{-6}
1.00	0.2	5.6×10^{-6}

(Ans: second order)

Q21. Some reactions taking place around room temperature have activation energies around 50kJ mol^{-1}.

(i) What is the value of the factor $e^{\frac{-E}{RT}}$ at 25°C ?

(Ans: 1.72×10^{-9})

(ii) Calculate this factor at 35 °C anat 45 ^{0}C and note1 the increase in this factor for every 10 ^{0}C rise in temperature.

(Ans:3.31×10^{-9})

(iii) Prove that for every 10°C rise in of temperature, the factor doubles and so rate constant also doubles.

(Ans:6.12×10^{-9})

Q22. H_2 and I_2 react to produce HI. Following data for rate constant at various temperatures (K) have been collected.

(i) Plot a graph between $\frac{1}{T}$ on x-axis and log k on the y-axis.

(ii) Measure the slope of this straight line and calculate the energy for activation of this reaction.

Temp. (K)	Rate constant ($cm^3\ mol^{-1}\ s^{-1}$) (K)
500	6.814×10^{-4}
550	2.64×10^{-2}
600	0.56×10^{0}
650	7.31×10^{0}
700	66.67×10^{0}

(Ans: 8326.32,160.6kJmol^{-1})

APPENDIX

Animation: Appendix
Source & Credit: olivergoodwin

Table A.1 The SI System

Physical Quantity	Name in Units	Symbol	Physical Quantity	Name in Units	Symbol
Length	meter	m	Volume	cubic meter	m^3
Mass	kilogram	kg	Length	angstrom	Å (0.1nm)
Time	second	s	Pressure	atmosphere	atm(101.325kPa)
Temperature	Kelvin	K		torr	mmHg(133.32Pa)
Electrical current	ampere	A	Energy	calorie	cal(4.184J)
Luminous intensity	candela	cd		electron volt	ev(1.6022x10^{-19}J)
Amountofsubstance	mole	mol	Temperature	degree celsius	^{o}C (K-273.15)
			Concentration	molarity	M(mol/L or mol/dm^3)

Table A.2 Common Derived Units in SI

Physical Quantity	Name in Unit	Symbol
Energy	joul	J(kg-m^2/s^2)
Frequency	hertz	Hz(cycles/s)
Force	newton	N(kg-m/s^2)
Pressure	pascal	P_a(N/M^2)
Power	watt	W(j/s)
Electrical charge	coulomb	C(amp-s)
Electrical potential	volt	V(j/c)
Electrical resistance	ohm	Ù(v/amp)
Electrical conductance	siemens	S(amp/V)
Electrical capacitance	farad	F(C/V)

TableA.3 Fraction and Multiplies for Use in SI

Fraction and Multiplies for Use in SI			
exa, E	10^{18}	deci, d	10^{-1}
peta, P	10^{15}	centi, c	10^{-2}
tera, T	10^{12}	milli, m	10^{-3}
giga, G	10^{9}	micro, μ	10^{-6}
mega, M	10^{6}	nano, n	10^{-9}
kilo, k	10^{3}	pico, p	10^{-12}
hecto, h	10^{2}	femto, f	10^{-15}
deca, da	10^{1}	atto, a	10^{-18}

Table A.4 Values of Selected Fundamental Constants

Speed of light in vacuum (c)	$c = 2.99792458\text{x}10^{8}\text{m/s}$
Charge on an electron (q_e)	$q_e = 1.6021892\text{x}10^{-19}\text{C}$
Rest mass of electron (m_e)	$m_e = 19.109534\text{x}10^{-28}\text{g}$ $m_e = 5.4858026\text{x}10^{-4}\text{amu}$
Rest mass of proton (m_p)	$m_p = 1.6726485\text{x}10^{-24}\text{g}$ $m_p = 1.00727647\text{amu}$
Rest mass of neutron (m_n)	$m_n = 1.6749543\text{x}10^{-24}\text{g}$ $m_n = 1.00865012\text{amu}$
Faraday's constant (F)	F = 96484.56 C/mol
Planck's constant (h)	$h = 6.626176\text{x}10^{-34}\text{J-s}$
Ideal gas constant (R)	R = 0.0820568 L-atm/mol-K R = 8.31441 J/mol-K
Atomic mass unit (amu)	$1\text{ amu} = 1.6605655\text{x}10^{-24}\text{g}$
Boltzmann's constant (k)	$k = 1.380662\text{x}10^{-23}\text{ J/K}$
Aogadro's constant (N_A)	$N_a = 6.022045\text{x}10^{23}\text{mol}^{-1}$
Rydberg constant (R_H)	$R_H = 1.09737318\text{x}10^{7}\text{m}^{-1}$ $= 1.09737318\text{x}10^{-2}\text{nm}^{-1}$
Molar Volume of a gas at s.t.p	$V_m = 2.24\text{x}10^{-2}\text{m}^{3}\text{mol}^{-1}$
Heat capacity of water	C = 75.276J/mol-K

Table A.5 Selected Conversion Factors

Energy	1 J = 0.2390 cal = 10^7erg
	1 cal = 4.184 J
	lev/atom = $1.6021892\text{x}10^{-19}$J/atom = 96.484 kJ/mol
Temperature	K = C + 273.15
	^{0}C = 5/9 (F-32)
	^{0}F = 9/5 (C) + 32
Pressure	1am = 760 mmHg = 760 torr = 101.325kPa
Mass	1kg = 2.2046 lb
	1lb = 453.59 g = 0.45359 kg
	1oz = 0.06250 lb = 28.350 g
	1ton = 2000 lb = 907.185 kg
	1tonne (metric) = 1000 kg = 2204.62 lb
Volume	1 mL = 0.001 L = 1 cm^3
	1 oz (fluid) = 0.031250 qt = 0.029573 L
	1 qt = 0.946326 L
	1 gal = 0.946 L
Length	1 mile = 1.60934 km
	1 in. = 2.45 cm
	10mm = 1 cm
	1000mm = 1 m
	1000m = 1 km
	1m = 39.370 in.
	Å = 10^{-10} m = 10^{-8} cm

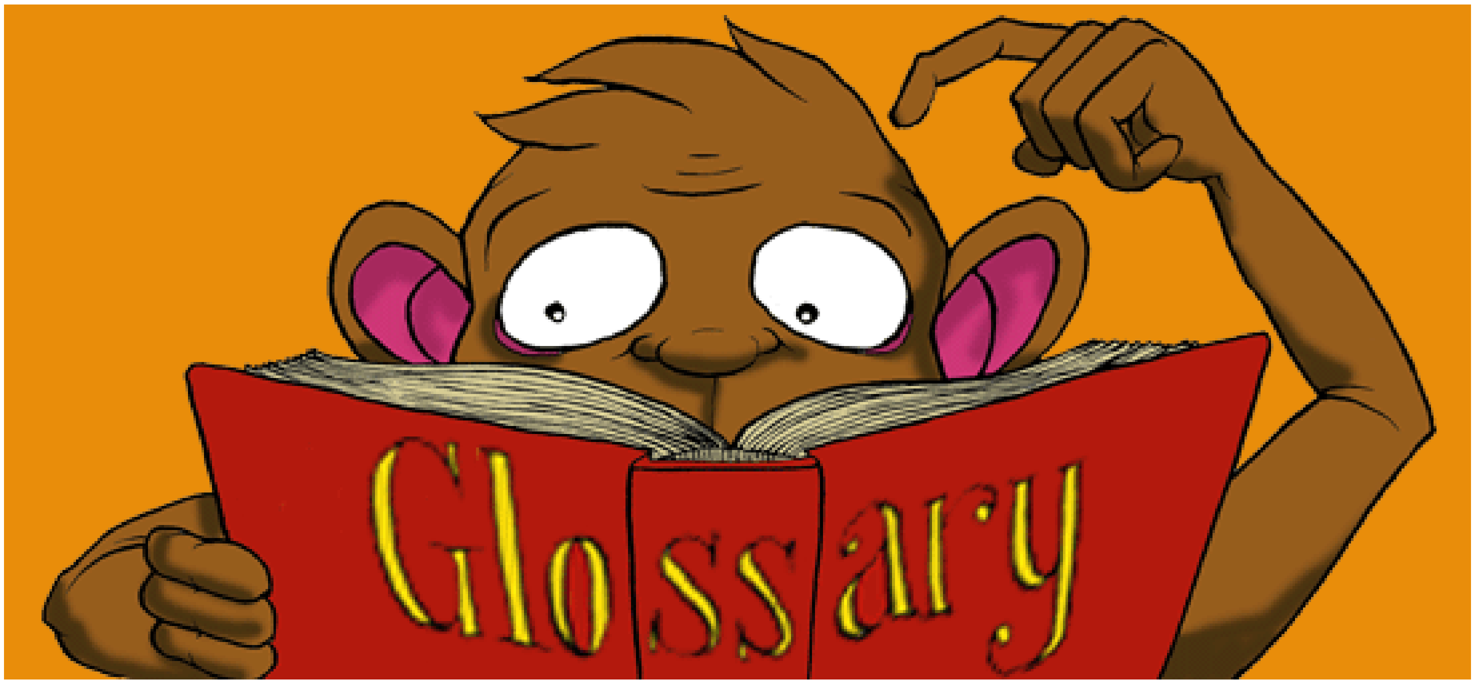
Table A.6 Solubility Table

	F^-	Cl^-	Br^-	I^-	O^{2-}	S^{2-}	OH^-	NO_3^-	CO_3^{2-}	SO_4^{2-}	CH_3COO^-
H^+	S	S	S	S	S	s	S	S	s	S	S
Na^+	S	S	S	S	S	S	S	S	S	S	S
K^+	S	S	S	S	S	S	S	S	S	S	S
NH_4^+	S	S	S	S	-	S	S	S	S	S	S
Ag^+	S	I	I	I	I	I	-	S	I	I	I
Mg^{2+}	I	S	S	S	I	d	I	S	I	S	S
Ca^{2+}	I	S	S	S	I	d	I	S	I	I	S
Ba^{2+}	I	S	S	S	s	d	s	S	I	I	S
Fe^{2+}	s	S	S	S	I	I	I	S	s	S	S
Fe^{3+}	I	S	S	-	I	I	I	S	I	S	I
Co^{2+}	S	S	S	S	I	I	I	S	I	S	S
NI^{2+}	s	S	S	S	I	I	I	S	I	S	S
Cu^{2+}	s	S	S	-	I	I	I	S	I	S	S
Zn^{2+}	s	S	S	S	I	I	I	S	I	S	S
Hg^{2+}	d	S	I	I	I	I	I	S	I	d	S
Cd^{3+}	s	S	S	S	I	I	I	S	I	S	S
Sn^{2+}	S	S	S	s	I	I	I	S	I	S	S
Pb^{2+}	I	I	I	I	I	I	I	S	I	I	S
Mn^{2+}	s	S	S	S	I	I	I	S	I	S	S
Al^{3+}	I	S	S	S	I	d	I	S	-	S	

Key : S = Soluble in water **I = Insoluble in water (less than 1g/100g H_2O)**

s = Slightly soluble in water **d = Decompose in water**

GLOSSARY



Animation: Glosssary
Source & Credit: speedyromeo

Absolute zero:	The temperature of -273.16 °C at which the volume of a gas theoretically becomes zero is called absolute zero. It is taken as Zero on the kelvin scale of temperature.
Actual yield:	Actual yield is the amount of the product actually obtained in a chemical reaction.
Amorphous solids:	Those solids in which the structural units i.e. atoms, ions or molecules are fixed in their positions but are not regularly arranged.
Anisotropy:	It is the variation of a certain physical property with direction.
Atomic absorption spectrum:	When a beam of white light is passed through the vapours or a gas, the element absorbs certain wavelengths, while rest of the wavelengths are passed through it. The spectrum of this radiation is called atomic absorption spectrum. The missing wavelengths appear as dark lines in the spectrum.
Atomic emission spectrum:	It is the spectrum formed by the elements or their compounds when they are heated in a flame. The spectrum consists of a series of bright lines with a dark background.
Atomic radius:	If an atom is assumed to be spherical then the atomic size means the average distance between the nucleus of the atom and its outermost shell. This distance is called atomic radius and it can not be measured precisely.
Auf-bau principle:	The electrons should be filled in energy sub-levels in order of increasing energy values. The electrons are first placed in Is, then 2s, then 2p and so on.
Average Rate of Reaction:	The rate of reaction between two specific time intervals is called average rate of reaction.
Avogadro's law:	Equal volumes of all ideal gases at same temperature and pressure contain equal number of molecules.
Avogadro's number:	Avogadro's number is the number of atoms, molecules or ions in one gram atom of an element, one gram mole of a compound or one gram ion of an ionic substance.
Azimuthal quantum number:	The quantum number that defines the shape of the orbital of an electron.
Balmer series:	A series of lines present in the visible region of hydrogen spectrum formed when an electron jumps from higher orbits to the 2nd orbit.

Boiling point:	The temperature at which the vapour pressure of a liquid becomes equal to the external pressure, is called boiling point of the liquid.
Bond energy:	The average amount of energy required to break all bonds of a particular type in one mole of the substance.
Bond order:	Half of the difference between the number of bonding electrons and anti-bonding electrons.
Boyle’s law (1662):	The volume of the given mass of a gas is inversely proportional to the pressure of that gas when the temperature is kept constant.
Brackett series:	A series of lines in the infra red region of hydrogen spectrum formed when the electron jumps from higher orbits to the fourth orbit.
Catalyst:	The substance which alters the rate of a chemical reaction but remains chemically unchanged at the end of reaction.
Cathode rays:	Negatively charged rays which originate from the cathode when electricity is passed through a gas at very low pressure.
Charles’s law (1787):	The volume of a given mass of a gas is directly proportional to absolute temperature when the pressure is kept constant.
Chromatography:	It is a method used for the separation of components of a mixture.
Colligative properties:	These are the properties of solutions that depend only on the number of solute and solvent molecules or ions.
Common ion effect:	The decrease in the solubility of an electrolyte in a solution in the presence of a common ion is called common ion effect.
Conjugate acid of a base:	The positively charged ion produced by the acceptance of a proton by a base is the conjugate acid of the base.
Conjugate base of the acid:	The negatively charged ions or a neutral species produced by the release of proton is the conjugate base of the compound releasing the proton.
Covalent crystals:	Those crystals in which the non-metallic atoms are held together in a network of single covalent bonds.
Covalent radius:	It is half the length of a covalent bond between tw’o atoms.
Critical temperature:	That temperature of a gaseous substance above which it cannot be converted into the liquid state no matter how much the pressure is applied on it.
Crystal lattice or space lattice:	A particular three dimensional arrangement of particles i.e. atoms, ions or molecules in a crystal is. called a crystal lattice or space lattice.

Crystal:	A three dimensional shape bounded by plane surfaces which intersect at definite angles with each other.
Crystallization:	A process in which a crude product is purified and obtained in the form of crystals.
Dalton's law of partial pressures:	Total pressure of a mixture of gases is equal to the sum of the partial pressures of all the gases in the mixture.
Diffusion of gases:	The spontaneous mixing of the molecules of different gases by random motion and collisions to form homogeneous mixture is called gaseous diffusion.
Dipole moment:	It is a product of charge and the distance between the positive and negative centers present in a compound.
Dipole:	Partial separation of charges on a bond between two atoms.
Dipole-Dipole forces:	The attractive forces between the positive end of one molecule and the negative end of the another polar molecule are called dipole-dipole forces.
Discharge tube:	A glass tube containing a gas at low pressure and is provided with electrodes for the passage of electricity through the gas.
Effusion of gases:	With the passage of the gas molecules one by one without collisions through a pin hole in their container into an evacuated space is called effusion.
Electrochemical Cell:	It is a system consisting of electrodes that dip into an electrolyte and in which a chemical reaction either uses or generates electric current.
Electrode potential:	It is the tendency of a metal to form its ions or to get deposited on the metal when a metal is dipped into the solution of its own ions.
Electrolysis:	It is the decomposition of ionic compounds by the passage of electric current.
Electrolytic conduction:	It is the passage of electric current through electrolytes present in the fused state or in the solution form.
Electron affinity:	Attraction of nucleus of an atom for an extra electron.
Electronegativity:	Tendency of a bonded atom to attract the shared electron pair towards itself.
Empirical formula:	That formula of a compound which is based on the formula unit and gives the simple whole number ratio of the atoms in the molecule is called empirical formula.

Endothermic reactions:	The chemical reactions, which are accompanied by absorption of heat, are called endothermic reactions.
Enthalpy or heat of solution:	It is defined as the heat change when one mole of a substance is dissolved in a specified number of moles of solvent at a given temperature.
Enthalpy:	The total heat content of a system is termed as enthalpy of a system.
Equilibrium constant:	Equilibrium constant is the ratio of forward rate constant and backward rate constant for a reaction at given condition.
Evaporation:	The spontaneous change of a liquid into its vapours at the surface of liquid at a given temperature is called evaporation.
Exothermic reaction:	The chemical reactions, which are accompanied by the evolution of heat, are called exothermic reactions.
First law of thermodynamics:	It states that energy can neither be created nor be destroyed but can be changed from one form to another.
Graham 's law of diffusion:	The rate of diffusion of a gas is inversely proportional to the square root of the density of the gas or the molar mass of gas under the given conditions of temperature and pressure.
Half-life period:	Half-life period of a reaction is the time required to convert 50% of the reactants into products.
Heisenberg's uncertainty principle:	It is not possible to measure simultaneously the exact position and momentum of an electron in an atom.
Hess's law of constant heat summation:	If a chemical change takes place by several different routes, the overall energy change is the same, regardless of the route by which the chemical change occurs, provided the initial and final conditions are the same.
Hund's rule:	If degenerate orbitals are available and more than one electrons are to be placed in them, they should be placed in separate orbitals with the same spin rather than putting them in the same orbital with opposite spins.
Hybridization:	Mixing of orbitals to form new orbitals with specific orientations.
Hydration:	The process in which water molecules surround and interact with solute molecules or ions is called hydration.

Hydrogen bonding:	Hydrogen bondingis the electrostatic force of attraction between hydrogen atom (bonded to a small highly electronegative atom) and the electronegative atom of another molecule.
Ideal gas:	A gas which obeys the gas laws at all temperatures and pressures.
Ideal solutions:	Those solutions which obey Raoult's law.
Instantaneous Rate of Reaction:	The rate of reaction at any one instant during the interval.
Intermolecular forces:	The attractive forces which exist between individual particles i.e. atoms, ions and molecules.
Ion dipole interactions:	The electrostatic forces of attraction between an ion (positive or negative) and the polar molecules of the solvent.
Ionic crystals:	Those crystals in which the oppositely charged ions are held together by an ionic bond.
Ionic radius:	It is the radius of an ion considered spherical in shape.
Ionization Energy:	It is the minimum amount of energy required to remove the most loosely bound electron from an isolated gaseous atom.
Irreversible reaction:	An irreversible reaction is that in which products of the reaction do not react to form the original reactants under the same set of conditions.
Kinetic molecular theory of gases:	A model of gases which explains the physical behaviour of gases.
Law of mass action:	The rate at which a substance reacts is proportional to its active mass and the rate of a chemical reaction is proportional to the product of the active masses of the reacting substances.
Le-Chatelier's principle:	If a system at equilibrium is disturbed, it behaves in such a way as to nullify the effect of that disturbance.
Limiting reactant:	Limiting reactant is that reactant which is present in lesser amount and controls the amount of the products in a chemical reaction.
Liquid crystal:	That crystalline state of a substance which exists between two temperatures i.e. the melting temperature and the clearing temperature.

London dispersion forces:	The attractive forces between the temporary dipole in one molecule and temporary induced dipole in an adjacent molecule are called London dispersion forces, adjacent molecule are called London dispersion forces.
Lowry-Bronsted Concepts of acids and bases:	Acids are those species which give proton or have a tendency to give proton. Bases are those species which accept proton or have a tendency to accept proton.
Lyman series:	A series of lines in the ultraviolet region of hydrogen spectrum which are obtained when electron jumps from higher orbits to the first orbit of hydrogen atom.
Magnetic quantum number:	The quantum number that defines the orientation of an orbital in a magnetic field.
Mass spectrometer:	It is the instrument employed to separate positively charged particles on the basis of their m/e values and get the record on the photographic plate or electrometer.
Metallic crystals:	Those crystals in which the metal atoms are held together by metallic bonds.
Molality (m):	It is the number of moles of the solute dissolved in 1000 grams (1 kg) of the solvent.
Molar volume:	The volume occupied by one mole of an ideal gas at standard temperature and pressure - 22.414 dm^3 is called the molar volume.
Molarity (M):	It is the number of moles of the solute dissolved per dm^3 of the solution.
Mole fraction:	Mole fraction of any component in a mixture is the ratio of the number of moles of it to the total number of moles of all the components present in the solution.
Mole:	A quantity which contains Avogadro's number of units i.e. atoms, molecules, ions or whatever under consideration is called a mole.
Molecular crystals:	Those crystals in which the molecules are held together by van der Waal's forces.
Molecular formula:	A chemical formula which gives the total number of atoms present in a molecule of a substance.

Molecular ions:	Those ions which are produced by the removal of one or more electron or electrons from the molecule of a substance are called molecular ions. They are mostly positive and rarely negative.
Non-ideal solution:	Those solutions which do not obey Raoult's law.
Non-spontaneous Process:	It is the reverse of the spontaneous process. It does not take place on its own and does not occur in nature.
Orbit:	An orbit is a definite path at a definite distance from the nucleus in which the electron revolves around the nucleus; actually an orbit indicates an exact position or location of an electron in an atom.
Orbital:	A region around the nucleus where the probability of finding the electron is maximum, s, p, d and f are different types of orbitals which exist in an atom.
Order of Reaction:	It is the sum of the exponents of the concentration terms in the rate expression of a chemical reaction.
Oxidation Number:	It is the apparent charge on an atom of an element in a compound or a radical.
Paper Chromatography:	It is a technique of partition chromatography in which the stationary phase is water adsorbed on paper and mobile phase is usually an organic liquid.
Partial pressure:	The pressure exerted by an individual gas in a gaseous mixture is called the partial pressure of that gas.
Parts per million:	It is defined as the number of the parts (by weight or volume) of a solute per million parts (by weight or volume) of the solution.
Paschen series:	A series of lines in the infra red region of hydrogen spectrum which results from the transitions of electron from higher orbits to the third orbit.
Pauli's exclusion principle:	According to this principle, it is impossible for two electrons residing in the same orbital of a poly electron atom, to have the same values of four quantum numbers. Thus two electrons in the same orbital should have opposite spins.
Percentage yield:	$\%\text{yield}=\dfrac{\text{Actual yield}}{\text{Theoretical yield}}\text{x}100$
Pfund series:	A series of lines in the infra red region of hydrogen spectrum which results from the transition of electron from higher orbits to the fifth orbit.

pH of the solution:	The negative log of $[H^+]$ is called pH of the solution.
Phase:	Every sample of matter with uniform properties and a fixed composition is called a phase.
pi (π) bond	A bond formed by the parallel overlap of the two planar p-orbitals present on the adjacent atoms which are already bonded with a ct bond.
pK_w:	It is the negative log of dissociation constant of water.
pOH of the solution:	The negative log of $[OH^-]$ is called pOH of the solution.
Polarizability:	Polarizability is the quantitative measurement of the extent to which the electronic cloud can be polarized.
Positive rays or canal rays:	Rays travelling in a direction opposite to the cathode rays in a discharge tube. They consist of positively charged ions formed by the ionization of gas molecules with the passage of cathode rays.
Principal quantum number:	The quantum number that defines the shell of an electron in an atom. Its symbol is n.
Quantum Numbers:	These are the sets of numerical values which give the acceptable solutions.
Raoult's law:	The lowering of the vapour pressure of a solvent by a solute, at a given temperature, is directly proportional to the mole fraction of solute.
Rate Constant:	Itistherateofreactionwhentheconcentrationsofthereactantsareunity.
Rate of Reaction:	It is defined as the change in concentration of a reactant or a product divided by the time taken for the change.
Real gas:	A gas which does not obey the gas laws at all temperatures and pressures.
Redox Reaction:	A chemical reaction in which oxidation and reduction take place.
Relative abundance of isotope:	The percentage of isotope of an element in comparison to other isotopes of the same element is called relative abundance of isotope.
Relative atomic mass:	Relative atomic mass of an atom of an element is the mass as compared with the mass of one atom of carbon taken as twelve. It is expressed in a.m.u.

Retardation Factor (R_f):	A component of a mixture may be identified by a specific retardation factor called R, value. It is related to the partition coefficient by the following relationship, $R_f = \frac{\text{Distance travelled by a component from the original spot}}{\text{Distance travelled by a solvent from the original spot}}$
Reversible reaction:	A reversible reaction is that one in which products of a reaction can react to form the original reactants.
Sigma (σ)-bond:	A bond formed by the linear overlap of atomic orbitals.
Solubility:	It is the number of grams of a solute that can be dissolved in 100 grams of the solvent to prepare a saturated solution at a particular temperature.
Solvent Extraction:	It is a technique in which a solute can be separated from a solution by shaking the solution with a solvent in which the solute is more soluble and the added solvent does not mix with the solution.
Spectrum:	A band of seven colours formed by the dispersion of the components of white light, when it is passed through a prism.
Spontaneous Process:	Process, which takes place on its own without any outside assistance and moves from a non-equilibrium state towards an equilibrium state, is termed as spontaneous process.
Standard Electrode Potential:	When a metal is dipped into the solution of its own ions having concentration 1.0 mol per dm^3 or a gas is passed at a pressure of one atmosphere through a solution of 1.00 mol per dm^3 strength of its ions having an inert electrode, the potential developed is called standard electrode potential. The temperature of the system is maintained at 25^0 C.
Standard Enthalpy of Atomization:	It is the change of enthalpy when one mole of gaseous atoms is formed form the element under standard conditions.
Standard Enthalpy of Combustion:	It is the amount of heat produced when one mole of the substance is completely burnt in excess of oxygen under standard conditions.
Standard Enthalpy of Formation:	It is the change of enthalpy when one mole of a compound is formed from its elements under standard conditions.

Standard Enthalpy of Neutralization:	It is the amount of heat evolved when one mole of hydrogen ions H^+ from an acid react with one mole of hydroxide ion OH^- from an alkali under standard conditions.
Standard temperature and pressure:	The standard temperature is 0^0C (273 K) and the standard pressure is 1 atm or 760 mm of Hg or 760 torr or 101325 Nm^{-2}.
State Function:	It is a macroscopic property of a system which has some definite value for each state and which is independent of path in which the state is reached.
Stoichiometry:	Stoichiometry is the branch of chemistry which deals with the quantitative relationship between reactants and products in a balanced chemical equation.
Sublimation:	It is a process in which a solid, when heated, vapourizes directly without passing through the liquid state.
Surroundings:	The remaining portions around a system are called surroundings.
System:	Anything (materials) under test or under consideration, is termed as a system.
Theoretical yield:	The oretical yield is the amount of the products calculated from the balanced chemical equation.
Thermochemistry:	The study of heat changes during a chemical reaction is known as thermochemistry.
Unit cell:	The smallest unit of the volume of a crystal which when repeated in three dimensions can generate the structure of the entire crystal.
Vacuum distillation:	The process of heating a liquid under reduced pressure to change it into vapours at a lower temperature and then condensing the vapours to a liquid.
van der Waal's equation:	It is an equation of state of gases that modifies the ideal gas equation to represent more accurately the behaviour of real gases.
Vapour pressure:	The pressure exerted by the vapours of a liquid in equilibrium with the liquid at a given temperature.
Water of crystallization:	Those water molecules, which have combined with some compounds as they are crystallized from aqueous solutions is called water of crystallization or water of hydration.