International Edition

Understanding CHEMISTRY

C N R Rao

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and
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Cover: The burning candle shown in the cover picture has traditionally symbolized chemistry. The bucky ball (C_{60}) next to it is obtained from carbon soot.

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The external boundaries and coastline of India as depicted in the maps are neither correct nor authentic.

UNDERSTANDING CHEMISTRY (International Edition)

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To
Kartik and Suggi

PREFACE

Understanding Chemistry is an elementary introduction intended for high school students and others interested in an appreciation of chemistry. It is not a textbook. Everything is not said. Some ideas and facts are presented, and a few questions raised, in order to interest the reader in the subject and to arouse curiosity. Several topics of human interest such as the environment, energy, food and water are discussed, besides giving life sketches of chemists, historical accounts and procedures for a few experiments. I believe that the book provides a flavour of the subject and shows how it works. I hope that students, teachers and enthusiasts for science will find the book useful and educational.

I am most thankful to the members of the Education Technology Unit of the Jawaharlal Nehru Centre for Advanced Scientific Research, Jatinder Kaur, Bhaskar, Indu Rao and Sanjay Rao, for their invaluable assistance in illustrating and formatting the book as well as in preparing the final version for production.

I thank the Indian National Science Academy and the Council for Scientific and Industrial Research (CSIR) for supporting this venture.

C N R Rao
Banglore

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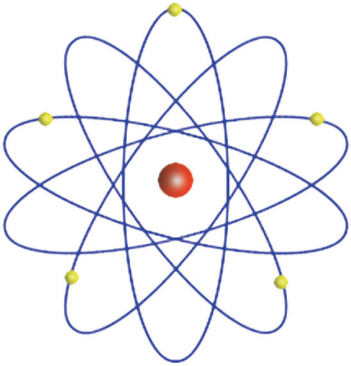
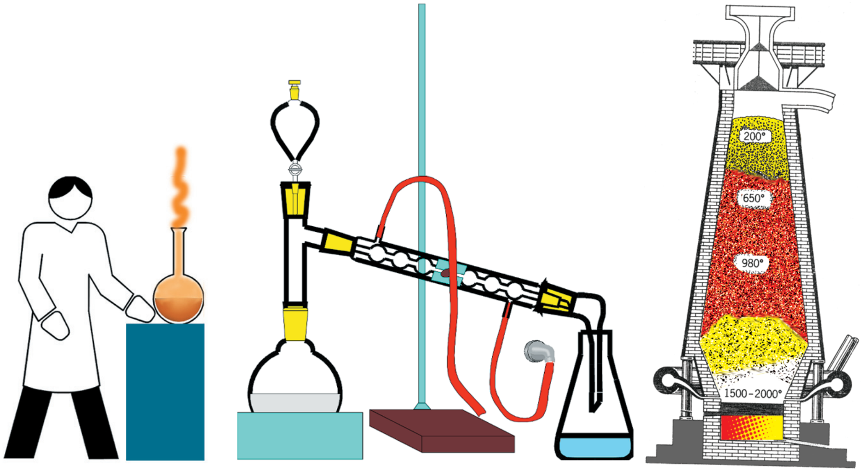


CHEMISTRY IN A CAPSULE



Objectives

- In this lesson, we shall try to understand certain essential aspects of chemistry. Colours and smells are associated with chemicals. The world is full of chemical substances. Life is associated with chemicals and we need chemicals for many useful purposes. And, our body is a huge chemical factory.
- Chemistry involves observing changes in substances. In chemistry, we prepare substances, classify them and describe their properties. We shall examine some aspects of metals and materials, alkalis and acids as well as carbon compounds. We end up with a look at our food, the atmosphere and water.
- The last three topics are of concern to all of us. We depend on food and water for living. We have to take care of the atmosphere.

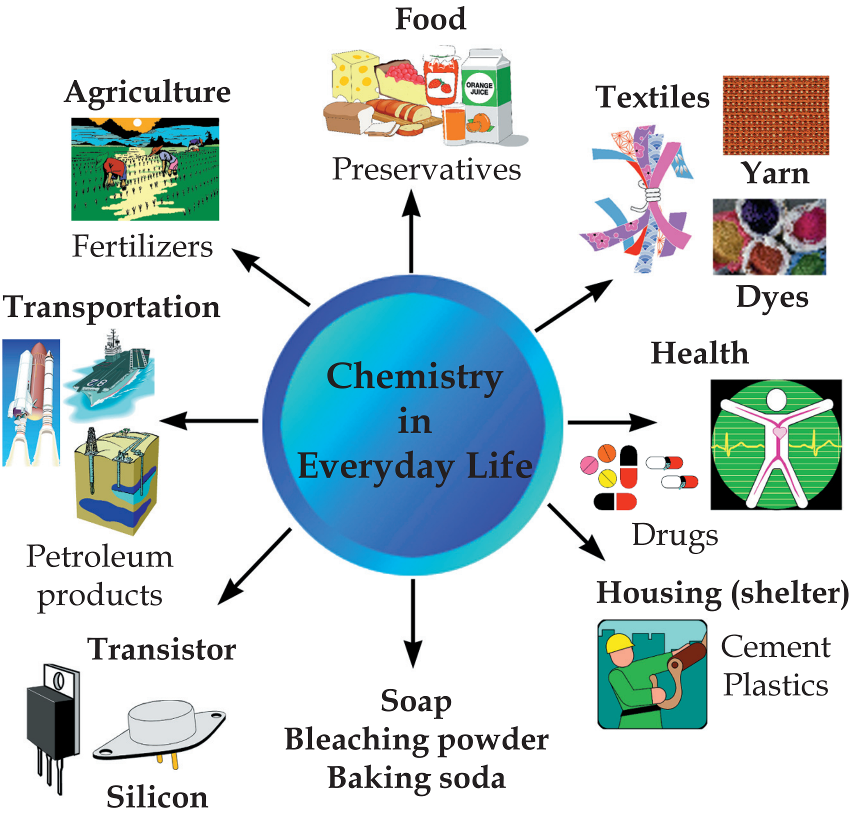
Chemistry is a study of substances, their properties, structures and transformations. Because there is such a large variety of substances in Nature, the scope of chemistry is immense. Chemists use their skills and methods to design and synthesize molecules of great complexity. It is jokingly said that given enough time, chemists can even synthesize a camel!

Whether it is a computer chip or cough syrup, chemistry is needed to make it. Progress in modern society is indeed based on advances in chemistry. Thus, some of the most essential needs for living require the use of chemical compounds.

A few examples are given below:

Fertilizers:	(NPK) Ammonimum nitrate + Ammonium phosphate + Potassium chloride
Insecticides:	DDT, Endosulfan, Monocrotophos, Isoproturon
Herbicides:	Sulfonylureas, Butachlor
Medicinal drugs:	Aspirin, antibiotics (penicillin), contraceptives for family planning
Sugar substitute:	Aspartame (for diabetics and weight-watchers)
Soap:	Sodium salt of a fatty acid

Besides making compounds (molecules) of different compositions, structures and properties, chemists extract active principles from natural products (plants), characterize them and also make them independently in the laboratory. For example, the active principle in neem (*azadirachta indica*) is found to be azadirachtin. The tranquilizer, reserpine, is found in the roots of the plant, *rauwolfia serpentina*. Forskolin extracted from the makandi plant (*celeus forskohlli*) is good for treatment of asthma. Vincristin and vinblastin are drugs for blood cancer extracted from the plant *vinca rosia*. Medicinal properties of turmeric are due to curcumin and its derivatives.



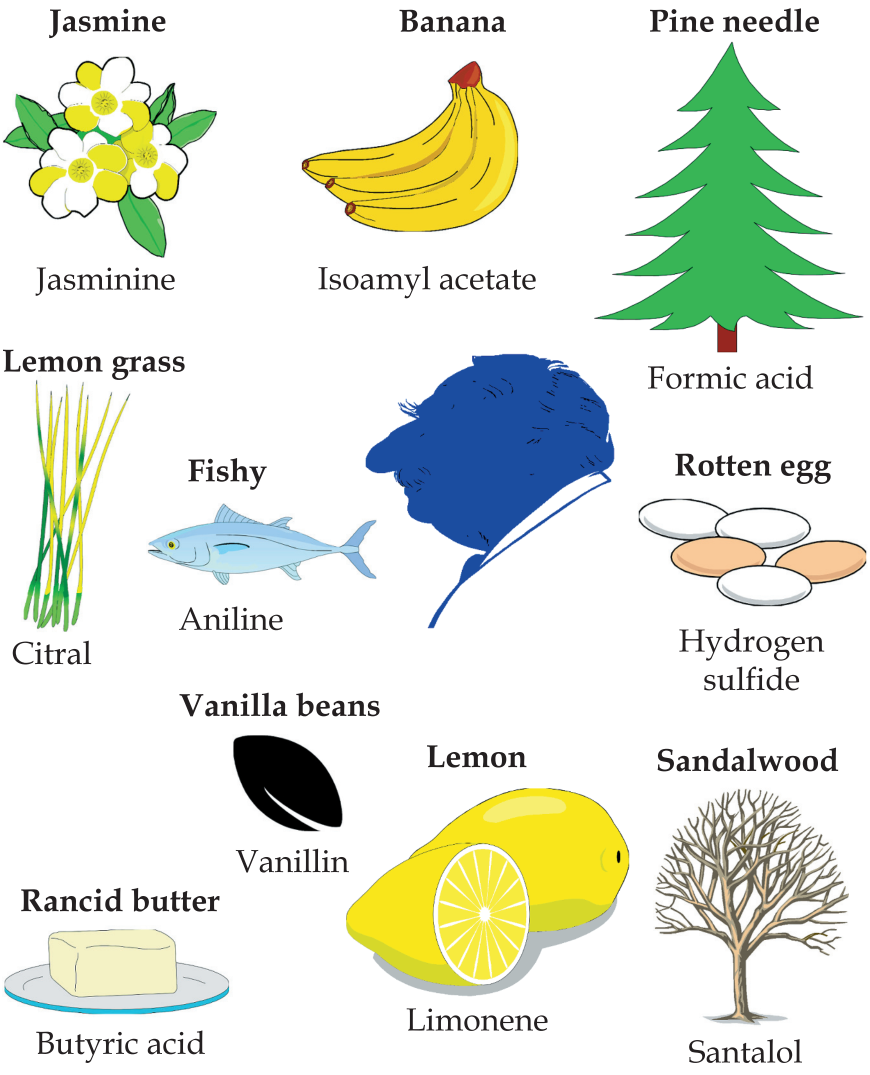
Sodium stearate
Calcium hypochlorite
Sodium bicarbonate

Chemistry deals with vivid colours, different smells and flavours, and even sounds (explosions).

The origin of colours is chemical.

Chemical	**Colour**
Iodine	Violet
Indigo	Indigo
Copper sulfate in water	Blue
Nickel sulfate, Chlorophyll	Green
Barium chromate Copper chloride	Yellow
Potassium dichromate Carotene	Orange
Cobaltous nitrate	Red

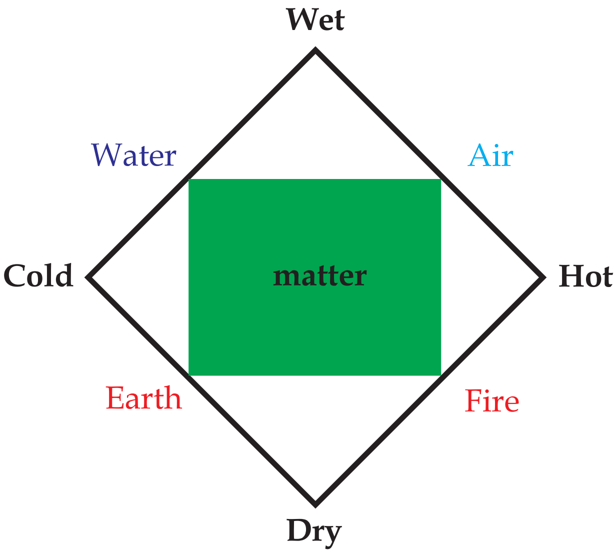
The origin of smell and flavours is also chemical. The smell of garlic is due to the chemical, allicin.



1.1 What is matter made of?

Philosophers of ancient Greece and India sought an answer to this question centuries before Christ.

Early Greek Idea: Empedocles (500 – 430 B.C.) suggested that fire, water, air and the earth constituted the primary elements of matter. Aristotle (384 – 322 B.C.) agreed with Empedocles's concept of the four primary elements constituting all matter. He added a crucial component to this idea — properties of the elements.



The properties of any particular substance were believed to be due to the composition ratio of these four primary elements.

Early Indian Concept: Interestingly, almost an identical concept was developed independently in India during this period (600 – 500 B.C.). According to Samkhya philosophy, matter was made up of five "bhutas" or elements consisting of akasa (sky), vayu (air), tejas (fire), ap (water) and kshiti (earth). The "bhutas" shared properties like colour, taste, smell, touch and at the same time, each "bhuta" had distinguishing properties of its own. The distinguishing properties were: kshiti — smell, ap — coolness, tejas — hotness, and vayu — touch. The difference in the properties of the same "bhuta class" was due to the difference in the grouping.

The only significant part of the early concept of the elements that has survived is that elements have distinctive properties.

What is an element?

Cut a piece of antimony into two or break them into flakes, or grind it into powder. All the pieces in the flakes or powder contain identical particles of antimony.

An element is a substance which cannot be further reduced to a simpler substance by ordinary processes, and is made up of particles of one kind only.

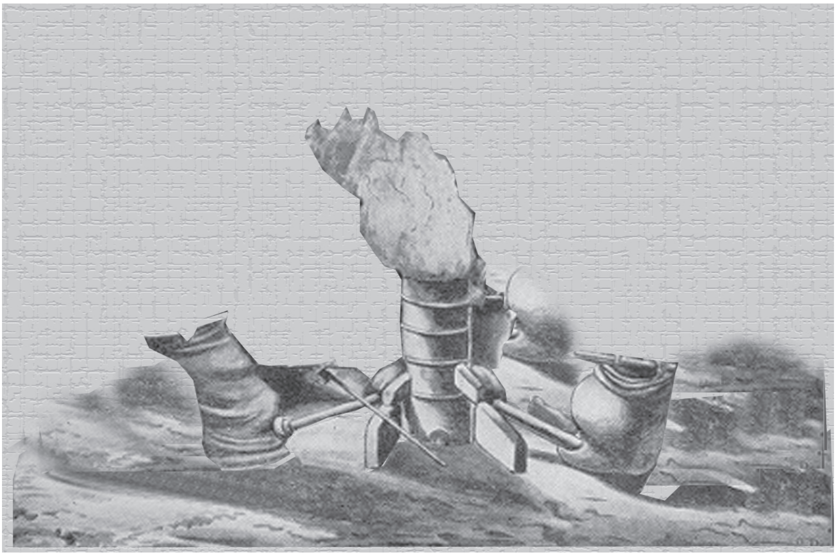
It took many centuries of observation and experiment to arrive at this simple understanding of what an element is.

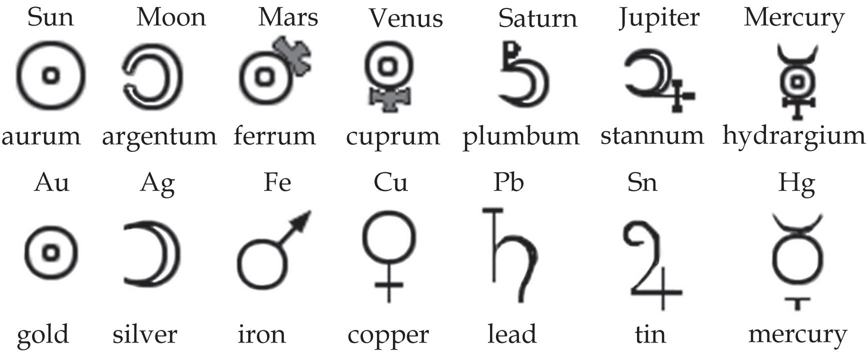
How and when were elements discovered?

The story of elements is linked to the story of human civilization.

From the Stone Age to modern times, man has used many metals and their compounds to suit his needs.

Man learnt to extract elements from ores, and fashioned them into implements without knowing what an element was.





A few metals like gold, silver, iron, copper, lead, tin and mercury were extensively used even by the first century A.D. These metals were known in ancient India as well. They have been mentioned in Charaka Simhita — a medical treatise of ancient India. But they were not identified as chemical elements. Each of these metals was associated with a particular heavenly body. In addition to the above seven elements, sulfur and carbon were also known.

Middle Ages and the Alchemists: Alchemists are the forerunners of present-day chemists. They were perhaps the earliest experimentalists. They tried various experiments to convert base metals into gold by using "philosopher's stone" — an illusionary substance. While they did not succeed in converting "base" elements to gold, alchemists succeeded in separating and identifying arsenic, antimony and bismuth. Do you know that the celebrated physicist Newton was an alchemist!

Arsenic, antimony and bismuth are indeed members of a chemical family sharing similar properties.

Alchemists added three more properties to Aristotle's list of properties: Combustibility (sulfur), Volatility (mercury), and Incombustibility (chemical salts). Properties of elements, however, remained mere abstractions.

As time went on, more and more elements were discovered. Thanks to the contributions of a number of chemists, the manner of arranging elements in relation to their properties came to be understood. And, the modern **periodic table** came into being. We will discuss the periodic table in Lesson 2.

1.2 What are we made of?

The world around us consists of compounds made of various elements. The Earth's core consists of heavy elements like iron. The Earth's crust, on the other hand, consists of light elements like oxygen, hydrogen, carbon and silicon. Much of the Earth's crust is made up of silicon and oxygen. (Note that sand consists of silicon and oxygen). The human body also consists of various elements, but the composition is very different from that of the Earth's crust. Human body consists mainly of carbon, oxygen, nitrogen and hydrogen. It has a lot of water. In the table below, we compare the compositions of the Earth's crust and of the human body.

Elements in Earth's crust and human body

Element	**% by weight of**	
	Earth's crust	**Human body**
Hydrogen (H)	0.14	9.5
Carbon (C)	0.03	18.5
Oxygen (O)	46.6	65.0
Nitrogen (N)	very little	3.3
Sulfur (S)	0.03	0.3

cont'd…

cont'd…

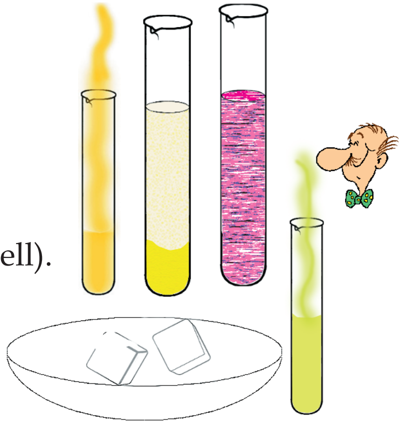
Sodium (Na)	2.8	0.2
Calcium (Ca)	3.6	1.5
Magnesium (Mg)	2.1	0.1
Silicon (Si)	27.7	very little
Aluminium (Al)	6.5	very little
Iron (Fe)	5.0	very little
Manganese (Mn)	0.1	very little

Above all, life processes depend on various molecules. Proteins and DNA are two of the important molecules of life. Our body is one big chemical factory.

1.3 Let us observe chemical changes

Chemistry is an experimental science. The best way to study chemistry is to make observations of chemical changes. How can we know that a chemical reaction has occurred?

- A gas comes out.
- A solid gets precipitated.
- The colour changes.
- A substance disappears.
- There is a new odour (smell).

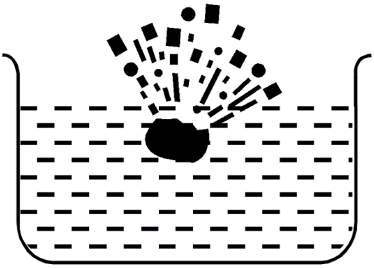


Observe what happens when you:

1. Throw a tiny piece of sodium into a bucket of water.
2. Take a piece of sulfur in a test tube, and heat it in a flame.
3. Take a piece of copper, and put it in a test tube containing nitric acid.
4. Take a little water in a test tube, and add a few drops of concentrated sulfuric acid to it.
5. Take a piece of zinc metal in a test tube, and add dilute hydrochloric acid.
6. Take a strip of magnesium and stick it through the stopper of a flask containing water. Heat the flask.
7. Add an aqueous solution of common salt (NaCl) or hydrochloric acid to a solution of silver nitrate.
8. Add a small quantity of zinc powder to a solution of copper sulfate.

Let us examine each of the above reactions.

1. When a piece of sodium is thrown into water, we hear a fizzing sound. Sodium reacts vigorously with water.



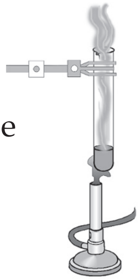
$$2Na + 2H_2O \longrightarrow 2NaOH + H_2(gas)$$

sodium + water ⟶ sodium hydroxide + hydrogen

2. When sulfur is heated in a test tube, the yellow solid changes into a pale orange liquid. On further heating, the colour of the liquid turns black and becomes more viscous, giving off pungent fumes of sulfur dioxide.

$$S + O_2 \longrightarrow SO_2\ (gas)$$

sulfur + oxygen ⟶ sulfur dioxide



3. Copper reacts with nitric acid to form nitrogen oxide. We see brown fumes of nitrogen dioxide.

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

copper + nitric acid ⟶ copper nitrate + water + nitrogen dioxide

4. The test tube becomes warm due to the heat generated in the reaction between water and sulfuric acid. The acid often spurts out because of the formation of steam. (The reaction can be violent.)

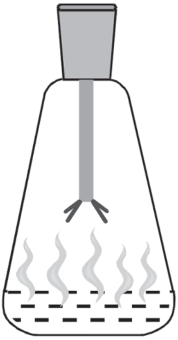
$$H_2SO_4 + H_2O \longrightarrow H_2SO_4.H_2O$$

5. Zinc dissolves in hydrochloric acid and liberates hydrogen gas. We see bubbles of hydrogen.

$$\mathrm{Zn} + 2\,\mathrm{HCl} \longrightarrow \mathrm{ZnCl_2} + \mathrm{H_2}\ \text{(gas)}$$

zinc + hydrochloric acid ⟶ zinc chloride + hydrogen

6. Magnesium reacts with steam liberating hydrogen and forming magnesium oxide. We see intense light emitted in the reaction.



$$\mathrm{Mg} + \mathrm{H_2O} \longrightarrow \mathrm{MgO} + \mathrm{H_2}$$

magnesium + steam ⟶ magnesium oxide + hydrogen

7. Addition of sodium chloride (NaCl) or hydrochloric acid (HCl) to the silver nitrate ($AgNO_3$) solution gives a white precipitate of silver chloride (AgCl).

$$\mathrm{AgNO_3} + \mathrm{NaCl} \longrightarrow \mathrm{NaNO_3} + \mathrm{AgCl}$$

$$\mathrm{AgNO_3} + \mathrm{HCl} \longrightarrow \mathrm{HNO_3} + \mathrm{AgCl}\ \text{(precipitate)}$$

8. When a powder of zinc metal is added to a solution of a copper salt, copper metal is formed. Zinc displaces copper from solution.

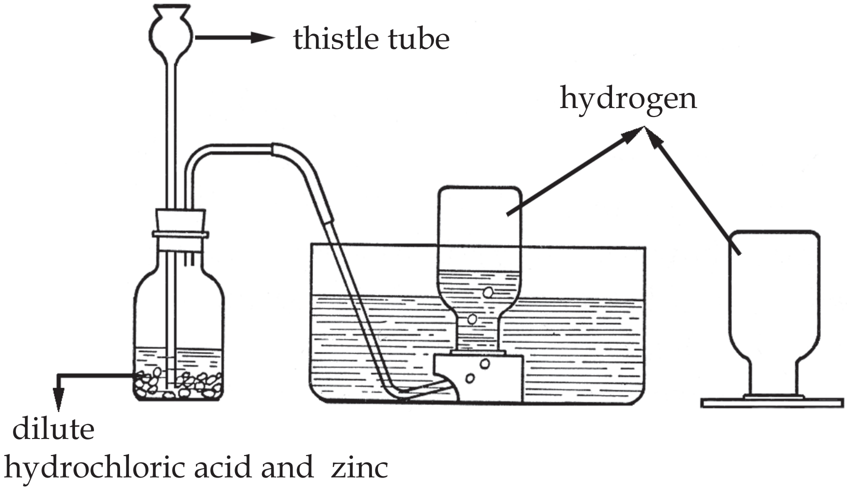
$$CuSO_4 + Zn \longrightarrow ZnSO_4 + Cu$$

$$\text{copper sulfate} + \text{zinc metal} \longrightarrow \text{zinc sulfate} + \text{copper metal}$$

1.4 Let us prepare a few elemental gases

Preparation of Hydrogen: Hydrogen is prepared by the displacement of hydrogen from dilute hydrochloric acid by metals such as zinc and magnesium. The reaction is given by:

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$$



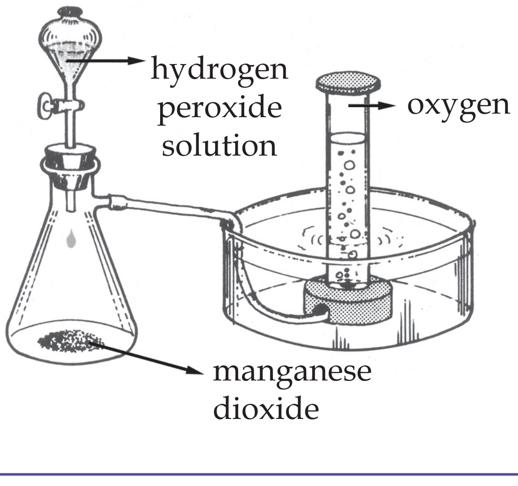
The reaction takes place at room temperature. The liberated hydrogen is collected over water.

Write the equation for the reaction of Mg (magnesium) with dilute HCl (Hydrochloric acid).

Preparation of Oxygen: Oxygen can be prepared by the decomposition of hydrogen peroxide (H_2O_2) in the presence of manganese dioxide (MnO_2). The reaction is written as follows:

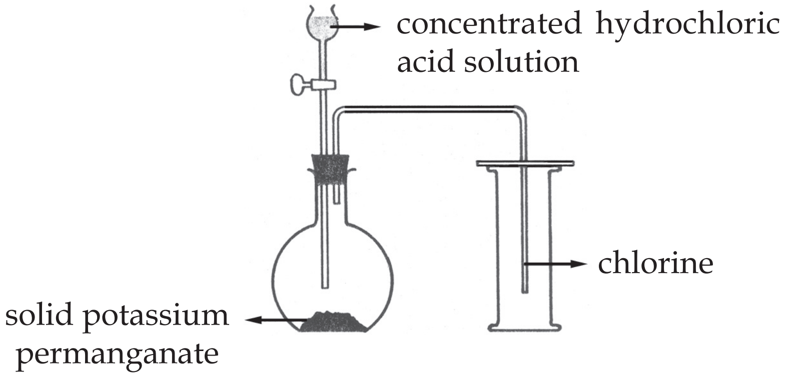
$$\underset{\text{hydrogen peroxide}}{2H_2O_2} \xrightarrow[\text{catalyst}]{MnO_2} \underset{\text{water}}{2H_2O} + \underset{\text{oxygen}}{O_2\ (\text{gas})}$$

The reaction takes place at room temperature.



What is a catalyst? We will learn about it later. We will just state here that a catalyst is a substance that makes a reaction go smoothly and faster.

Preparation of Chlorine: Chlorine is prepared by the oxidation of chloride ions by potassium permanganate ($KMnO_4$) in acidic solution. A hydrochloric acid solution is added dropwise over solid $KMnO_4$. Hydrochloric acid provides the acidic medium required for the reaction to take place. This reaction occurs at room temperature and is written as:



$$2KMnO_4 + 16HCl \longrightarrow 5Cl_2 + 2MnCl_2 + 2KCl + 8H_2O$$

1.5 Atomic and molecular nature of substances

What is an atom?

> Atoms are eternal, indestructible and cannot exist in the free state.
>
> — *Kanaada, an Indian saint*

The Indian concept of the atom bears a close resemblance to the Greek concept of the atom. Unfortunately, the Indian concept was not known outside India and the Indian contributions do not therefore get mentioned sufficiently.

> An atom is that which cannot be cut up further.
>
> — *Democritus* (560 – 470 B.C.)

The modern idea of the atom originated with Dalton (1803).

- All the atoms of an element are alike.
- Atoms of different elements differ.
- The mass of an atom of an element is fixed.
- Atoms can neither be created nor destroyed.

The first three statements are still valid. The last statement, however, is no longer correct. (Do you know why?)

It is only since 1911 that we know that atoms contain negatively charged **electrons** and positively charged **nuclei**. We shall examine the structure of atoms in some detail in Lessons 2 and 3. Electrons are responsible for most of chemistry.

Molecules: Molecules are made of atoms.

A molecule of hydrogen, H_2, contains two atoms of hydrogen.
A molecule of oxygen, O_2, contains two atoms of oxygen.
A molecule of ozone, O_3, contains three atoms of oxygen.
A molecule of HCl contains one atom of hydrogen and one atom of chlorine.
A molecule of methane, CH_4, has one atom of carbon and four atoms of hydrogen.

JOHN DALTON (1766 – 1844)

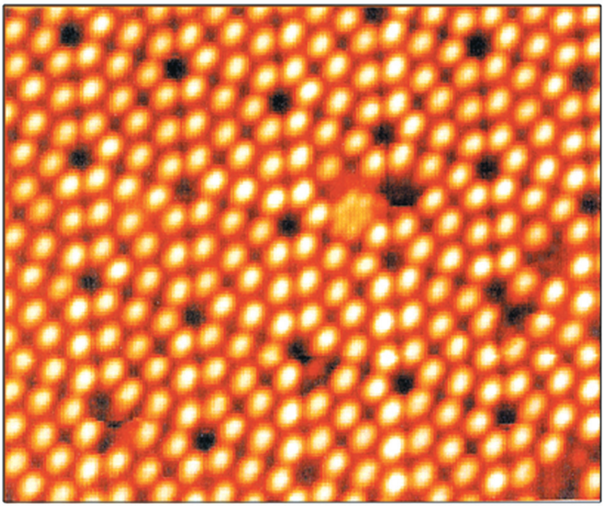
John Dalton was born in the family of a poor weaver in England. He began his career as a teacher at a village school when he was twelve years old. Seven years later, he became a school principal. In 1793, he left for Manchester, to teach mathematics, physics and chemistry in a college. He soon resigned from this post since teaching duties interfered with his scientific work. Dalton never got married and lived a simple life.

Dalton propounded the atomic theory in 1803. He suggested that compounds were formed by the combination of atoms of different elements in small, whole number ratios. He had no way to determine the ratios in which the different atoms combine. When only one compound between two elements A and B was known, he assumed that it had the simplest possible formula, AB. He deduced relative atomic masses, on the basis of such assumptions. He published a table of relative atomic masses. Since his assumptions were not always correct, there were errors in his table. These errors were corrected in 1858. Yet, the credit for first putting the atomic theory on a quantitative basis goes to Dalton.

From his early years to his death, Dalton carefully recorded each day, the temperature, pressure, amount of rainfall and so on. Dalton suffered from protanopia, an inability to see red at all. This sight defect became known as “daltonism”.

Are atoms for real?

Atoms were originally proposed as an idea. Although their presence was proved by various means, people did not think that they could see them directly. This was so until recently. We are now able to directly see atoms by employing powerful microscopic techniques. Typical of these techniques are electron microscopy and scanning tunneling microscopy (STM). Given below is an image of the atoms in a crystal of silicon obtained by STM.



Silicon

What is a compound?

A compound is made of two or more elements. A compound can be transformed to simpler substances. Remember that an element cannot be transformed to simpler substances. Compounds generally consist of molecular units.

Let us consider the case of water (H_2O). It has two hydrogen atoms and one oxygen atom. When we take water in a vessel, it contains a large number of molecules of water. Each molecule of water has the formula H_2O.

Atomic Mass: Atomic mass is also called atomic weight. The atomic mass (weight) of the carbon isotope 12 (^{12}C) is taken as the reference for defining atomic masses of elements.

$$\begin{array}{c}\text{Atomic mass}\\ \text{(Atomic weight)}\end{array} = \frac{\text{Mass (weight) of one atom of the element}}{{}^{1}\!/_{12}\ \text{of the mass (weight) of one atom of}\ {}^{12}\text{C}}$$

Note! The same elements can have different atomic masses. These are called **isotopes**. Naturally-occurring carbon has different isotopes and its average atomic mass is 12.011. The species having atomic mass 12 is one of the isotopes. The unit of atomic mass of an element is $g\ mol^{-1}$ or $amu\ atom^{-1}$ where amu is the atomic mass unit ($^1/_{12}$ of the mass of a single ^{12}C atom). The other isotopes of carbon are of mass 13 and 14.

Mole: The mole is the amount of a substance containing the same number of chemical units as there are atoms in exactly 12 grams of ^{12}C. Chemical units may be atoms or molecules. The same number is the **Avogadro number**, which has a value $6.02214 \text{ X } 10^{23}$ units mol^{-1}. One atomic weight (mass) of copper, therefore, contains $\sim 6.022 \times 10^{23}$ atoms.

The molecular weight (mass) of a compound is obtained by adding the atomic weights (masses) of all the constituent atoms. For example, molecular weight of $H_2 = 2 \times 1.008 = 2.016$. Molecular weight of $H_2O = 2 \times 1.008 + 15.999 = 18$.

Atomic masses of some elements

Element	Symbol	Atomic mass
Hydrogen	H	1.00794
Helium	He	4.002602
Lithium	Li	6.941
Boron	B	10.811
Carbon	C	12.011
Nitrogen	N	14.00674
Oxygen	O	15.9994
Fluorine	F	18.99840
Sodium	Na	22.989768
Chlorine	Cl	35.4527

How many molecules are there in one spoon of water? Or, for that matter, in the Indian Ocean? If we are to answer this question, we must be able to quantify the number of molecules in some way.

In terms of moles, $H_2 + \frac{1}{2} O_2 \longrightarrow H_2O$, means one mole of H_2 and half a mole of O_2 combine to give one mole of H_2O. $2H_2 + O_2 \longrightarrow 2H_2O$, means 2 moles of H_2 and 1 mole of O_2 give 2 moles of H_2O.

Gram molecular weight of a substance: It is the quantity of a compound that has the weight in grams numerically equal to its molecular weight. For example, the gram molecular weight of water (H_2O) is 18. There is an Avogadro number of molecules in one gram molecular weight of water.

The Avogadro number is such a large number that the number of molecules in a spoon of water will be comparable to the number of molecules of water in the Indian Ocean! Think about this.

Concentration: The concentration of a substance in solution is generally given by the number of moles of the substance in a litre (1000 ml) of solution. The unit is called **molarity** (M).

1 mole (gram mol. wt) of NaCl is = 22.99 + 35.45 = 58.44 g

One molar (1M) solution of NaCl in water contains 58.44 g of NaCl in one litre of the solution. A 0.1M NaCl solution contains 5.844 g of NaCl in one litre of the solution.

1.6 Laws of chemical combination

Law of conservation of mass: This law states that matter can neither be created nor destroyed.

In a chemical reaction, the total mass of the reactants is equal to the sum of the masses of the products.

In a chemical reaction, $A + B \longrightarrow C + D$,

Mass of A + Mass of B = Mass of C + Mass of D

For example,

$$\begin{array}{ccccc} C & + & O_2 & \longrightarrow & CO_2 \\ (12.011) & + & (2 \times 15.999) & & [12.011 + (2 \times 15.999)] \end{array}$$

$$\begin{array}{ccccc} H_2 & + & \frac{1}{2} O_2 & \longrightarrow & H_2O \\ (2 \times 1.00794) & + & \frac{1}{2}(2 \times 15.999) & & [(2 \times 1.00794) + 15.999] \end{array}$$

Law of definite proportions: This law states that the proportion in which two or more elements combine in forming a particular compound is always identical.

$$\begin{array}{ccccc} \text{Zinc} & + & \text{Sulfur} & \longrightarrow & \text{Zinc sulfide} \\ Zn & + & S & \longrightarrow & ZnS \end{array}$$

This proportion will remain the same no matter how zinc sulfide is formed.

Law of multiple proportions: This law states that when two elements combine to form more than one compound, the different masses of one of the elements which combine separately with a fixed mass of the other element, bear a simple ratio. Example: Carbon and oxygen combine to form carbon monoxide (CO) and carbon dioxide (CO_2). Here the mass of carbon is fixed while the mass of oxygen varies in the two compounds. The ratio of oxygen combining with a fixed mass of carbon is 1:2.

Idea of valence: Valence is defined as the combining capacity of an atom in forming compounds. To understand valence, we shall examine three sets of compounds.

1	2	3
HCl	NaCl	$FeCl_2$
HBr	NaBr	FeO
H_2O	Na_2O	$FeCl_3$
H_2S	Na_2S	Fe_2O_3

Let us look at the compounds in column 1 containing hydrogen.

HCl	One atom of hydrogen combines with one atom of chlorine in HCl.
HBr	One atom of hydrogen combines with one atom of bromine in HBr.
H_2O	Two atoms of hydrogen combine with one atom of oxygen in water, H_2O, or,
H_2S	with one atom of sulfur in H_2S.

If we take the valence of hydrogen as one, then, chlorine (Cl) and bromine (Br) will have valence of one, and oxygen will have valence of two. We take the valence of hydrogen (H) or oxygen (O) as the reference.

What is the valence of sulfur? Two.

We now look at column 2 with compounds of sodium (Na). One atom of sodium, combines with one atom of chlorine in sodium chloride (NaCl) or with one atom of bromine in NaBr. Since the valence of Cl or Br is one, the valence of Na (sodium) is one.

Na_2O That is why two atoms of sodium combine with one atom of oxygen in sodium oxide (Na_2O).

Na_2S Remember, sulfur has a valence of two.

> Since Na has valence of one, all other elements of the same kind (that is, the alkali elements, K, Rb, Cs) also have a valence of one.

Let us now look at the iron compounds in column 3.

$FeCl_2$ One atom of iron (Fe) combines with two atoms of chlorine in $FeCl_2$. Therefore, Fe has a valence of two (since valence of chlorine is one).

FeO One atom of Fe combines with one atom of oxygen in FeO. Therefore, here the valence of Fe is two just as in $FeCl_2$ (Again, remember oxygen has valence of two).

$FeCl_3$	One atom of iron combines with three atoms of chlorine in $FeCl_3$. Therefore, here Fe has a valence of three.
Fe_2O_3	Two atoms of Fe combine with three atoms of oxygen in Fe_2O_3. Here also, Fe has a valence of three.

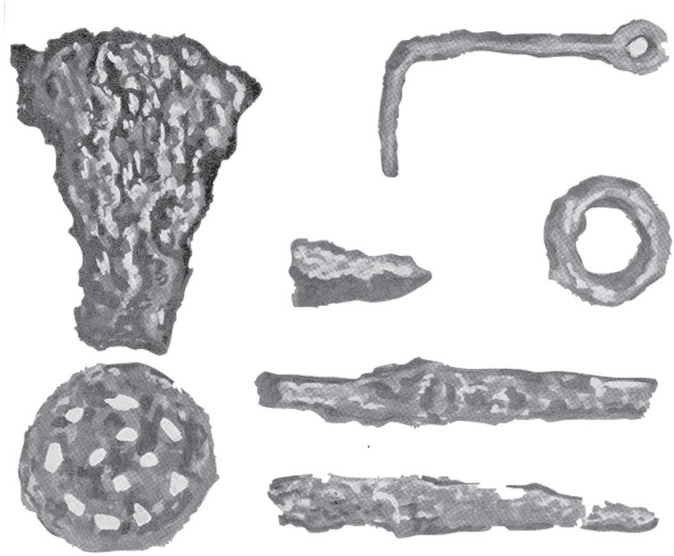
Calculate the valence of manganese (Mn) in the compounds listed below.

Compound	Answer
MnO	2
Mn_2O_3	3
MnO_2	4
$KMnO_4$	7

You see that manganese can have several valences.

1.7 Man and Metals

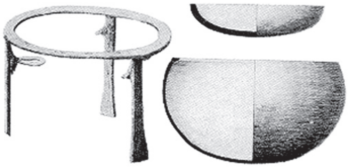
Man's search for metals goes back to prehistoric times. Metals have been used for several thousand years in India. Certain periods in history are associated with specific metals used extensively during that period.



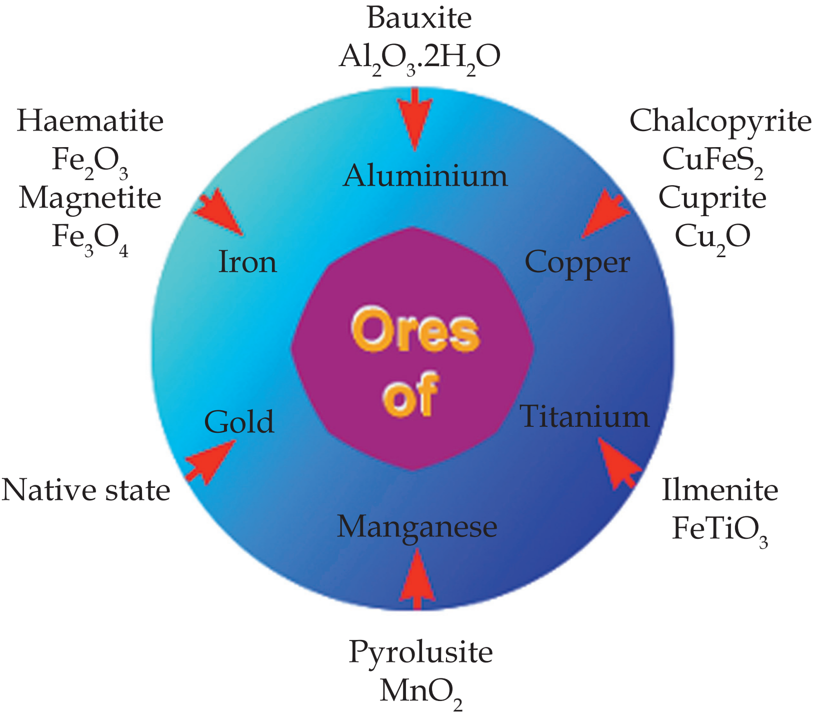
Copper Age: During this period, copper metal was extracted by smelting. This was a cottage industry!

Bronze Age: During this period, alloys of metals were used.

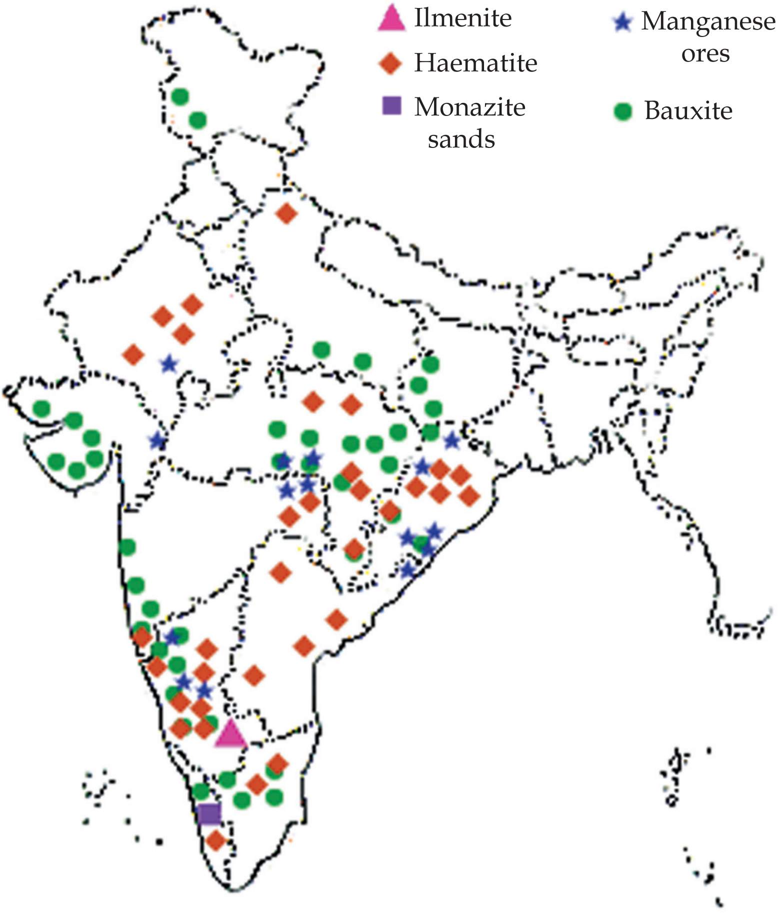
Iron Age: By this time, man had mastered the skill of extracting metals from iron ores.



Metals are generally found as ores of minerals in the Earth's crust.



India has large deposits of



Ilmenite is found in abundance in India. We can make titanium (Ti) metal from this mineral. Titanium is an important metal in modern industry. It is light but strong.

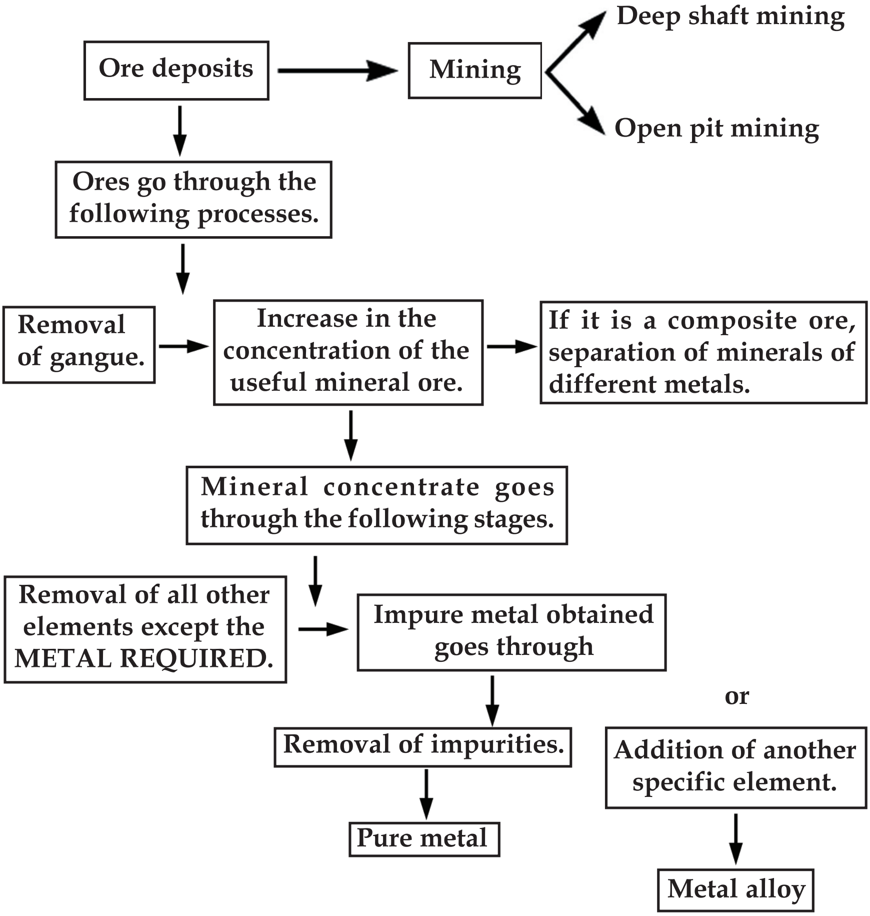
Monazite sands in Kerala contain large quantities of rare earth elements. India has large deposits of manganese (Mn) ore as well.

Properties of metals:

Metals:
- conduct electricity and heat.
- are malleable.
- are ductile.
- have lustre.

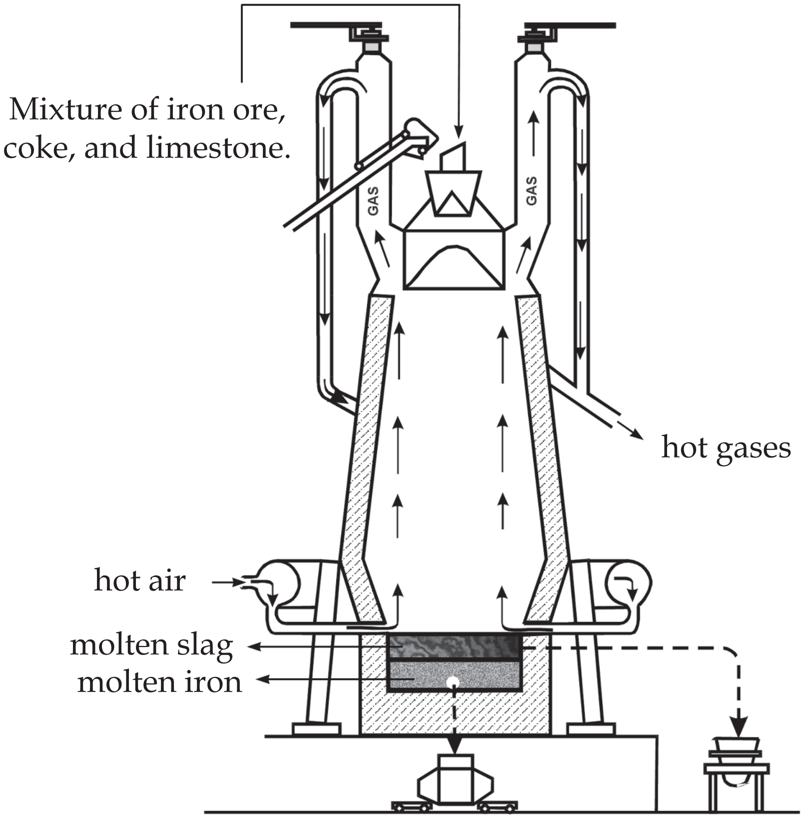
How do we get metals out of ores and minerals?

Various processes are employed to obtain metals from ores as shown in the chart below.



Iron

Iron is the workhorse of man. It is obtained by the reduction of iron oxide. The reduction is carried out in a blast furnace.



The reduction takes place in stages.

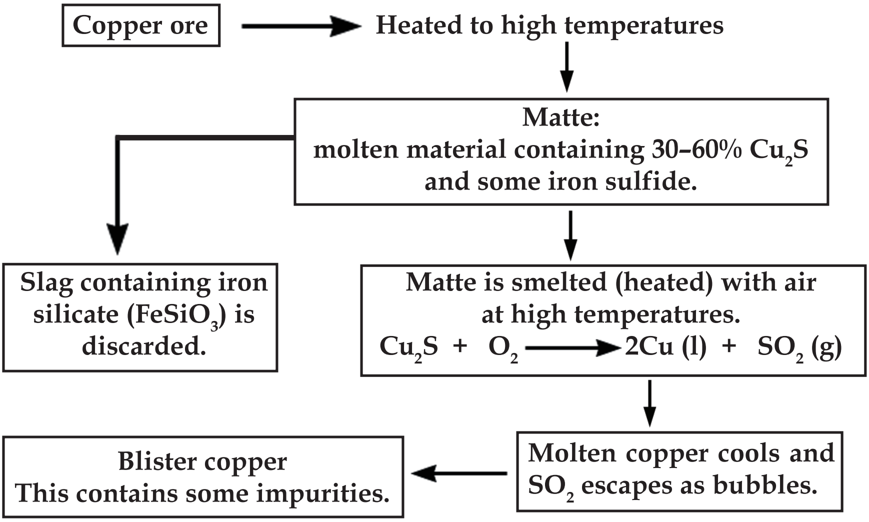
$$3Fe_2O_3\,(s) + CO\,(g) \longrightarrow 2\,Fe_3O_4\,(s) + CO_2\,(g)$$

$$Fe_3O_4\,(s) + CO\,(g) \longrightarrow 3\,FeO\,(s) + CO_2\,(g)$$

$$FeO\,(s) + CO\,(g) \longrightarrow \underset{\text{molten}}{Fe\,(l)} + CO_2\,(g)$$

s — solid, g — gas, l — liquid

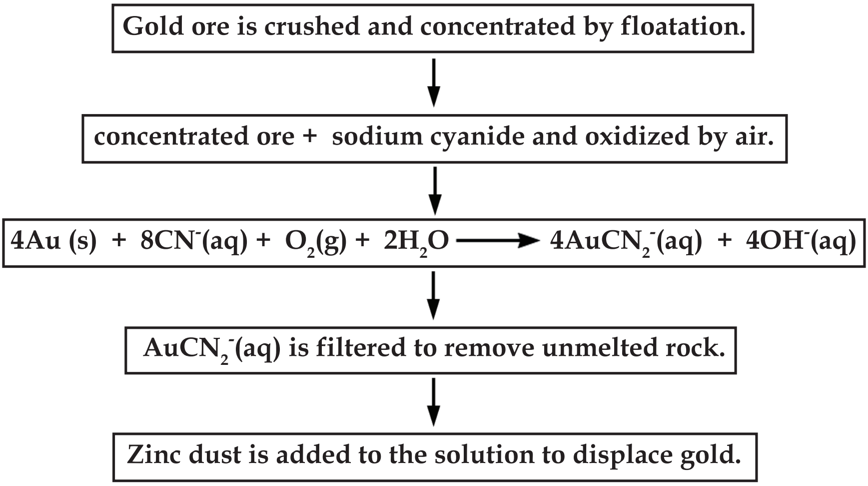
Copper



Blister copper is purified by electrolysis

What is electrolysis? We will learn later in this lesson.

Gold



What is corrosion? You will have noticed that things made of iron rust. The reddish brown rust is nothing but an oxide of iron. Corrosion is the oxidation of metals by substances in the surroundings, or by the constituents of the atmosphere. Both water and oxygen play a role in corrosion. The composition of rust may be represented as FeOOH. Certain chemicals are used to inhibit corrosion. Some of the alloys of iron (e.g., stainless steel) do not corrode easily.

Copper vessels become black or greenish due to corrosion. Why do people wear gold jewellery? Gold does not get corroded. It is a **noble metal**. Other noble metals are platinum and silver, but silver gets slightly corroded.

The Rustless Iron Pillar of Delhi

The famous iron pillar in Delhi, erected in the Gupta period (over 1500 years ago), is a marvel. After all these years, this pillar stands erect without deterioration. This rustless iron pillar is a tribute to the great ingenuity of our forefathers. The approximate chemical composition of this pillar is as follows:

Carbon	0.25% (by weight)
Silicon	0.04%
Phosphorus	0.17%
Sulfur	0.002%

The rest is all iron. The specific gravity is 7.6.

1.8 Classification of substances

We can classify substances based on their properties. Metallic materials form an important class of substances. They have unique properties that we have read earlier. There are about 100 elements in nature and a majority of them are metals.

Other than metallic substances, there are two other types of substances which can be easily recognized. These are salt-like substances (or ionic substances) and covalent substances.

Ionic substances: Ionic substances consist of positively charged metal ions and negatively charged nonmetal ions.

The positive ions are called **cations** and the negative ions are called **anions**.

Ionic substances:

- are soluble in water.
- have high melting points.
- conduct electricity either in solution or in molten state (i.e., they form **electrolytes**).

Let us look at some examples of salts (ionic substances).

Sodium chloride	Na^+Cl^-
Potassium chloride	K^+Cl^-
Zinc chloride	$Zn^{2+}(Cl^-)_2$
Magnesium bromide	$Mg^{2+}(Br^-)_2$
Copper sulfate	$Cu^{2+}(SO_4)^{2-}$
Iron oxide	$Fe^{2+}O^{2-}$
Iron oxide	$(Fe^{3+})_2\,(O^{2-})_3$
Manganese oxide	$Mn^{4+}\,(O^{2-})_2$
Copper sulfide	$Cu^{2+}S^{2-}$

Simple ions

Positive ions (cations)	
Sodium	Na^+
Potassium	K^+
Calcium	Ca^{2+}
Magnesium	Mg^{2+}
Ferrous	Fe^{2+}
Ferric	Fe^{3+}
Zinc	Zn^{2+}

Negative ions (anions)	
Fluoride	F^-
Chloride	Cl^-
Bromide	Br^-
Iodide	I^-
Oxide	O^{2-}
Sulfide	S^{2-}

Some polyatomic ions

Hydroxide	OH^-
Cyanide	CN^-
Nitrate	NO_3^-
Carbonate	$(CO_3)^{2-}$ or CO_3^{2-}
Sulfate	$(SO_4)^{2-}$ or SO_4^{2-}

An ionic substance, when dissolved in water or some other solvent, gives an electrolyte solution. In solution state, an ionic substance does not always break up into free ions. This process, called **dissociation**, is complete in the case of substances such as NaCl and KCl. They are called strong electrolytes. Some substances dissociate partly and they are called weak electrolytes. A strong acid like HCl dissociates more (giving H^+ and Cl^- in aqueous solution) than a weak acid like vinegar (acetic acid). There will be a smaller proportion of H^+ in an acetic acid solution.

Acids and Alkalis: There are some substances which turn blue litmus to red. They are the acids.

Examples:

Hydrochloric acid	HCl
Nitric acid	HNO_3
Sulfuric acid	H_2SO_4

Alkalis have a hydroxyl or a OH group. They turn red litmus to blue.

Examples:

Sodium Hydroxide	$NaOH$
Potassium Hydroxide	KOH
Calcium Hydroxide	$Ca(OH)_2$

When an alkali is added to an acid, we get salt and water.

$$\underset{\text{acid}}{HCl} + \underset{\text{alkali}}{NaOH} \longrightarrow \underset{\text{salt}}{NaCl} + \underset{\text{water}}{H_2O}$$

$$HBr + KOH \longrightarrow KBr + H_2O$$

Certain substances change colour when a solution is alkaline. For example, phenolphthalein becomes pink in alkali solution. Such substances are called indicators.

When we add a solution of an alkali (NaOH) to a solution of an acid (HCl) containing phenolphthalein, the solution becomes pink as soon as the acid is neutralized.

Acids undergo dissociation in water giving H^+ or more correctly H_3O^+ ions. This can be written as:

$$HA + H_2O \longrightarrow H_3O^+ + A^-$$

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

$$H_2CO_3 + H_2O \longrightarrow H_3O^+ + HCO_3^-$$

Acids which dissociate greatly are strong acids (e.g., HCl, HNO_3, H_2SO_4). Water itself dissociates giving H_3O^+ and OH^- ions. A measure of the acidity of a solution is **pH**.

$$pH = -\log [H^+] \quad \text{or} \quad -\log [H_3O^+]$$

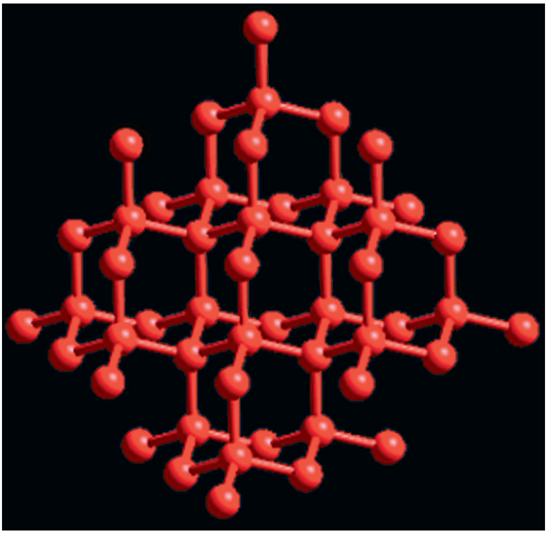
Here $[H^+]$ or $[H_3O^+]$ is the concentration of the ionized species. In ordinary water, $[H_3O^+] = 10^{-7}$ M. Therefore pH = 7. Neutral water has a pH of 7. If the pH of a solution is less than 7, it is acidic. If it is greater than 7, it is alkaline.

Covalent substances:
- do not conduct electricity.
- have low melting and boiling points.

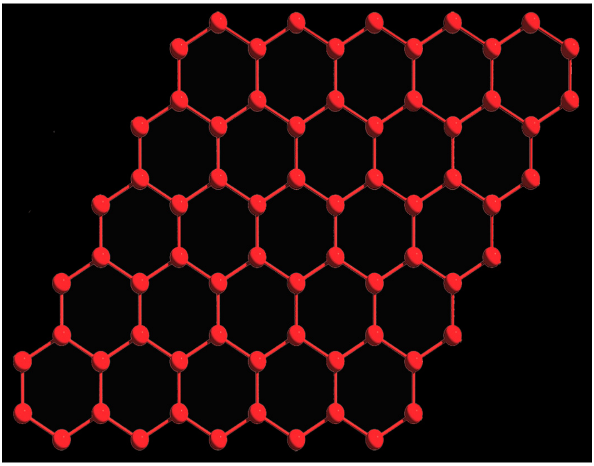
The simplest examples of covalent compounds are carbon compounds. We shall discuss them in the next section. Covalent solids are generally soft. Typical examples of covalent substances are paraffin wax and camphor.

Covalent networks: Well-known examples of covalent networks are diamond and graphite. Both diamond and graphite are formed by networks of carbon atoms.

Diamond is the hardest substance known. It is also the best conductor of heat. Diamond can be made in the laboratory starting from graphite, at high temperatures and pressures, using catalysts. Laboratory diamonds are used in machine tools, but cannot be used for jewellery. Diamond films are made by the decomposition of hydrocarbons (e.g., CH_4).

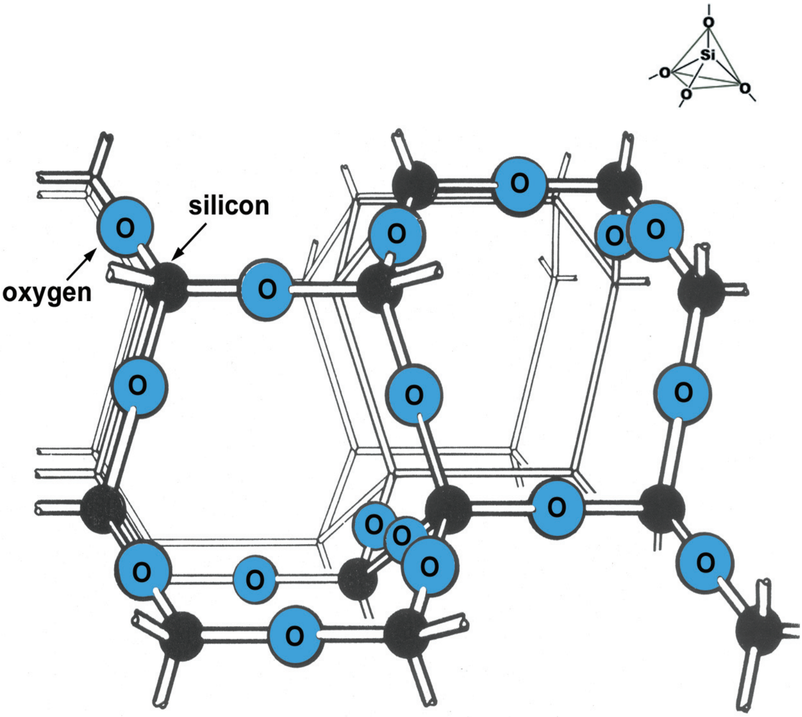


In diamond, the network consists of a carbon atom bound to four other carbon atoms. The four bonds are connected to the corners of a tetrahedron.



Graphite conducts electricity and consists of a two-dimensional network where each carbon atom is bound to three other carbon atoms.

Silicon and **germanium** have the same structure as diamond. Boron nitride (BN) has a structure similar to graphite. It can be made in the diamond structure as well.

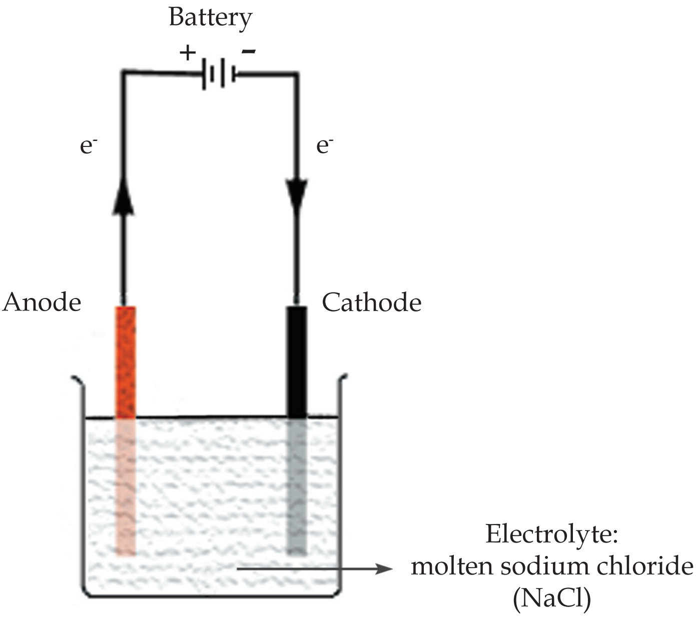


Another example of a covalent network is **silica**, SiO_2 (silicon dioxide). It contains Si—O—Si linkages. Sand consists of pure silica.

Glass is made of silicates (e.g., sodium silicate). It also contains networks formed by Si—O—Si linkages.

1.9 Electrolysis

Electrolysis is a chemical reaction brought about by passing electricity through a substance. During electrolysis, electrical energy is converted to chemical energy. The electrodes can be of an inert material like graphite. Electrons flow from the **anode** to the **cathode**. Positively charged ions (cations) move to the cathode and negatively charged ions (anions) move to the anode. If we have molten NaCl in the vessel, the following changes occur:



At the cathode, reduction occurs : $Na^+ + e^- \longrightarrow Na$

At the anode, oxidation occurs : $Cl^- \longrightarrow \frac{1}{2} Cl_2 + e^-$

If two graphite electrodes are immersed in a beaker of pure water and the electrodes connected to a source of electricity like a battery, nothing happens. This is because water does not conduct electricity. If a few drops of acid are added to the water, we soon notice hydrogen produced at the cathode and oxygen at the anode. The reactions are:

Cathode : $2H^+ (aq) + 2e^- \longrightarrow H_2 (g)$ Reduction

Anode: $2OH^- (aq) \longrightarrow H_2O (l) + \frac{1}{2} O_2 (g)$ Oxidation

Here, (aq) stands for aqueous (in water solution).

Michael Faraday gave the laws of electrolysis in 1833. These laws relate the extent of chemical change occurring in electrolysis to (a) the current, and to
(b) the time of passage of electricity.

The quantity of electricity is expressed in terms of the **Faraday**. The Faraday is the charge of one mole of electrons and has the value 96,500 coulombs mol^{-1}. One Faraday produces one mole of silver from a solution containing silver salt (Ag^+ ions). Two moles of silver are produced by 2 Faradays. Two Faradays are required to produce a mole of lead (Pb) from a solution of a lead salt (containing Pb^{2+}). Why?

$$Ag^+ + e^- \longrightarrow Ag$$

$$Pb^{2+} + 2e^- \longrightarrow Pb$$

Similarly,

$$2Br^- \longrightarrow Br_2 + 2e^-$$

Two Faradays are required to produce a mole of bromine.

Electrolysis is employed to make various compounds. It is also used for electroplating and to extract metals from compounds.

Electroplating: Electroplating is employed to coat one material with another. Shining metal coatings are obtained by this means (for example, gold plating of silver articles and anodizing aluminium articles). The metal or the metallic object that is to be plated is made the **cathode**. The plating metal is taken as the **anode.** The electrolyte contains ions of the plating metal. The cathode and the anode are immersed in the electrolyte, and electric current is passed through the electrolyte. The metal from the anode, gets deposited on the cathode.

If one wants to plate a metal article (say of silver) with gold, the anode is made of pure gold. The (silver) article to be electroplated is made the cathode. The electrolyte solution will have a salt of gold. The gold ions produced by oxidation at the anode, get reduced to form the metal at the cathode, and the article gets the shine of gold.

Electroplating involves many stages. For successful electroplating, the following conditions are necessary:

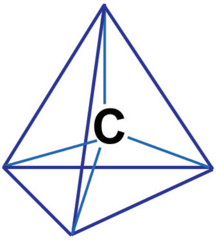
- correct concentration of the electrolyte.
- the right temperature.
- required electric current.
- a clean cathode.

Some of the important chemicals are produced by electrochemical processes. The most well-known example is the industrial production of **caustic soda** or sodium hydroxide (NaOH) and **chlorine** (Cl_2). The process involves the electrolysis of a solution of NaCl. At the anode, Cl^- ions get oxidized to chlorine gas, and at the cathode, Na^+ ions get reduced to sodium metal. Na + H_2O gives NaOH.

If chlorine is mixed with sodium hydroxide in a controlled manner one gets sodium hypochlorite (NaOCl) or sodium chlorate ($NaClO_3$). NaOCl is a bleaching powder. $NaClO_3$ is a weed killer.

1.10 Carbon compounds

Carbon has a valence of four. That is why carbon forms methane CH_4. It was shown by van't Hoff and Le Bel that the four valences of carbon are pointed towards the four corners of a tetrahedron. This is so in a molecule like CH_4 as well as in diamond (solid).



Let us look at several hydrocarbons that belong to the same family as methane. These are the saturated hydrocarbons and are called **paraffins**. They have the general formula C_nH_{2n+2}.

When n = 1, we have CH_4, methane.

n = 2,	C_2H_6,	ethane
n = 3,	C_3H_8,	propane
n = 4,	C_4H_{10},	butane
n = 5,	C_5H_{12},	pentane
n = 6,	C_6H_{14},	hexane
n = 7,	C_7H_{16},	heptane

We can obtain derivatives of methane by substituting other elements or groups in place of hydrogen.

The following are a few examples.

CH_3Cl	methyl chloride or chloromethane
CH_2Cl_2	methylene chloride or dichloromethane
$CHCl_3$	chloroform or trichloromethane
CCl_4	carbon tetrachloride
CH_3OH	methyl alcohol
CH_3NH_2	methyl amine
CH_3COOH	acetic acid

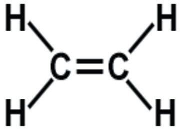
OH group is referred to as the hydroxyl and NH_2 as the amino group. Ketones and aldehydes have C=O groups. The COOH (carboxyl) group has both C=O and OH groups. COOH is present in acids like acetic acid, CH_3COOH. When H in COOH is replaced by a group such as CH_3 we get an ester. $CH_3COOC_2H_5$ is the ethyl ester of acetic acid. It is called ethyl acetate. CH_3COOCH_3 is methyl acetate.

Halogen atoms as well as OH, NH_2 and other groups can substitute hydrogen in other hydrocarbons as well. Thus,

C_2H_5Cl	ethyl chloride
C_2H_5Br	ethyl bromide
C_2H_5OH	ethyl alcohol
C_3H_7Cl	propyl chloride
C_3H_7OH	propyl alcohol
$C_7H_{15}OH$	heptyl alcohol
CH_3CHO	acetaldehyde
CH_3COCH_3	acetone

In carbon compounds, the valence of carbon (4) is satisfied in different ways. Let us look at two important examples, ethylene and acetylene.

Ethylene, C_2H_4



Ethylene is also referred to as ethene. The four valences of each carbon atom here are satisfied as follows. The double bond between two carbon atoms (each bond is counted for a valence) and the two single bonds (between each carbon atom and two hydrogen atoms) make up the total valence of four.
Let us list a few derivatives of C_2H_4.

C_2H_3Cl	chloroethylene or ethylene chloride
$C_2H_2Cl_2$	dichloroethylene or ethylene dichloride

Acetylene, C_2H_2

$$H{-}C{\equiv}C{-}H$$

Identify the number of bonds formed by each carbon atom. How is the valence of carbon satisfied here? It is still four.

Saturated hydrocarbons are also called **alkanes** (e.g., methane, ethane). Unsaturated hydrocarbons containing double bonds are called **alkenes** (e.g., ethylene or ethene). Another example of an alkene is propylene, $CH_3{-}CH{=}CH_2$. Hydrocarbons containing triple bonds are called **alkynes** (e.g., acetylene). Unsaturated compounds can be made saturated by adding hydrogen, halogens and other species.

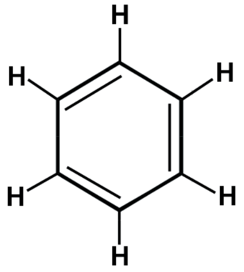
e.g., ethene (C_2H_4) + $H_2 \longrightarrow$ ethane (C_2H_6)

The presence of double bonds can be tested by adding bromine water to alkenes. The colour of bromine (brown) disappears. This is because bromine adds to the double bond.

Carbon compounds containing hydrogen and other elements are called ORGANIC compounds. Let us list a few of the familiar organic compounds.

Chloroform	$CHCl_3$
Alcohol	C_2H_5OH
Benzene	C_6H_6
Phenol	C_6H_5OH
Vinegar (Acetic acid)	CH_3COOH
Napthalene	$C_{10}H_8$
Camphor	$C_{10}H_{16}O$
Sugar (Sucrose)	$C_{12}H_{22}O_{11}$
Aspirin	$C_9H_8O_4$

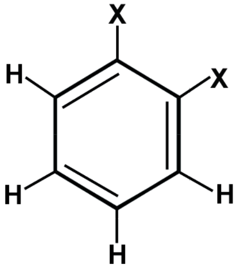
Benzene, C_6H_6, has the following structure.



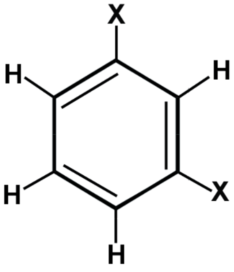
Derivatives of benzene are obtained by substituting the hydrogens:

$C_6H_5CH_3$	Toluene
C_6H_5Cl	Chlorobenzene
C_6H_5OH	Phenol
$C_6H_5NH_2$	Aniline
C_6H_5COOH	Benzoic acid

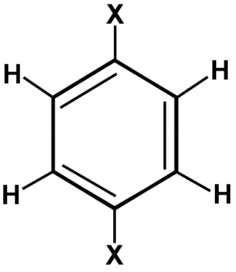
When two hydrogens of benzene are substituted by other groups, we have three possible choices as below:



ortho

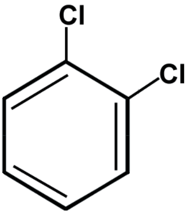


meta

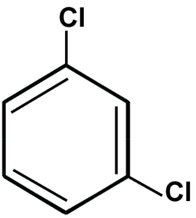


para

Let us write the structures of the three dichlorobenzenes:



ortho



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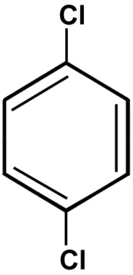
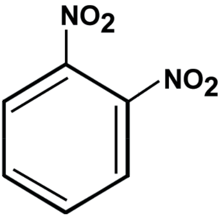
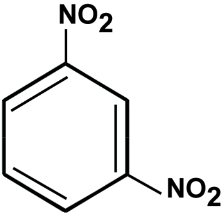
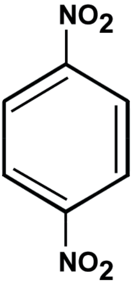


para

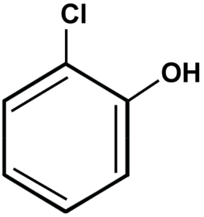
For simplicity, we have not shown the four hydrogens in the above structures. The dinitrobenzenes are:

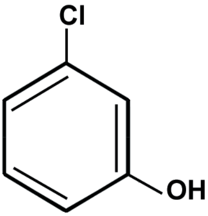


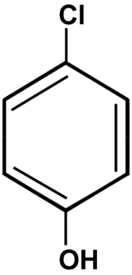




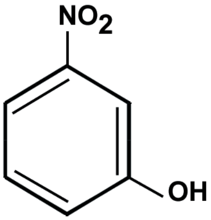
Let us substitute two of the hydrogens in benzene by two different groups Cl and OH to get the chlorophenols.



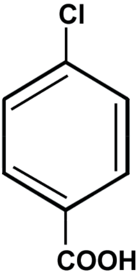




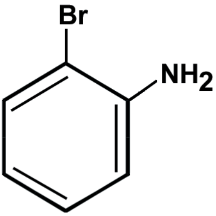
The following are a few other examples of disubstituted benzenes.



meta-nitrophenol

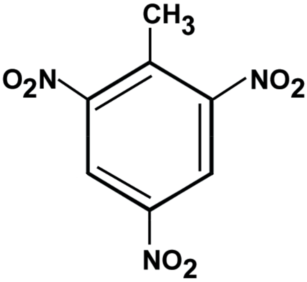


para-chlorobenzoic acid

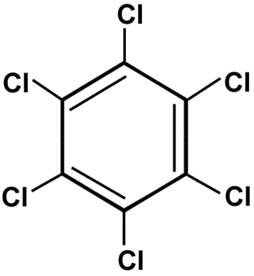


ortho-bromoaniline

We can have three, four, or all the six hydrogens in benzene substituted by different groups.



Trinitrotoluene (TNT)



Hexachlorobenzene

We often find more than one name for a compound or a new name which does not relate to the hydrocarbon from which it is derived. Let us look at the names of a few compounds.

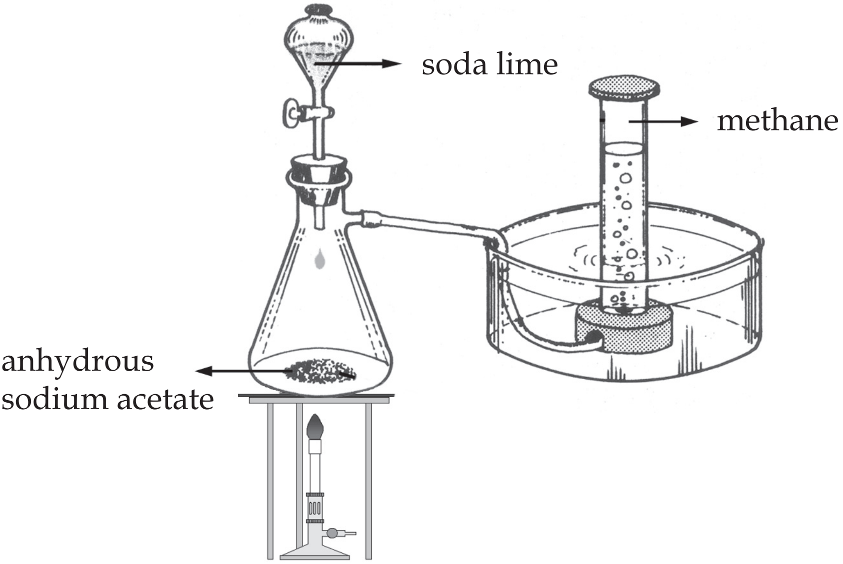
CH_3Cl	chloromethane or methylchloride
CH_2Cl_2	dichloroethane or methylene dichloride
CH_3OH	methyl alcohol or methanol
$CHCl_3$	chloroform
C_6H_5OH	phenol (not hydroxy benzene)
CH_3NH_2	methylamine (not aminomethane)
$C_6H_5NH_2$	aniline (not aminobenzene)
C_6H_5COOH	benzoic acid
CH_3COOH	acetic acid

Because of the innumerable compounds made by chemists, it is necessary to have standard names to be used by people all over the world. Standard names for compounds are given by the International Union of Pure and Applied Chemistry (IUPAC). IUPAC rules can be found in most of the chemistry textbooks.

Preparation of simple organic substances

Methane: Place a mixture (of equal quantities) of anhydrous sodium acetate and soda lime (mixture of sodium hydroxide and calcium hydroxide) in a flask. Heat the flask. Collect the gas by displacement of water. The equation for the reaction is shown as:

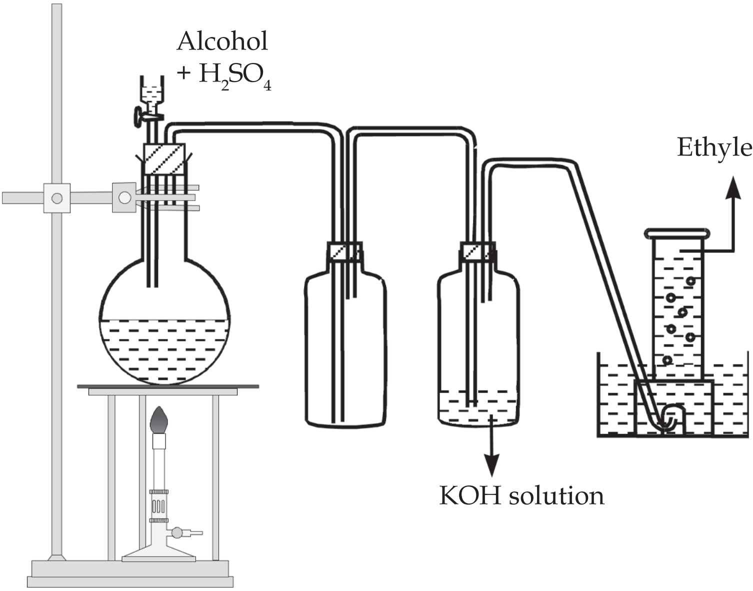
$$\underset{\text{sodium acetate}}{CH_3COONa} + \underset{\text{sodium hydroxide}}{NaOH} \longrightarrow \underset{\text{sodium carbonate}}{Na_2CO_3} + \underset{\text{methane}}{CH_4\ (\text{gas})}$$



Ethylene: Ethyl alcohol is mixed with concentrated sulfuric acid carefully and the mixture heated. The gas is then passed through a concentrated solution of potassium hydroxide to remove the sulfur dioxide and carbon dioxide present in it.

The equation for the above reaction is as follows:

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + \underset{\text{sulfuric acid}}{H_2SO_4} \longrightarrow H_2SO_4.H_2O + \underset{\text{ethylene}}{C_2H_4}$$



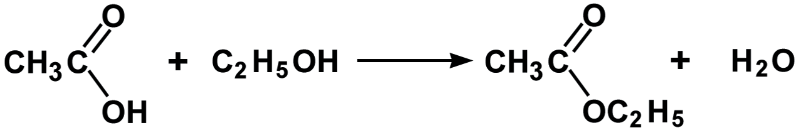
Benzene: Benzene is obtained from coal tar. Coal tar contains large quantities of benzene and other organic substances. Benzene is collected by the distillation of coal tar.

Ethyl alcohol: Ethyl alcohol (ethanol) is prepared by the action of an enzyme on sugar (sucrose). This process is referred to as fermentation. The reaction is given by:

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{(yeast)}]{\text{enzyme}} \underset{\text{ethanol}}{4C_2H_5OH\ (l)} + \underset{\text{carbon dioxide}}{4CO_2\ (g)}$$

Preparing an Ester

Let us carry out an organic chemical reaction. For this, we choose a reaction that gives an odour (not a bad one). We will, therefore, prepare an ester. Esters are obtained by the reaction of alcohols with carboxylic acids. We will prepare ethyl acetate by the reaction:

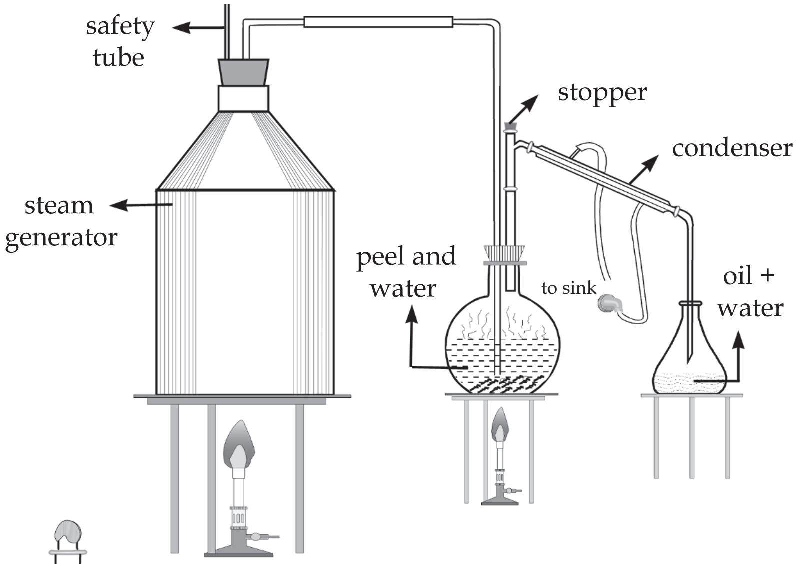


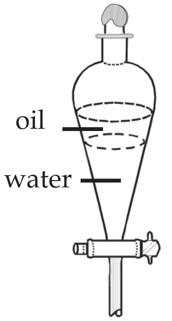
Acetic acid ethyl alcohol ethyl acetate

Take a few drops (2 ml) of glacial acetic acid in a test tube. Add to it, an equal volume of ethyl alcohol. Then, add 1 ml of concentrated sulfuric acid and place the test tube in boiling water. After 5 minutes, pour the contents of the test tube into about 10 ml of water. The ester (ethyl acetate) floats on water and gives its characteristic odour. (The unreacted acetic acid and alcohol dissolve in the water).

Extraction of essential oils from plant materials: We mentioned earlier that many natural products are obtained by extraction from leaves, flowers, bark and such materials of plant origin. To illustrate this, we shall prepare lemon oil or oil of orange by steam distillation.

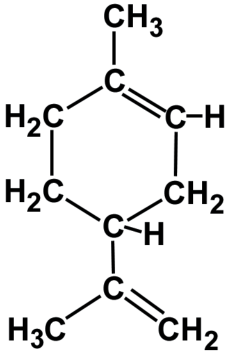
Collect some lemon or orange peel (from 5 or 6 fruits) and grind it into a pulp, using a food blender (or mortar and pestle). Add the peel pulp to the water in the flask (see figure). Pass steam through the mixture of peel pulp and water. The steam carries the essential oil which condenses and collects in the conical flask.



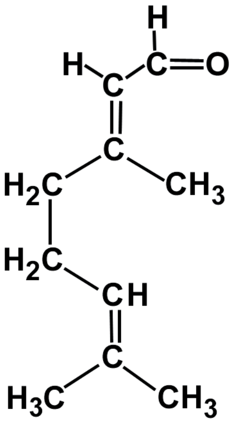


separating funnel

The distilled liquid contains both water and the oil. You can separate the oil from water by using a separating funnel (see figure). Note the fine odour of the oil. Limonene is the main constituent in the oil from lemons and oranges. Citral is the compound that gives lemon oil its distinctive flavour.



Limonene



Citral

1.11 States of substances

Substances can exist in three states — gas, liquid and solid. Water exists in all the three states : gas (steam or water vapour), liquid (ordinary water) and solid (ice). Properties of gases, liquids and solids are different. For example, a liquid takes the shape of the container and gases occupy the entire volume of the container. Atoms and molecules in the gaseous state move freely or randomly. Some of them move very fast (high kinetic energy) and some move slowly (small kinetic energy), but most molecules move with an average speed (average kinetic energy). In other words, atoms and molecules in gases have a distribution of speeds or kinetic energies. The atoms and molecules in the gaseous state keep colliding with one another.

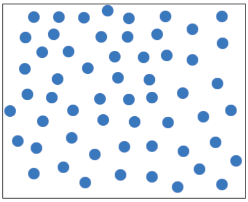
If we take ice in a glass of water, the ice remains floating for a considerable time, and eventually attains a constant temperature (0°C or 273 K). We then say that ice and water are in equilibrium and represent this as

$$\text{ice} \rightleftharpoons \text{water.}$$

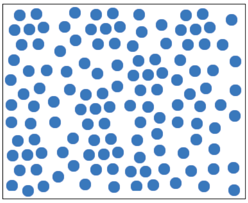
This is an example of solid–liquid equilibrium. We are familiar with the liquid–vapour equilibrium. Above liquid water, there is always a certain amount of vapour. With increase in temperature, the pressure of the vapour increases. Liquids with an odour are recognized by the smell because of the presence of some molecules in the vapour phase. We smell camphor because there is a solid–vapour equilibrium.

When gases are cooled, they become liquids which occupy a smaller volume. In the liquid state, a smaller number of atoms (or molecules) get together to form "groups" or "clusters". Yet, the liquid state is not rigid because the molecules can still move around.

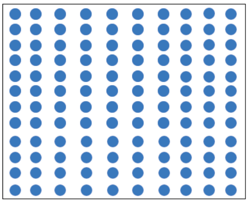
When liquids are cooled further, they become solids. In the solid state, the atoms (or molecules) are fixed in position and become rigid.



Gas



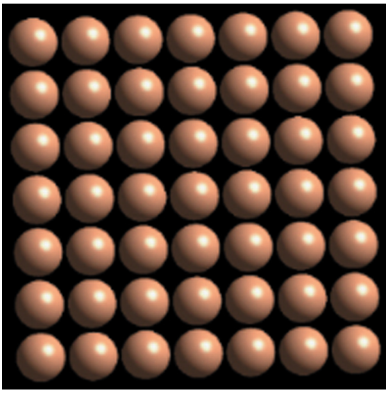
Liquid

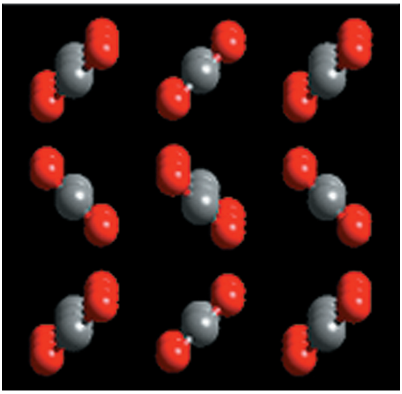


Crystalline solid

There are substances which appear as solids, but the atoms or molecules in them are disordered. Such solids are called amorphous solids. **Glass** is an amorphous solid. One can make any substance into a glass by rapidly cooling the liquid. For example, we have metals formed in the glassy state (metglasses).

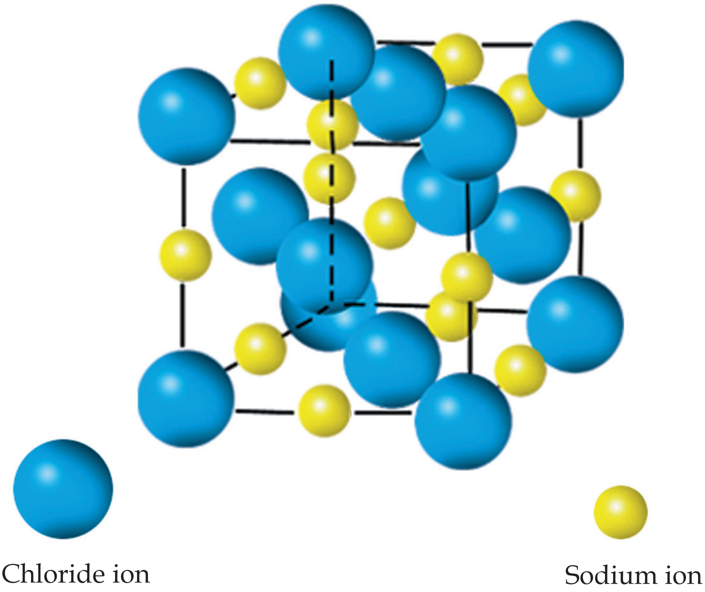
Solids where the atoms or the molecules are arranged regularly in all the three directions are called **crystals**. We show below the arrangement of atoms or molecules in crystals of copper, carbon dioxide and sodium chloride.





Notice that in copper crystals, the copper atoms occur in a regular manner. In solid carbon dioxide, CO_2 molecules occur in a regular manner.

In sodium chloride, which is a salt (an ionic substance), Na^+ and Cl^- ions are present in a regular manner.



1.12 Materials

Substances that possess unusual properties are also chemicals. For example, some materials conduct electricity. Metals like copper are conductors. We use wires made of copper, or sometimes of aluminium, to transmit electricity. Chemists have made many other substances which conduct electricity just like copper. Metal oxides like ReO_3 (rhenium trioxide) and RuO_2 (ruthenium dioxide) conduct like metals.

Even metals offer some resistance for the passage of electricity. Some materials conduct electricity without any resistance. Such materials are called **superconductors.** Chemists have made many new superconductors. The important ones are $YBa_2Cu_3O_7$ and $HgCa_2Ba_2Cu_3O_8$. These two become superconducting at 98 K and 135 K respectively.

Some substances are magnetic. Iron is a well-known magnetic metal. Cobalt and nickel are also magnetic metals. Lodestone, used by travellers for centuries to find the direction, is a chemical (Fe_3O_4, magnetite). There are other substances which are good magnets (e.g., alloys of samarium and cobalt).

Divided matter (Nano materials)

If you take a piece of solid matter (say a metal) containing an Avogadro number of atoms and go on dividing it to smaller bits, you will ultimately end up with an atom of the substance. Before that, you will reach a stage of very tiny particles containing 100 to 10,000 atoms. Such particles with diameters of 1–50 nm (10–500 Å) are referred to as **nanoparticles**. Nanomaterials exhibit properties entirely different from bulk materials and constitute materials of the future.

Let us look at some other materials that are familiar to us.

Transparent roof: The transparent roofs that we see in some buildings or sheds are made of fibre-reinforced plastic (plastic containing glass fibre) or of polycarbonate (plastic).

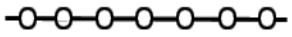
Radio and solar cell: The transistor used in the radio and television contains silicon (Si), generally with some impurities (e.g., phosphorus, boron) carefully put into it. Silicon is also used in solar cells to convert sunlight into electricity.

Tape (cassette) recorder: The tape has the coating of a magnetic oxide (gamma-iron oxide, Fe_2O_3, or chromium dioxide, CrO_2).

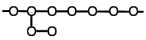
MRI: Hospitals carry out brain or total body scans by magnetic resonance imaging. The magnet is a superconducting one, containing wires made of niobium and tin (Nb_3Sn).

Plastics are long-chain molecules (polymers) containing repeating units. They have large molecular weights which can go up to several hundred thousands.

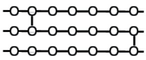
Some **polymers** contain linear chains formed by a repeating unit (monomer). Some others contain branched chains. In some polymers, chains are linked by bonds. Crosslinking increases the rigidity and strength of polymers.



linear



branched



crosslinking

Thermoplastic polymers are those which can be moulded when heated. They do not have crosslinking.

Thermosets are polymers whose shapes cannot be changed, even by heating. They are highly crosslinked. Many of the resins (epoxy, phenol–formaldehyde) are thermosets.

Soap

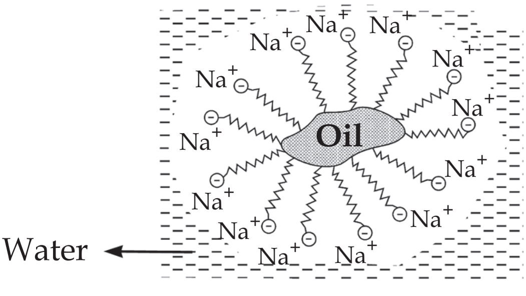
It has been known for a long time that soap can be made by boiling vegetable oils or animal fats with caustic soda (NaOH) solution. Chevreul in 1816 established that soap is formed by the reaction of alkali with the acid part of the oil or the fat. Soap is therefore a sodium salt of an organic acid.

Animal fats are esters formed between glycerol (glycerine) and stearic acid (long-chain carboxylic acid, $C_{17}H_{35}COOH$). When NaOH is added to the ester, it forms the sodium salt of stearic acid and glycerine. This is called **saponification.**

Glyceryl tristearate (fat) $+ 3NaOH \longrightarrow 3C_{17}H_{35}COO^{-}Na^{+}$ + glycerine

The essential feature of a soap is the long-chain hydrocarbon part with a charged group at the end. This is what gives soap its useful properties. The hydrocarbon part can readily mix with oily substances and the ionic part can mingle with water. This role of soap makes it an **emulsifying agent.**

Soap cleans clothes or any other object (including animal bodies) because of two reasons. It emulsifies oily substances and also lowers the surface tension of water. Soap is a **surfactant**. Many synthetic detergents also contain sodium salts of long-chain acids. An example is $C_{15}H_{31}SO_4^{-}Na^{+}$.



Emulsifying action of soap

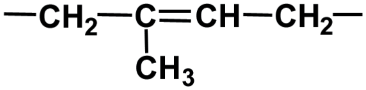
In the table below, we list a number of polymers and their uses. In addition to these, there are polymers which act as **adhesives**. Instant glue has methylcyanoacrylate which polymerizes on contact with moisture (H_2O).

Polymer	Uses
poly(ethylene)	plastic bags; containers; water piping; film and sheet.
poly(propylene)	moulded plastic chairs; carpets.
poly(vinyl chloride) or PVC	water piping; electrical conduit; flexible laboratory tubing; upholstery covering; toys.
poly(styrene)	as a foam in insulated food containers; packaging; glass-fibre reinforced plastic; plastic plates, cups and trays.
poly(methyl methacrylate)	car tail light mouldings; aeroplane windows.
poly(ethylene terephthalate)	shirts and blouses (with cotton); trousers and coats (with wool); soft drink bottles; tyre cord (Terylene).
poly(butadiene)	rubber tyres
nylon 6,6, poly(amide)	carpets; panty-hose; clothing; bearings.
poly(urethanes)	foam insulation in refrigerators; mattresses; cushions.
poly(tetrafluoroethylene)	non-stick pans (Teflon).
poly(acrylonitrile)	acrylic sweaters; carpets (Orlon, Acrilan).
cellulose acetate	rayon clothing; toothbrush handles.

Copolymers contain more than one type of monomer.

Wood is an important material. It mainly contains cellulose (50%) and lignin (30%). Cellulose is a carbohydrate made up of glucose units. Cellulose in wood is used to make paper, cellulose acetate and other materials. Lignin is a complex substance made of phenolic molecules. Wood is a beautiful composite material that is not possible to make in the laboratory. Wood substitutes have been made with the use of plastics and other materials for making doors, windows, panels and furniture.

Natural rubber is a long-chain hydrocarbon polymer consisting of



$-CH_2-\underset{\underset{CH_3}{|}}{C}=CH-CH_2-$

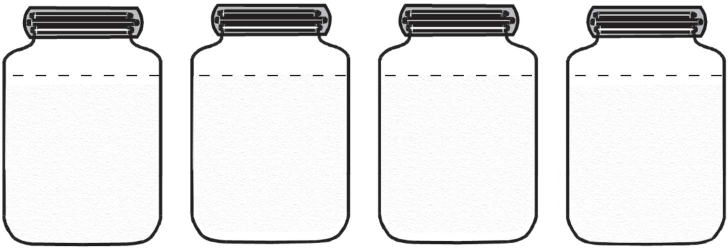
units, called isoprene units. Products made of natural rubber do not last long. Rubber is therefore vulcanized by heating it with sulfur. Synthetic rubber (neoprene) is produced starting from a chloroalkene.

Waxes are esters of long-chain carboxylic acids (fatty acids). Bees-wax has the formula $C_{15}H_{31}COOC_{30}H_{61}$. Esters of the steroid, cholesterol, are used in ointments.

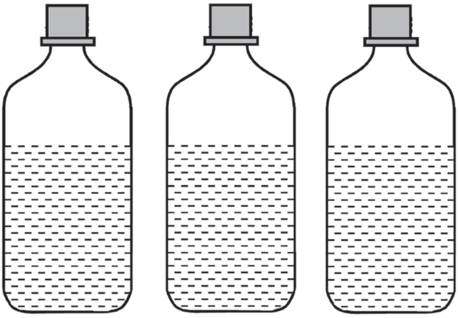
1.13 Similar looks but different properties

A cook was preparing a sweet dish. He was in a hurry. When the time came to add sugar, he took a bottle containing a white crystalline powder and added several spoons of it. He then proudly served the sweet. As soon as people put a spoon of the sweet in their mouths, their faces became awkward and some started shouting. What had happened? The cook had added salt instead of sugar. This can happen in a laboratory.

Let us say, there are four bottles containing white powdery materials. They all look the same. One bottle may have sugar and the second bottle may have potassium cyanide which is a terrible poison. The third bottle could be ammonium phosphate which is a fertilizer. The fourth may be baking soda. All look-alikes are not the same.



Sometimes, we can distinguish look-alikes. For example, if we had three bottles containing colourless liquids, water, alcohol, and ether. We can pick out which is which by the smell. Smelling can be dangerous if the liquid is a strong acid or a poisonous chemical. It is therefore necessary to label the bottles and not to use, taste or smell chemicals in bottles without labels on them. Clearly, it is not nice to taste a strong acid in trying to find out whether the syrupy liquid in the bottle was honey.



1.14 Pure and impure

A substance can be pure or in mixture with other substances. It becomes necessary to find out whether a substance is pure and if so, how pure. Many methods are available to analyze purity. Nowadays, chemists employ different instruments to check the purity of substances. A common method is **chromatography**. This general technique uses a medium (a column containing a solid absorbent or a porous medium such as filter paper) to separate the components in an impure substance or a mixture of substances.

Suppose you want to find out whether a sample of green writing ink is a pure liquid or a mixture of substances. Then, get a strip of filter paper (3 cm long) and fix it in a test tube as shown in the **Fig. 1(a)**. Take an appropriate solvent (a mixture of ethyl alcohol and ammonia solution) in the tube and wet the filter paper with a spot of green ink. Leave the test tube for some time and let the solvent rise to the top of the paper. You may see two spots above the original green spot, one yellow and the other blue as shown in **Fig. 1(b)**. Clearly, the green ink is a mixture of two substances, one yellow and another blue. Here, paper chromatography was employed to identify the components of green ink. In principle, a piece of chalk can also provide such a separation of components.

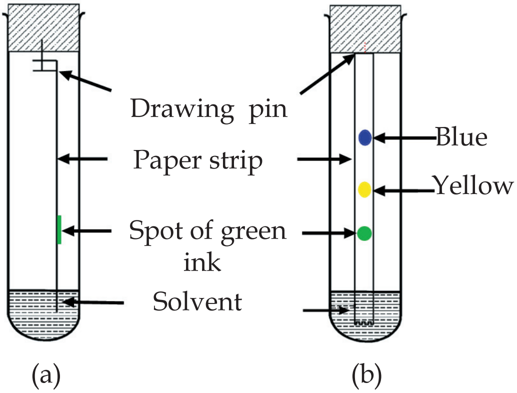


Figure 1

Mixtures of substances in the solid state can be separated and identified by paper chromatography or column chromatography. In column chromotography, a solution of the mixture is passed through an adsorbent column. Usually a material such as alumina or chalk is used as the adsorbent. Different substances go to different heights in the column as shown in the **Fig. 2**. Mixtures of gases and vapours are separated by passing them through solid adsorbent columns (e.g., alumina).

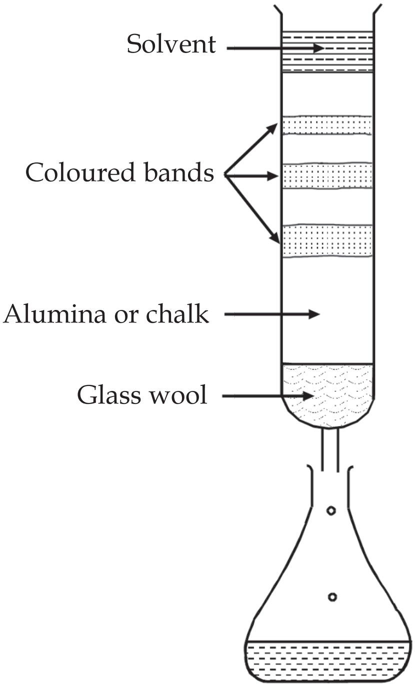


Figure 2

Mixtures of substances can be separated, or impure substances purified, by several means. With solids, crystallization from a suitable solvent can be used for purification. Repeated crystallization gives pure solids. A mixture of two immiscible liquids (e.g., oil and water) can be separated simply by using a separating funnel. If they are miscible (e.g., benzene and alcohol, benzene and carbon tetrachloride, water and alcohol), distillation is employed. In distillation, a liquid that boils at a lower temperature vapourizes first and is collected through a condenser. In **Fig. 3**, a simple apparatus for distillation is shown. For proper separation of liquids from mixtures, fractional distillation is employed.

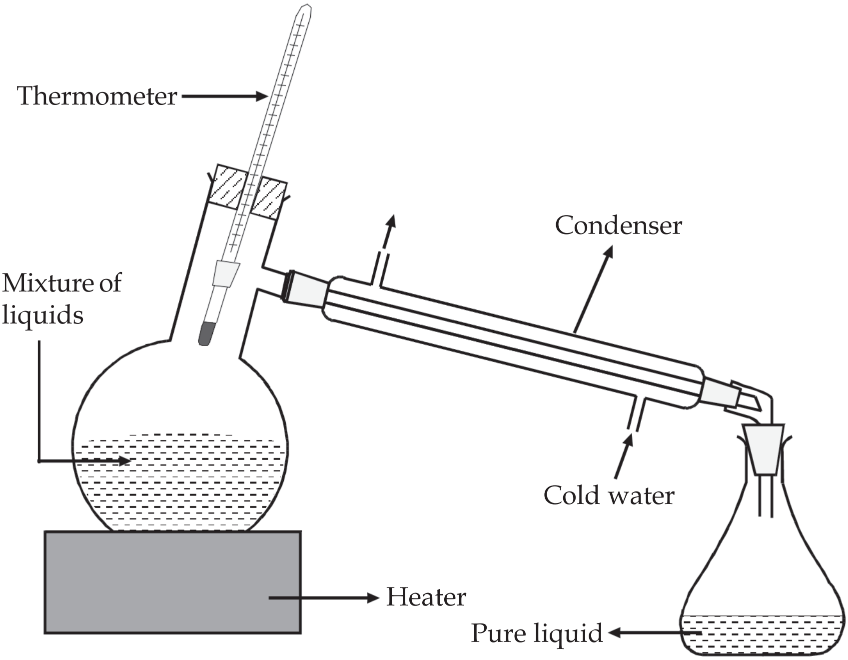
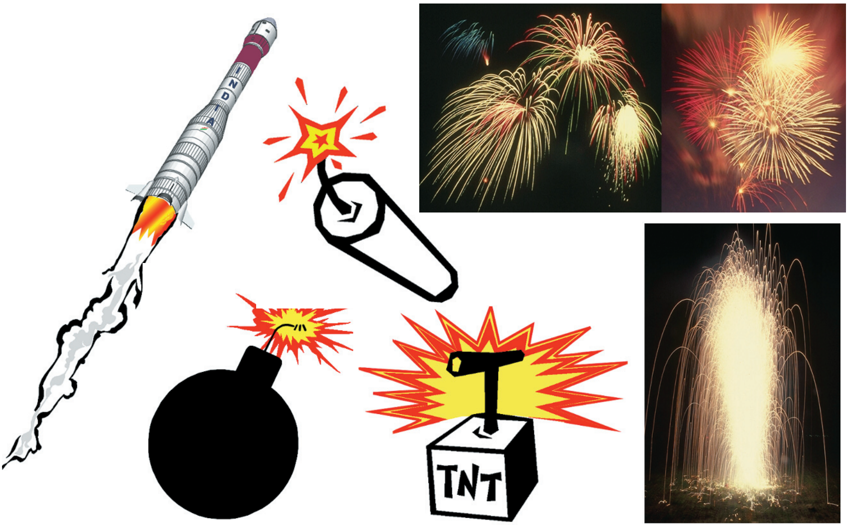


Figure 3

Purification of substances is essential for their use in medicinal and chemical practice. This is done industrially with much effort and at considerable expense. Some distillation columns in the industry can be several metres high.

1.15 Explosions and fireworks

It is not uncommon to witness explosions and fire in a chemical laboratory. Some compounds explode as they decompose. Thus, some peroxides decompose explosively giving stable compounds along with oxygen. Azides and diazo compounds explode to give the stable compounds along with nitrogen. When people carelessly throw sodium into a sink, it immediately reacts with water, and any combustible compound that may be present in the sink (e.g., ether) catches fire. This is why, while working in a laboratory, one has to be careful and wear safety glasses to protect the eyes. Sometimes explosions can be violent and risky. For example, hydrogen in the presence of oxygen can explode under certain conditions of temperature and pressure (normally, hydrogen and oxygen combine to make water). In 1967, three American astronauts were killed by a fire in the Apollo module. The cabin contained



100% oxygen and fire was caused by an accidental spark which ignited the plastic material.

The greatest tragedy in a chemical factory was caused in Bhopal in 1984, probably due to a water leak into a storage tank containing MIC (methyl isocyanate). This gave rise to a runaway reaction and explosion. MIC leaked into the atmosphere and killed or injured a large number of citizens. This points to the need to take greater care in maintaining high safety standards in laboratories and industries.

Other than the above kinds of explosions, human beings have always been in search of explosives for use in war and for entertainment. Around 1,000 years ago, the Chinese and the Arabs discovered gunpowder, a mixture of potassium nitrate (KNO_3), sulfur and charcoal. This was replaced in 1845 by nitrocellulose (gun cotton). Soon after, a terribly unstable explosive, nitroglycerine, was discovered. When nitroglycerine explodes, about 10,000 times its own volume of hot gases are produced within a second. Alfred Nobel combined nitroglycerine with silaceous earth (and later with wood pulp) to make dynamite, in 1867. He also instituted Nobel prizes for science, out of the profit made by selling dynamite. The more modern explosives are ammonium nitrate (NH_4NO_3), trinitrotoluene (TNT) and mixtures of such compounds. Explosives are used for construction (e.g., opening tunnels, making large pits, demolition work), besides military purposes.

Rockets were first employed by the Chinese in the 13th century. Tippu Sultan used them in his war against the British in Srirangapatna. Rockets use chemical propellents. The early rockets used gun powder as the propellent. Modern-day rockets employ liquids as well as solids as propellents. Typical liquid propellents are a mixture of liquid oxygen and hydrogen. Germans used a mixture of liquid oxygen and alcohol during the Second World War. Instead of oxygen, N_2O_4 is also used as an oxidizer. Other than hydrogen (or alcohol), hydrazine (N_2H_4) derivates are used as fuel. Common solid propellents use ammonium perchlorate (NH_4ClO_4) and ammonium nitrate as oxidizers, along with polyurethane and synthetic rubber. Aluminium is added in some instances.

During diwali, we play with firecrackers. Firecrackers contain oxidizers such as potassium chlorate ($KClO_3$) and potassium nitrate. The oxidizers are mixed with fuels such as carbon (charcoal) and sulfur. White phosphorus is used as the kindling material. Magnesium and other additives give out sparks. Copper oxide (CuO), barium nitrate ($Ba(NO_3)_2$), strontium carbonate ($SrCO_3$) and other materials give rise to different colours. Some people try to make firecrackers at home by mixing and grinding the above chemicals. They often end up with explosions, resulting in severe injuries and even death.

1.16 The food we eat

Our food generally consists of carbohydrates, proteins, fats, vitamins and minerals. **Carbohydrates** are made up of carbon, hydrogen and oxygen. Rice, wheat and sugar, by and large, consist of carbohydrates. Carbohydrates provide energy, but nothing else.

Proteins are organic nitrogen compounds and consist of long chain molecules. Proteins are present in muscles, blood, cartilage and hair. Foods that are rich in proteins are milk, nuts and pulses, fish and meat. When we eat proteins they get hydrolyzed by enzymes in the digestive system to smaller nitrogen containing molecules called amino acids. The amino acids are then used by the body to replenish its own proteins. Proteins are therefore not merely a source of energy but are essential for maintaining the protein levels in the body.

Fats are present in oil, butter, ghee, and other dairy products and in some types of meat. Fats contain long hydrocarbon chains and acid groups. We really do not need to eat fat. Excess carbohydrate gets converted into fat in the body.

Some oils contain unsaturated fatty acids (possessing double bonds) while some contain saturated fatty acids. Animal fats contain triglycerides (glycerine esters of saturated fatty acids). Butter contains 45% saturated fats. Peanut oil and safflower oil contain 18% and 9% of saturated fats respectively. We should avoid saturated fats (oils) in our diet.

Vitamins and minerals are found in fruits and vegetables. They are essential for our health. Vitamin C is an antioxidant and is good for general health. Oranges and other citrus fruits contain vitamin C. Vitamin C gets destroyed when heated during cooking.

Folic acid is another main need of our body, and its deficiency leads to serious disorders. It is found in leafy vegetables, fruits, and legumes. Much of the folic acid gets destroyed while cooking.

Balanced food intake is necessary to satisfy the requirements of the body. Nutritional deficiency is common in the populations of many of the poor countries, including India. Certain deficiencies cause serious diseases. For example, lack of iodine causes goitre which results in the swelling of the thyroid gland. Diabetes is caused when the pancreas gland does not produce sufficient insulin. The body can use the sugar which it absorbs from food, only if insulin is available.

Our blood consists of haemoglobin (red part of the blood). Haemoglobin has iron in it. Haemoglobin can be made in the body only if there is iron. An adult requires around 0.01 g of iron per day. The absence of iron from the diet causes anaemia.

We do not really need additional sugar in our food intake. The carbohydrates we eat bring in enough sugar (glucose). Excessive fat intake increases the chance of heart attack, because of the blockage of the arteries by cholesterol.

In the table below, the recommended daily nutritional requirements for young adults are shown.

Recommended daily dietary intakes for young people (Age: 15 - 18 years)*								
	Protein							
Male	59 g							
Female	44 g							
Vitamins	**A**	**D**	**E**	**K**	**C**	**Niacin**	**B_6**	**Folic acid**
Male	1000 µg	10 µg	10 mg	65 mg	60 mg	20 mg	2 mg	200 µg
Female	800 µg	10 µg	8 mg	55 mg	60 mg	15 mg	1.5 mg	180 µg
Minerals	**Ca**	**P**	**Mg**	**Fe**	**Zn**	**I**	**Se**	
Male	1200 mg	1200 mg	400 mg	12 mg	15 mg	150 µg	50 µg	
Female	1200 mg	1200 mg	300 mg	15 mg	12 mg	150 µg	50 µg	
* From the National Academy of Sciences, USA.								

It is useful to look at what happens to the food we eat. The breakdown of food molecules involves oxidation. For example, glucose gets oxidized as follows:

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O + \text{energy}$$

The breakdown of glucose helps to form high energy molecules (ATP). For example, one mole of glucose in the absence of oxygen breaks down to produce two moles of a molecule containing three carbon atoms (pyruvate or lactate) and the net energy stored in this process is 20 kcal mol^{-1}. In the presence of oxygen, the lactate or pyruvate oxidizes to CO_2 and H_2O, and in the process considerable energy is captured.

Eat a Banana!

When you are tired (and feeling a bit weak), eat a banana. It is a source of instant energy. It has many good ingredients (find out which).

Tea: Tea is a truly popular beverage in India and in the world at large. The three common types of tea are unfermented green tea, partly fermented oolong tea and fermented black tea. Green tea (commonly used in China and Japan) contains a high proportion (up to 30%) of polyphenols or flavanols. When tea is fermented to make black tea, flavanols undergo transformations and give rise to theaflavins (red-orange in colour) and thearubigins. Tea also contains alkaloids such as caffeine, and phenolic acids (e.g., gallic acid). In addition, inorganic components such as potassium, calcium, phosphorus, iron and manganese are also present in tea.

Have you noticed that the same brand of tea gives different colours in different places? Flavanols and the related constituents of tea react with metal ions, giving a range of coloured complexes. The colour of tea depends on the acidity and the hardness of the water used. With alkaline water (containing Ca, Mg), we get dark brown colours. On addition of acid (say, lemon juice), the colour becomes lighter.

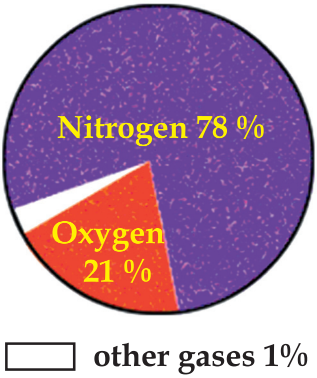
Caffeine in tea is a stimulant. It increases cardiac and brain activity. Coffee also contains caffeine, but a cup of strong coffee has much more caffeine than a cup of tea. That is why many people prefer decaffeinated coffee.

Did you know?
Many of the **colas** are acidic (low pH).

Did you know?
Milk is an emulsion, consisting of fat molecules suspended in water.

1.17 Our atmosphere

We live under an ocean of air called the atmosphere. There can be no life without the various components of gases that make the atmosphere. The atmosphere is mainly a mixture of gases. The major gases in the atmosphere are nitrogen 78% and oxygen 21%. Other gases make up only 1%.



Gases present in the atmosphere	**% of particles present in air**
nitrogen, N_2	78.00
oxygen, O_2	21.00
argon, Ar	0.93
carbon dioxide, CO_2	0.033
neon, Ne	0.0018
helium, He	0.00052
methane, CH_4	0.00015
krypton, Kr	0.00011
others	each < 0.0001

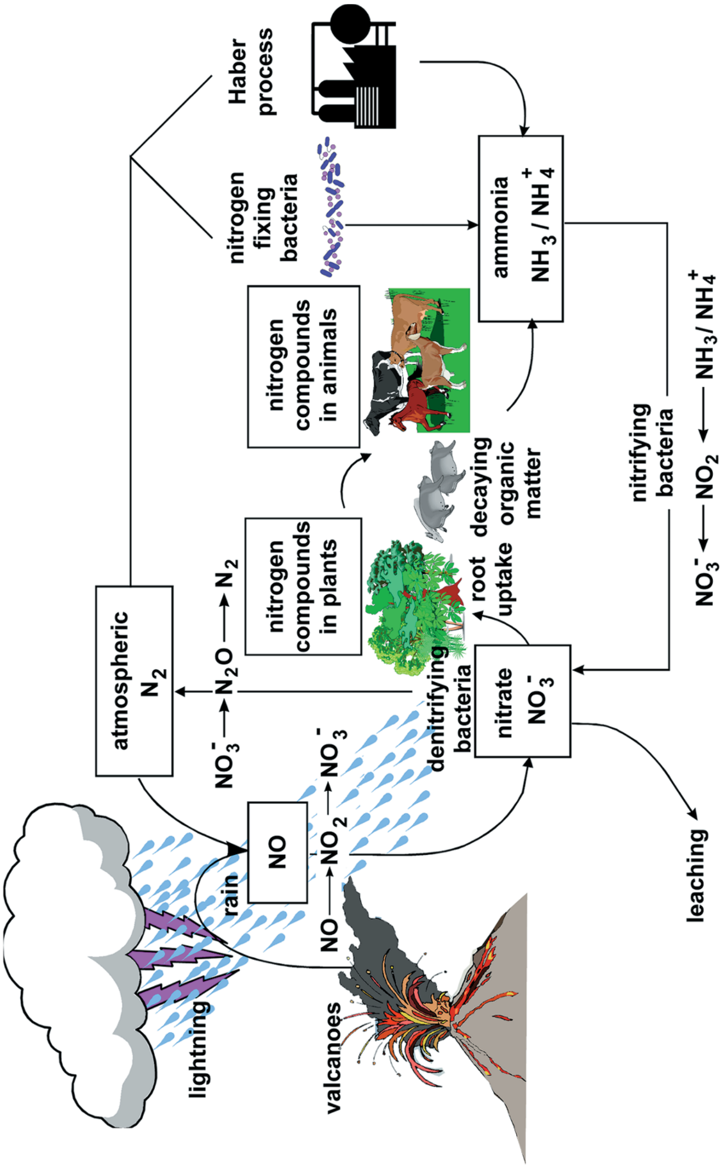
In addition to the above gases, there are some minor gases in the atmosphere.

Ozone	O_3
Carbon monoxide	CO
Sulfur dioxide	SO_2
Nitrous Oxide	N_2O
Nitric Oxide	NO
Ammonia	NH_3

Nitrogen (N_2) is essential for plants to produce amino acids and proteins. However, plants cannot use the atmospheric nitrogen directly. Nitrogen in the atmosphere is converted to ammonium compounds by certain bacteria in the root nodules of legumes. This process is called **nitrogen fixation**.

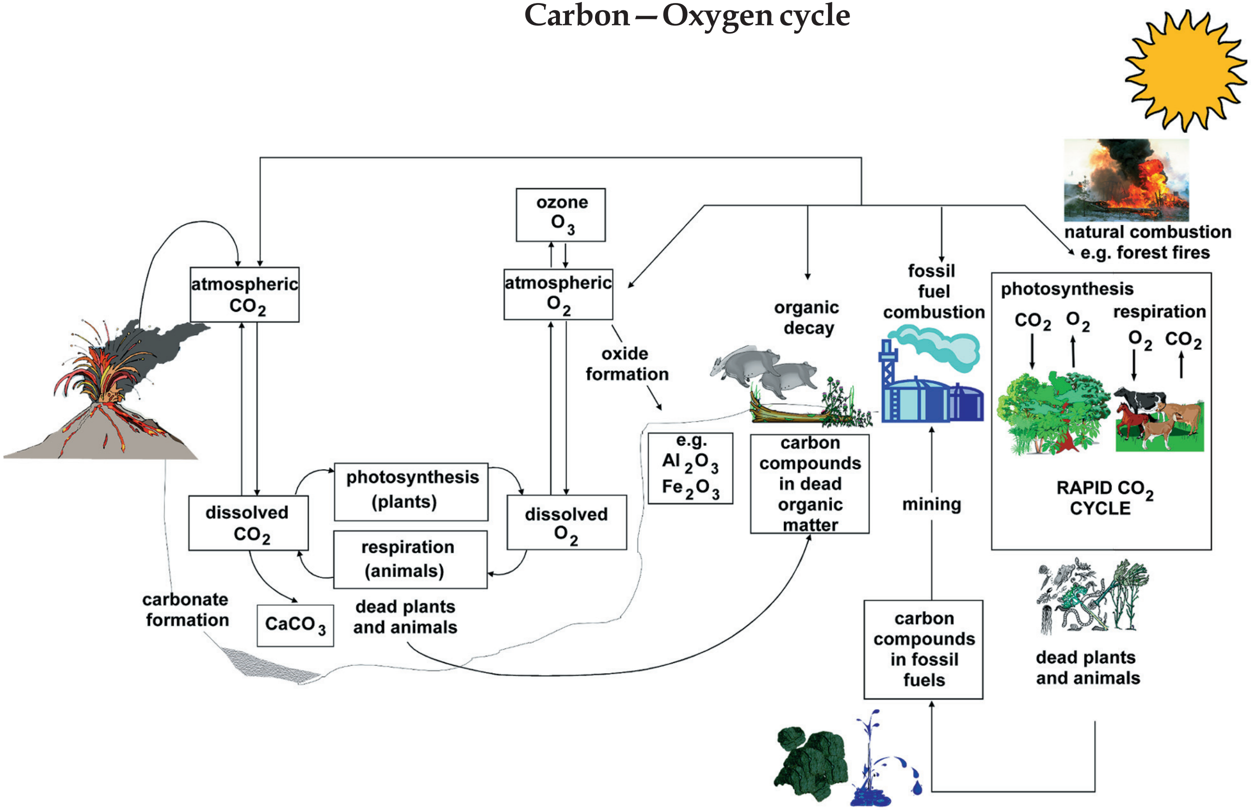
Twenty kilometres above the earth's surface, the incoming solar radiation helps oxygen to react to form ozone (O_3). The **ozone layer** absorbs harmful ultraviolet rays present in the incoming solar radiation.

Most of the phenomena in the atmosphere are cyclic. We shall now look at a few important cyclic processes that occur in nature.



Nitrogen cycle

Carbon — Oxygen cycle

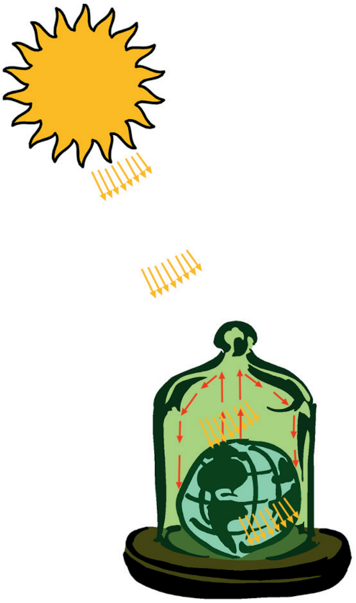


Pollutants: Pollutants are substances which have an undesirable effect on life. Some of the common pollutants are:

sulfur dioxide	(SO_2)
nitric oxide	(NO)
carbon dioxide	(CO_2).

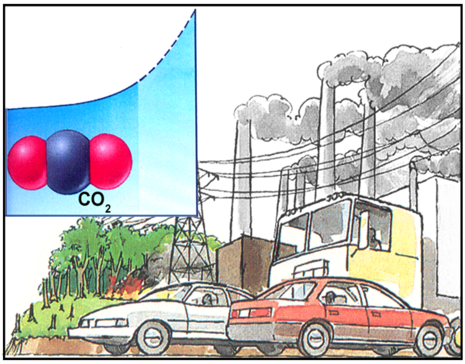
The presence of some of these substances in high concentrations in the atmosphere causes pollution. Pollutants can be **primary** or **secondary**. Primary pollutants are released into the atmosphere as a consequence of natural phenomena or human activities (examples: sulfur dioxide, carbon monoxide, oxides of nitrogen, hydrocarbons, freons and minute solid particles). Secondary pollutants are produced by the chemical changes involving primary pollutants (examples: sulfuric acid and nitric acid).

Greenhouse effect: The term Greenhouse effect was first used in 1822 by the French mathematician, Jean Fourier. What is greenhouse effect ? Atmospheric gases allow the solar radiation to pass through, but do not allow the terrestrial radiation to escape. This is what the glass does in a greenhouse. Life on earth would not have been possible without its beneficial effects. Because of various human activities, increased greenhouse effect poses a threat to life on earth. Callender of Great Britain warned as far back as 1939, of the dangers of upsetting the delicate balance of carbon dioxide levels!

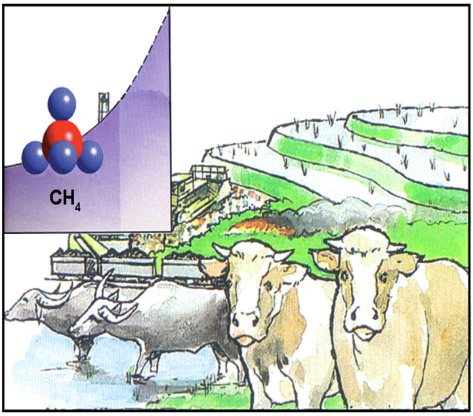


Greenhouse gases

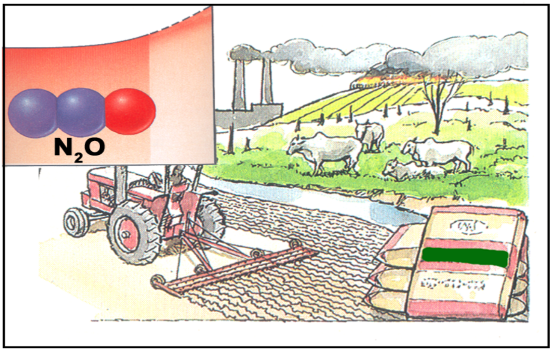
Burning of fossil fuels and clearing of forests contribute to the rising level of carbon dioxide.



Flooded rice fields, cattle and landfills increase the levels of methane. It lasts in the atmosphere for up to 10 years and its absorbing capacity is 20–30 times more than that of carbon dioxide.



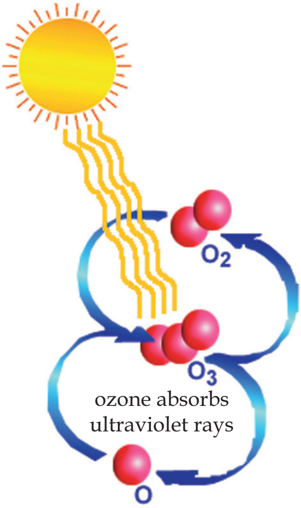
Nitrous oxide is produced by chemical fertilizers and "slash and burn" agriculture. It lasts up to 180 years in the atmosphere and absorbs heat 200 times more than carbon dioxide.



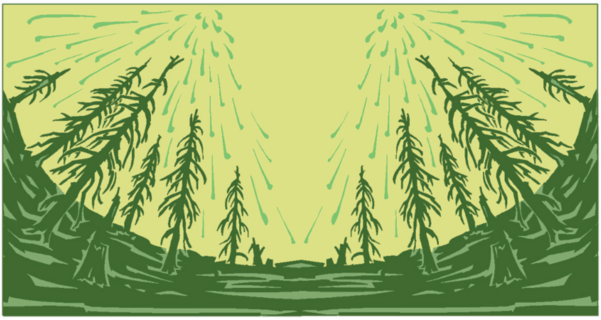
Refrigerators, air conditioners and air sprays all send CFCs (chlorofluorocarbons e.g., CF_2Cl_2) to the atmosphere. CFCs can last up to 400 years in the atmosphere and absorb heat 16,000 times more than carbon dioxide.

Consequences of global warming: This will have a disastrous effect in the frozen tundra regions. With the melting of the permafrost, methane gas can be released in large quantities. Thawing of frozen soils will release large quantities of water, causing flooding and subsidence of land. The tundra ecosystem can no longer support the diverse fauna. With increase in temperatures, many species of trees of the temperate forests can become extinct. The sea levels will rise and submerge many low-lying islands. Salt water will invade the estuaries and ground water sources, polluting the freshwaters. This will also have a disastrous effect on the flora and fauna of many regions.

Ozone layer: Ozone (O_3) occurs in minute quantities in the upper layers of the atmosphere (concentrated mainly in the upper stratosphere). Ozone is unstable and is easily split into O_2 and O by the ultraviolet rays present in the incoming solar radiation. Oxygen molecule (O_2) and oxygen atom (O) again combine to form new ozone molecules. This ongoing cycle protects the earth. Harmful ultraviolet rays are thus prevented from reaching the earth's surface by the ozone layer.



Acid rain: Primary pollutants (sulfur dioxide and oxides of nitrogen) occur in the gaseous state in the atmosphere. These get dissolved in the rain droplets in the atmosphere and precipitate as sulfurous acid, sulfuric acid, nitrous acid and nitric acid. Acid rain has destroyed thousands of acres of forests. Acid rain increases the acidity of lakes and rivers, which in turn can kill marine life.



Acid rain causes corrosion of metals, erosion of marble, limestone and mortar. Acid rain is responsible for dissolving heavy metals like zinc and cadmium into ground water, making it poisonous.

1.18 Water

Water is the most abundant chemical compound on earth. Much of the earth's surface is covered by water. The total quantity of water on earth is 10^{18} tonnes or 10^{24} grams. The human body is mainly made up of water.

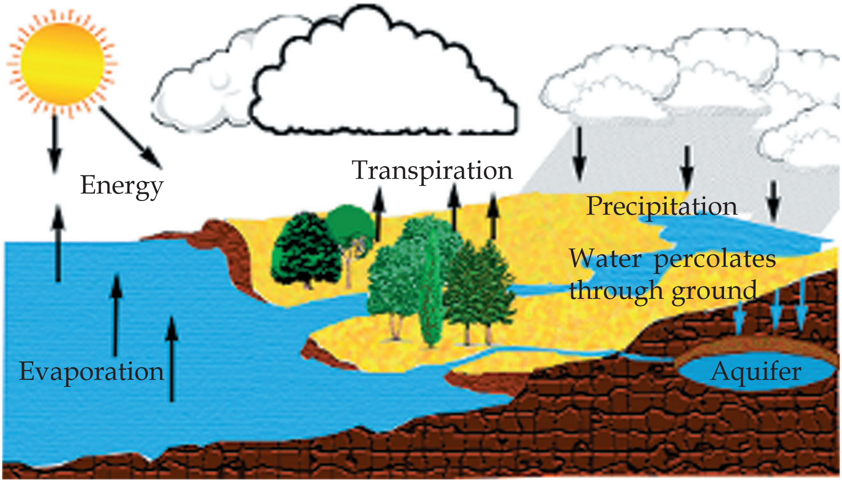
Water is essential for life. Therefore, we can have life in some other planet only if it has water.

Water is the only substance which exists in the gaseous (water vapour), liquid and the solid (ice/snow) states in nature.

Many substances dissolve in water. For example, salt and sugar are highly soluble in water. We can carry out many chemical reactions in water.

Several chemical substances contain water, as H_2O molecules. A good example is copper sulfate, $CuSO_4.5H_2O$.

There are substances which have a tendency to absorb water. Typical examples are $CaCl_2$, P_2O_5 and H_2SO_4.



Water is available to us through the water cycle.

Water quality: Since water can dissolve many things, the quality of water can vary widely. Some samples of water may be acidic while some others may contain various salts. Water can also contain microorganisms.

Hard water: Substances present in water vary from place to place, depending on the soil and rocks present. A common substance present in water is the calcium salt, calcium bicarbonate, $Ca(HCO_3)_2$. Water that contains appreciable amounts of dissolved calcium, magnesium and iron salts is called hard water.

There are two types of hardness:

- temporary hardness caused by calcium bicarbonate, $Ca(HCO_3)_2$, or magnesium bicarbonate, $Mg(HCO_3)_2$.
- permanent hardness caused by calcium sulfate ($CaSO_4$), or magnesium sulfate ($MgSO_4$).

Removal of hardness of water: Temporary hardness of water can be removed by boiling. When water with temporary hardness is boiled, calcium and magnesium ions precipitate as carbonates. The reaction can be shown as:

$$2HCO_3^{2-}\,(aq) \longrightarrow CO_3^{2-}(aq) + H_2O\,(l) + CO_2\,(g)$$

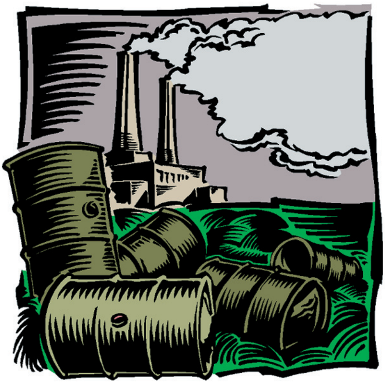
$$Ca^{2+}\,(aq) + CO_3^{2-}\,(aq) \longrightarrow CaCO_3\,(s)$$

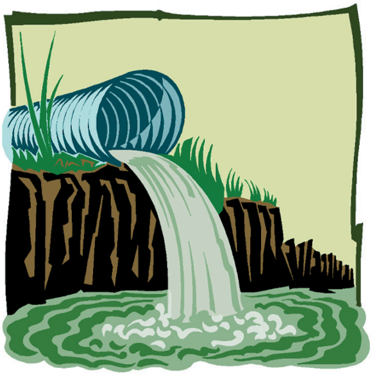
Permanent hardness of water cannot be removed by boiling. The simplest method of removing permanent hardness of water is by adding washing soda or sodium carbonate (Na_2CO_3). The calcium ions (magnesium ions) get precipitated as calcium carbonate (magnesium carbonate). The reaction can be shown as follows:

$$Ca^{2+}SO_4^{2-} + (Na^+)_2CO_3^{2-} \longrightarrow CaCO_3(s) + Na_2SO_4$$

Biological pollution: Biological pollution of water is generally measured in terms of the biological oxygen demand (BOD). The oxygen content of water is determined before and after incubation in the dark for 5 days at 20°C. The BOD is given in milligrams/dm^3 ($decimetre^3$). If BOD is less than 30 mg/dm^3, the water is not polluted.

Chemical pollution: Chemical pollution of water is a serious problem. Many industries discharge polluted water into rivers and lakes. For example, 24 tonnes of waste water is generally discharged for every tonne of paper produced. Several thousands of tonnes of untreated sewage water are also let out into oceans and rivers.





Water pollution is responsible for most of the diseases in poor countries. Diseases like typhoid, cholera, dysentery and diarrhoea are caused by the consumption of polluted water.

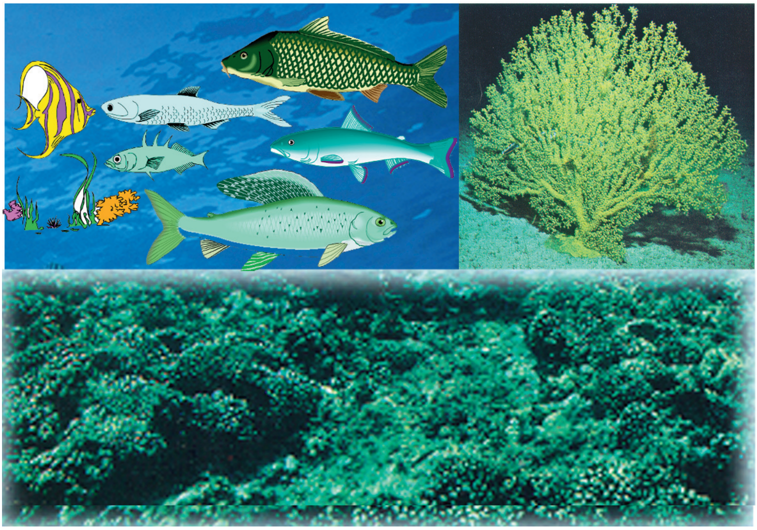
Fluoride pollution: A high concentration of dissolved fluoride salts is unfit for human consumption and is extremely harmful. It causes bone decay, dental decay and related deformities. Fluoride pollution is a serious problem in some parts of India.

Purification of water: Polluted water can be cleaned by appropriate chemical treatment and by other methods. Let us not forget that most people in India do not have clean drinking water. If they can have clean drinking water, most diseases can be avoided.

Distillation of water: If we want very pure water, it is obtained by distillation. We use distilled water in car batteries and also for many purposes in laboratories. Distilled water is used to give injections to patients. Do you know that tender coconut (coconut water) is as pure as distilled water?

The oceans of the world contain many salts. The average salinity of sea water is 35 grams of dissolved salts in one kilogram of sea water. Many minerals are present in the seas. Bromine is obtained from sea water.

The oceans are a rich source of food. Seaweed is a source of chemicals.



Distillation of sea water is one way of getting water for domestic use.

Many parts of the world including India are short of drinking water although there is plenty of sea water available.

A way of purifying sea water is to pass it through certain films (membranes) with small pores. The **membranes** allow only clean water to pass through. Certain substances, such as ion exchange resins, are commonly used to eliminate various ions or salts from water.

Conclusions

Chemistry is an experimental science and involves observation of transformations in substances, and making substances.

Chemistry pervades the world around us. Chemistry helps us to understand Nature and life processes. It is through chemistry that we can make a variety of materials with novel properties.

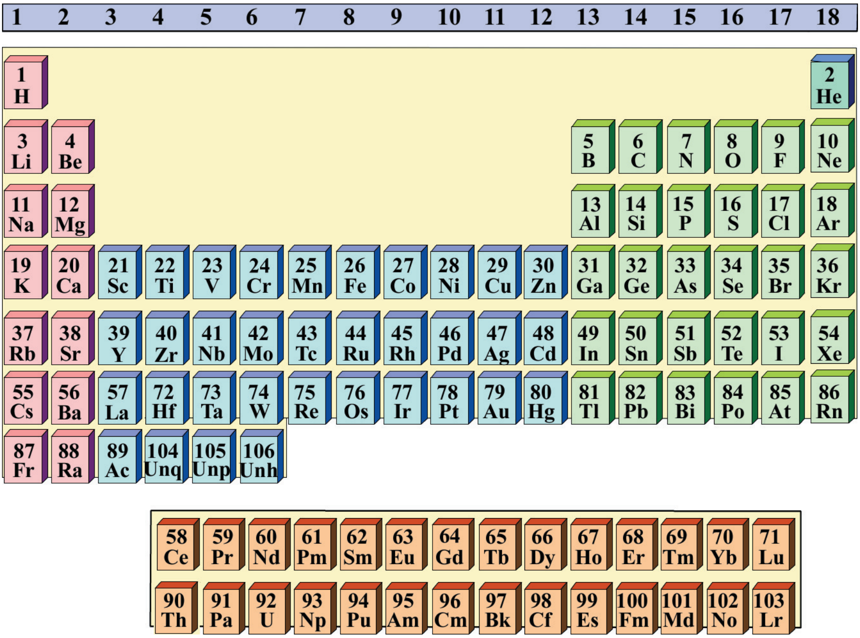
Without a knowledge of chemistry, we cannot improve our quality of life.

Little things make big things happen

In January 1986, the American space shuttle Challenger had a disastrous explosion. The famous physicist Richard Feynman showed how this was caused by the failure of the rubber O-rings. At low temperatures, rubber loses its resilience. So, the O-rings did not act as good seals, and caused hot gases to leak, which caused the explosion.

2

ELEMENTS AND THE PERIODIC TABLE



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Unq	105 Unp	106 Unh												

58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Objectives

- In this lesson, we examine how our knowledge of the elements has developed over a period of time and learn to describe the elements in terms of the electronic structure of atoms. We then try to understand the classification of elements, and how efforts to classify gave birth to the periodic table.
- We discuss the important features of the modern periodic table and see how it provides a basis to explain and predict properties of substances. We also make use of this lesson to follow some aspects of the history of chemistry.

There are millions of substances of different compositions and properties. They can be present in the form of solids, liquids and gases. However, the amazing fact is that these millions of substances are varied combinations of less than 100 naturally occurring elements. Up to the 16th century, only 10 elements were known.

Iron Fe
Carbon C
Copper Cu
Tin Sn
Silver Ag
Lead Pb
Gold Au
Antimony Sb
Mercury Hg
Sulfur S

2.1 Modern concept of elements

By 1661, the fundamental difference between a mixture and a chemical compound had been understood. Robert Boyle pointed out how Aristotle's concept of elements was wrong.

Boyle argued that fire, water, air and earth could not be considered as elements because

- they could not combine to form other substances and
- they could not be separated or extracted from other substances.

Boyle emphasized the importance of the physical properties of the elements. According to Boyle, elements

- were simple, unmixed bodies.
- were not made up of other similar or dissimilar bodies.
- were unique substances.

From this time on, the term element meant a material substance.

Twenty elements were known by 1775.

Iron (Fe)	**Cobalt (Co)**	**Nickel (Ni)**	**Platinum (Pt)**
Silver (Ag)	**Mercury (Hg)**	**Carbon (C)**	**Tin (Sn)**
Lead (Pb)	**Copper (Cu)**	**Nitrogen (N)**	**Oxygen (O)**
Phosphorus (P)	**Arsenic (As)**	**Bismuth (Bi)**	**Sulfur (S)**
Gold (Au)	**Zinc (Zn)**	**Hydrogen (H)**	**Antimony (Sb)**

Chemical criteria for identifying elements based on experimental data were established by the middle of 18th century. In 1789, Lavoisier of France published the first list of chemical elements. On the basis of experimental data, his list had 23 elements. He used chemical decomposition as the basis of classification of elements.

In 1807, Humphry Davy of Britain added two more elements to the list of known elements — Sodium and Potassium.

Davy

There was no agreed format for naming the elements up to early 19th century. In 1814, Baron Jons Jakob Berzelius suggested that

- the initial letter of the name of an element be used as the chemical symbol.
- if the element had a latin name which was no longer used, the chemical symbol should be from the latin name.
- if two or more elements had names beginning with the same alphabet, then the next distinctive letter should be added to the first letter (H, He, Ni, Na, Ne).

Need for arranging elements in an order: Advances in chemistry improved the understanding of the properties of the elements. There was a need to arrange the known elements in an order. To do this, an understanding of the structure of the atom became necessary.

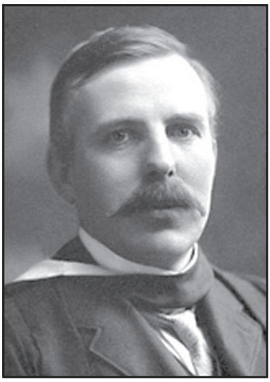
LAVOISIER (1743 – 1794)

Antoine Laurent Lavoisier is regarded by many as the father of chemistry. He was the son of a wealthy French lawyer and graduated in law. Chemistry fascinated Lavoisier and he devoted his life to the study of chemical phenomena. He was perhaps the first chemist to recognize the importance of quantitative measurements. He derived the law of conservation of mass by carefully weighing reactants and products in chemical reactions. Lavoisier made many discoveries which explained the nature of combustion. Lavoisier established that air consists of oxygen and nitrogen. It is a delight to see the old papers of Lavoisier where he graphically describes experiments with beautiful drawings. He became a victim of the French Revolution, during which he was guillotined. As Laplace said: “It took a minute to behead Lavoisier, but it will take thousands of years to make a head like that.”

2.2 The modern atom

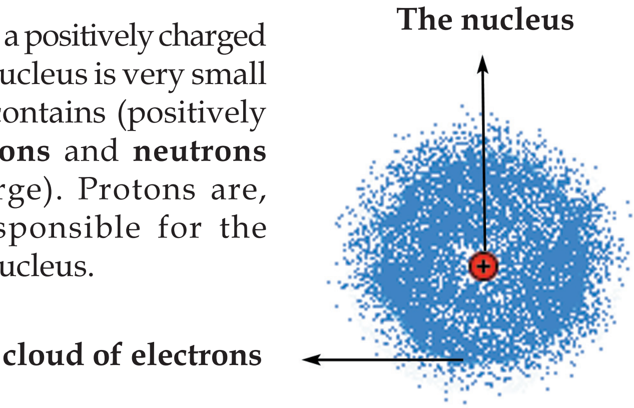
In 1904, J. J. Thomson discovered the electron. He proposed that the **electron**

- had negligible mass;
- had negative charge; and
- was a constituent of all elements.



The first ideas of the modern atom are due to Lord Rutherford (1911). Both Thomson and Rutherford worked at Cambridge (U.K.).

The atom has a positively charged nucleus. The nucleus is very small in volume. It contains (positively charged) **protons** and **neutrons** (without charge). Protons are, therefore, responsible for the charge of the nucleus.



Negatively charged electrons surround the nucleus and occupy most of the volume. The mass of an atom is almost entirely due to protons and neutrons.

Mass number: The mass number of an element is the sum of protons and neutrons in the nucleus.

Atomic number: The atomic number of an element is equal to the number of protons in the nucleus. Atoms are neutral because they have the same number of electrons and protons. The number of electrons in a neutral atom is also equal to the atomic number.

Isotopes of an element have the same atomic number, but different mass numbers. Deuterium (D) and tritium (T) are isotopes of hydrogen (H) with mass numbers of 2 and 3 respectively.

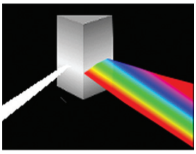
Niels Bohr (Denmark) proposed in 1913, that electrons move around the nucleus in **orbits**. Each orbit is associated with a specific energy. The different orbits are distinguished by giving numbers to them. These numbers are called **principal quantum numbers** (with the symbol **n**). They have values 1, 2, 3, ... Electrons with different values of **n** are also referred to as belonging to different **shells**. As the number **n** increases, the energy of the electron increases.

If an electron jumps from one orbit to another, there will be a change in energy. For example, if an electron goes from orbit 1 (energy E_1) to orbit 2 (energy E_2), the change in energy is given by $E_2 – E_1$. This energy change is accompanied by absorption of radiation. The energy of the radiation is given by the equation,

$$E_2 - E_1 = h\upsilon$$

where υ is the frequency of radiation and h is the Planck constant. The value of h is 6.626×10^{-34} J-s. The absorption and emission of light due to electron jumps in atoms are measured by using spectrometers.

THE SPECTROMETER



Spectroscopy is a powerful tool of modern science. The early spectrometer (spectroscope) dissected light, by the use of a prism or a diffraction grating. By using a spectrometer, one can identify elements, for example, by the colour of light they emit. Sodium, strontium and copper compounds when placed in a flame give yellow, crimson and green colours respectively.

The source of light can be a carbon arc (or a laser). The sample is placed in front of the light source and the light absorbed or emitted is analyzed by the spectrometer. The wavelengths or frequencies of absorption or emission depend on the transitions of the electrons in an element. Thus, hydrogen, lithium and every other element has its characteristic spectrum.

The frequency of radiation υ, is related to the wavelength, λ, by the relation,

$$\upsilon = \frac{c}{\lambda}$$

Here, c is the velocity of light (3×10^8 ms^{-1}).

It was pointed by de Broglie in 1924, that the electron, just like light, has wave properties. The wave associated with an electron is called an **orbital**. How do we specify the energies of different electron orbitals? To do this, it is necessary to describe electrons or their energies much more specifically.

This requires more than one quantum number. We will first make use of two numbers (quantum numbers) to illustrate how electrons can be individually described.

First, we have the quantum number with values 1, 2, 3, … with the symbol, **n**. We now define another quantum number "**l**" (letter "el") For each value of "**n**", there can be different values of "**l**" varying between 0 and (**n**–1).

Let us see how this works.

n = 1, "**l**" can only be 0

n = 2, "**l**" can be 0 or 1

n = 3, "**l**" can be 0, 1 and 2

n = 4, "**l**" = ?

Electrons with "**l**" = 0, 1, 2, 3 ...... are called **s**, **p**, **d** and **f** electrons. We shall now list the different types of electrons (electrons with different energies).

n = 1, 1**s**
n = 2, 2**s**, 2**p**
n = 3, 3**s**, 3**p**, 3**d**
n = 4, 4**s**, 4**p**, 4**d**, 4**f**

The maximum number of electrons in an **s** orbital is 2.
The maximum number of electrons in a **p** orbital is 6.
The maximum number of electrons in a **d** orbital is 10.
The maximum number of electrons in an **f** orbital is 14.

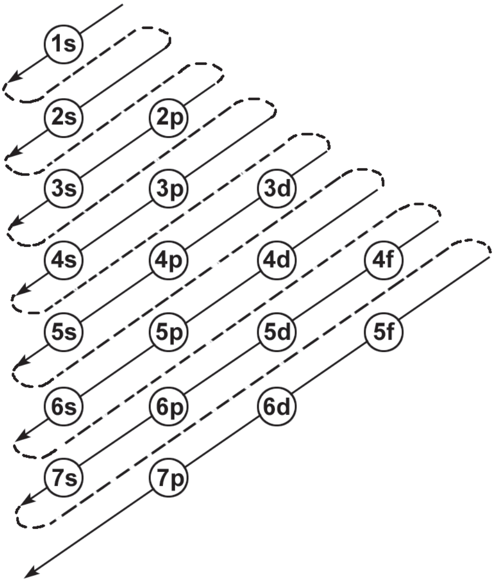
We can now see how electrons can be arranged in atoms with increasing atomic number.

Atomic number	Element	Description of electrons
1	H	$1s^1$
2	He	$1s^2$
3	Li	$1s^2\ 2s^1$
4	Be	$1s^2\ 2s^2$
5	B	$1s^2\ 2s^2\ 2p^1$
6	C	$1s^2\ 2s^2\ 2p^2$
7	N	$1s^2\ 2s^2\ 2p^3$
8	O	$1s^2\ 2s^2\ 2p^4$
9	F	$1s^2\ 2s^2\ 2p^5$
10	Ne	$1s^2\ 2s^2\ 2p^6$

Aufbau principle: The order of filling the orbitals is called the Aufbau principle. Aufbau in German means **building up**.

According to this principle,

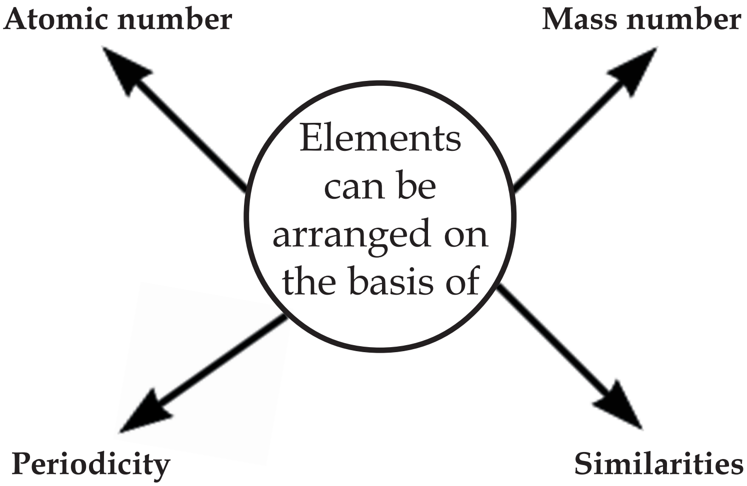
- electrons should be arranged in the order of their increasing energies.
- The order **1s**, **2s**, **2p**, **3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d** … is the order of increasing energy.



The above orbital filling diagram helps to understand the electronic configuration of an element. Electrons always occupy orbitals with the lowest energy first. For example, in lithium, two electrons occupy the 1s orbital, the third electron occupies the 2s orbital. The 2s orbital is filled in beryllium ($1s^2$, $2s^2$). In the next six elements, i.e., boron to neon, the 2p orbitals get filled.

Note! After 3p, 4s gets filled, and NOT 3d.

2.3 Arranging elements



By the early nineteenth century, about 50 elements had been identified and their properties studied. The need for arranging the elements in a logical manner led to various attempts to produce a periodic table.

In 1817, Dobereiner discovered that when calcium (Ca), barium (Ba) and strontium (Sr) were listed one below the other, they had similar properties.

Ca
Sr
Ba

The atomic mass of strontium was close to the average of the atomic masses of calcium and barium.

The properties of strontium were also an average of the properties of calcium and barium.

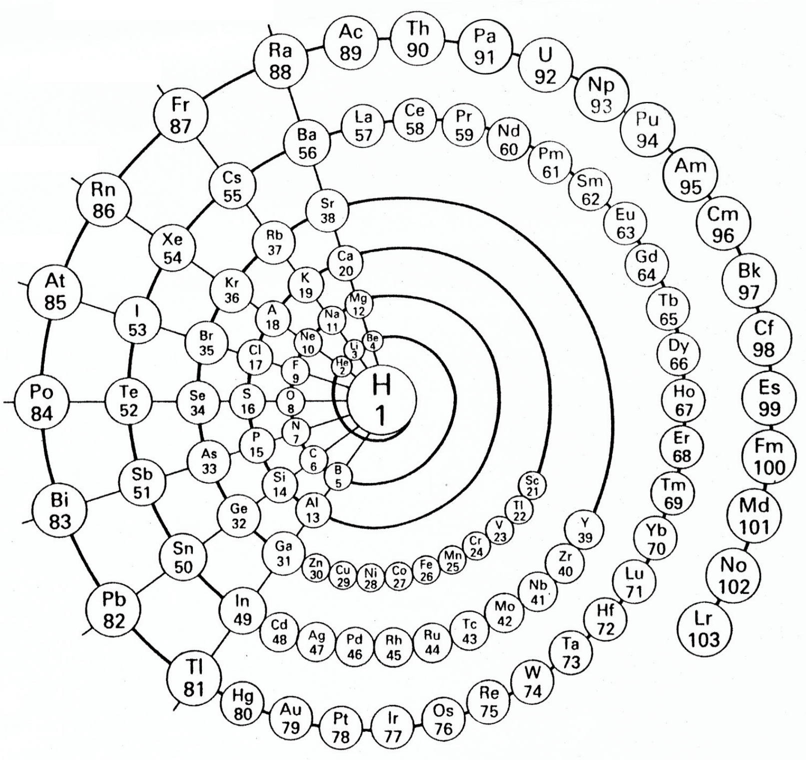
Dobereiner was the first to identify the **triads** and to use the atomic mass as the basis for grouping.

By 1829, two more triads were discovered.

Cl	**Chlorine**	**Lithium**	**Li**
Br	**Bromine**	**Sodium**	**Na**
I	**Iodine**	**Potassium**	**K**

In 1862, De Chancourtois (France) proposed that the properties of elements are the properties of numbers. How did he come to this important conclusion?

De Chancourtois selected a cylinder with a circumference of 16 units. Why did he select 16 units? It was the approximate atomic mass of oxygen. Elements were then arranged in an increasing order of the atomic mass.

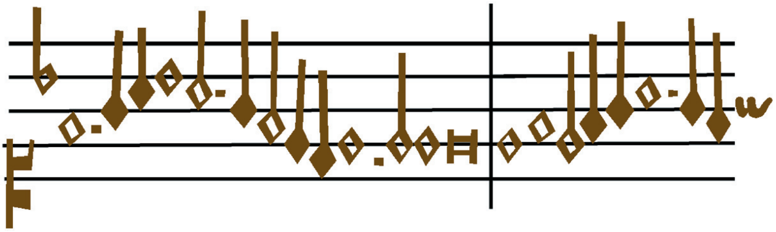


Chancourtois noticed that elements with similar properties fell on a vertical line from the centre of the spiral. The figure illustrates the arrangement of all the elements following Chancourtois' idea.

In 1864, Newland (England) selected hydrogen, lithium, beryllium, boron, carbon, nitrogen and oxygen as the first seven elements.

H	Li	Be	B	C	N	O
1	2	3	4	5	6	7

He found that when these elements were serially numbered as 1, 2, 3, . . . 7, and arranged in order, the properties of the eighth element was repeated as the eighth note in western musical notes.



Based on this observation Newland postulated the Law of Octaves. The eighth element, starting from a given one is a kind of repetition of the first, like the eighth note of an octave in music.

What was the major drawback of the law of Octaves?

It was good only for the first 17 elements.

H **1**	**Li** **2**	**Be** **3**	**B** **4**	**C** **5**	**N** **6**	**O** **7**
F **8**	**Na** **9**	**Mg** **10**	**Al** **11**	**Si** **12**	**P** **13**	**S** **14**
Cl **15**	**K** **16**	**Ca** **17**	**Cr** **18**	**Ti** **19**	**Mn** **20**	**Fe** **21**

Newland was the first to use numbers in a serial order and to predict periodicity.

2.4 The modern periodic table

In 1869, Mendeleyev, the great Russian chemist, published the first version of his periodic table.

	I	II	III	IV	V	VI	VII	VIII
1	**Li**	**Be**	**B**	**C**	**N**	**O**	**F**	
2	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	
3	**K**	**Ca**	*	**Ti**	**V**	**Cr**	**Mn**	**Fe Co Ni**
4	**Cu**	**Zn**	*	*	**As**	**Se**	**Br**	
5	**Rb**	**Sr**	**Y**	**Zr**	**Nb**	**Mo**		

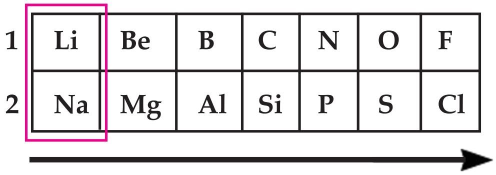
Group ↓

Period →

Periods are “rows” and **groups** are “columns”.

How was Mendeleyev's classification of elements an improvement over the earlier versions? While earlier periodic tables focused on a single observed characteristic, Mendeleyev correlated all the known and observed features such as periodicity, triads (groups), and chemical properties.

Mendeleyev first listed the known elements in an ascending order of their atomic mass.



1	**Li**	**Be**	**B**	**C**	**N**	**O**	**F**
2	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**

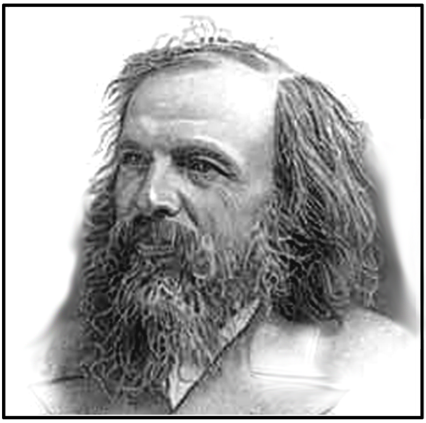
Each row (period) had seven elements. In each row (period), the first element had similar properties as the first element in the previous row (period). As hydrogen did not fit into the pattern, Mendeleyev (and also Meyer earlier) started the first row with lithium.

What are the outstanding features of Mendeleyev's periodic table?

Mendeleyev

- arranged the known elements in a tabular form.
- numbered the elements according to their atomic mass (mass number).
- arranged them in an increasing order of the atomic mass.
- did not place odd elements in the main groups (Fe, Co, Ni).

DMITRI MENDELEYEV (1834 – 1907)



Dmitri Mendeleyev was born in a large family of seventeen, in Siberia, Russia. He obtained a Master's degree in chemistry from the University of St. Petersburg in 1856, and then taught at the University. He was appointed professor of inorganic chemistry in 1867. His great textbook called **Principles of Chemistry** led to the systematic and periodic arrangement of the elements. It is most creditable that he considered the properties of elements to be related to their atomic masses, since the structure of atoms was unknown at that time. To bring certain elements into the correct group because of their chemical properties, he reversed the order of some of the elements and asserted that their atomic masses were incorrect. When the periodic table was formed, many vacant spaces became evident. Mendeleyev was faced with the choice between abandoning his scheme as invalid or declaring that these vacant spaces must belong to undiscovered elements. He predicted the properties of some of the unknown elements from the trends observed among the properties of related elements.

Mendeleyev was a genius interested in many fields of science. He worked on many problems associated with Russia's natural resources. He invented an accurate barometer. He was the director of the Bureau of Weights and Measures until his death in 1907.

Why did Mendeleyev leave gaps in his periodic table?

When Mendeleyev arranged the elements, he had to skip places to maintain the similarity in properties of the elements in the vertical columns (groups). He was certain that there were missing elements (elements that were yet to be discovered). For example, in group IV (the carbon group), he knew that tin could not occupy the place immediately below silicon. He left a gap for the element that was yet to be discovered and called this element eka-silicon. By studying the properties of the elements in this group, he was able to predict the properties of eka-silicon.

In 1886, Winkler, in Germany, discovered the missing element and named it germanium!

Properties of eka-silicon predicted by Mendeleyev		**Properties of Germanium**
Colour	light grey	dark grey
Atomic mass	72	72.6
Density	5.5	5.47
Atomic volume	13	13.2
Oxide	XO_2 High melting point Density 4.7 g cm^{-3}	GeO_2 Melting point >1000°C Density 4.703 g cm^{-3}
Chloride	Boiling point <100°C Density 1.9 g cm^{-3}	Boiling point 86.5°C Density 1.887 g cm^{-3}

Mendeleyev also predicted two more elements between aluminium and yttrium. He called them:

B
Al
eka-boron
eka-aluminium
Y

eka-boron (scandium discovered in 1879 by Lars Nilson of Scandinavia)

eka-aluminium (gallium discovered in 1875 by Lecoq de Boisbaudran of France)

Mendeleyev summed up his observations in the form of the **Periodic Law**. "The properties of elements vary periodically with the atomic mass".

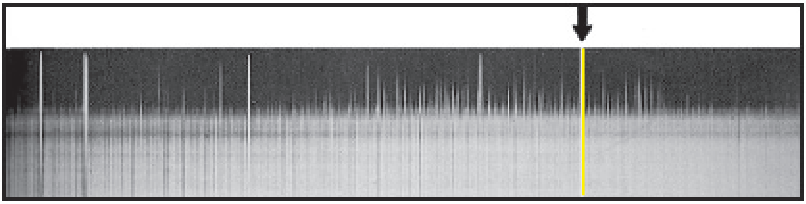
What were the drawbacks of Mendeleyev's Periodic Table? Like Newland's law of octaves, Mendeleyev's periodic law could not satisfactorily explain the positions of all the elements. (For example, the positions of tellurium and iodine.) And, there was no place for noble gases.

In spite of the drawbacks, a modified version of Mendeleyev's periodic table was used for nearly 50 years.

Group 0	**I**		**II**		**III**		**IV**		**V**		**VI**		**VII**		**VIII**
	a	b	a	b	a	b	a	b	a	b	a	b	a	b	
	H 1														
He 2	Li 3		Be 4		B 5			C 6		N 7		O 8		F 9	
Ne 10	Na 11		Mg 12		Al 13			Si 14		P 15		S 16		Cl 17	
Ar 18	K 19	Cu 29	Ca 20	Zn 30	Sc 21	Ga 31	Ti 22	Ge 32	V 23	As 33	Cr 24	Se 34	Mn 25	Br 35	Fe 26, Co 27, Ni 28
Kr 36	Rb 37	Ag 47	Sr 38	Cd 48	Y 39	In 49	Zr 40	Sn 50	Nb 41	Sb 51	Mo 42	Te 52	Tc 43	I 53	Ru 44, Rh 45, Pd 46
Xe 54	Cs 55	Au 79	Ba 56	Hg 70	57-71*	Tl 81	Hf 72	Pb 82	Ta 73	Bi 83	W 74	Po 84	Re 75	At 85	Os 76, Ir 77, Pt 78
Rn 86	Fr 87		Ra 88		Ac 89		Th 90		Pa 91		U 92		Np 93		Pu 94,Am95,Cm 96

* Lanthanum and lanthanides

Discovery of Noble Gases: Mendeleyev had no clue of the existence of noble gases. While studying the spectrum of the light from the chromosphere during a solar eclipse in 1868, the French astronomer Janssen observed brilliant yellow lines which came from an unknown element.



The element was named Helium – from Helios (the sun). The discovery of helium was purely accidental! It took another 27 years before helium was discovered on earth. After 1894, Lord Rayleigh, Ramsay and Travers in England discovered other noble gases.

Ramsay isolated a gas unknown till then, which

- had no colour,
- had no odour,
- had no taste, and
- did not react chemically with other elements.

Ramsay had no hesitation in picking a name for this element. He called it "argon" (lazy in Greek). Ramsay and Travers discovered neon (new), krypton (hidden) and xenon (stranger). Ernst Dorn of Germany discovered the last element of this group – radon. With this, the last group of the modern periodic table was complete.

Ne
He
Ar
Kr
Xe
Rn

Earlier, noble gases were also called inert gases. It was found in 1962 that elements like Xe form compounds (e.g., XeF_4). Clearly they were not inert.

Radioactivity: Becquerel discovered radioactivity in uranium in 1896. He found that an uranium compound darkened photographic plates even in the dark.

A more spectacular discovery was made by Marie Curie who found that certain minerals containing uranium were more radioactive than expected on the basis of the uranium content alone. She found that this was due to the presence of the element polonium (Po) of atomic number 84. It was named polonium after Poland, the native country of Marie Curie.

Radioactive elements decay, giving alpha particles (doubly charged helium), beta particles (electrons) or gamma radiation (hard X-rays).

Periodic table as we have today: With the various discoveries, the arrangement of elements in the periodic table changed to something close to what we have today. Moseley (England) suggested in 1914, that elements should be arranged in the order of increasing atomic numbers. This is advantageous because of the following reasons:

- The number of electrons increases by the same number as the increase in the atomic number.
- As the number of electrons increases, the electronic structure of the atom changes.
- The filling up of electrons in an atom occurs according to the Aufbau principle.

- Electrons in the outermost shell of an atom (**valence electrons**) determine the chemical properties of the element.

Properties of elements vary periodically with the atomic number.

element 1	**element 2**	**element 3**	and so on.
H	**He**	**Li**	

Members of a chemical family have similar chemistry. Therefore, understanding the chemical behaviour of one element of a family (group) helps to predict the chemical behaviour of the other members of the family.

Two of the well-known chemical families are:

Noble gases			**Alkali metals**
Helium	**2e** **He**	**3e** **Li**	Lithium
Neon	**10e** **Ne**	**11e** **Na**	Sodium
Argon	**18e** **Ar**	**19e** **K**	Potassium
Krypton	**36e** **Kr**	**37e** **Rb**	Rubidium
Xenon	**54e** **Xe**	**55e** **Cs**	Cesium
Radon	**86e** **Rn**	**87e** **Fr**	Francium

What do you notice about the number of electrons in the noble gases and alkali metals?

Chemical properties of these two families (groups) are different.

Alkali metals

- are excellent conductors of heat and electricity.
- have low melting points in comparison with the melting points of other metals.
- are soft and malleable.
- are reactive.
- react with water to form hydroxides.

Noble gases

- are the only elements to exist as unbound atoms.
- have low boiling points and densities.
- exist as gases at room temperature and pressure.
- do not easily take part in chemical reactions.

Let us now compare the noble gases and halogens.

Halogens		**Noble gases**	
		2e **He**	Helium
Fluorine	**9e** **F**	**10e** **Ne**	Neon
Chlorine	**17e** **Cl**	**18e** **Ar**	Argon
Bromine	**35e** **Br**	**36e** **Kr**	Krypton
Iodine	**53e** **I**	**54e** **Xe**	Xenon
Astatine	**85e** **At**	**86e** **Rn**	Radon

What do you notice about the number of electrons in a halogen, compared with the corresponding noble gas?

The properties of halogens differ from the properties of the noble gases. Halogens, like the alkali metals, are reactive.

Halogens		**Noble gases**		**Alkali metals**	
		2e **He**	Helium	**3e** **Li**	Lithium
Fluorine	**9e** **F**	**10e** **Ne**	Neon	**11e** **Na**	Sodium
Chlorine	**17e** **Cl**	**18e** **Ar**	Argon	**19e** **K**	Potassium
Bromine	**35e** **Br**	**36e** **Kr**	Krypton	**37e** **Rb**	Rubidium
Iodine	**53e** **I**	**54e** **Xe**	Xenon	**55e** **Cs**	Cesium
Astatine	**85e** **At**	**86e** **Rn**	Radon	**87e** **Fr**	Francium

The number of electrons in a halogen is one less than the corresponding noble gas. The number of electrons in an alkali metal is one more than the corresponding noble gas.

Elements display similar properties at regular periods.

Physical properties ← **It can be periodicity in** → **Chemical properties**

All these features are incorporated in the present-day periodic table.

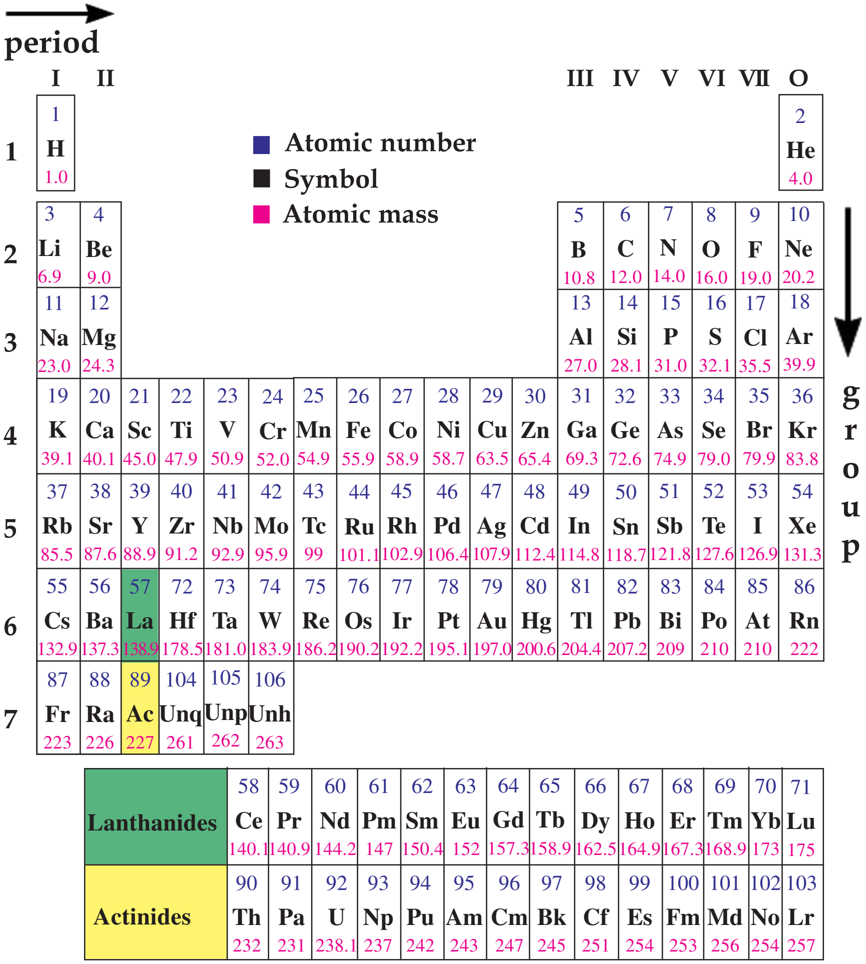
The first period has only two elements (Hydrogen and Helium).

The second and third periods have eight elements each.

The fourth, fifth and the sixth have eighteen elements each.

The seventh period is an incomplete period. Space for accomodating elements yet to be discovered is provided in this period (Unq, Unp …).

Note! The elements in a Group are similar.



■ **Atomic number**
■ **Symbol**
■ **Atomic mass**

	I	II											III	IV	V	VI	VII	O
1	1 **H** 1.0																	2 **He** 4.0
2	3 **Li** 6.9	4 **Be** 9.0											5 **B** 10.8	6 **C** 12.0	7 **N** 14.0	8 **O** 16.0	9 **F** 19.0	10 **Ne** 20.2
3	11 **Na** 23.0	12 **Mg** 24.3											13 **Al** 27.0	14 **Si** 28.1	15 **P** 31.0	16 **S** 32.1	17 **Cl** 35.5	18 **Ar** 39.9
4	19 **K** 39.1	20 **Ca** 40.1	21 **Sc** 45.0	22 **Ti** 47.9	23 **V** 50.9	24 **Cr** 52.0	25 **Mn** 54.9	26 **Fe** 55.9	27 **Co** 58.9	28 **Ni** 58.7	29 **Cu** 63.5	30 **Zn** 65.4	31 **Ga** 69.3	32 **Ge** 72.6	33 **As** 74.9	34 **Se** 79.0	35 **Br** 79.9	36 **Kr** 83.8
5	37 **Rb** 85.5	38 **Sr** 87.6	39 **Y** 88.9	40 **Zr** 91.2	41 **Nb** 92.9	42 **Mo** 95.9	43 **Tc** 99	44 **Ru** 101.1	45 **Rh** 102.9	46 **Pd** 106.4	47 **Ag** 107.9	48 **Cd** 112.4	49 **In** 114.8	50 **Sn** 118.7	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 **Xe** 131.3
6	55 **Cs** 132.9	56 **Ba** 137.3	57 **La** 138.9	72 **Hf** 178.5	73 **Ta** 181.0	74 **W** 183.9	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.1	79 **Au** 197.0	80 **Hg** 200.6	81 **Tl** 204.4	82 **Pb** 207.2	83 **Bi** 209	84 **Po** 210	85 **At** 210	86 **Rn** 222
7	87 **Fr** 223	88 **Ra** 226	89 **Ac** 227	104 **Unq** 261	105 **Unp** 262	106 **Unh** 263												

Lanthanides	58 **Ce** 140.1	59 **Pr** 140.9	60 **Nd** 144.2	61 **Pm** 147	62 **Sm** 150.4	63 **Eu** 152	64 **Gd** 157.3	65 **Tb** 158.9	66 **Dy** 162.5	67 **Ho** 164.9	68 **Er** 167.3	69 **Tm** 168.9	70 **Yb** 173	71 **Lu** 175
Actinides	90 **Th** 232	91 **Pa** 231	92 **U** 238.1	93 **Np** 237	94 **Pu** 242	95 **Am** 243	96 **Cm** 247	97 **Bk** 245	98 **Cf** 251	99 **Es** 254	100 **Fm** 253	101 **Md** 256	102 **No** 254	103 **Lr** 257

Unq, Unp, Unh: Unq = unnilquadium, (un = 1, nil = 0, quad = 4) for element with atomic number 104.Unp is unnilpentium and Unh is unnilhexium.

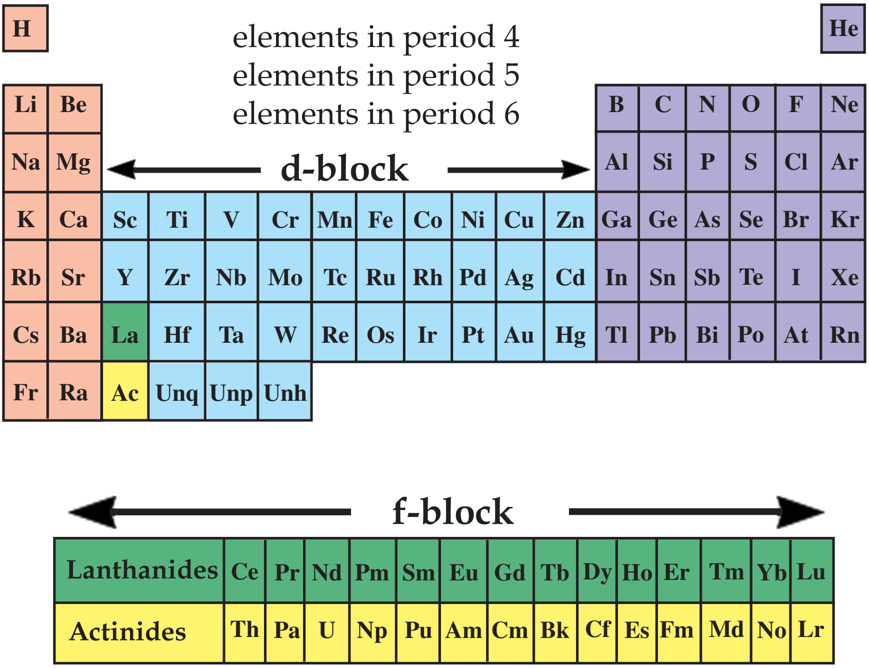
Elements in the different groups are classified as s-block, p-block, d-block and f-block elements.

Elements in groups I and II are s-block elements.

Elements in groups III, IV, V, VI, VII and 0 are p-block elements.

Elements in these two blocks are called as main group elements.

There are three series of d-block elements.



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Unq	Unp	Unh												

Lanthanides	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Actinides	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Elements belonging to the f-block form two series: rare earth elements or lanthanides in period 6 and actinides in period 7.

Elements beyond uranium in period 7 are called **transuranium** elements.

All transuranium elements are artificial elements (they do not occur in nature).

Artificial elements: In 1934, Enrico Fermi proposed that new elements could be made by bombarding the atomic nucleus of an element by particles such as neutrons. In 1936, Segre (Italy) did such an experiment by bombarding molybdenum (element no. 42) with deuterons and obtained the first man-made element (43), called technetium (Tc). The next man-made element was a transuranium element (93) obtained by irradiating uranium (92) with neutrons. This element was named neptunium (Np) by the discoverers, Mcmillan and Abelson at the University of California, Berkeley (1940), because Neptune is the planet after Uranus.

During 1940 – 1950, Seaborg and coworkers at Berkeley made many transuranium elements: plutonium (Pu, 94), americium (Am, 95), Curium (Cm, 96), berkelium (Bk, 97), californium (Cf, 98), einsteinium (Es, 99) and fermium (Fm, 100). All these elements can be produced in reasonably large quantities.

Seaborg (1912 – 1999)

Today, we have up to 112 elements. We list these elements on the next page, along with the place and the year of discovery.

101	mendelevium, Md	(Berkeley, 1955)
102	nobelium, No	(Dubna, Russia, 1965)
103	lawrencium, Lr	(Berkeley, 1961)
104	rutherfordium, Rf	(Dubna, Berkeley, 1964)
105	dubnium, Db	(Dubna, Berkeley, 1970)
106	seaborgium, Sg	(Berkeley, 1974)
107	bohrium, Bh	(Darmstadt, Germany, Dubna, 1974–1989)
108	hassium, Hs	(Darmstadt, 1980s)
109	meitnerium, Mt	(Darmstadt, 1980s)
110–112	**Not named**	(Darmstadt, after 1993)

How stable an artificial element is depends on the number of neutrons and protons in the nucleus. Thus, certain isotopes of elements are more stable than others. Calcium (Ca) isotope 40 (20 protons + 20 neutrons) and lead (Pb) isotope 208 (82 protons and 126 neutrons) are very stable. The isotope of element 114 with 114 protons and 184 neutrons is expected to be stable. Scientists are therefore trying to explore this **island of stability** by making element 114.

What are the other features of periods in the modern periodic table?

The core electrons of elements in a particular period is similar, and the structure is the same as that of the noble gas of the previous period.

Remember that the core electrons do not determine the chemical properties of elements. They are determined by the electrons in the outermost shell (valence electrons).

How does the periodic table help to predict chemical properties? Let us first examine the variation in the properties of the elements across periods. The 3rd period is the best to illustrate the variations across a period.

From element 11 to 17, there is a change from metallic to non-metallic nature.

Metallic Elements	Non-metallic Elements	
• Na Mg Al • form basic oxides. • form chlorides with high melting points. • chlorides are electrolytes. • form compounds with anions.	• Si P S Cl • form acidic oxides. • form chlorides with low melting points. • chlorides are non-electrolytes. • form compounds with cations.	**Ar**

How is the 4th period different? This is the first period in which the elements are in the s, d and p-blocks. The elements Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn in this period are called **transition elements**.

Transition elements: In these elements, the 3d gets filled after 4s. That is, 4s comes after 3p, not 3d.

Sc	scandium
Ti	titanium
V	vanadium
Cr	chromium
Mn	manganese
Fe	iron
Co	cobalt
Ni	nickel
Cu	copper
Zn	zinc

In water solution, most ions of transition elements are coloured.

Some of these elements exhibit more than one valency (Fe^{2+}, Fe^{3+}; Mn^{2+}, Mn^{3+}, Mn^{4+},…, Mn^{7+}). Some of the metals and their ions have catalytic properties.

Iron, cobalt and nickel are magnetic. These are permanent magnets (**ferromagnetic**). Compounds of these and many other transition elements are attracted by a magnet. They are **paramagnetic**.

The d-block elements in the 5th and the 6th periods are also the transition elements. Here, 4**d** (or 5**d**) gets filled before 4**p** (5**p**).

Elements in a group: Groups are chemical families. Remember the alkalis, halogens and noble gases!

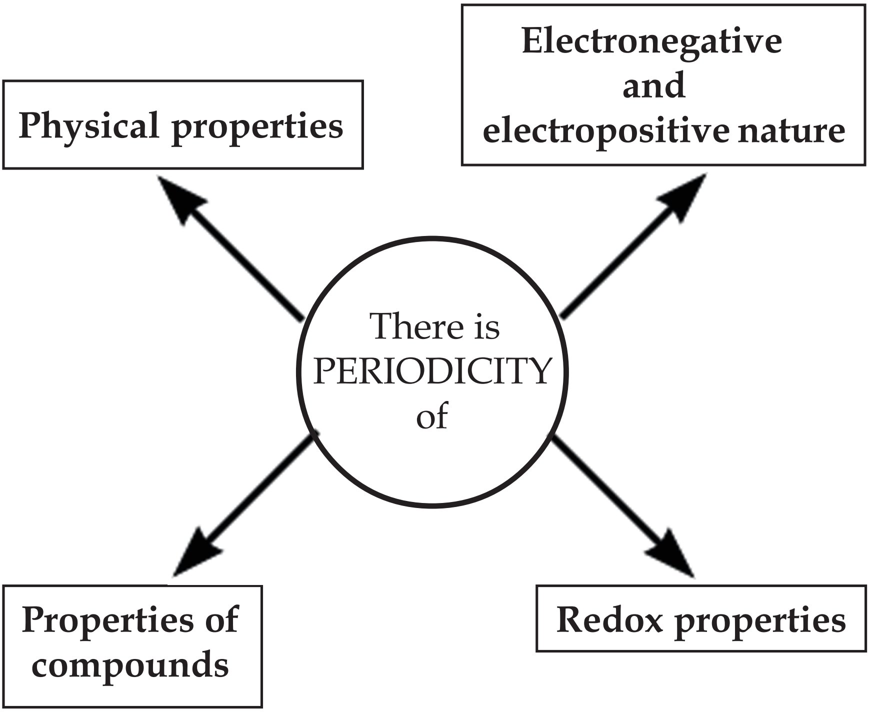
Elements in a group

- have the same number of valence electrons.
- have similar properties.
- become more metallic in character down the group.

Properties of an element in a group can be predicted on the basis of the properties of another element in the same group.

2.5 Periodic table and properties of elements

Periodicity in the modern periodic table is a function of the electronic configuration.



Physical properties:

- Melting point, boiling point and density of elements increase across a period until maximum values are reached. Then they decrease. Noble gases have low values.
- Elements become less metallic across a period and more metallic down a group.
- The atomic size and ionic size decrease across a period and increase down a group.

The variation in the ionization energy and the electron affinity of elements is particularly important. **Ionization energy** (IE) is the energy required to remove an electron from a free atom. We shall be concerned mainly with the first IE which is the energy required to remove the electron in the outermost shell. The first IE values of elements show periodic variations. The highest values are found for noble gases. Alkali metals like Na have low IEs. Atoms with low IE readily become positive ions.

We list below the first ionization energies (in electron volts) of a few elements:

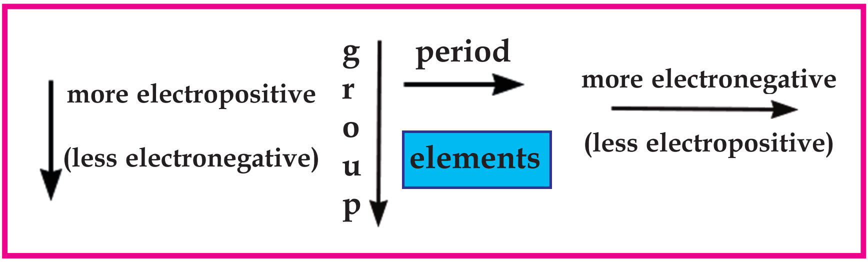
H	13.6	C	11.3	Na	5.1
He	24.6	N	14.5	Mg	7.6
Li	5.4	O	13.6	Cl	13.0
Be	9.3	F	17.4	K	4.3
B	8.3	Ne	21.6	Rb	4.2

Electron affinity is the energy change that occurs when an atom accepts an electron. Atoms with high electron affinity readily become negative ions. Halogen atoms have high electron affinities.

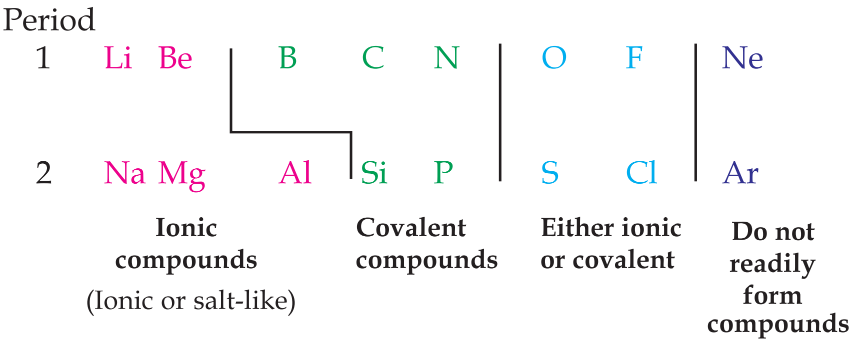
Electron affinities of a few elements (in electron volts) are given below:

F	3.40	I	3.06
Cl	3.61	H	0.75
Br	3.36	O	1.46

There is a direct relation between the electronegative or electropositive nature of the elements and the types of chemical compounds they form.



Let us see how this is seen in the nature of compounds formed by the elements in the 2nd and 3rd periods.



We have given the present-day version of the long-form of the periodic table in the following pages.

Long form of the Periodic Table of elements recommended by IUPAC [1]

Representative elements — d- transition elements — Representative elements — Noble gases

Group Number (1, 2; 3 – 12; 13 – 17; 18) — period number (1 – 7)

period number	Group 1	Group 2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	Group 18
1	1 **H** $1s^1$																	2 **He** $1s^2$
2	3 **Li** $2s^1$	4 **Be** $2s^2$											5 **B** $2s^22p^1$	6 **C** $2s^22p^2$	7 **N** $2s^22p^3$	8 **O** $2s^22p^4$	9 **F** $2s^22p^5$	10 **Ne** $2s^22p^6$
3	11 **Na** $3s^1$	12 **Mg** $3s^2$											13 **Al** $3s^23p^1$	14 **Si** $3s^23p^2$	15 **P** $3s^23p^3$	16 **S** $3s^23p^4$	17 **Cl** $3s^23p^5$	18 **Ar** $3s^23p^6$
4	19 **K** $4s^1$	20 **Ca** $4s^2$	21 **Sc** $3d^14s^2$	22 **Ti** $3d^24s^2$	23 **V** $3d^34s^2$	24 **Cr** $3d^54s^1$	25 **Mn** $3d^54s^2$	26 **Fe** $3d^64s^2$	27 **Co** $3d^74s^2$	28 **Ni** $3d^84s^2$	29 **Cu** $3d^{10}4s^1$	30 **Zn** $3d^{10}4s^2$	31 **Ga** $4s^24p^1$	32 **Ge** $4s^24p^2$	33 **As** $4s^24p^3$	34 **Se** $4s^24p^4$	35 **Br** $4s^24p^5$	36 **Kr** $4s^24p^6$
5	37 **Rb** $5s^1$	38 **Sr** $5s^2$	39 **Y** $4d^15s^2$	40 **Zr** $4d^25s^2$	41 **Nb** $4d^45s^1$	42 **Mo** $4d^55s^1$	43 **Tc** $4d^55s^2$	44 **Ru** $4d^75s^1$	45 **Rh** $4d^85s^1$	46 **Pd** $4d^{10}$	47 **Ag** $4d^{10}5s^1$	48 **Cd** $4d^{10}5s^2$	49 **In** $5s^25p^1$	50 **Sn** $5s^25p^2$	51 **Sb** $5s^25p^3$	52 **Te** $5s^25p^4$	53 **I** $5s^25p^5$	54 **Xe** $5s^25p^6$
6	55 **Cs** $6s^1$	56 **Ba** $6s^2$	57 **La*** $5d^16s^2$	72 **Hf** $4f^{14}5d^26s^2$	73 **Ta** $5d^36s^2$	74 **W** $5d^46s^2$	75 **Re** $5d^56s^2$	76 **Os** $5d^66s^2$	77 **Ir** $5d^76s^2$	78 **Pt** $5d^96s^1$	79 **Au** $5d^{10}6s^1$	80 **Hg** $5d^{10}6s^2$	81 **Tl** $6s^26p^1$	82 **Pb** $6s^26p^2$	83 **Bi** $6s^26p^3$	84 **Po** $6s^26p^4$	85 **At** $6s^26p^5$	86 **Rn** $6s^26p^6$
7	87 **Fr** $7s^1$	88 **Ra** $7s^2$	89 **Ac**** $6d^17s^2$	104 **Rf** $5f^{14}6d^27s^2$	105 **Db** $6d^37s^2$	106 **Sg** $6d^47s^2$	107 **Bh** $6d^57s^2$	108 **Hs** $6d^67s^2$	109 **Mt** $6d^77s^2$									

f - inner transition elements

* **Lanthanides** $4f^n\ 5d^{0-1}\ 6s^2$	58 **Ce** $4f^15d^16s^2$	59 **Pr** $4f^35d^06s^2$	60 **Nd** $4f^45d^06s^2$	61 **Pm** $4f^55d^06s^2$	62 **Sm** $4f^65d^06s^2$	63 **Eu** $4f^75d^06s^2$	64 **Gd** $4f^75d^16s^2$	65 **Tb** $4f^95d^06s^2$	66 **Dy** $4f^{10}5d^06s^2$	67 **Ho** $4f^{11}5d^06s^2$	68 **Er** $4f^{12}5d^06s^2$	69 **Tm** $4f^{13}5d^06s^2$	70 **Yb** $4f^{14}5d^06s^2$	71 **Lu** $4f^{14}5d^16s^2$
** **Actinides** $5f^n\ 6d^{0-1}\ 7s^2$	90 **Th** $5f^06d^27s^2$	91 **Pa** $5f^26d^17s^2$	92 **U** $5f^36d^17s^2$	93 **Np** $5f^46d^17s^2$	94 **Pu** $5f^66d^07s^2$	95 **Am** $5f^76d^07s^2$	96 **Cm** $5f^76d^17s^2$	97 **Bk** $5f^96d^07s^2$	98 **Cf** $5f^{10}6d^07s^2$	99 **Es** $5f^{11}6d^07s^2$	100 **Fm** $5f^{12}6d^07s^2$	101 **Md** $5f^{13}6d^07s^2$	102 **No** $5f^{14}6d^07s^2$	103 **Lr** $5f^{14}6d^17s^2$

---

[1] IUPAC stands for the International Union of Pure and Applied Chemistry.

In the IUPAC periodic table, while the number of periods remain the same, there are 18 groups. This has been done to avoid confusion.

Let us look at some other features.

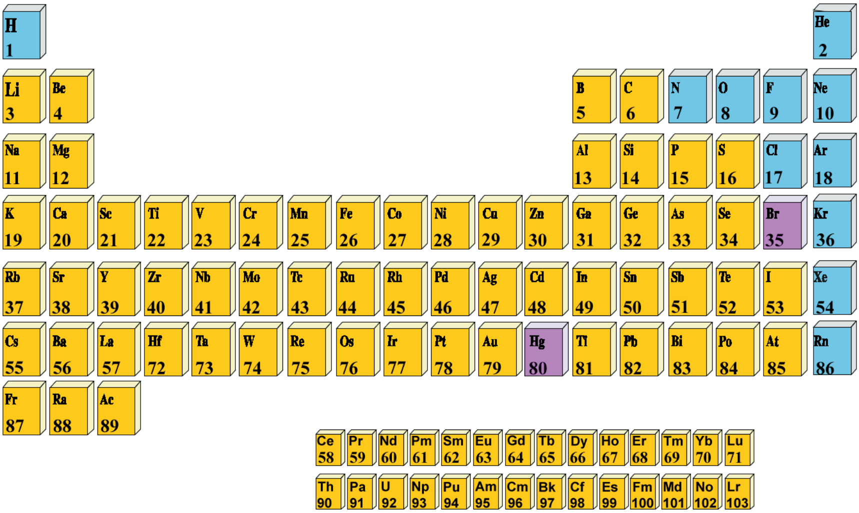
Elements occur in one of the three states of matter at room temperature.

🟨 **Solids**

🟪 2 **Liquids**

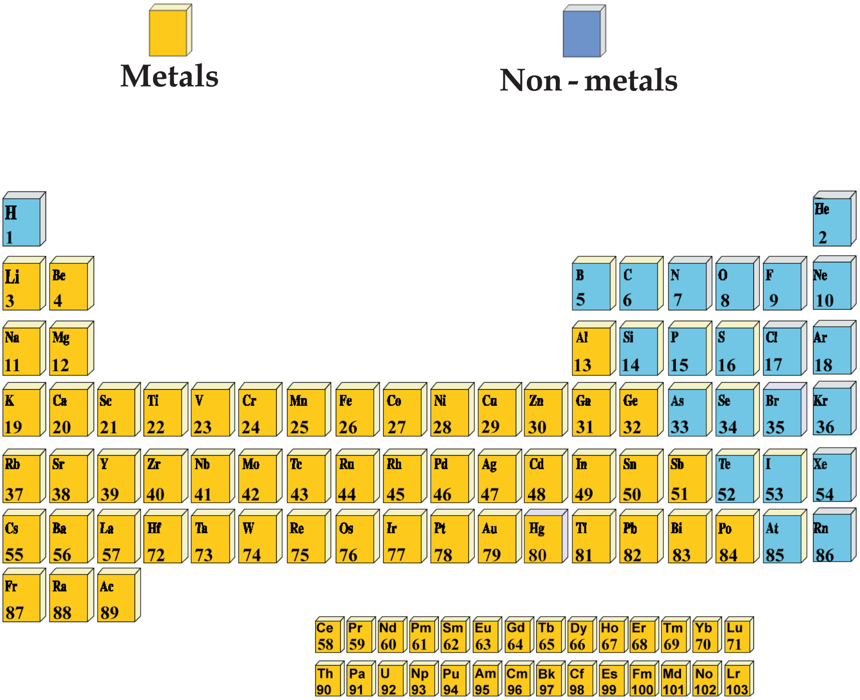
(Mercury and Bromine)

🟦 11 **Gases**



Most elements are metallic.

Did the creator want the world to be metallic!



In addition, Si, Ge, Se and Te are metallic in the liquid (molten) state.

Elements having atomic number above 83 are naturally radioactive. The exceptions to this are "Technetium" (Z = 43), and "Promethium" (Z = 61).

2.6 Coming back to the story of the elements

Let us look at the chronology of the Modern Periodic Table.

de Chancourtois	Spiral	1862
Newlands (UK)	Law of octaves	1864
Meyers (Germany)	Atomic volume	
Mendeleyev (Russia)	Periodic law (short-form)	1869
Henry Moseley (UK)	Atomic number	1914
Long-form of the periodic table		1985
Present-day periodic table		1994

Scientists from many countries have contributed to the discovery of elements.

Country	**No. of elements discovered**
Sweden	23
Britain	20
France	15
Germany	10
Russia	5
Austria	3

Artificial elements have all been discovered in the USA, Russia and Germany (mainly in the USA).

Have you wondered why there is no relation between the symbols of certain elements and the name of the element? For example, the symbol for sodium is Na and for silver, it is Ag. They are abbreviations of Latin or Greek names.

Here is a list of some of them:

Sodium	Na	Natrium	Latin
Potassium	K	Kalium	Latin
Iron	Fe	Ferrum	Latin
Copper	Cu	Cuprum	Latin
Silver	Ag	Argentum	Latin
Tin	Sn	Stannum	Latin
Antimony	Sb	Stibium	Latin
Gold	Au	Aurum	Latin
Lead	Pb	Plumbum	Latin
Mercury	Hg	Hydrargyrum	Greek
Tungsten	W	Wolfram	Swedish

Story of Antimony (element no. 51): This metal has been known from the middle ages. How did it get its name? Antimony, a metallic substance, was found to combine with other elements. It is believed that the name antimony is derived from "antimonium", "enemy of solitude". However, its symbol Sb is from its Latin name "stibium".

Story of Vanadium (element no. 23): This was discovered by Nils Sefstrom in 1801. It was named after Vanadis, Nordic goddess of love and beauty.

Story of Mercury (element no. 80): This element has been known from prehistoric times. How did it get its name? The Greek name for mercury is “hydrargyrum”. “Hydros” means water and “argyros” means silver. Its symbol Hg is of Greek origin.

Story of Tantalum (element no. 73): This was discovered by A. Ekeberg in 1802. Ekeberg of Sweden found deposits of a white oxide mass near the village Itterbul. He tried to dissolve the oxide in strong acids to isolate the element. This element was very difficult to isolate from the white oxide mass. Ekeberg, in frustration, named it tantalum, after the torments of Tantalus. (Tantalus, the son of Zeus, was punished by forcing him to stand up to his chin in water, but he could not quench his thirst. The water in which he was standing receded whenever he tried to drink it.)

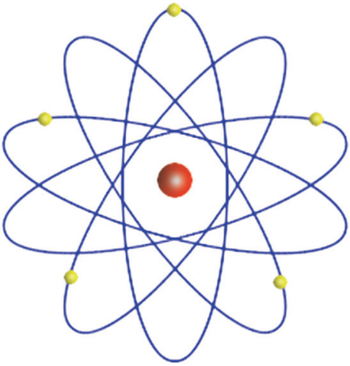
Conclusions

The modern periodic table is an encyclopedia of the properties of all the known elements.

It also provides space to accommodate elements yet to be discovered.

By using the various features of the modern periodic table, we can unravel the properties of elements and predict their chemical behaviour. The periodic table is a product of the contributions of chemists from many countries. It has taken centuries of work to arrive at this arrangement of elements.

Intelligent use of the periodic table continues to give rise to new discoveries.

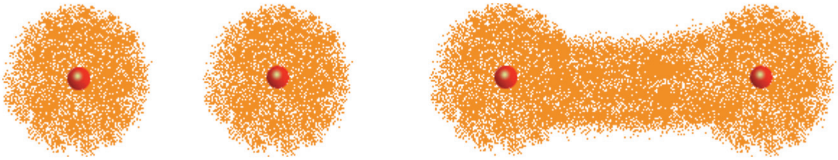


Understanding the nature and structure of the atom changed the face of physical sciences. The importance of the understanding of atoms to modern science can be best summed up by Richard Feynman's statement. "If, in some cataclysm, all of scientific knowledge were to be destroyed and only one sentence passed on to the next generation of creatures, what statement would contain the most information in the fewest words?

"I believe it is the atomic hypothesis … that all things are made of atoms … In that one sentence … there is an enormous amount of information about the world, if just a little imagination and thinking are applied." It is the understanding of the atom that has helped us to understand the elements.

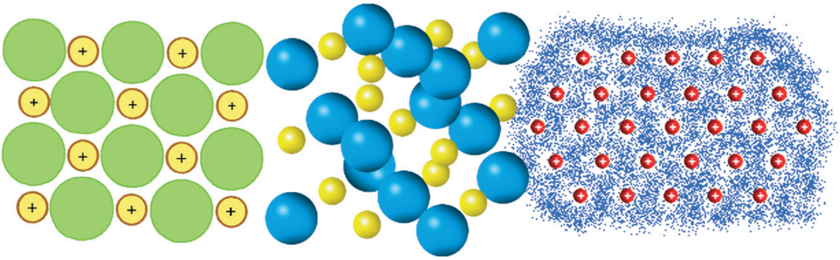
3

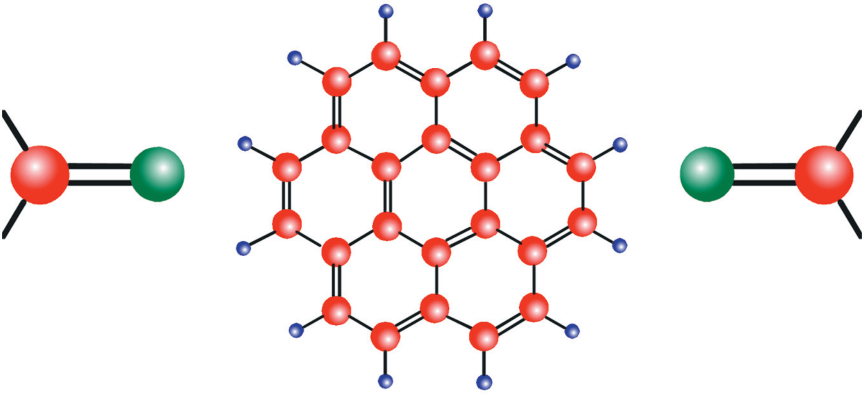
THE CHEMICAL BOND



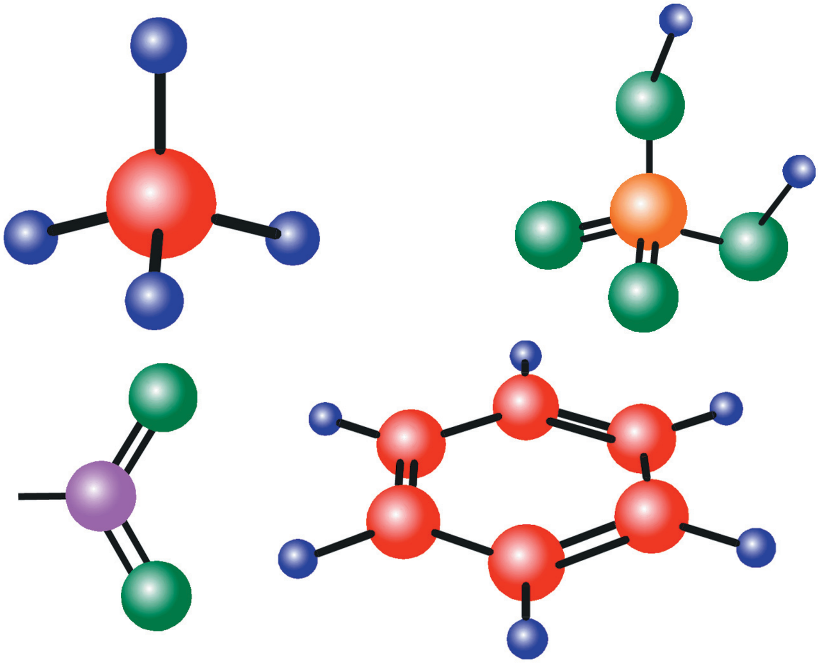
Objectives

- In this lesson, we shall try to understand the bonding between atoms in molecules and substances.
- The different kinds of chemical bonds that we examine are: the ionic bond, the covalent bond, the coordinate bond and the metallic bond.

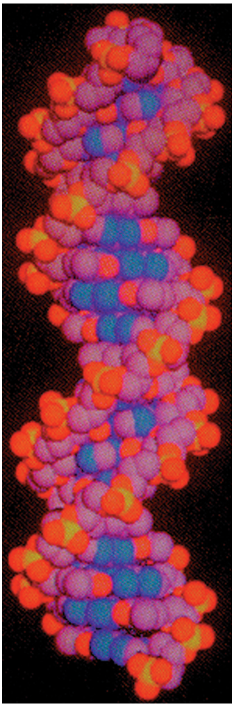




What are chemical bonds?



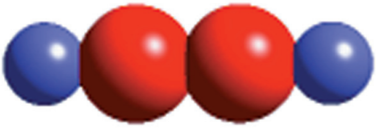
The answer to this question lies in the world around us. It is instructive to imagine what the world would have looked like without chemical bonds.

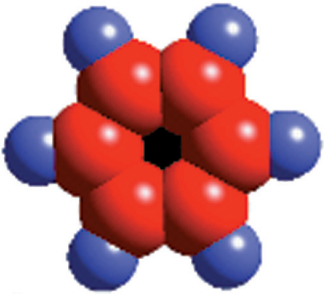


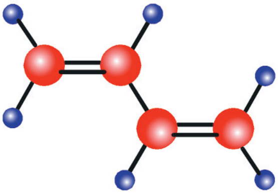
Without chemical bonds, the world would have only free atoms or ions. We would not have the amazing variety of substances. There would be no water and food. And, there would be no life! After all, all living things are made up of millions of atoms and ions bound together, forming molecules.

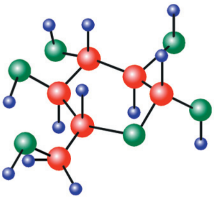
Molecules and materials are a result of bonding of atoms in different ways. This results in

- molecules of various shapes, and
- formation of various substances.



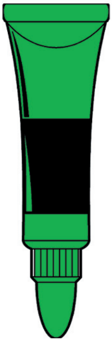


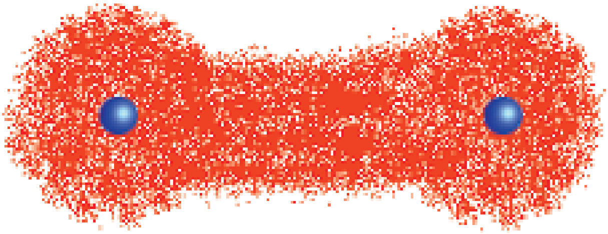




3.1 How are chemical bonds formed?

To bind atoms, we need a glue. Electrons present in atoms provide the magic glue. In other words, if there is sufficient electron density between the nuclei of two atoms, there will be a bond.





Do all the electrons in an atom act as the glue?

The answer is no. Only the valence electrons are involved in the formation of chemical bonds.

Lithium

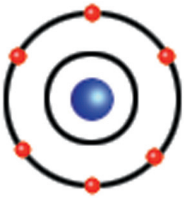
Atomic number — 3
Electronic Configuration, $1s^2$, $2s^1$

Sodium

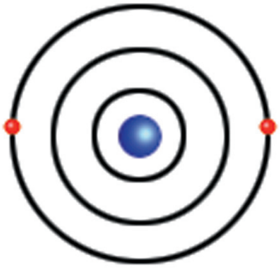
Atomic number — 11
Electronic Configuration, $1s^2\ 2s^2\ 2p^6\ 3s^1$

The 3s electron in the third shell of sodium is the valence electron. In lithium, the 2s electron is the valence electron.

C



O



Mg

Carbon has four electrons in the outermost shell

Oxygen has six electrons in its outermost shell

Magnesium has two electrons in its outermost shell

How many valence electrons are there in each of the above atoms?

The same number as the electrons in the outermost shell.

How do valence electrons bind the atoms together?

Valence electrons provide bonding between atoms in two simple ways:

- by transferring an electron or electrons from one atom to another.

  The bond formed by the transfer of an electron (or electrons) is called the IONIC BOND.

- by sharing of electrons between two or more atoms. This type of bond is called the COVALENT BOND.

In both cases, the atoms involved attain a stable electronic configuration. The stable electronic configuration is that of a noble gas (He, Ne or Ar).

The Octet rule: When chemical bonds are formed, the atoms involved in bond formation achieve the electronic configuration of a noble gas. The noble gases, except helium, have eight electrons in their outermost shells. (Noble gases are at the end of the periods in the periodic table.) This rule applies to both covalent and ionic bonds.

Let us look at the common octet configurations attained by the ions while forming chemical bonds.

Argon — electronic configuration: (Ar – 2,8,8)
Neon — electronic configuration: (Ne – 2,8)

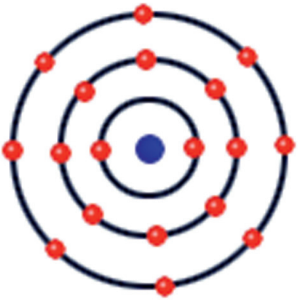
These are the octet configurations attained by most ions. A few ions also attain the helium configuration ($1s^2$).

Ions that have the electronic configuration of neon/argon are:

Neon electronic configuration (2,8)

Ne
O^{2-}
Na^{+}
Mg^{2+}
F^{-}

Argon electronic configuration (2,8,8)



Ar
S^{2-}
Cl^{-}
K^{+}
Ca^{2+}

3.2 Ionic bond

In an ionic bond,

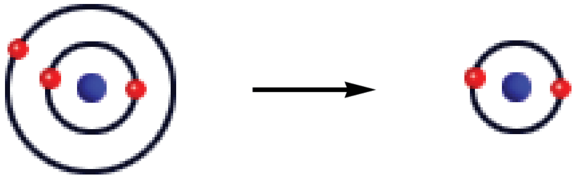
- An electron is (or Electrons are) transferred from one atom to another.
- The atom that transfers the electron (or electrons) attains a positive charge. The atom, therefore, becomes a positive ion or a CATION.
- The atom that receives (or gains) the electron (or electrons) attains a negative charge. The atom, therefore, becomes a negative ion or an ANION.

The idea of the ionic bond was first proposed by Kossel in 1916.

For example,

Lithium atom
Electronic Configuration, $1s^2$, $2s^1$ (2,1)

Lithium ion
Electronic Configuration, $1s^2$ (2)



(Li)

(Li^+)

The outermost shell contains a single electron.

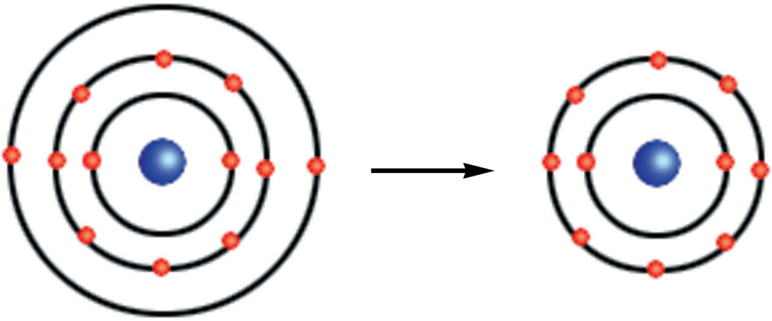
The lithium atom loses the valence electron, and becomes Li^+ cation. This has the electronic configuration of helium. Note that Li^+ is smaller in size than Li. The magnesium atom loses two electrons from the outermost shell to form Mg^{2+} cation. Note that Mg^{2+} is smaller in size than Mg. Think why!

Magnesium atom

Electronic Configuration,
$1s^2$, $2s^2$, $2p^6$, $3s^2$ (2,8,2)

Magnesium ion

Electronic Configuration,
$1s^2$, $2s^2$, $2p^6$ (2,8)

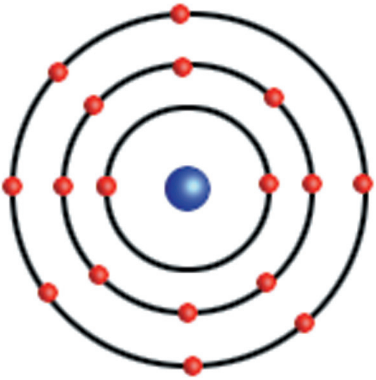


Magnesium atom has two valence electrons.

Remember that the atom that receives an electron (or electrons) gets a negative charge and becomes an anion. The chlorine atom gains (accepts) an electron to become chloride (Cl^-) anion.

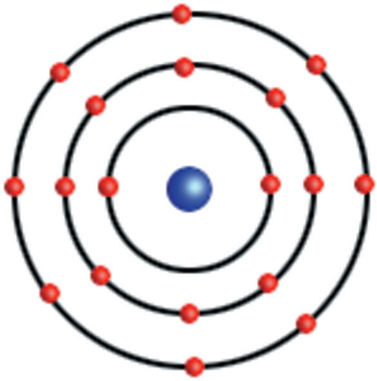
Chlorine atom

Electronic Configuration, (2,8,7)



Chloride ion

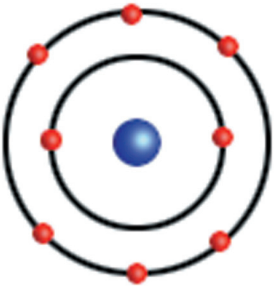
Electronic Configuration, (2,8,8)



The oxide ion (anion) has a negative charge of two (O^{2-}).

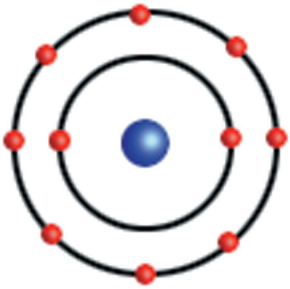
Oxygen atom

Electronic Configuration, (2,6)



Oxide ion

Electronic Configuration, (2,8)

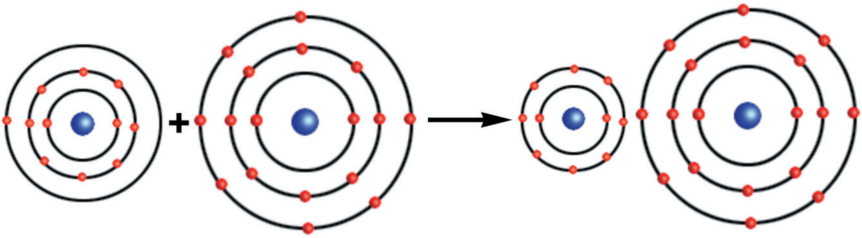


It accepts two electrons.

How is the bond between sodium atom and chlorine atom formed?

Sodium has one valence electron. Chlorine has seven valence electrons. An electron is transferred from the sodium atom to the chlorine atom.

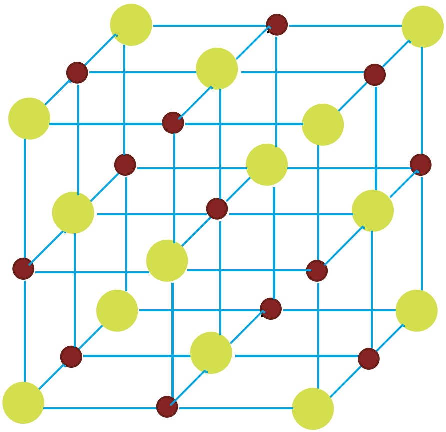
Thus, an ionic bond is formed.



The sodium atom becomes Na^+ (cation) with a single positive charge and the chlorine atom becomes Cl^- (anion) with a single negative charge. Both Na^+ and Cl^- now have stable electron configurations (of Ne and Ar respectively).

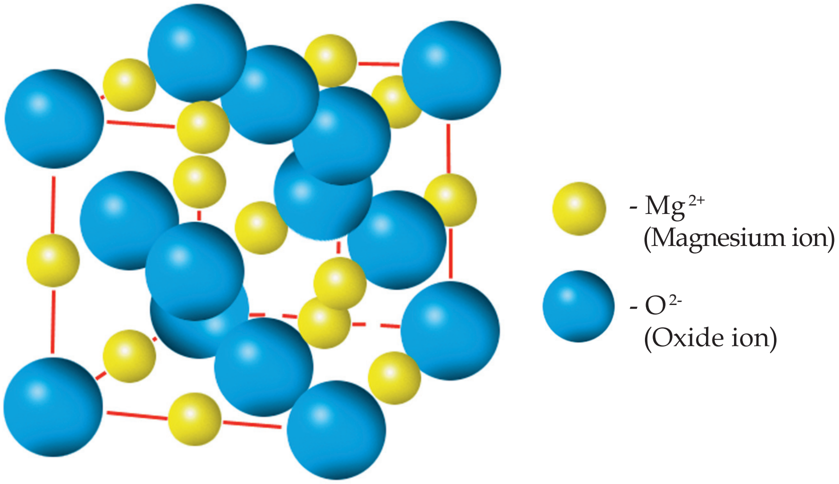
What we showed above was the ionic bond in a NaCl molecule. Such a molecule occurs in vapour phase at high temperatures. NaCl, as we use it, exists as a solid (common salt).

Solid NaCl has alternating Na^+ and Cl^- ions in all directions.



● - Na^+ (Sodium ion)

🟡 - Cl^- (Chloride ion)



Solid MgO has alternating Mg^{2+} and O^{2-} ions in all directions. It has the same structure as solid sodium chloride (NaCl).

Note that both in solid NaCl and MgO, the cations are next to (or surround) the anions. Similarly, the anions are next to (or surround) the cations.

Ionic bonds are generally formed between

- metallic elements of groups 1 and 2,
- non-metallic elements of groups 16 and 17.

H
Li
K
Rb
Cs
Fr

Be
Mg
Ca
Sr
Ba
Ra

and

O
S
Se
Te
Po

F
Cl
Br
I
At

Metallic elements of groups 1 and 2

The metallic elements transfer electrons and become cations.

Non-metallic elements of groups 16 and 17

The non-metallic elements receive electrons and become anions.

Clearly, elements with low ionization energy (e.g., Na, K and other alkali metals) which can give out electrons to become positive ions, readily form ionic bonds with elements of high electron affinity (e.g., halogens).

What would happen if all the chemical bonds were ionic?

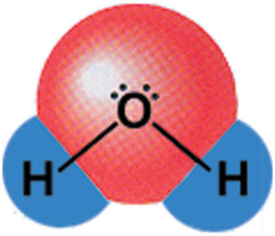
There would be:

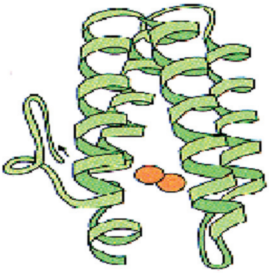
- No oxygen!
- No water!
- No sugar!
- No carbon dioxide!

3.3 Covalent bond

What makes life on earth possible?

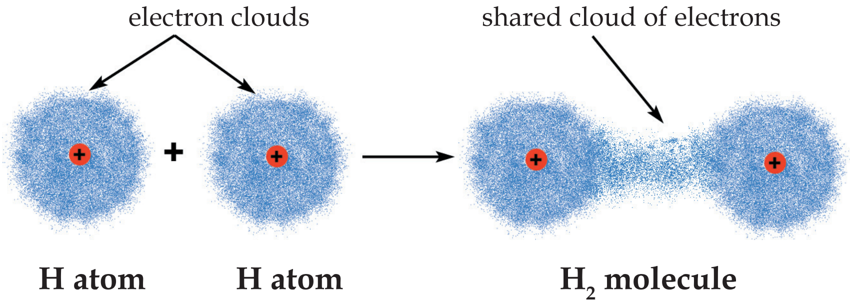
Oxygen, carbon dioxide, nitrogen, proteins and such molecules make life possible on earth. All these compounds in Nature have COVALENT BONDS formed by the sharing of electrons.





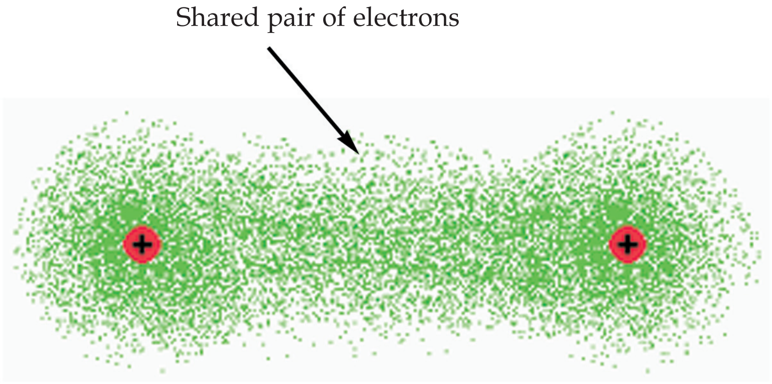
Covalent bonds are formed by the atoms sharing their valence electrons. The shared electrons reside between the nuclei of the atoms forming the bond.

This can be shown in the form of an electron density diagram.



Note that the electron density is high between the nuclei (The valence electron in hydrogen is 1s).

The two atoms in a fluorine molecule share a pair of electrons.



F_2 molecule

(The valence electron in fluorine is 2p).

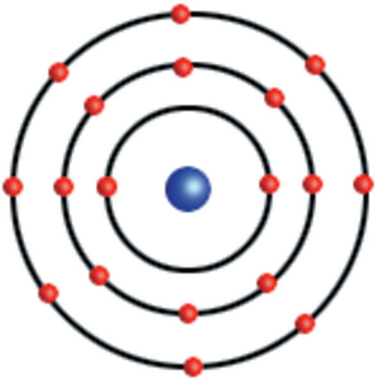
The number of bonds varies with the number of shared electrons. In oxygen, two electrons of each atom are shared. The bond between two oxygen atoms, therefore, involves four electrons.

Chlorine atoms form sodium chloride (NaCl) and chlorine (Cl_2) molecules. **How are the chemical bonds in the two molecules different?**

Chlorine reacts with sodium to form sodium chloride. Here, chlorine receives an electron from sodium and becomes chloride ion (anion).

Chloride ion

Electronic Configuration, (2,8,8)



In a chlorine molecule, the two chlorine atoms share a pair of electrons with each other.

The Cl atom has the electronic configuration $1s^2, 2s^2, 2p^6, 3s^2, 3p^5$. The valence electrons are 3p. Note that both in NaCl and Cl_2, the Cl atoms attain the noble gas configuration (Ar), as required by the octet rule.

The shared electrons between atoms can be from two atoms of the same element as in,

Cl_2 (between two Cl atoms) →

Br_2 (between two Br atoms) →

OR

from two different atoms as in,

HCl (between hydrogen and chlorine atoms) →

HBr (between hydrogen and bromine atoms) →

Hydrogen atoms form a covalent bond as given by:

The two atoms of hydrogen share a pair of two electrons.

Oxygen atoms form covalent bonds as given by:

The two atoms of oxygen share two pairs of electrons.

Nitrogen atoms form covalent bonds as given by:

The two nitrogen atoms share three pairs of electrons.

The covalent bond can be represented in different ways. For example, we can represent HCl, O_2 and N_2 as follows:

HCl

O_2

N_2

Electrons in the valence shell of an atom are represented by dots and crosses. This way of representing bonds is known as the Lewis representation, after G. N. Lewis who first proposed the method. The idea of covalent bond was mooted by Lewis in 1916.

In a covalent bond, two atoms share as many pairs of electrons as are required to attain the stable electronic configuration. Such bonds that connect atom centres are referred to as **sigma bonds** (σ-bonds). In a σ-bond, the electron density is concentrated between the atom centres.

A covalent bond is generally expressed as a line “—” and each line represents a bond. **The number of lines signifies the number of bonds**.

In H_2, there are two electrons forming the covalent bond. In H_2^+ ion, only one electron is involved in bonding the two hydrogens. In other words, H_2^+ ion has a **one-electron bond**.

In H_2, one pair of electrons is shared by two hydrogen atoms (**single bond**).

$$\mathrm{H-H}$$

In O_2, two pairs of electrons are shared by two oxygen atoms (**double bond**).

$$\mathrm{O=O}$$

In N_2, three pairs of electrons are shared by two nitrogen atoms (**triple bond**).

$$\mathrm{N\equiv N}$$

> **Note:** One covalent bond is formed by a pair of electrons. Therefore, to form a double bond, there is need for 4 electrons and to form a triple bond, there is need for 6 electrons.

G. N. Lewis (1875 – 1946)

G. N. Lewis is regarded as one of the greatest chemists of the 20th century. He started as the Head of a little-known Department of Chemistry at the University of California, Berkeley, U.S.A. He went on to make it one of the most famous chemistry departments in the world.

As a chemist, he was far ahead of his time. He contributed to the understanding of chemical bonding, acids and bases, electrolytes and thermodynamics. He was the first to talk of the covalent bond (in 1916).

Lewis greatly enjoyed doing experiments and never lost the thrill of discovering new aspects of chemistry. Even though Lewis himself did not get the Nobel Prize, he produced a galaxy of great students, several of whom received Nobel prizes.

Lewis died as he would have liked, in his laboratory, after making a sample of liquid HCN.

Polar bond: We have learnt that in an ionic bond, there is a transfer of electron(s) from one atom to another ($Na \curvearrowright Cl \rightarrow Na^+ Cl^-$). In a covalent bond, electrons are shared between two atoms ($H : H$). The situation can be in-between. In molecules that contain two different types of atoms (e.g., HCl), the bond will be partly ionic and partly covalent. There will be a small charge, δ, on the two atoms ($H^{\delta+}{-}Cl^{\delta-}$), because the atom which has high electron affinity pulls the electrons more towards it. Such bonds are called **polar bonds**.

Pauling gave a scale that measures the attraction of an atom for an electron. This is called the **electronegativity scale**. The values of electronegativity of a few elements are given below:

H (2.1)
Li (1.0), Be (1.5), B (2.0), C (2.5), N (3.0), O (3.5), F (4.0)
Cl (3.0)

We see that oxygen and halogens have high electronegativity.

In order to understand how electrons in atoms are involved in forming a covalent bond, we need to probe more into the electron structure of atoms. We said before that it is convenient to classify electrons in atoms and designate them as **s**, **p**, **d**, and **f** orbitals. Actually, there is need for an even greater categorization of electrons in atoms to provide individual identities to them. **Thus, p, d, and f orbitals are further subdivided into 3, 5, and 7 sub-orbitals respectively, with different directional or spatial features.**

In each of such sub-orbital, there can be a maximum of two electrons.

That is, each of the three **p** sub-orbitals can have two electrons, making a total of 6 electrons in the **p** orbital. The **s** orbital cannot be further subdivided and it can have a maximum of two electrons.

Let us now take a count of the maximum number of electrons in different orbitals, remembering that any given sub-orbital can have only two electrons.

Orbital	**Maximum number of electrons**
s-orbital	2
p-orbital	3 x 2 = 6
d-orbital	5 x 2 = 10
f-orbital	7 x 2 = 14

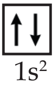
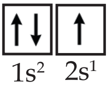
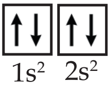
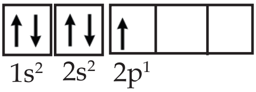
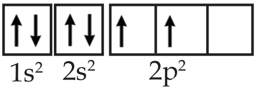
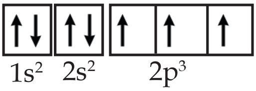
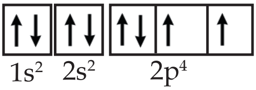
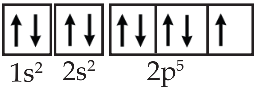
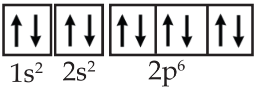
The two electrons in each sub-orbital are further distinguished by a property called **spin**. This is indicated by arrows pointing up ↑ or down ↓ as follows:

s-orbital : 2 electrons $\boxed{\uparrow\downarrow}$

p-orbital: 3 x 2 electrons $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}$

Let us now write down the electronic configuration of a few elements using the above prescription.

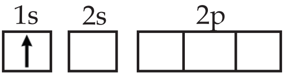
Atomic number	**Name**	**Number of electrons**	**Description of electrons**
1	Hydrogen(H)	1	$\boxed{\uparrow}$ $1s^1$

2	Helium (He)	2	 $1s^2$
3	Lithium (Li)	3	 $1s^2$ $2s^1$
4	Beryllium (Be)	4	 $1s^2$ $2s^2$
5	Boron (B)	5	 $1s^2$ $2s^2$ $2p^1$
6	Carbon (C)	6	 $1s^2$ $2s^2$ $2p^2$
7	Nitrogen (N)	7	 $1s^2$ $2s^2$ $2p^3$
8	Oxygen (O)	8	 $1s^2$ $2s^2$ $2p^4$
9	Fluorine (F)	9	 $1s^2$ $2s^2$ $2p^5$
10	Neon (Ne)	10	 $1s^2$ $2s^2$ $2p^6$

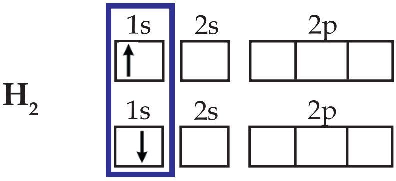
By writing the electronic structure in the above manner, we have made sure that no two electrons in an atom have the same description. Or, each electron in an atom has a unique description.

Now, let us see how simple covalent bonds between two atoms are formed. To do so, we shall look at four simple molecules: H_2, F_2, HF and H_2O.

The electronic structure of a hydrogen atom is given by $1s^1$. We write this as follows:

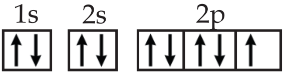


The 1s orbital is partially filled.
The formation of H_2 molecule can be represented as the sharing of two 1s electrons belonging to the two H atoms.



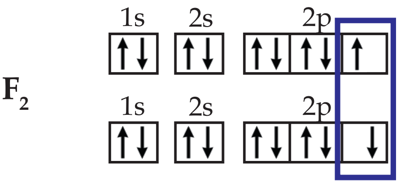
The two electrons involved in forming the bond are shown by arrows in opposite directions (spins). The rectangular box encompassing the two electrons represents the overlap of the two electron orbitals.

The electronic configuration of a fluorine atom, $1s^2\,2s^2\,2p^5$ is pictorially written as follows:

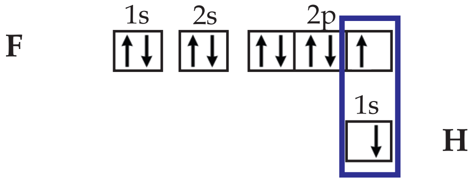


In a fluorine atom, one 2p orbital is only partially filled.

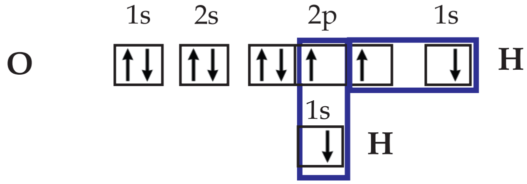
A fluorine molecule is formed by sharing of the partially filled **p** orbitals belonging to two F atoms.



The formation of the bond in HF can be shown as:



The formation of H_2O can be written as:

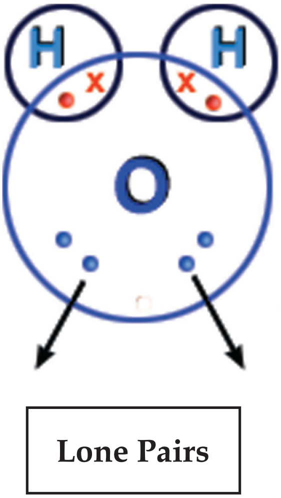


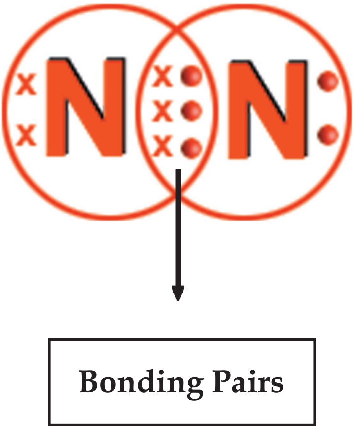
Why helium does not form He_2 molecule?

Helium gas contains He atoms. (In fact, all noble gases contain only atoms.) This is because helium has two electrons in the outermost (valence) shell ($1s^2$).

We see that two electrons with opposite spins are already present in the atom. There is no way an electron from another atom can form a bond. Note that overlap can occur only when there is one electron in a sub-orbital (only one arrow).

All the valence electrons of an atom may not participate in the **formation of covalent bonds**. The pair of electrons that participate in bond formation is called the **bonding pair**. The pair of electrons that does not participate in bond formation is called the **non-bonding pair** or **lone pair**.





3.4 Bond distances and bond energies

One can determine structures of molecules, by studying crystals containing the molecules, using X-rays. Such studies give distances between the atoms and the angles between them.

Bond distances are measured in Angstroms.
1 Angstrom (Å) = 10^{-8} cm = 0.1 nanometer = 0.1 nm

For example,

$C-H$	1.0 Å	=	0.1 nm
$C-C$	1.54 Å	=	0.154 nm
$C=C$	1.34 Å	=	0.134 nm
$C\equiv C$	1.20 Å	=	0.12 nm

Bond angles are important parameters. In CH_4 (methane), the HCH angle is the tetrahedral angle (~ 109° 28′). In acetylene, the HCC angle is 180° and it is linear. In benzene, the CCC and CCH angles are 120° each.

Will there be a change in energy when two atoms combine? When two atoms combine to form a chemical bond, ENERGY IS RELEASED. By releasing energy, greater stability is attained. That is, a molecule of two atoms is more stable, or has a lower potential energy, than two separate atoms. Typical bond energies (in kcal mol^{-1}) are given below:

H—H	104
Cl—Cl	58
C—H	99
C—C	83
C=C	147
C≡C	201

Note that 1 kcal = 4.187 kJoules (kJ).

A double bond has roughly twice the energy of a single bond and a triple bond has roughly three times the energy of a single bond.

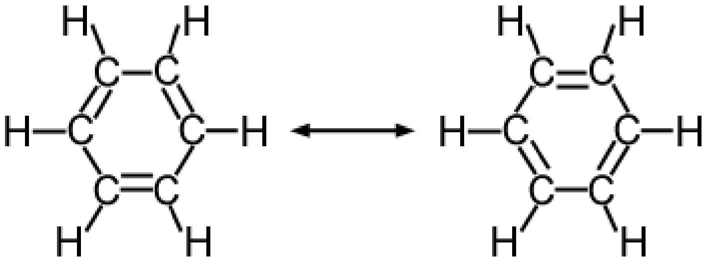
The energy of the bond between the nitrogen atoms in N_2 is greater than that of the bond in H_2. This is because N_2 has a triple bond and H_2 has a single bond.

Which of the following compounds requires most energy to break it into its elements?

Hydrogen chloride (HCl)	HCl has a single bond.
Oxygen (O_2)	Oxygen atoms share two pairs of electrons.
Carbon monoxide (CO)	The total number of electrons in CO is the same as in N_2.

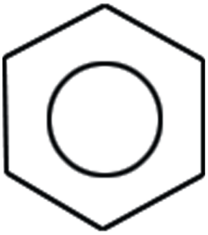
3.5 Resonance

Benzene is a resonance hybrid of two structures.



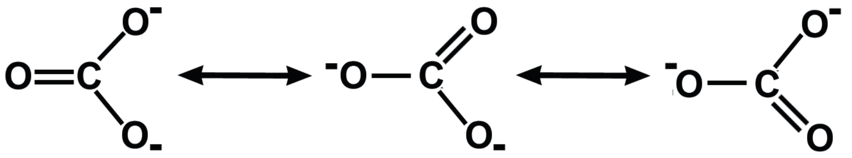
These structures were proposed by Kekule in 1866. Here, the carbon–carbon double bonds and single bonds exchange places. Therefore, these bonds are between single and double bonds. The length of the C—C bond in benzene is 1.4 Å.

Benzene is conveniently represented as,

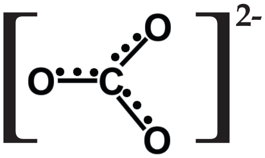


Resonance structures are not real structures, and therefore cannot be prepared or isolated in the laboratory. They are "imaginary" and contribute to the real structure which imbibes the properties from all the resonance structures. Such resonance stabilizes molecules. Resonance structures are not unique to benzene. Even simple molecules and ions involve resonance structures. We give two examples as follows.

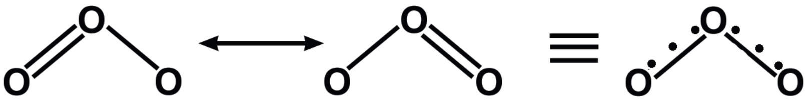
Carbonate ion, CO_3^{2-}:



This may be represented by

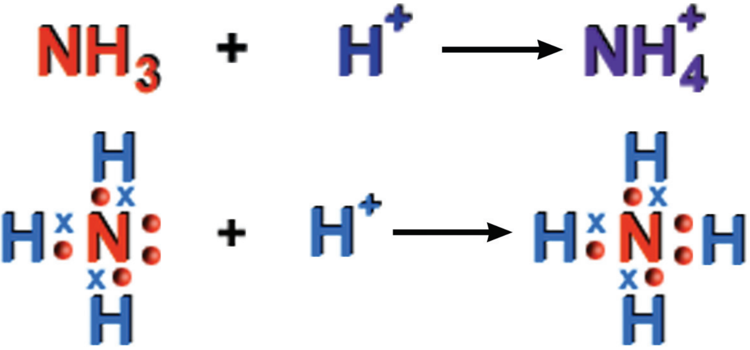


Ozone, O_3:



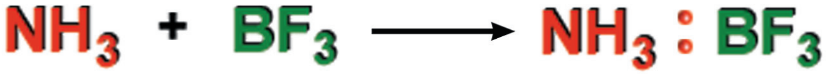
3.6 Coordinate bond

There is another type of bond called the coordinate bond. Here, an atom forming the bond donates a pair of electrons to another atom. Let us look at the simplest example of this bond, the ammonium ion (NH_4^+).

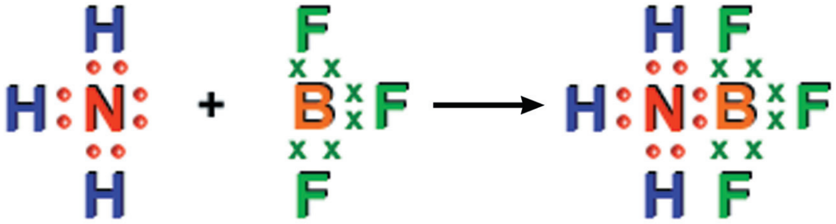


Here, H^+ has no electron. NH_3 donates its lone pair of electrons. H^+ loves to receive the electrons from NH_3.

Another example is the bond formed between the nitrogen atom in NH_3 and the boron atom in BF_3.



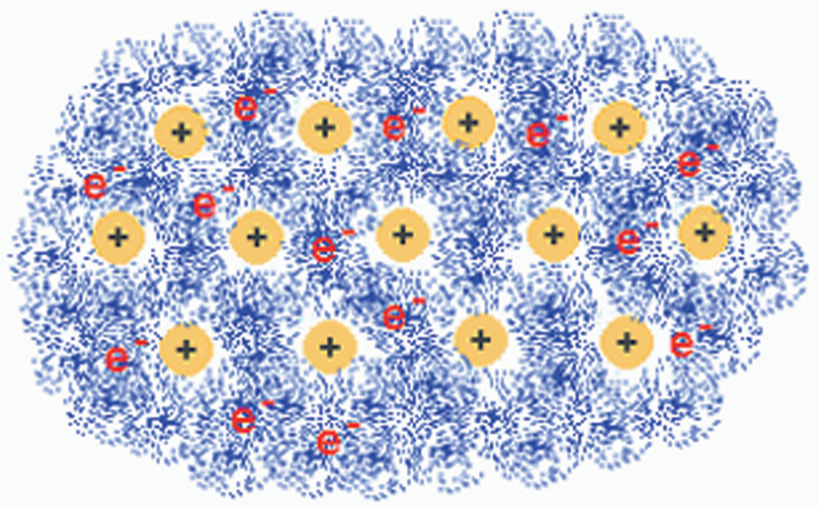
The nitrogen atom in NH_3 donates a pair of electrons to BF_3. BF_3 is **electron deficient** and loves to accept the electrons.



Such bonds are commonly found in certain transition metal compounds which are called **coordination compounds**. In these compounds, molecules generally donate their lone pair of electrons to the metal.

Molecules which donate electrons (like NH_3) are called **Lewis bases**. Molecules which receive electrons (like BF_3 and $AlCl_3$) are called **Lewis acids**. Lewis bases surround simple metal ions in the solution state. For example, Na^+ in water is present as $Na^+ (H_2O)_6$. Here, H_2O is the Lewis base. Lewis acids and bases are different from the regular acids that we read about in Lesson 1. Acids like HCl, HNO_3 and H_2SO_4 are acids by virtue of giving out a proton (H^+) in water solution. These acids are called **Brönsted acids**.

3.7 Metallic bond

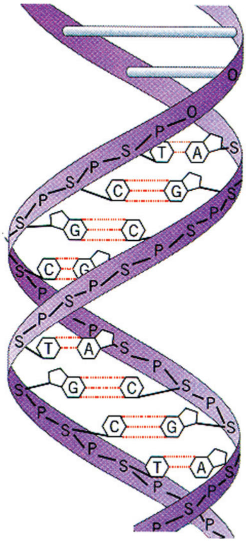


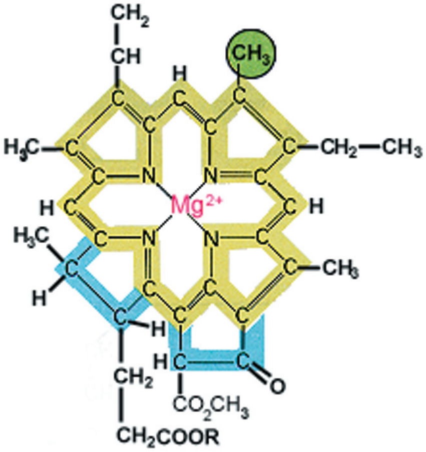
It is common practice to call the bonds in metals as metallic bonds.

Metals have loosely moving electrons. Since the valence electrons move freely, metals can be considered to have positively charged ions instead of neutral atoms. The attraction between the positively charged ions and the loosely moving electrons bind the atoms in metals.

Conclusions

We have looked at bonds in simple molecules. The world around us is full of complex molecules of varied shapes and forms.





Chlorophyll

Deoxyribose nucleic acid (DNA)

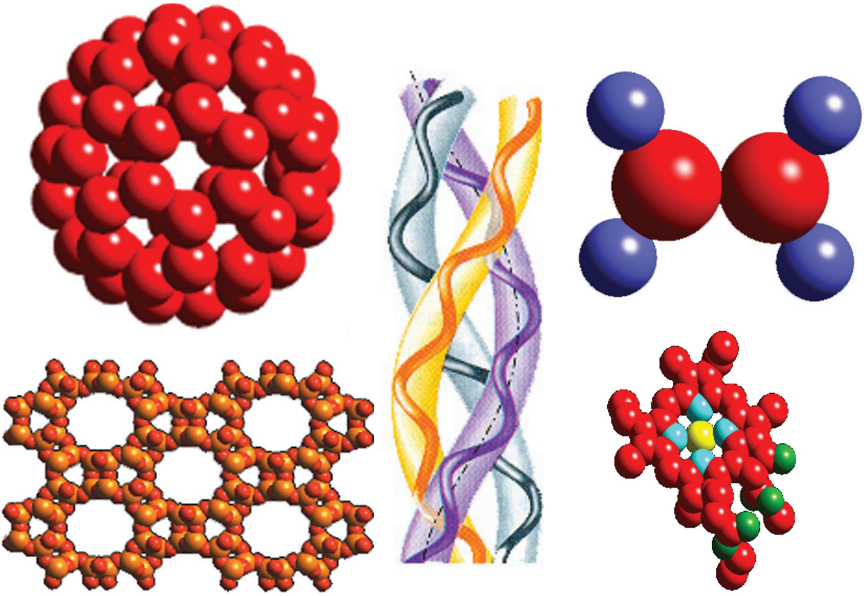
DNA

To understand the shapes and properties of such molecules, we need to probe more into the nature of chemical bonds.

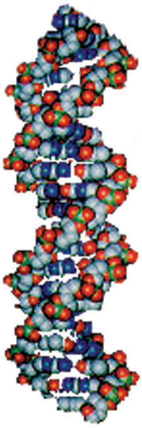
Chemistry saved my life!

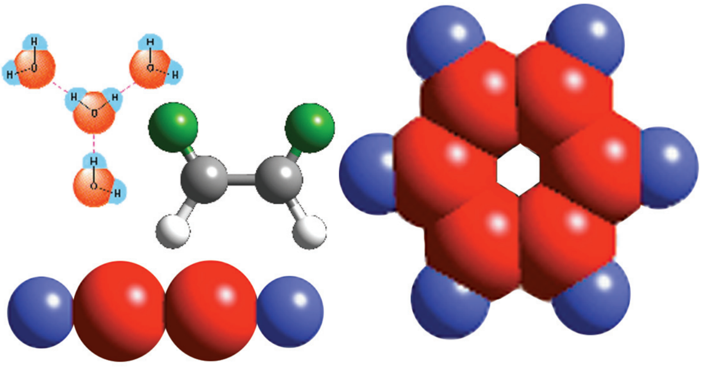
An elderly gentleman went to the chemistry department of a major university and wanted to make a donation. When he was asked why, he gave the following story. “During the Second World War, I was caught with some others by enemy troops. The captain of the troops decided to send us to a concentration camp. Before sending us, he asked each of us about our professions. I told him that I was a chemist. He immediately asked me: ‘Do you know the Kekule structures of benzene?’ I wrote them. For some reason, he let me free.”

4



STRUCTURES AND SHAPES OF MOLECULES





Objectives

We shall try to understand the following aspects of molecules in this lesson:

- the relation between structures and shapes of molecules.
- the Valence Shell Electron Pair Repulsion (VSEPR) method to understand shapes.
- hybridization and its relation to shapes.
- diversity in shapes and structures of molecules.
- the seminal importance of the hydrogen bond.
- biopolymers and man-made polymers.

The world of molecules is fascinating. This is because molecules show a great variety of forms and properties. One of the main tenets of modern chemistry is that the properties of all forms of matter depend on the properties of molecules, particularly their structures and shapes.

In the previous lesson (Lesson 3), we examined different types of chemical bonds. We also saw how bond distances and bond energies are related to the nature of the chemical bond. Bond distances and other structural features of molecules are determined mainly by using X-ray diffraction of crystals. In recent years, instrumentation and computer capabilities have advanced so greatly that structures of most molecules can be determined within a matter of few hours. Structures of even larger molecules, such as proteins, are determined by means of X-ray diffraction, though the procedure takes considerably longer time. The structural information obtained by X-ray diffraction is supplemented or corroborated by the use of spectroscopic methods. Of the many spectroscopic methods that are employed today, nuclear magnetic resonance (NMR) spectroscopy is by far the most effective in solving structural problems.

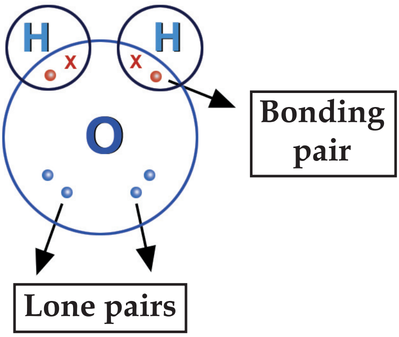
In this lesson, we shall first examine the relation between the structures and shapes of simple molecules and later extend these ideas to larger molecules including the molecules of life.

4.1 What are the factors that determine the shapes of simple molecules?

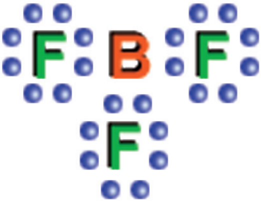
A simple way to understand the shapes of molecules is by the **VSEPR** method.

VSEPR stands for **Valence Shell Electron Pair Repulsion**. According to this method, the direction of bonds around an atom in a molecule depends upon the number of both bonding and non-bonding electron pairs in the valence shell of the atom. Generally, the geometrical shape that places the electron pairs as far as possible is favoured.

Let us recall that, the electron pairs that participate in bond formation are the **bonding pairs**. The electron pairs that do not participate in bond formation are the **non-bonding pairs** or **lone pairs**.



In the molecule BF_3, the three bonding electron pairs around B form an equilateral triangle, because this arrangement places them far apart.



BF_3 is, therefore, a planar molecule. In CH_4, the bonding electron pairs favour a tetrahedral arrangement.

In NH_3 and H_2O, we have non-bonding pairs in addition to bonding pairs. The four electron pairs around N (in NH_3) or O (in H_2O) occupy vertices of a tetrahedron. In NH_3, the three hydrogen atoms occupy the three corners of the tetrahedron forming a pyramid and the remaining lone pair occupies the apex of the pyramid. In H_2O, the two hydrogens occupy the two corners of the tetrahedron and the lone pairs occupy the remaining two positions (see the figure given earlier).

The geometry of $HgCl_2$ is linear because Hg (mercury) has only two electron pairs around it. They are best placed 180° with respect to each other.

Let us write down the rules.

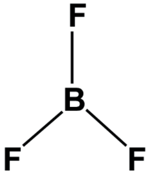
According to the **VSEPR** method, the shapes of molecules are determined by the repulsion between the electron pairs.

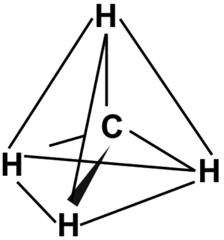
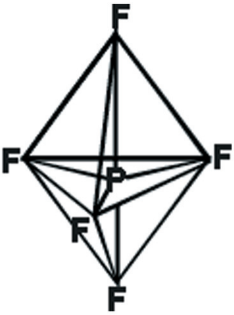
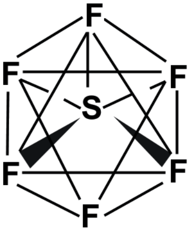
- The electron pairs arrange themselves in such a way that the repulsion between them is minimum.
- The molecule then acquires minimum energy and maximum stability.
- The lone pairs also participate in determining the shapes of molecules.
- The repulsion of the other pairs of electrons by the lone pair is stronger than that of a bonding pair.

The strength of repulsion between electron pairs is as follows: lone pair-lone pair > lone pair-bonding pair > bonding pair-bonding pair.

Thus, the number of bonding pairs and lone pairs in the central atom contribute towards determining the shapes of molecules and ions.

Shapes of simple molecules and ions

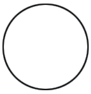
No. of electron pairs	Arrangement of electron pairs	Shape	Examples
2	Linear	**Cl——Hg——Cl**	$BeCl_2$, $HgCl_2$
3	Trigonal planar		BF_3, BCl_3 CO_3^{2-}, NO_3^-

4	Tetrahedral		SiF_4, CH_4, NH_4^+, PO_4^{3-}
5	Trigonal bipyramidal		PCl_5
6	Octahedral		SF_6, $[PF_6]^-$

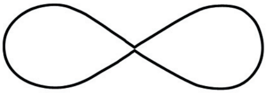
4.2 Hybridization

Electrons are not just particles. They have wave properties. Orbital is the term used to describe an electron in the wave picture. Because they are waves, we can mix the different types of waves (electrons).

Different orbitals (electrons) have different shapes.



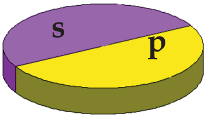
s-orbital



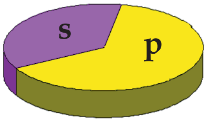
p-orbital

We add salt and pepper according to our taste. Similarly, we can mix **s** and **p** electrons to attain a desired mix. That such mixing can be done was first proposed by Linus Pauling.

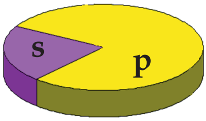
For example, **sp**, **sp^2** and **sp^3** contain different proportions of **s** and **p** electrons.



In **sp**, **s** character is ½ or 50%.
The **p** character is also 50%.



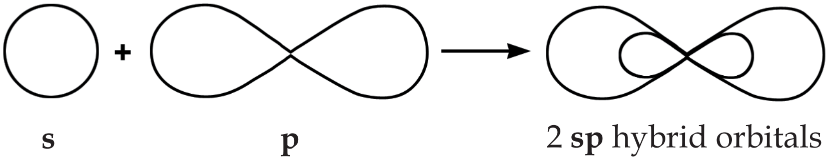
In **sp^2**, **s** character is ⅓ or 33.3%.
The **p** character is 66.7%.



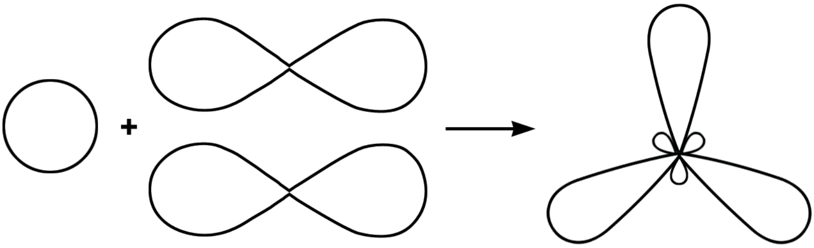
In **sp^3**, **s** character is ¼ or 25%.
The **p** character is 75%.

Since the **s** orbital is spherical and the **p** orbital is shaped like a dumbbell, mixing of **s** and **p** orbitals in different proportions results in different shapes. Mixing of orbitals is called **hybridization**. The mixed orbitals are called **hybrid orbitals**.

For example, when one **s** orbital and one **p** orbitals are mixed, we get two **sp** hybrid orbitals. The **sp** hybrid orbital is linear.

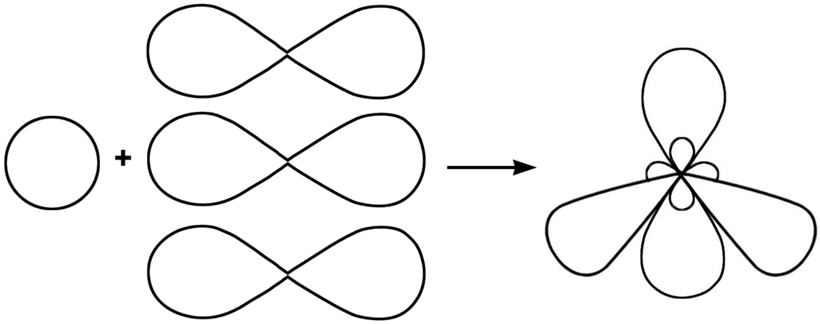


When one **s** orbital is mixed with two **p** orbitals, we get three **sp^2** hybrid orbitals. The **sp^2** hybrid orbital has a trigonal planar shape.



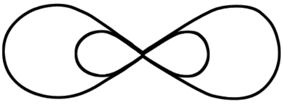
three **sp^2** hybrid orbitals
(trigonal planar)

When we mix one **s** and three **p** orbitals, we get four **sp^3** hybrid orbitals. The **sp^3** hybrid orbital has a tetrahedral shape.

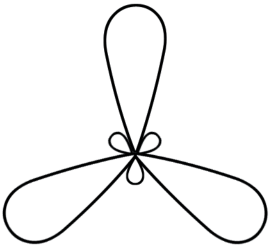


four **sp^3** hybrid orbitals
(tetrahedral)

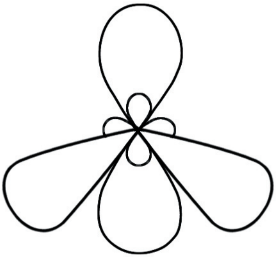
Let us summarize the shapes of the three orbitals formed by mixing the **s** and the **p** orbitals. **sp is linear, sp^2 is trigonal planar and sp^3 is tetrahedral.**



sp – linear



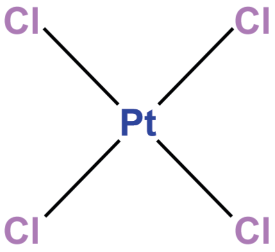
sp^2 – trigonal planar



sp^3 – tetrahedral

It is not only the **s** orbitals and the **p** orbitals that can be mixed to give different shapes. We can also mix other types of orbitals. Let us see how different shapes of molecules are obtained by mixing **d**, **s** and **p** orbitals. Mixing of one **d**, one **s**, and two **p** orbitals gives **dsp^2** hybrid orbitals.

Example of **dsp^2**:

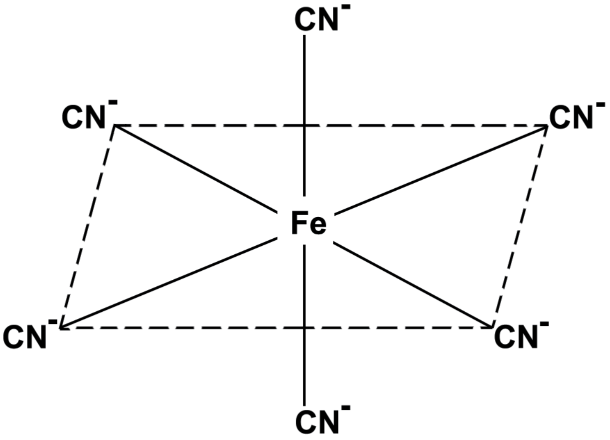


[$PtCl_4$]

This has a square-planar geometry.

We can mix two **d**, one **s** and three **p** orbitals to get **d^{2}sp^3** hybrid orbitals.

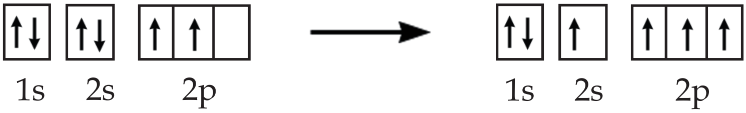
Example of $\mathbf{d^2sp^3}$:



$[Fe(CN)_6]^{3-}$

It is octahedral.

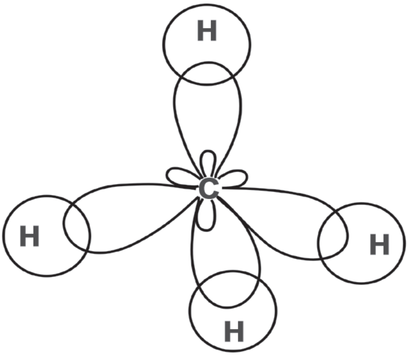
Let us look at the mixing of orbitals in carbon compounds. The electronic configuration of carbon is $1\mathbf{s}^2\,2\mathbf{s}^2\,2\mathbf{p}^2$. In order to form orbitals from the mixing of **s** and **p** orbitals, the electronic configuration of carbon changes to $1\mathbf{s}^2\,2\mathbf{s}^1\,2\mathbf{p}^3$.



Now, one 2**s** can be mixed with one 2**p**, two 2**p** or three 2**p** orbitals to give **sp**, $\mathbf{sp^2}$ and $\mathbf{sp^3}$ orbitals as follows:

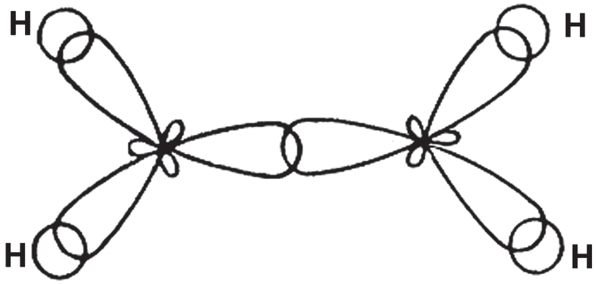
1 (**s**) + 1 (**p**) $\longrightarrow$ 2 (**sp**) + 2 (**p**) left remaining.
1 (**s**) + 2 (**p**) $\longrightarrow$ 3 ($\mathbf{sp^2}$) + 1 (**p**) left remaining
1 (**s**) + 3 (**p**) $\longrightarrow$ 4 ($\mathbf{sp^3}$)

In methane, CH_4, each of the $\mathbf{sp^3}$ orbitals of the carbon atom overlaps with the 1**s** orbital of a hydrogen atom.



Methane is a tetrahedral molecule. Just like CH_4, CCl_4 is also tetrahedral and so are many derivatives of methane. All the four C—H bonds in CH_4 are sigma bonds (σ-bonds). Remember that a sigma bond is a bond along the axis of the bond (or is due to the electron density between the two atom centres).

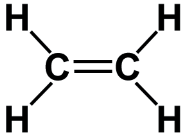
In ethylene, C_2H_4, two carbon atoms combine with four hydrogen atoms. Here, each carbon atom makes use of the **sp²** orbitals (which are trigonal). Two of the **sp²** orbitals of each carbon atom overlap with the 1s orbitals of hydrogen atoms. The remaining (third) **sp²** orbital of the carbon atom overlaps with that of the other, forming a C—C bond.



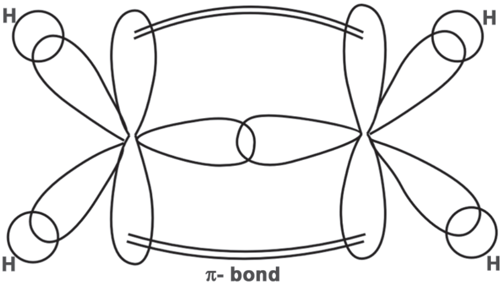
That is, each carbon atom forms two sigma bonds (σ-bonds) with two hydrogen atoms and one σ-bond with another carbon atom.

Note that after forming **sp²** orbitals, there will be one **p** orbital left on each carbon atom. These **p** orbitals remain in a direction perpendicular to the bond formed by **sp²** orbitals. The two **p** orbitals form a *π* bond (pi-bond).

When we write ethylene, C_2H_4 as



one of the bonds between the two carbon atoms corresponds to that formed by the two **sp²** orbitals. The other is due to the π bond. The π bond is perpendicular to the direction of the σ-bond between the two carbon atoms.



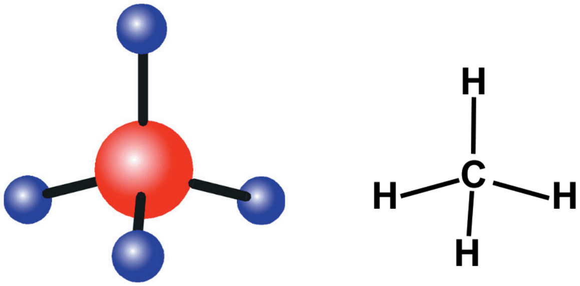
Acetylene is an example of **sp** hybridization.

$$H-C\equiv C-H$$

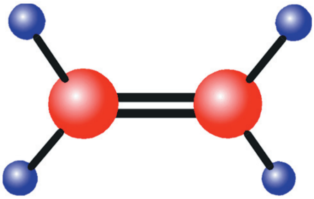
What is the interpretation of the triple bond here? How many π (pi) bonds do we have here? We have two π bonds between the carbon atoms and one σ-bond. The carbon-hydrogen bond is a σ–bond. The two π bonds are perpendicular to each other and they are both perpendicular to the C—C σ-bond.

4.3 Shapes of simple molecules

We often look at molecules using ball and stick models as shown below:



Methane

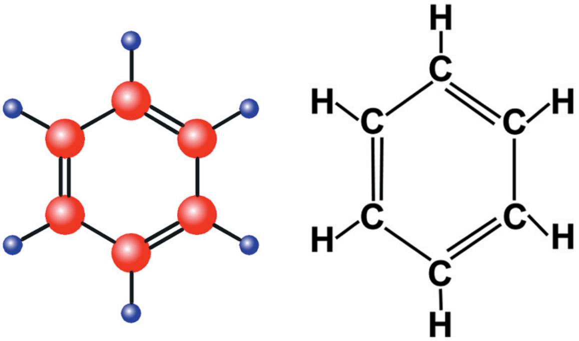


$H_2C{=}CH_2$

Ethylene

$HC{\equiv}CH$

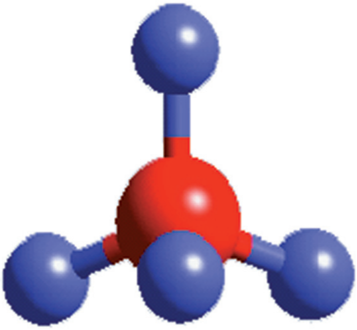
Acetylene



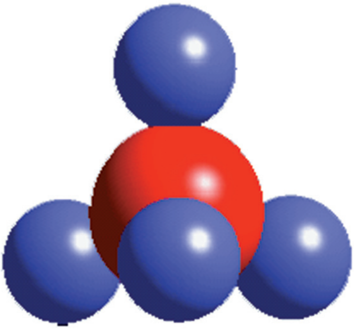
Benzene

Ball and stick models do not give an idea of the real molecular shapes. Space-filling models give a better picture of the shapes. Let us look at a few space-filling models.

Methane

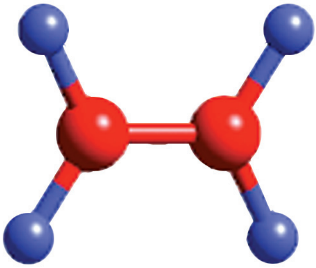


Ball and stick model

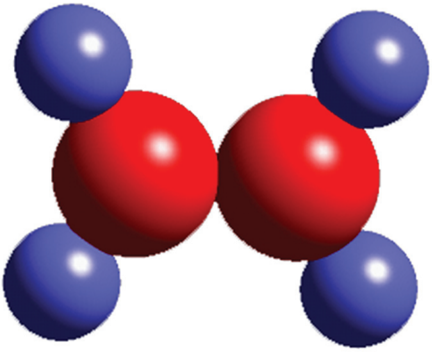


Space-filling model

Ethylene

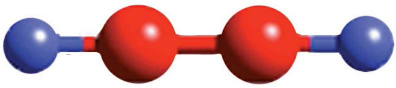


Ball and stick model

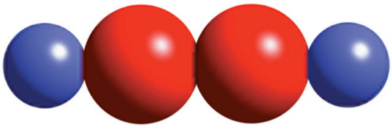


Space-filling model

Acetylene



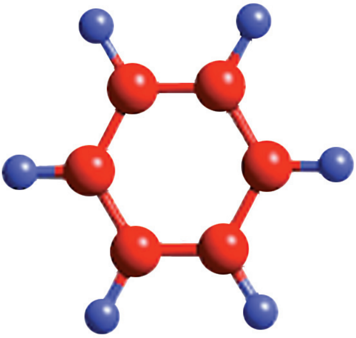
Ball and stick model



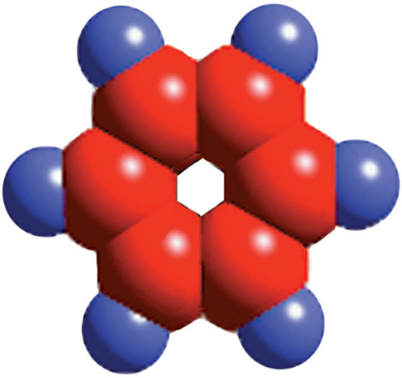
Space-filling model

🔵 – Hydrogen 🔴 – Carbon

Benzene



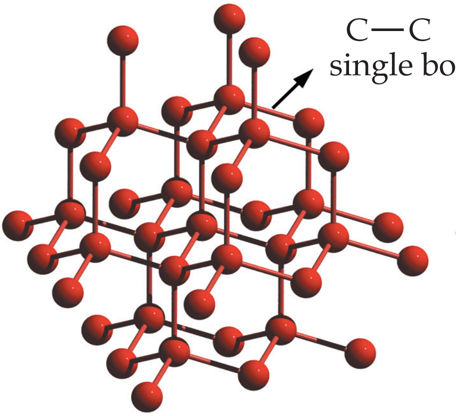
Ball and stick model

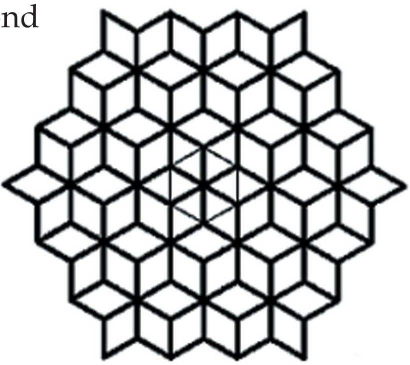


Space-filling model

Diamond consists of an infinite network of C—C single bonds of 1.54Å. The carbon atoms are tetrahedrally bonded (**sp**^{3}).

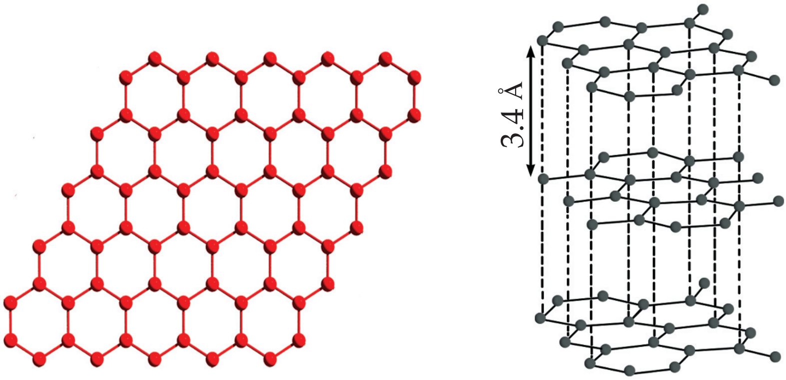
Diamond





Graphite consists of six membered rings made of carbon–carbon bonds of 1.34 Å. Observe how the carbon atoms are stacked in graphite.

Graphite

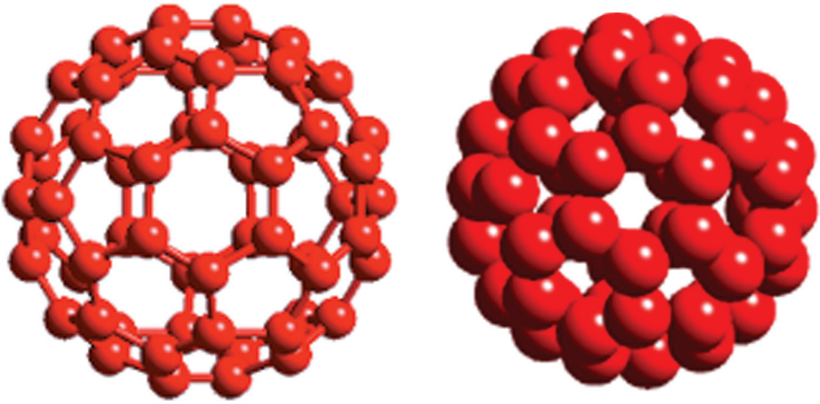


Graphite is an infinite planar structure formed by **sp²** carbons.

The new form of carbon discovered in 1985, **Buckminster fullerene**, has the formula C_{60}.

It is a perfect sphere and the bond distance between carbon atoms is around 1.4 Å. It looks like a football. C_{60} is popularly called **bucky ball**.

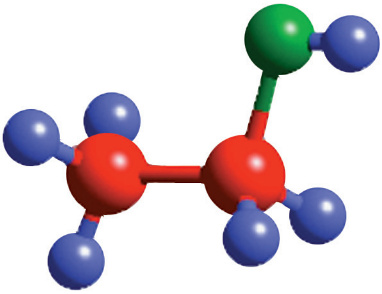
C_{60}



Ball and stick model Space-filling model

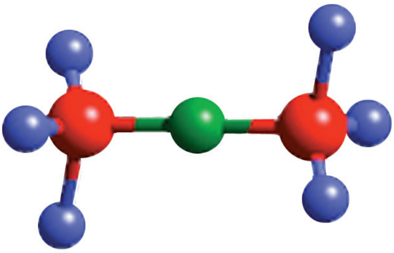
4.4 Isomers

Some carbon compounds have the same molecular formula, but have different structural formulae. For example, the compound C_2H_6O can have two different structural formulae.



Ethanol

C_2H_5OH



Methoxymethane
(Dimethylether)

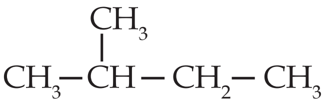
CH_3 O CH_3

● – Carbon ● – Hydrogen ● – Oxygen

These two are isomers.

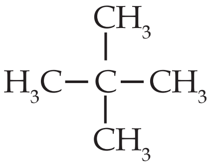
We can have different isomers of simple hydrocarbons as shown below:

$CH_3-CH_2-CH_2-CH_2-CH_3$ normal pentane



$CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_2-CH_3$

isopentane

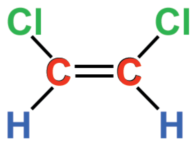


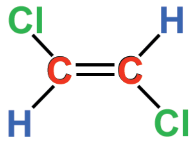
$H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$

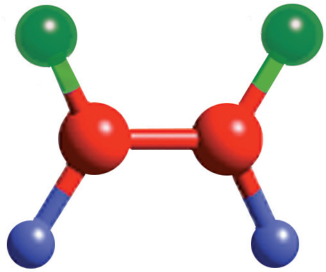
neopentane

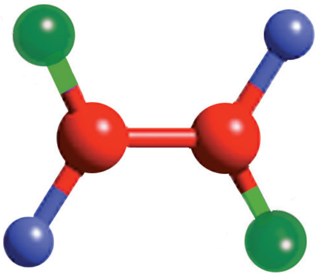
In disubstituted benzenes, ortho-, meta- and para- isomers are possible (see Lesson 1).

Look at the following structures of dichloroethylene or ethylenedichloride.



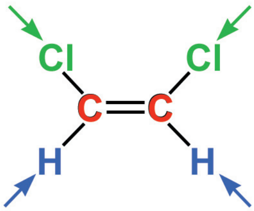




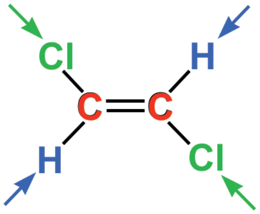


They have the same molecular formula $C_2H_2Cl_2$, but their structural formulae are different. The two structures are **geometrical isomers**.

Let us look again at $C_2H_2Cl_2$.



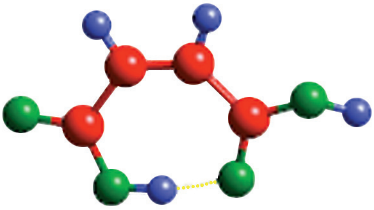
(a)



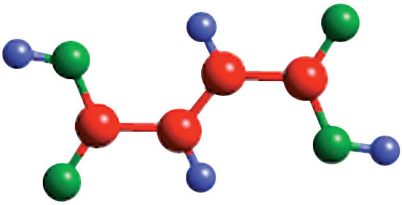
(b)

Note the position of Cl and H in figures (a) and (b). In figure (a), the chlorine atoms are on the same side of the double bond. In figure (b), they are on opposite sides of the double bond. Structure (a) is **cis form** and structure (b) is **trans form**.

Another example of **cis-trans isomers** is maleic and fumaric acids. They have the formula $\mathrm{HOOC(H)-C=C-(H)COOH}$.



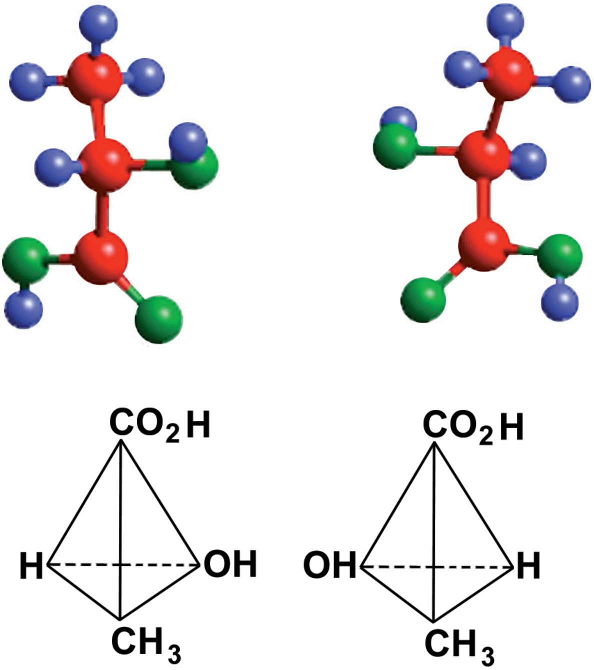
Maleic acid



Fumaric acid

🔴 – Carbon 🔵 – Hydrogen 🟢 – Oxygen

Louis Pasteur showed that isomers can exist in two different arrangements which are not superimposable, but are mirror images of each other. Such isomers are called **optical isomers**.



Optical isomers of lactic acid

These are like our hands; the left and right hands are mirror images.

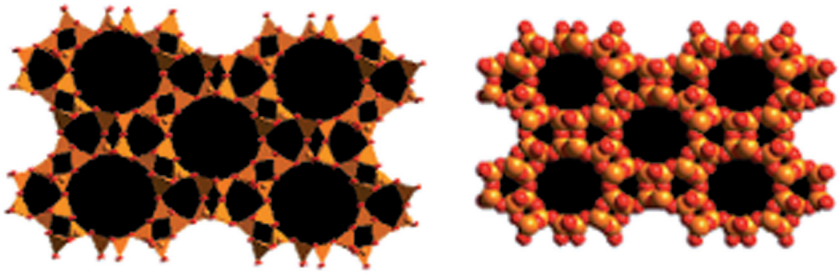
Several compounds that occur in Nature exhibit optical isomerism. The important property that distinguishes the two optical isomers is the optical activity. One of the isomers rotates the plane of polarized light to the right and another rotates it to the left. If we have a mixture containing equal amounts of the two isomers, there will be no rotation of the plane of polarized light. Such a mixture is called a **racemic mixture**. There are methods to separate the two isomers from such a mixture.

Optical activity (and isomerism) is found when a carbon atom is attached to four different groups (as in lactic acid above). Such carbon atoms are asymmetric. Asymmetric molecules are called **chiral molecules**. Chirality is an important property. Many of the drugs (medicines) we take are active (or have the desired effect) only when the molecules are chiral.

Cyclohexane, C_6H_{12}, can exist in **boat** and **chair** forms. These are called **conformers**. Find out what these are.

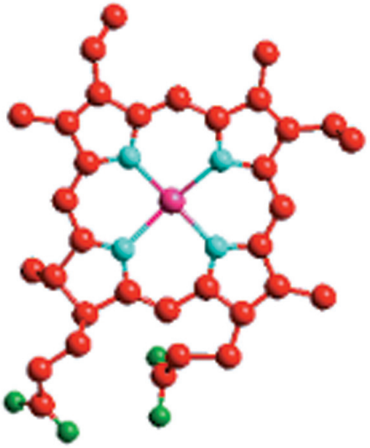
4.5 Some complex structures and shapes

Zeolites



Zeolites are aluminosilicates. They are used to prepare many important chemicals. The cages (big circular holes) are used for carrying out reactions of only those molecules which can be accommodated in the cages.

Haem in Haemoglobin



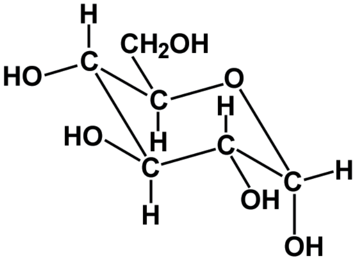
Ball and stick model

Space-filling model

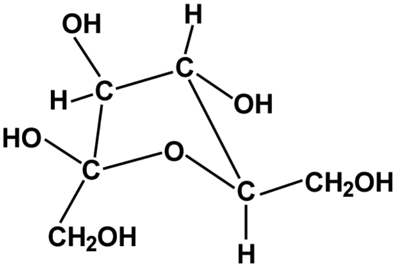
Haemoglobin has a globular structure. It is soluble in water. Haemoglobin is the red constituent of blood. Both haem and chlorophyll contain the porphyrin nucleus where the metal ion is located. In haem, iron is present. In chlorophyll, magnesium is present. Chlorophyll is responsible for the green colour of leaves.

Sugars

Monosaccharides

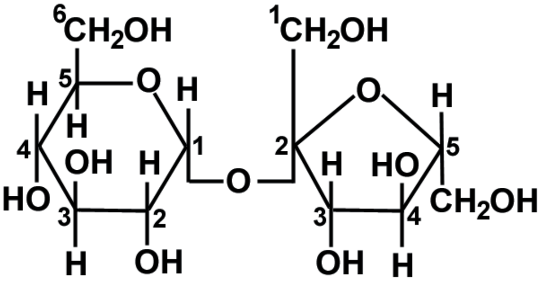


Glucose

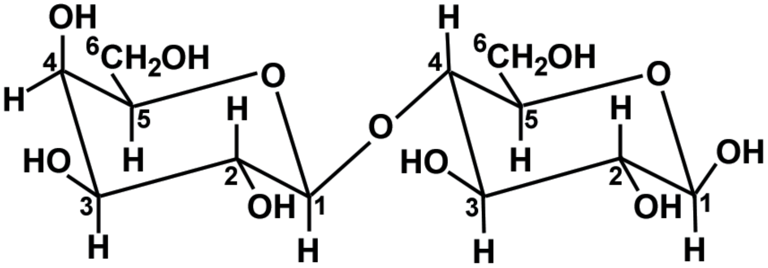


Fructose

Disaccharides

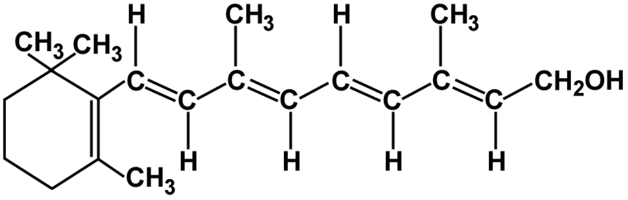


Sucrose

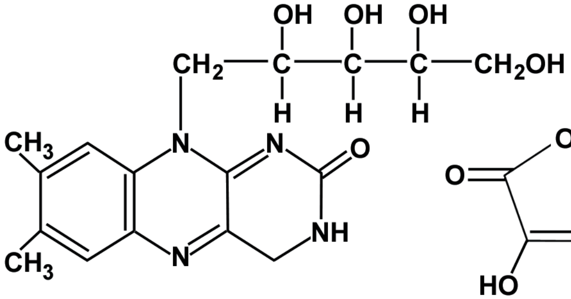


Lactose

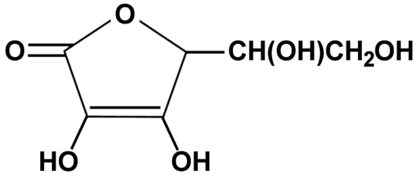
Vitamins



Vitamin A
(Retinol)



Vitamin B_2
(Riboflavin)



Vitamin C
(Ascorbic acid)

4.6 The Hydrogen bond

We generally think that the strongest succeed or survive best. It is not always the case. This is true at least for chemical bonds. One of the weakest bonds, known as the hydrogen bond, pervades all matter and life itself. Water would not be water without hydrogen bonds. The molecules of life, proteins and DNA, are held together by hydrogen bonds. What, then, is a hydrogen bond?

Hydrogen bonds are commonly formed between an O—H bond and an atom which can attract the hydrogen atom — for example, another oxygen atom, a halogen atom or a nitrogen atom. This is because in the O—H bond, the oxygen atom has a small negative charge (δ^-) and the hydrogen atom has a small positive charge (δ^+). Any atom that has a slight negative charge attracts the positively charged hydrogen atom as shown below:

$$\mathrm{O{-}H^{\delta+} \cdots O^{\delta-}}$$

The H · · · O bond is the hydrogen bond and it is weak. The energy of a hydrogen bond is around 3 kcal or 12kJ mol^{-1} compared to 60–100 kcal of ordinary single bonds.

Hydrogen bonds are formed by bonds other than the O—H bond. For example, an N—H bond can also form hydrogen bonds with electron-attracting atoms such as oxygen:

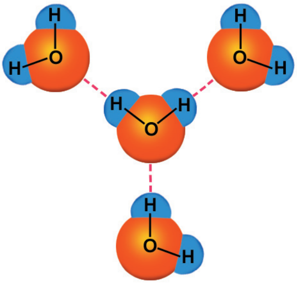
$$\mathrm{N{-}H \cdots O}$$

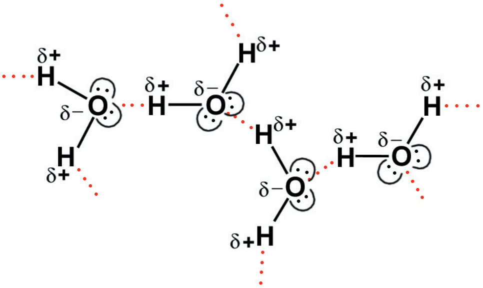
In general, hydrogen bonds are formed by an X—H bond (where X is an electronegative element such as O, N, S, halogen) and another electronegative atom, Y.

$$\mathrm{X{-}H^{\delta+} \cdots Y^{\delta-}}$$

Typical hydrogen bonds are O—H···O, O—H···N, O—H···Cl, O—H···S, N—H···O, N—H···S, S—H···O and S—H···S. In special instances, even a C—H bond forms a hydrogen bond with an electronegative atom.

Water is the most well-known example of hydrogen bonding.





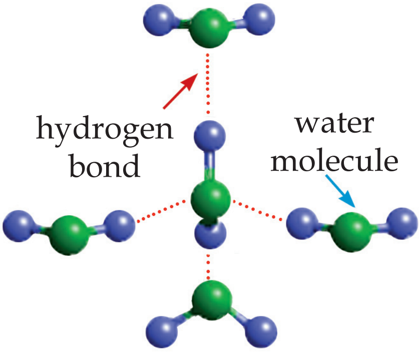
In water, the oxygen atom of one H_2O molecule (with a slight negative charge) attracts the proton of another H_2O molecule. This goes on and on, making water a highly "associated" liquid.

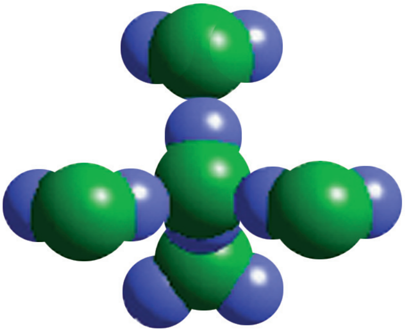
Many of the unique properties of water are due to the hydrogen bonding.

Water has a high

- boiling point (100°C or 373 K).
- surface tension.
- heat of vapourization.
- heat of fusion.

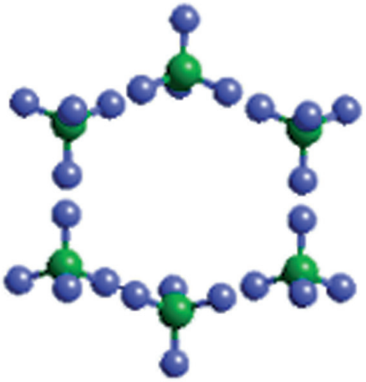
In ice, each water molecule is hydrogen bonded to four other water molecules.

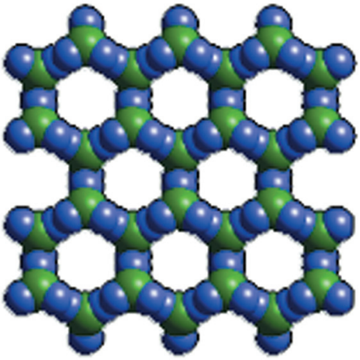




● – Oxygen ● – Hydrogen

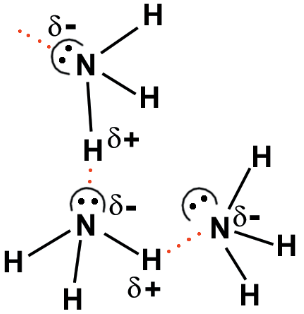
Different forms of ice, with different hydrogen bond patterns and shapes have been made in the laboratory.

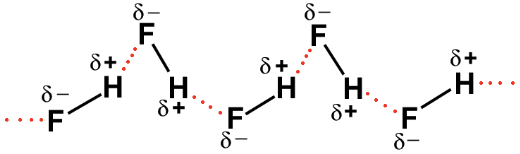




🟢 – Oxygen 🔵 – Hydrogen

Hydrogen bonding occurs in ammonia (with the nitrogen atom) and in hydrogen fluoride (with the fluorine atom).

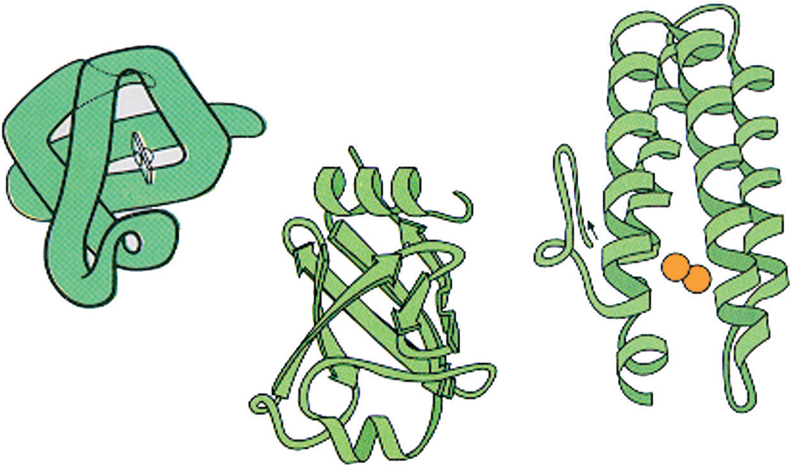


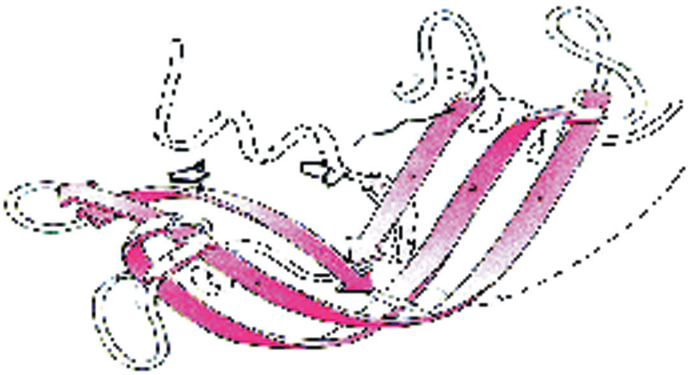


4.7 Molecules of life

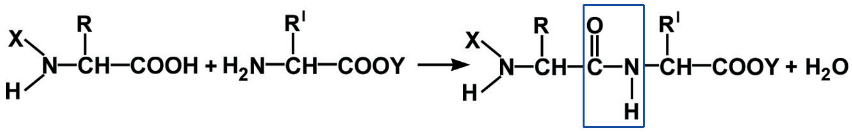
Let us look at some molecules of life where hydrogen bonds play a major role.

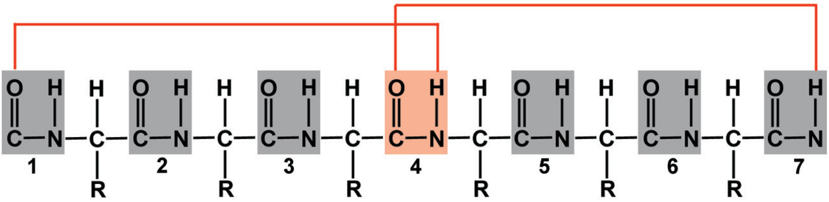
Proteins: Proteins of different shapes are known. Some are globular and some are fibrous. They have different types of hydrogen bonds.



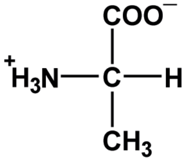


Proteins are essential constituents of life. Proteins perform various functions. The basic constituent of proteins is the peptide bond. These bonds are formed between amino acids.

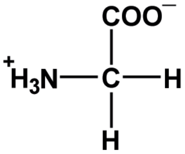




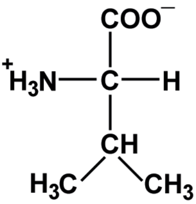
There are twenty amino acids in Nature. A few of them are shown below:



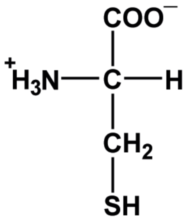
Alanine



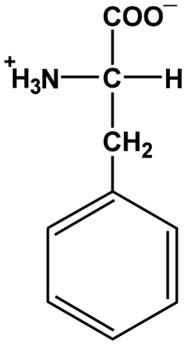
Glycine



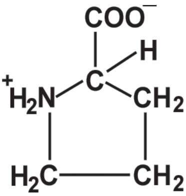
Valine



Cysteine

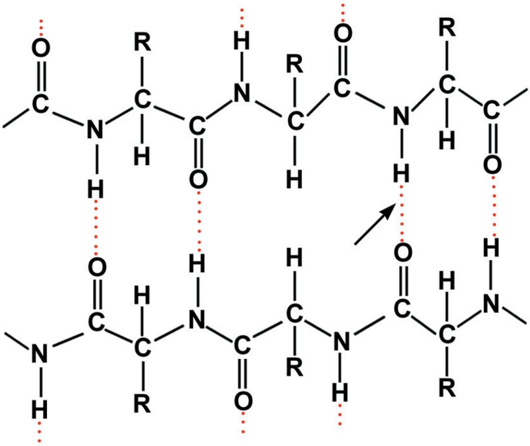


Phenylalanine

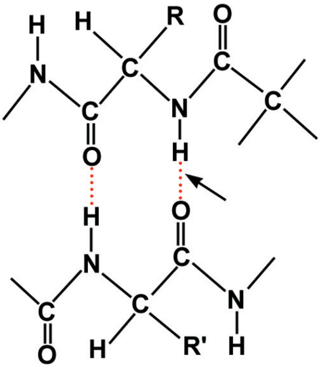


Proline

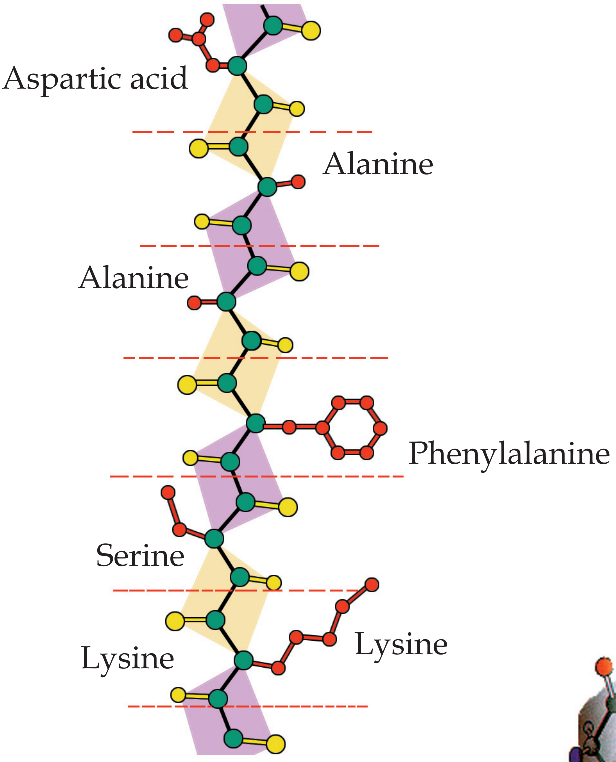
The peptide bonds get linked to each other by hydrogen bonds.

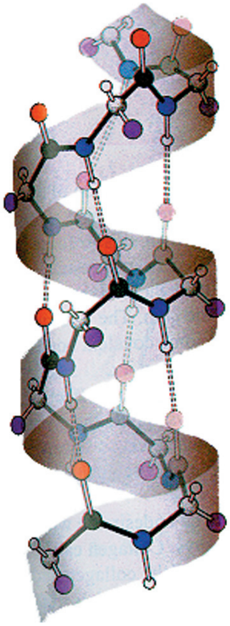


The hydrogen bond gives shapes to proteins.

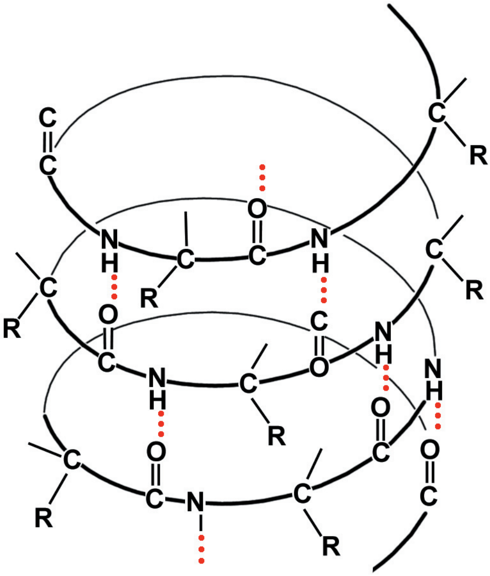


Protein–Polypeptide chain



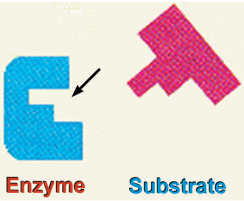


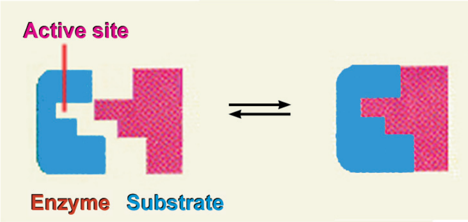
α-helix: The alpha-helix is one of the important features of proteins. The alpha-helix was discovered by Linus Pauling in 1951. This discovery marks the beginning of molecular biology.



Collagen is a protein consisting of three helices. It is a triple helix. It is found in bone, nails and hair. It has a fibrous structure and is an insoluble protein. The structure of collagen was determined by G. N. Ramachandran in Chennai.

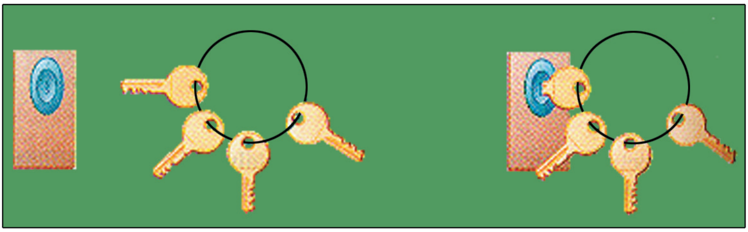
Enzymes: Enzymes are proteins, responsible for various reactions in biological systems. The way enzymes work is based on their shape. Enzyme molecules have a hole or a cleft.

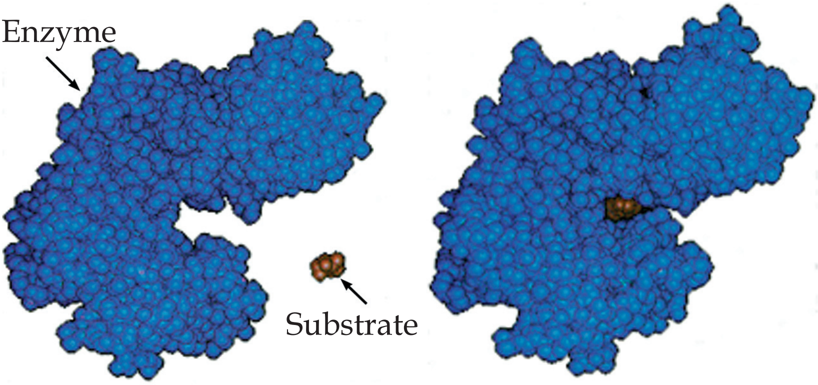




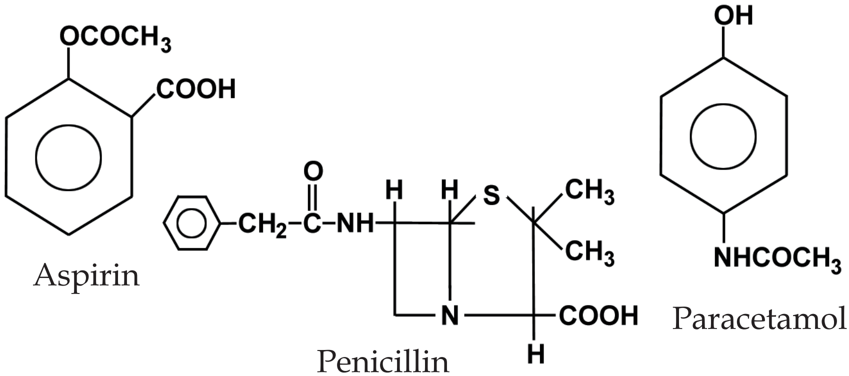
A substrate must have the right shape to fit into the cleft for the reaction to occur.

The hole or the cleft in an enzyme acts as the lock and the substrate acts as the key.





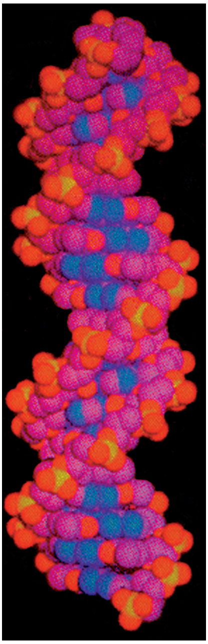
Drugs: The action of drugs also depends on the shape of the drug molecule as well as the site at which it interacts with a protein.



Aspirin

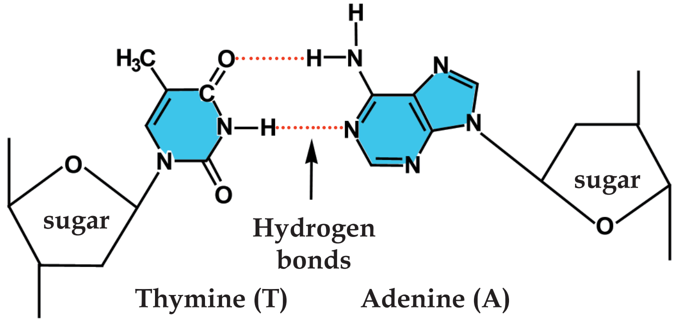
Penicillin

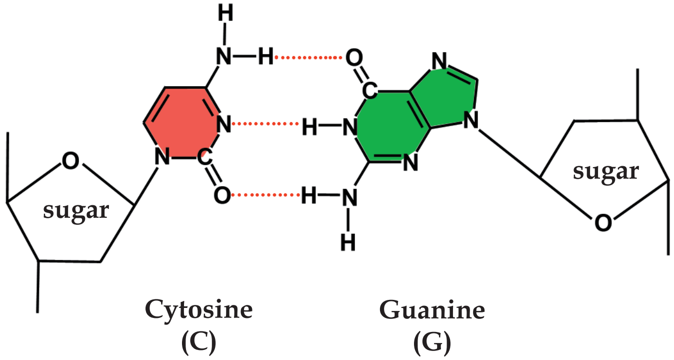
Paracetamol



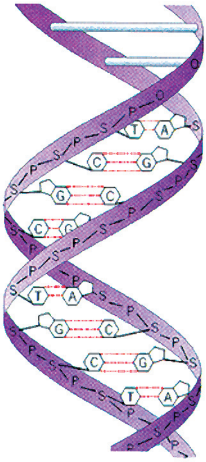
DNA: Without hydrogen bonds, we cannot have DNA. DNA is associated with the genetic code.

DNA has certain nitrogen-containing bases called purines and pyrimidines. The purines and pyrimidines are linked to one another by hydrogen bonds. These hydrogen bonds are specific and can occur only between specific molecules.





DNA consists of a double helix. Hydrogen bonds are present between the helices.

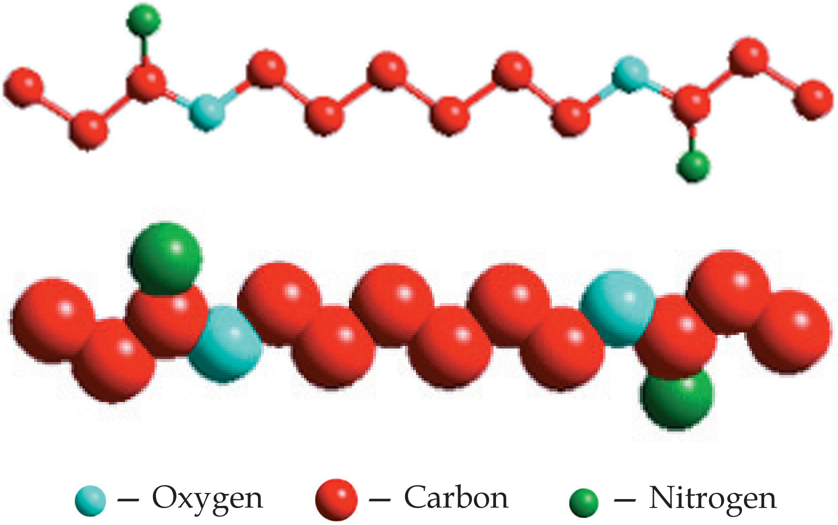


4.8 Man-made polymers

Polymers are high molecular weight substances. "Poly" means **many**. Polymers consist of **many** repeating units. That is, polymers are made starting from **monomers** which contain the repeating unit (Lesson 1).

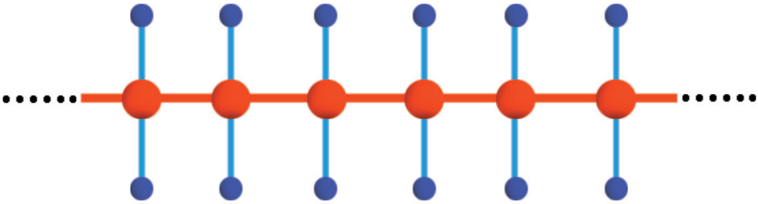
Ethylene is $H_2C{=}CH_2$. Polyethylene has repeating $-CH_2-CH_2-CH_2-$ units.

Proteins and DNA are biological polymers having definite shapes and structures. There are many man-made polymers of different types. Some examples of man-made polymers are given here.



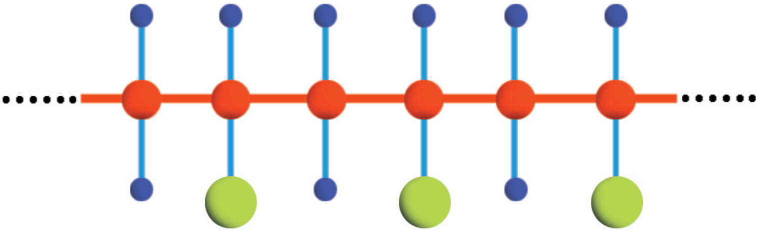
Repeating unit in Nylon 6,6

Two of the commonly used synthetic polymers are: polyethylene and polyvinyl chloride (see Lesson 1 for others).

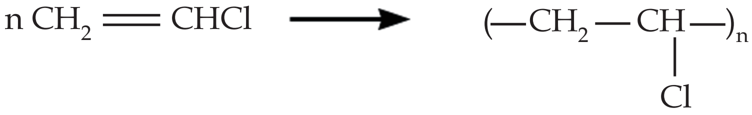


Polyethylene or polythene

$$n\,CH_2{=}CH_2 \longrightarrow (-CH_2-CH_2-)_n$$



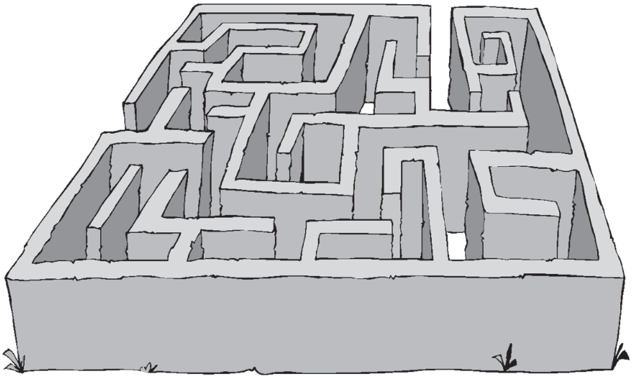
Polyvinyl chloride or PVC

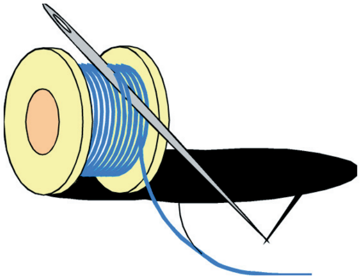


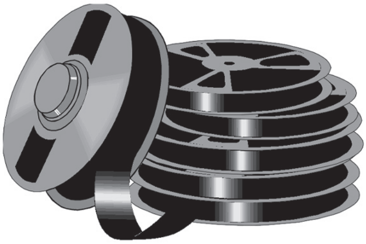
$$n\,CH_2{=}CHCl \longrightarrow \left(-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-\right)_n$$

There are many other important polymers. The artificial fibres used to make cloth, such as terylene or dacron, are polyesters. The artificial fibres blend with natural fibres such as cotton and wool. Some of the man-made fibres (e.g., kevlar) are very strong. There are polymers which can conduct electricity. There are some polymers which can be rolled into thin sheets (polyethylene), some made into soft and springy packing material (polyurethane) and some used as adhesives (polyvinylalcohol).

Structures and shapes of polymers determine their properties. Some can be moulded, some drawn into threads and some made into sheets.







However, man-made polymers are generally NOT biodegradable.

Conclusions

We have looked at the structures and shapes of molecules and tried to understand them on the basis of the chemical bonds in them. But, there are so many molecules in Nature and many more made by man. Most of them have complex structures resulting from intricate bonding patterns. Even the action of enzymes and drugs depends on their size and shape. We have also examined how the hydrogen bond, a weak bond, holds molecules and structures together. The hydrogen bond plays a crucial role in life processes.

Size is important!

Sizes and shapes of molecules have a big role in determining their chemical reactivity. There is a joke about a prominent chemist who showed the importance of the size (or bulk) of groups in organic compounds. He was so huge in size that he could not comfortably sit in a chair.

5

CHEMICAL ENERGY

Objectives

- In this lesson, we learn a few salient aspects of energy—how energy is conserved and can be transformed from one form to another.
- Chemical energy is an important form of energy. And, chemical transformations are associated with energy changes. Energy can be stored.
- We depend on the energy from the sun. As energy resources, such as petroleum, get depleted, we need to depend on alternative energy sources. We examine some of the alternatives.

Energy is one of the main needs of humans. The progress of a nation is measured by the amount of energy (say, electrical energy) consumed. In this respect, developing countries like India are far behind.

Chemical energy is an important form of energy. Chemical reactions are associated with energy changes.

Melting of iron ore

Candle burning

A torch

Burning of sugar

These are examples of chemical reactions.

Energy can be converted from one form to another, for example, from electrical energy to heat. Energy can also be stored as in a battery cell. But, energy cannot be created or destroyed.

5.1 Energy changes in chemical reactions

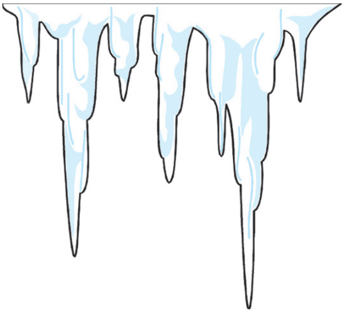
$$Na + Cl \longrightarrow NaCl$$

$$C + O_2 \longrightarrow CO_2$$

$$Cl_2 \longrightarrow Cl + Cl$$

In chemical reactions, bonds are either formed or broken. Making or breaking of bonds results in the rearrangement of atoms. This process involves a change in energy.

A reaction where heat is given out is **exothermic**.

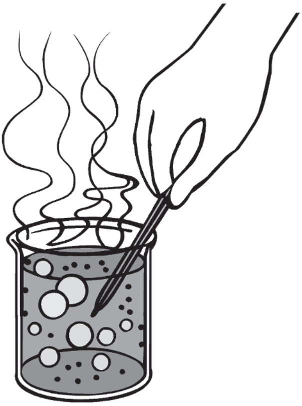


Heat is given out when water freezes into ice.

A reaction where heat is absorbed is **endothermic**.

Heat is absorbed when ice melts into water.

A common example of an **exothermic** reaction is the burning of wood or combustion. Burning anything gives out heat. Addition of water to quicklime or addition of sulfuric acid to water are other examples.



Common examples of **endothermic** reactions are: a liquid becoming vapour (water → steam) and ice melting to water.

The change in energy in a chemical reaction is generally given by the **heat of reaction**. It is the difference between the heat content of the reactants ($H_{reactants}$) and the heat content of the products ($H_{products}$). It is also called **enthalpy change**. The change in the heat content or the enthalpy change in a rection is represented as ΔH.

$$\mathbf{\Delta H = H_{products} - H_{reactants}}$$

When $H_{products}$ is $>$ $H_{reactants}$, ΔH is positive (endothermic).

When $H_{reactants}$ is $>$ $H_{products}$, ΔH is negative (exothermic).

$$H_2(g) + \tfrac{1}{2} O_2(g) \longrightarrow H_2O(l); \quad \Delta H = -286 \text{ kJ}$$

Note that (g) and (l) stand for gas and liquid respectively.

When a chemical bond is formed, heat is given out. Bond formation is, therefore, an exothermic reaction.

$$H_2O(l) \longrightarrow H_2(g) + \tfrac{1}{2} O_2(g); \quad \Delta H = +286 \text{ kJ}$$

To break a chemical bond, energy has to be supplied. Breaking a bond is an endothermic reaction.

> Depending on whether the reaction involves making or breaking of bonds, chemical reactions show release or absorption of energy (heat).

Heats of reactions are expressed in terms of kilocalories (kcal) or kilo Joules (kJ).

1 calorie = 4.184 joules

1 kilocalorie = 1 kcal = 1000 calories

Enthalpy changes of reactions are generally given for conditions when the reactants and products are in the so-called standard states. Example: H_2 (gas), H_2O (liquid). The standard states of substances correspond to those at the standard temperature (298 K or 25°C) and pressure (1 atm or 760 mm Hg).

Let us look at a few simple chemical reactions and determine whether they are exothermic or endothermic.

$$C\ (s) + O_2\ (g) \longrightarrow CO_2\ (g);\ \Delta H = -393.5\ kJ$$

$$H\ (g) + H\ (g) \longrightarrow H_2\ (g);\ \Delta H = -436\ kJ$$

In both reactions, bonds are formed, and heat is released. Therefore, the above two reactions are exothermic. The enthalpies of the products in the above reactions are less than the enthalpies of the reactants.

Let us consider the above two reactions in the reverse order.

$$H_2\ (g) \longrightarrow H\ (g) + H\ (g);\ \Delta H = 436\ kJ$$

$$CO_2\ (g) \longrightarrow C\ (s) + O_2\ (g);\ \Delta H = 393.5\ kJ$$

In these reactions, bonds are broken. Therefore, heat is absorbed and the reactions are endothermic.

The amount of energy required to form or break bonds is not the same for all bonds. Therefore, there will always be some energy change when products are formed from reactants.

The heat of a reaction or the enthalpy change in a chemical reaction can be measured in the laboratory. Heats of reactions can be used to
(a) understand the nature of chemical reactions and
(b) predict them.

Depending upon the nature of the transformation, the enthalpy change or the heat of reaction is described as shown below:

$\underset{\text{water}}{H_2O\,(l)} \longrightarrow \underset{\text{steam}}{H_2O\,(g)}$ heat of vapourization

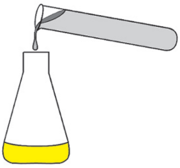
$CH_4\,(g) + 2O_2\,(g) \longrightarrow CO_2\,(g) + 2H_2O\,(l)$

$C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g)$ heat of combustion

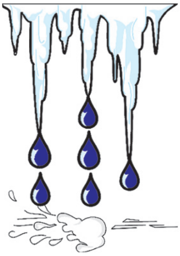
Note that (s) represents solid and (l) liquid.

$HCl\,(aq) + NaOH\,(aq) \longrightarrow NaCl\,(aq) + H_2O\,(l)$

heat of neutralization



Note that (aq) represents aqueous (solution in water)



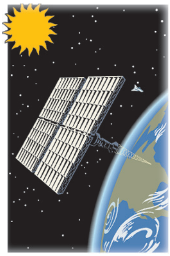
$\underset{\text{ice}}{H_2O\,(s)} \longrightarrow \underset{\text{water}}{H_2O\,(l)}$ heat of fusion

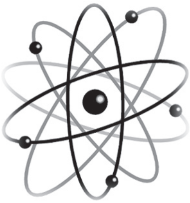
$I_2\,(s) \longrightarrow I_2\,(g)$ heat of sublimation

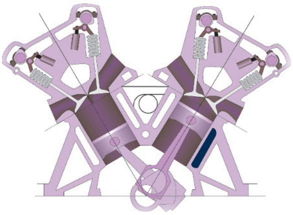
camphor (s) $\longrightarrow$ camphor (vapour)

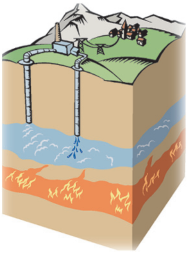
5.2 Nature of energy

Chemical energy is only one form of energy. Energy can be in the form of electrical energy, light energy, mechanical energy and so on. Some of the different forms of energy are shown below.





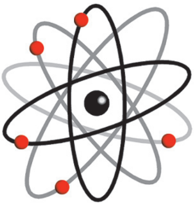




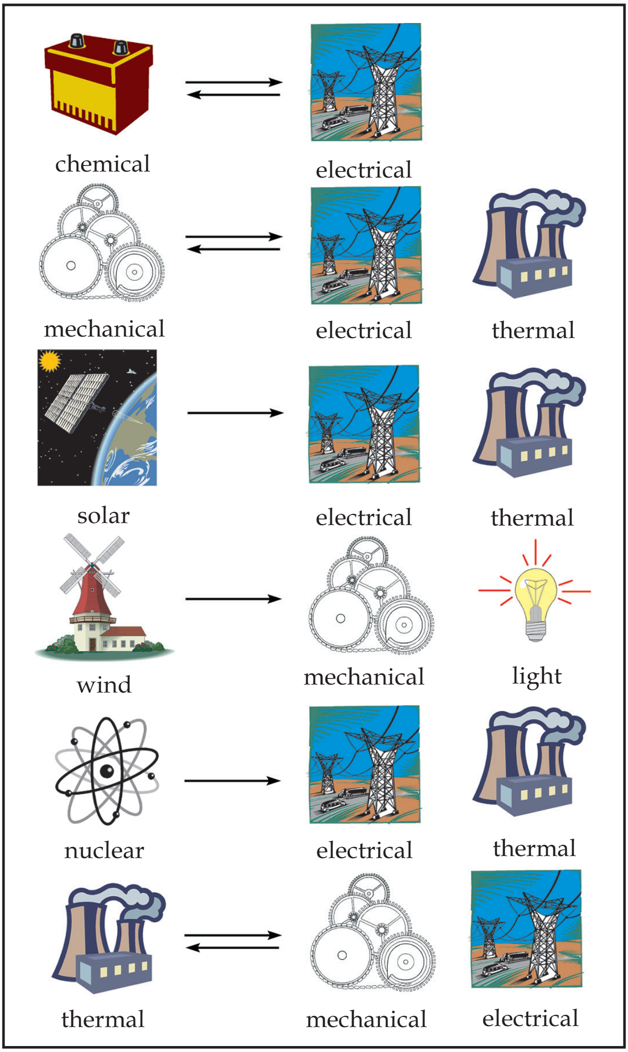
All forms of energy consist of the energy in the system (potential energy) and the energy due to motion (kinetic energy). Potential energy changes to kinetic energy when there is motion.

The energy of a system can be internal energy or external energy. The internal energy of a system can change. It increases if it gains energy or if work is done on the system. It decreases if it loses energy or if the system does work.

The internal energy of an atom is the sum of kinetic and the potential energies. The kinetic energy of electrons is due to the motion of electrons. Bond energy is an example of potential energy.



Energy can neither be created nor destroyed (**Law of Conservation of Energy**). It is always conserved. Energy can only be converted from one form to another as shown below.



5.3 Heats of reactions

We can write the equation for the formation of H_2O as follows:

$$H_2\,(g) \;+\; ½\,O_2\,(g) \longrightarrow H_2O\,(l) \;+\; 286\text{ kJ}$$

286 kJ of energy is released when one mole of water is formed. The decomposition of one mole of water requires 286 kJ of energy.

$$H_2O(l) \;+\; 286\text{ kJ} \longrightarrow H_2\,(g) \;+\; ½\,O_2\,(g)$$

In the above reactions, one mole of H_2O was involved. The above reactions for two moles of H_2O will be:

$$2H_2\,(g) \;+\; O_2\,(g) \longrightarrow 2H_2O\,(l) \;+\; 572\text{ kJ}$$

$$2H_2O\,(l) \;+\; 572\text{ kJ} \longrightarrow 2H_2\,(g) \;+\; O_2(g)$$

That is, the heat released or absorbed in a chemical reaction depends on the quantities of substances involved in the reaction.

$$4H_2\,(g) \;+\; 2O_2\,(g) \longrightarrow 4\,H_2O\,(l) \;+\; ?\text{ kJ}$$

In the neutralization of one mole of acid by one mole alkali, 57 kJ of energy is released,

$$H^+\,(aq) \;+\; OH^-\,(aq) \longrightarrow H_2O\,(l) \;+\; 57\text{ kJ}$$

The 57 kJ of energy is the heat of neutralization. If 0.5 mole of HCl is neutralized by 0.5 mole of NaOH, the heat change will be 28.5 kJ.

$$0.5H^+\,(aq) \;+\; 0.5\,OH^-\,(aq) \longrightarrow 0.5H_2O \;+\; 28.5\text{ kJ}$$

The food we eat in the form of carbohydrates (rice, wheat etc.) breaks down to glucose. Glucose is oxidised to CO_2 and H_2O, releasing energy.

$$C_6H_{12}O_6\,(s) \;+\; 6O_2\,(g) \longrightarrow 6CO_2(g) \;+\; 6H_2O(g) \;+\; 2900\text{ kJ}$$

The 2900 kJ of energy released is the heat of combustion.

The heat of combustion of n-butane, C_4H_{10}, present in cooking gas cylinders, is 2658 kJ.

$$C_4H_{10}(g) + 6.5\,O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(g) + 2658\text{ kJ}$$

Remember combustion (oxidation) is always exothermic. A small family may need about 25,000 kJ per day. If a cylinder contains about 12 kg of butane, the cylinder will last for about 21 days, assuming that about 30% of the gas is wasted.

The heat absorbed or given out when one mole of a substance is formed is called the **heat of formation**.

$$C(s) + O_2(g) \longrightarrow CO_2(g) + 393.5\text{ kJ}$$

The heat of formation of CO_2 is –393.5 kJ.

The heat of formation of H_2O is –286 kJ.

A chemical reaction can take place in more than one step. The heat change (ΔH) of the complete reaction is the sum of the ΔH values of the different steps.

The reaction

$$C(s) + O_2(g) \longrightarrow CO_2(g); \quad \Delta H = -393.5\text{ kJ}$$

takes place in two steps.

Step 1: $C(s) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g); \; \Delta H_1 = -110.5\text{ kJ}$

Step 2: $CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO_2(g); \; \Delta H_2 = -283.0\text{ kJ}$

$$C(s) + O_2(g) \longrightarrow CO_2(g); \quad \Delta H = -393.5\text{ kJ}$$

Step 1 + Step 2, $\Delta H_1 + \Delta H_2 = (-110.5\text{ kJ}) + (-283.0\text{ kJ}) = -393.5\text{ kJ}$

Heats of reaction can be added or subtracted because of the law of conservation of energy.

5.4 Energy storage

The conversion of energy from one form to another drives various activities on earth. However, when energy is converted, part of it becomes useless. Let us consider the conversion of the kinetic energy of a river to electrical energy. During this conversion, part of the total energy becomes useless.

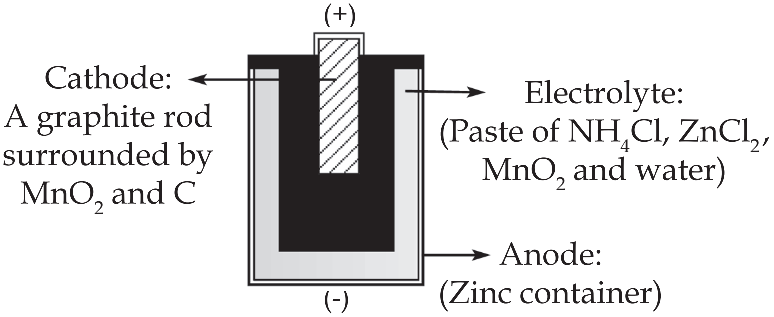
The energy change in chemical reactions need not always show up as release or absorption of heat. Chemical energy is often released as light. (Remember fireflies!)

Chemical energy can also be stored. Simple electrochemical devices convert chemical energy to electrical energy. Fuel (coal, oil, wood) is an energy source that is known to all of us. Fuel is easily converted into thermal energy, but when not used, it stores energy.

Batteries and fuel cells are stores of chemical energy. A battery is a portable source of electrical energy. In a fuel cell, chemicals are continuously used up, unlike in a battery.

Let us look at simple batteries. They can be primary cells (non-rechargeable) or secondary cells (rechargeable).

Battery cell or Dry cell: This is a primary cell and is non-rechargeable. It cannot be reused.



The reactions in the battery cell are as shown below:

anode: $Zn\ (s) \longrightarrow Zn^{2+}\ (aq) + 2e^-$

cathode:

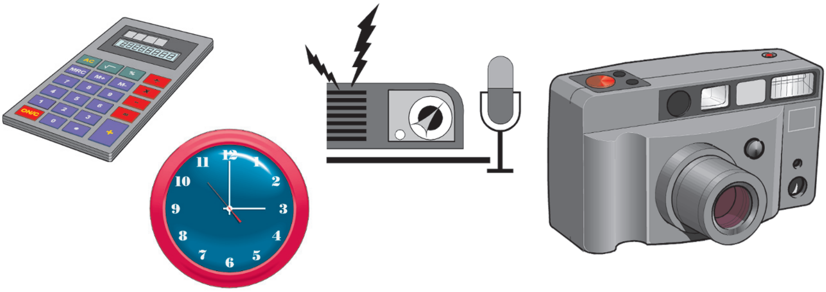
$$2MnO_2(s) + 2NH_4^+(aq) + 2e^- \longrightarrow Mn_2O_3(s) + 2NH_3(aq) + H_2O(l)$$

The total reaction is

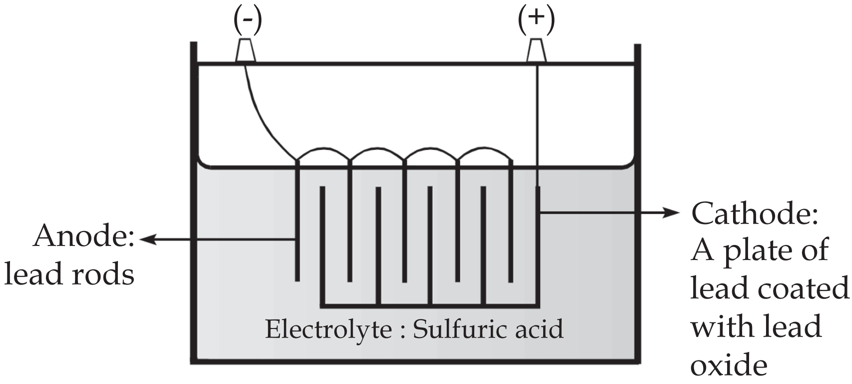
$$Zn\ (s) + 2MnO_2\ (s) + 2NH_4^+\ (aq) \longrightarrow Zn^{2+}\ (aq) + Mn_2O_3(s) + 2NH_3\ (aq) + H_2O\ (l)$$

The electrons (e^-) released at the anode go to the cathode where they are used up.

Such a storage cell generates between 1.25 and 1.5 volts.



Lead-acid battery (secondary cell): In this battery, a number of cells are connected in series.



The reactions in the lead-acid battery are as shown below:

anode: $Pb(s) + SO_4^{2-}(aq) \rightleftarrows PbSO_4(s) + 2e^-$

cathode:

$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \rightleftarrows PbSO_4(s) + 2H_2O(l)$

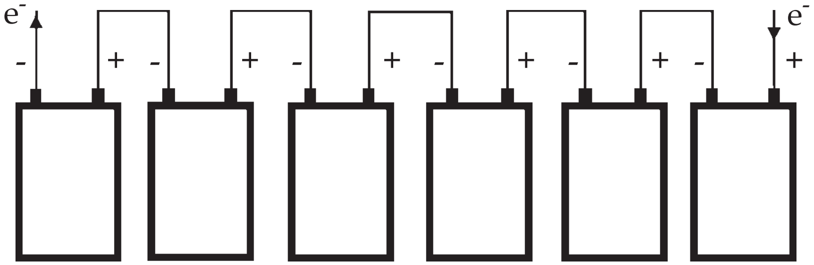
The total reaction is

$$Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq) \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} 2PbSO_4(s) + 2H_2O(l)$$

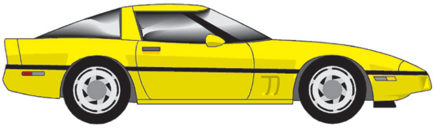
Electrons are released at the anode and consumed at the cathode. By applying a current from an external source, this battery can be recharged. This process reverses the reactions at the electrodes.

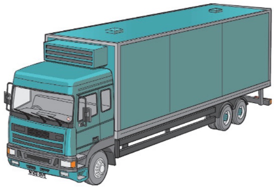
When fully charged, a lead storage cell gives around 2V. The relative density (specific gravity) of sulfuric acid is 1.275 when the cell is charged. Upon use (discharging), the concentration and the relative density of sulfuric acid decreases.

The car battery is a lead-acid battery having six storage cells in series.

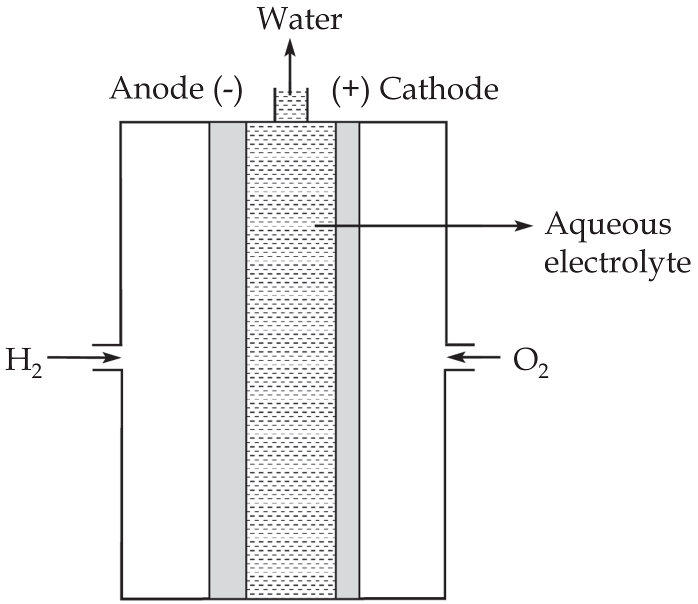


Car battery





Hydrogen-oxygen fuel cell: This is a primary cell where the reactants (hydrogen and oxygen) are continuously replaced as they form water. Power is produced by the electrochemical conversion of hydrogen and oxygen.



The reactions in the hydrogen-oxygen fuel cell are as shown below:

anode: $2H_2\,(g) + 4OH^-\,(aq) \longrightarrow 4H_2O\,(l) + 4e^-$

cathode: $O_2\,(g) + 2H_2O\,(l) + 4e^- \longrightarrow 4OH^-$

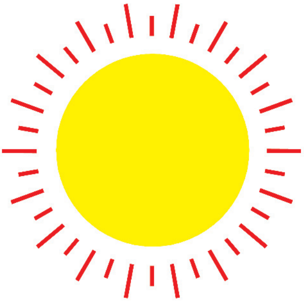
The total reaction is

$$2H_2\,(g) + O_2\,(g) \longrightarrow 2H_2O\,(l)$$

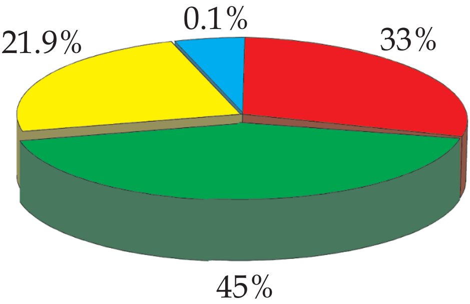
The reaction is the burning of hydrogen. A fuel cell can generate 12 kilowatts of power at peak (7kW on average). Instead of hydrogen, some fuel cells use methyl alcohol. Fuel cells are used in various situations.

5.5 Energy from the sun

Of all the forms of energy, it is the energy from the sun that drives most activities on the earth. The tremendous amount of energy released by the sun in the form of heat energy is due to the nuclear fusion in its core. Since the birth of the sun 5 billion years ago, hydrogen is being converted into helium. Yet another example of a chemical reaction!



How is the sun's energy reaching the earth distributed?



- 🟩 45% is used to heat the earth's crust and waters of the oceans.
- 🟥 33% is reflected back to space through dust particles and clouds.
- 🟨 Approximately 21.9% is consumed in the evaporation process of the water cycle.
- 🟦 0.1% drives winds, waves, ocean currents and **out of this, 0.03% is used for photosynthesis**.

This minute amount of energy from the sun is responsible for life on earth.

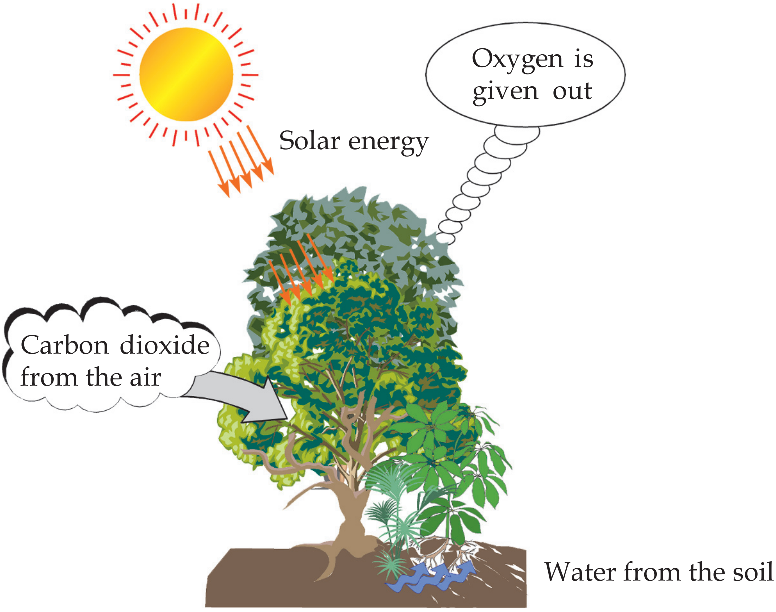
"All flesh is grass": Prophet Isaiah, 8th century B.C.

Using light energy from the sun (with chlorophyll or the "green blood" acting as the conveyer of light energy), plants convert the inactive inorganic compounds, CO_2 and H_2O, into an organic compound, glucose ($C_6H_{12}O_6$), by the chemical transformation called **photosynthesis**.

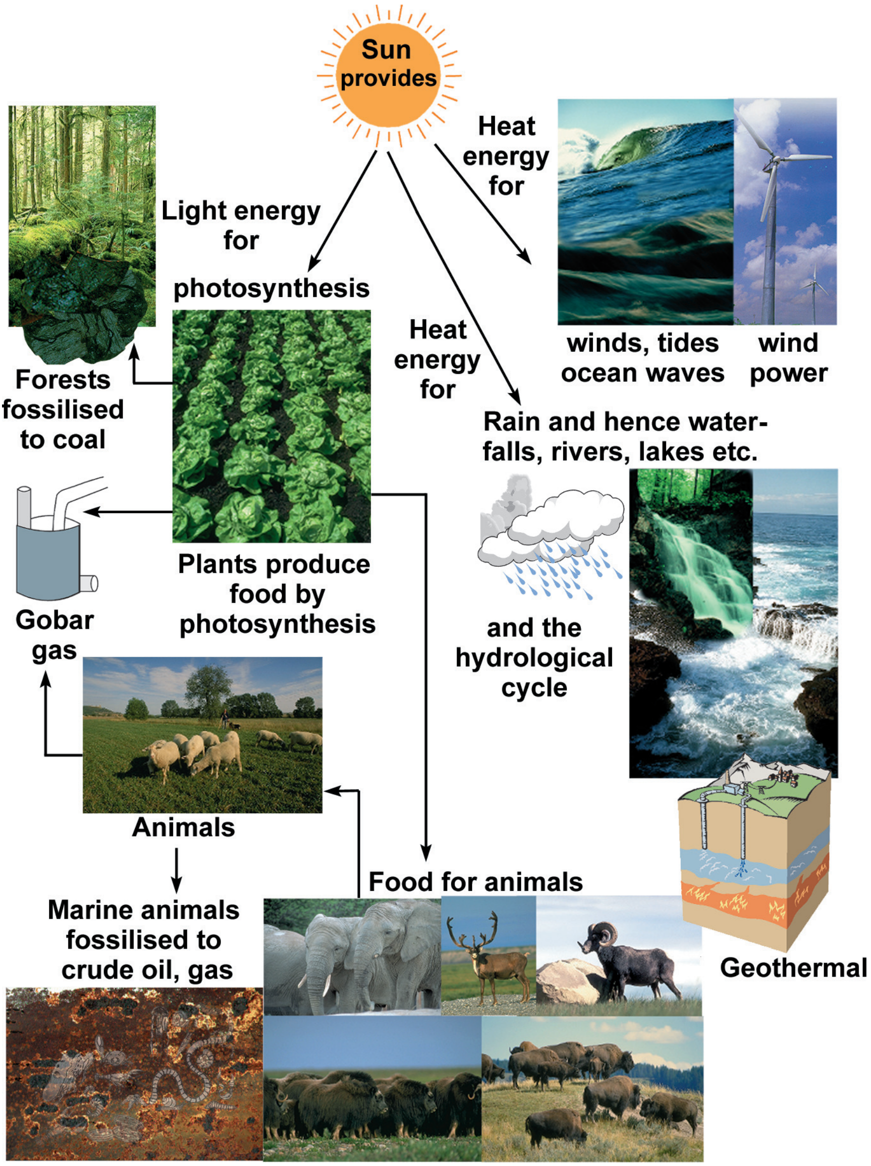
Photosynthesis is the reverse of combustion and respiration and is described by this reaction:

$$6CO_2 + 6H_2O + \text{light energy} \longrightarrow C_6H_{12}O_6 + 6O_2$$

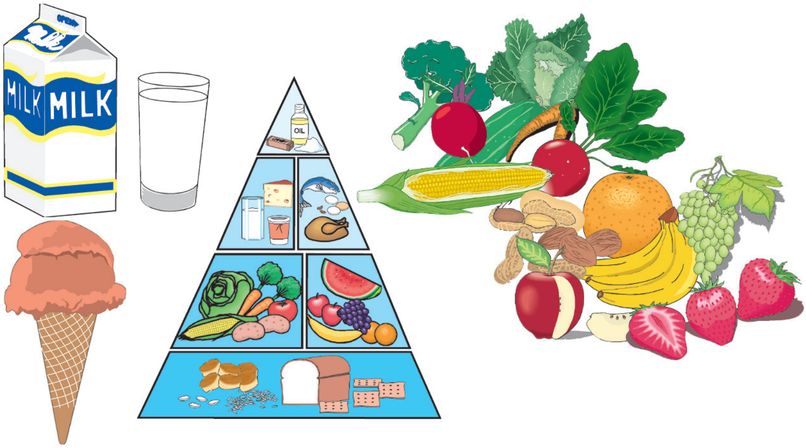
Photosynthesis is responsible for both the biomass and the fuels. Unraveling the exact mechanism of this conversion holds the key to man's future needs of food and energy.



The sun is also responsible for various forms of stored energy such as wood energy, biomass energy and food energy.



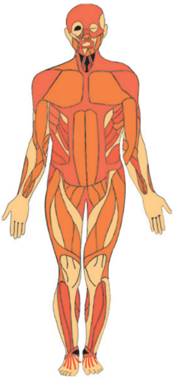
Food energy is required by all living beings. All living beings literally eat and drink for a greater part of their lives!



Energy value of some foods — a guide for good eating

Butter	7.40 kcal/g
Peanuts	5.70 kcal/g
Cheese	4.06 kcal/g
White sugar	3.94 kcal/g
Rice	3.61 kcal/g
White bread	2.33 kcal/g
Raw chicken	2.30 kcal/g
Ice cream	1.66 kcal/g
Eggs	1.47 kcal/g
Raw potatoes	0.86 kcal/g
Fish	0.76 kcal/g
Apples	0.46 kcal/g
Oranges	0.35 kcal/g
Beer	0.31 kcal/g
Raw Green Cabbage	0.22 kcal/g

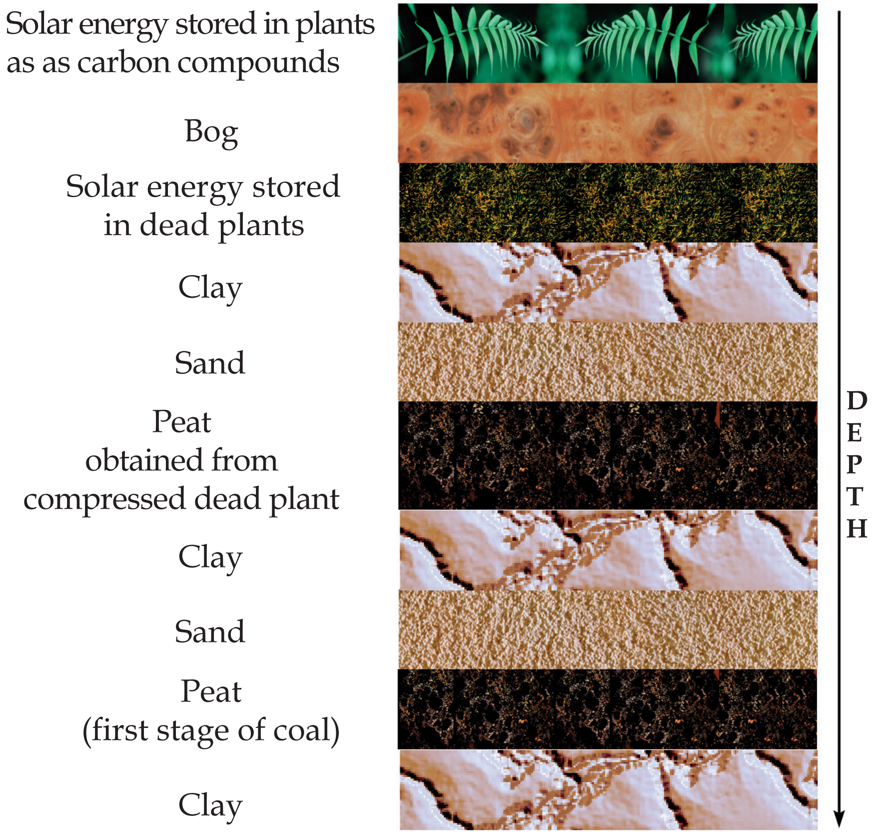
What happens to the energy consumed by us? Energy from food is essential for the chemical changes that go on in our system all the time. How do we use the energy provided by food? Energy is needed for the metabolic changes that take place in our bodies, to keep our bodies warm and for physical activities.



Not all of the energy in the food is used by our bodies. Of the food not used by metabolic changes in our bodies, part of it is wasted and excreted (in normal adults, this is very small). Surplus food is stored as fat. Therefore, either control your eating or exercise to burn the excess energy from the food you consume. A balanced diet is important to avoid malnutrition and to provide the energy required for various activities.

Wood energy: Wood energy is actually stored energy from the sun. Fuel energy from the burning of wood has been known to man from antiquity! Even today, firewood or charcoal cooks more meals than any other source of energy in India. Around 80% of the wood is used as fuel in many developing countries.

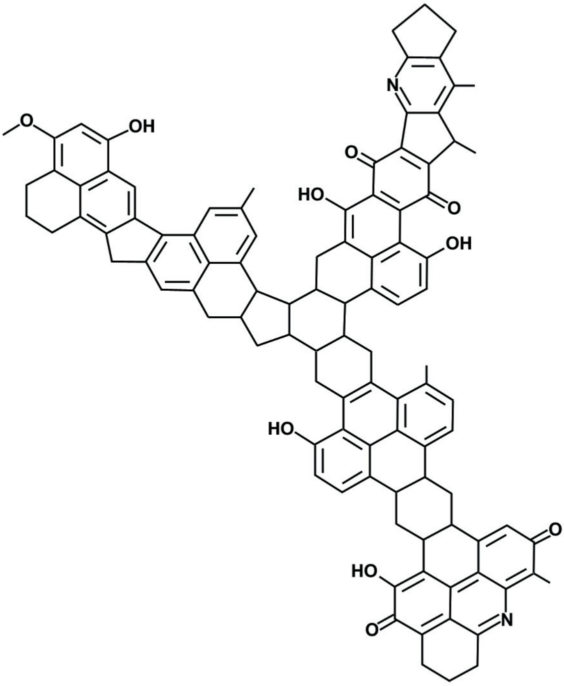
Coal, petroleum and natural gas: Coal is an important source of fuel and energy. It is also called "**buried sunshine**". Let us find out why?



Coal, petroleum and natural gas are sources that drive the modern world. Coal was the energy that propelled the industrial revolution. However, it is the discovery of petroleum and the technology of fractional distillation that changed the industrial scenario of the world. Natural gas has assumed great importance as it is easy to transport and is an important raw material.

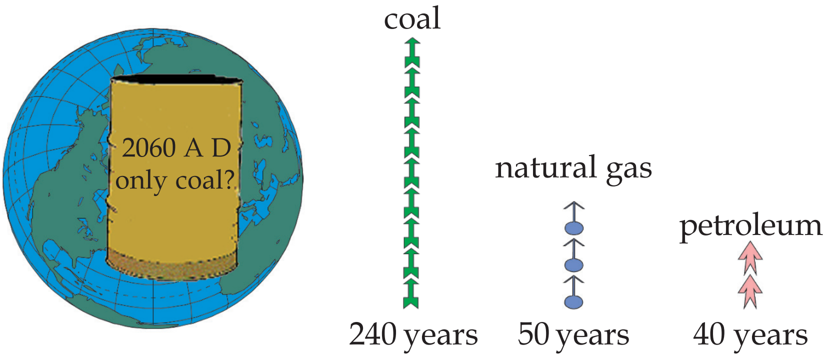
Coal, petroleum and natural gas are also natural sources of hydrocarbons. They are essential for fertilizer, chemical and pharmaceutical industries.

Coal is a complex mixture of substances. A "model" structure for coal is given below.



Petroleum consists of gaseous hydrocarbons dissolved in oil. The gases are separated from the oil. Hydrocarbons such as ethane, propane, butane and pentane are liquefied. Ethane is used in petrochemical industry as a feedstock. The mixture of propane and butane (in liquid form in cylinders) is sold as **liquefied petroleum gas** (LPG). Methane is also liquefied at low temperatures to **liquefied natural gas** (LNG). Methane is the main constituent of natural gas.

It has taken millions of years of chemical reactions for these energy sources to be formed. If we continue to use them recklessly, from the year 2000, the reserves will last approximately for:



Crude oil contains a large number of hydrocarbons. By distillation, different fractions are separated in oil refineries.

Composition of hydrocarbons		**Uses**
C_{1-4}	Refinery gas	gaseous fuel used to make synthetic gas ($CO + H_2$)
C_{5-12}	Petrol	car fuel
C_{12-16}	Kerosene	jet engines, cooking etc.
C_{15-18}	Diesel	engines, automobiles
C_{18+}	Residue	lubricating oil, wax, bitumen

5.6 Future options

What then are our future options?

The possible solutions are: biomass conversion and directly harnessing and harvesting nonconventional sources of energy.

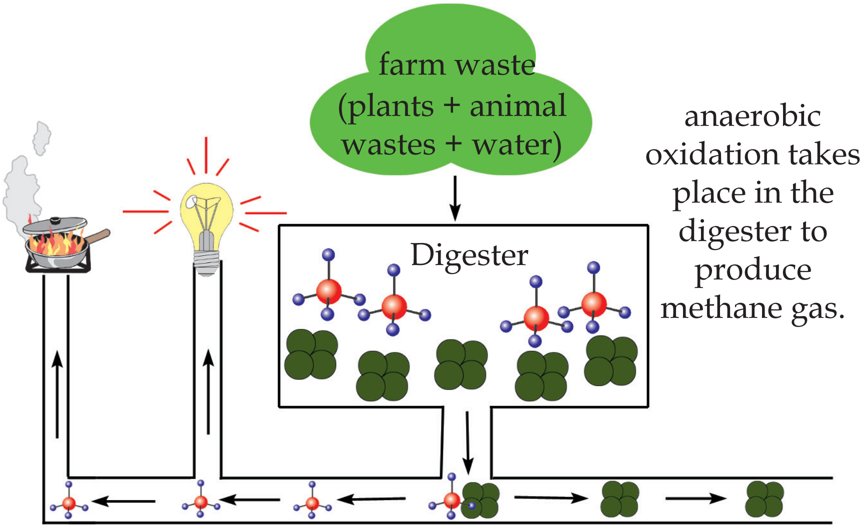
Bioconversion: Here, we convert a naturally occurring material to a chemical source of energy.

$$\text{Sugarcane} \longrightarrow \text{ethanol or ethyl alcohol}$$

$$\text{Ethanol} + \text{Petrol} \longrightarrow \text{Gasol (automobile fuel)}$$

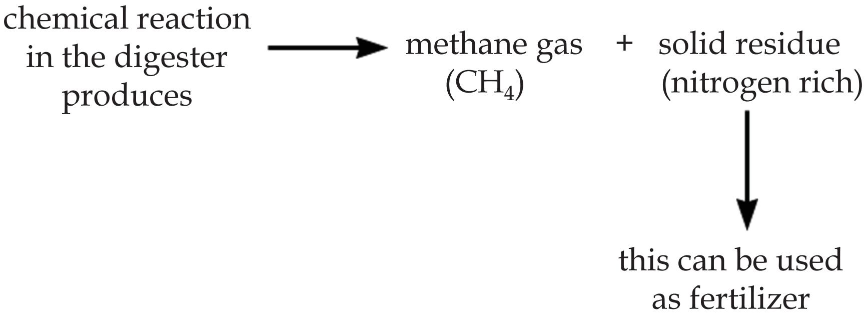
Brazil is the leading user of this alternative automobile fuel.

Wealth from waste: Conversion of organic waste to energy or organic fertilizers is an example of creating wealth from waste. Ethanol production from sugarcane, cassava, corn or beet uses food crops. Conversion of biowaste, on the other hand, offers an alternative means for the production of energy. This can be done by using a simple digester.



anaerobic oxidation takes place in the digester to produce methane gas.

Bio gas plant

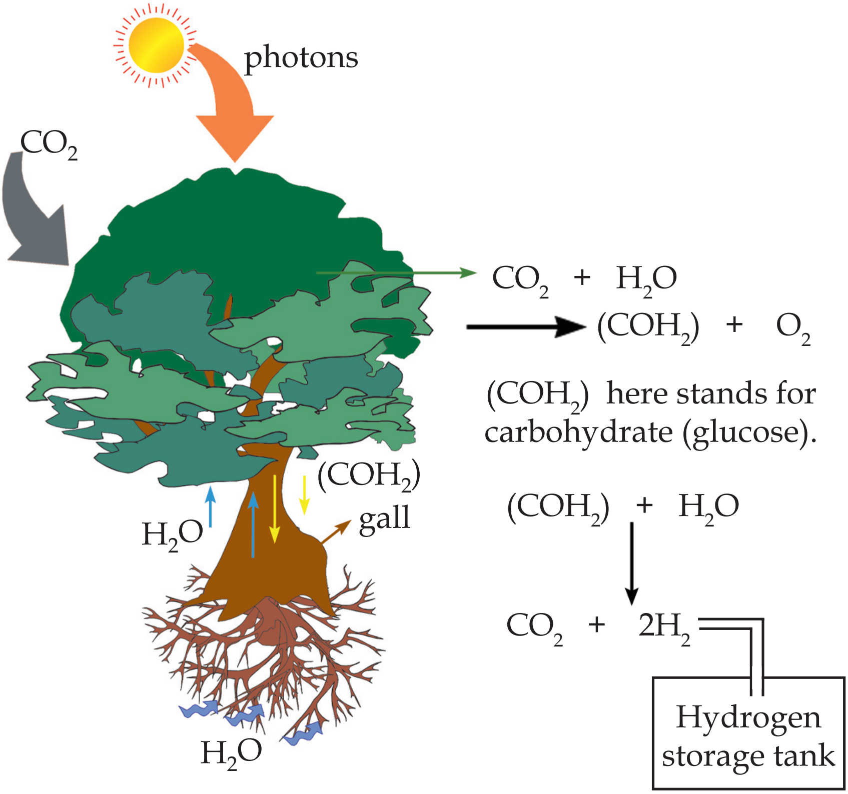


The advantages of biomass conversion are:

- it needs only simple technology.
- bio gas plant can be set up easily.
- raw material required is waste material.
- sufficient energy can be produced for both rural and urban use.

The hydrogen tree: Many types of swollen plant tissues (gall) are formed in plants by insects and bacteria. Gall caused by rhizobium bacteria in leguminous plants produces hydrogen (which escapes to air). This gave man the clue of splitting water using photons to produce hydrogen as a source of energy.

Cesare Marchetti working in Austria designed the first hydrogen tree. The hydrogen tree differs from the natural process in a significant way. In the hydrogen tree, the liberated hydrogen is piped to a central storage tank.



Direct conversion of energy from nonconventional energy sources: Direct conversion of light and heat energy from the sun provides an inexhaustible source of energy. Energy from the sun can be converted to heat energy by using solar panels. It can also be converted to electrical energy by using **photovoltaic cells**. The cells are made of silicon. This type of solar energy conversion has wide applications. Solar voltaic cells can provide electricity to remote villages to pump water or for domestic lighting. Solar voltaic cells provide electricity to spacecraft.

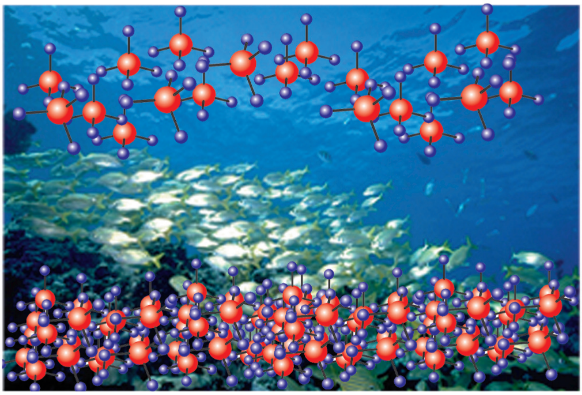
Hydrogen is considered to be a possible source of clean energy. The problem is to make hydrogen cheaply. Various methods of obtaining hydrogen are being explored. One method uses sunlight and electrolysis. Better ways of storing hydrogen are also being discovered. If we can manage to make and store hydrogen at a low cost, we then make use of the reaction,

$$2H_2 + O_2 \longrightarrow 2H_2O$$

to produce energy. We can then run cars, produce electricity and so on, without polluting the atmosphere.

While biomass conversion and harnessing energy directly from non-conventional sources may solve the energy crisis to some extent, depletion of hydrocarbons in Nature remains a major problem. It is necessary to identify newer sources of hydrocarbons. The most likely source is the ocean floor.

It is now known that millions of tonnes of **gas hydrate** are found on the ocean floor (1km or below). Methane gas under high pressure occurs as gas hydrate on the ocean floor. If appropriate technology can be developed to excavate and exploit these reserves, our hydrocarbon needs may be solved for centuries to come.



It is believed that there are rich deposits of gas hydrate near the Indian coast.

Conclusions

Human beings require energy for many purposes. Of the many forms of energy, chemical energy is an important one. There are energy changes in chemical reactions and we can calculate and measure these changes. Energy can be stored as in batteries and fuel cells.

Many sources of energy such as coal and petroleum are really from the sun, and we depend much on the energy from the sun. We have to exploit solar energy more, as our natural sources of petroleum get depleted. We have to look for other sources of energy as well. The gas hydrates in the ocean beds constitute a future source.

Brighter than a thousand suns!

Nuclear energy is an important form of energy used for many purposes, including the generation of electric power. Considerable energy is released when an atom bomb is exploded. When the first atom bomb was tested, people were transfixed with fright at its power. Robert Oppenheimer was in the control room. A passage from the Bhagvad Gita flashed into his mind.

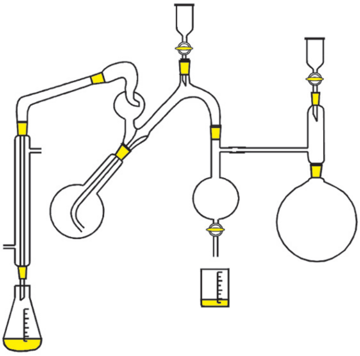
"If the radiance of a thousand suns were to burst into the sky, that would be like the splendour of the Mighty One."

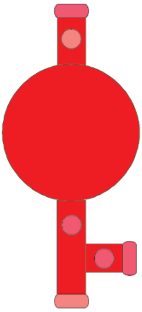
When the sinister and gigantic clouds rose up, he was reminded of yet another line from the Gita.

"I am become Death, the shatterer of the world."

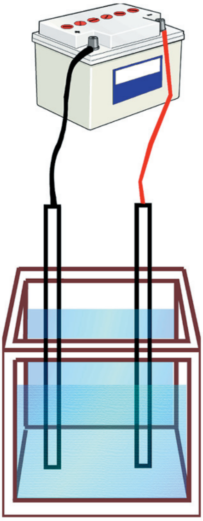
(*from Robert Jungk*)

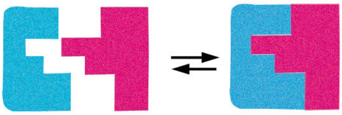
6





CHEMICAL REACTIONS





Objectives

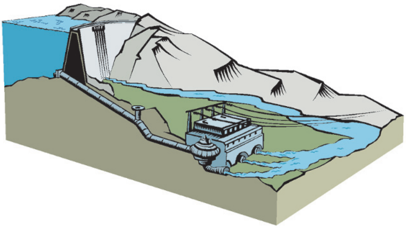
- In this lesson, we shall try to understand why and how chemical reactions occur and the factors that affect them.
- We then go through different types of reactions, which include catalysis and light-induced reactions.
- A combination of chemical reactions is necessary to prepare complex compounds. Chemists continue to discover new ways of assembling molecules. The supramolecular route provides a rich resource for new molecular systems.

Chemistry is a study of reactions between substances. It is therefore important to understand the nature of chemical reactions. One can make new substances by making use of various chemical reactions.

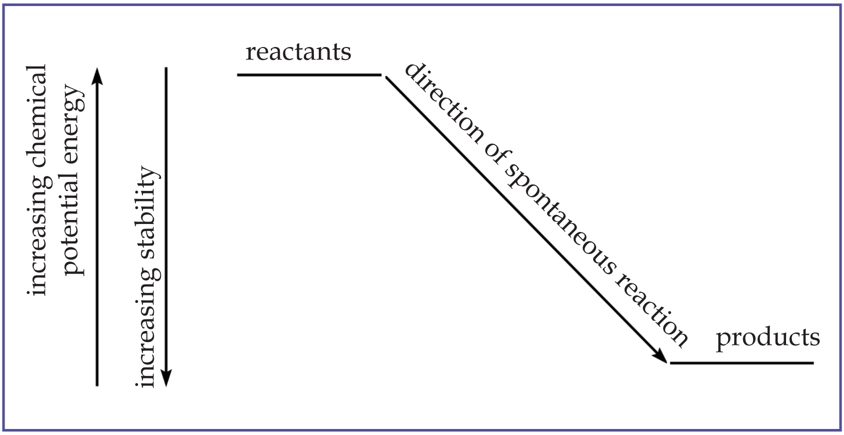
We shall try to understand how reactions can be associated with rates, and the factors that influence the rates. We then survey a few simple types of reactions and show how chemists innovate new strategies for making molecules using catalysts and new routes for synthesis.

6.1 Which reactions occur?

Some reactions occur spontaneously. We can understand this by analogy with potential energy. If we store water in a dam at the top of a hill, it has high potential energy. If there were no dam, water would have flowed down.



Chemical reactions occur spontaneously when the potential energy of the products is lower than the potential energy of the reactants.



In other words, the products have to be more stable than the reactants. One may, therefore, say that when energy is released in a chemical reaction, it will be spontaneous. This is the case of exothermic reactions. Thus, combustion (burning) is a spontaneous reaction. Remember combustion is associated with the release of heat (energy).

This does not mean that endothermic reactions do not occur. Endothermic reactions are made to occur by providing the necessary energy to the reactants.

Although we have mentioned that the change in energy in a reaction is a measure of the ease with which the reaction can occur, in reality, the situation is a bit more complex. One uses the concept of free energy, rather than that of potential energy, to determine how readily chemical reactions occur. The change in the free energy of a reaction takes into account not only the change in the potential energy that we considered before, but also the change in the order in the system. We will not go into the details here.

6.2 Chemical equilibrium

We used the word equilibrium when describing states of substances in Lesson 1. In a vessel containing ice and water, ice is in equilibrium with water. We indicate such an equilibrium situation by double arrows.

$$\underset{\text{solid}}{H_2O\,(s)} \rightleftharpoons \underset{\text{liquid}}{H_2O\,(l)}$$

Similarly,

$$\underset{\text{liquid}}{H_2O\,(l)} \rightleftharpoons \underset{\text{vapour}}{H_2O\,(g)}$$

We know that water is in equilibrium with its vapour. We suffer when there is a lot of water vapour in the air on a hot day. The double arrows are meant to show that the equilibrium is **dynamic**. That is, both the forward and reverse changes occur at the same time, and at the same rate. In $H_2O\ (l) \rightleftharpoons H_2O\ (g)$, the rate of evaporation is equal to the rate of condensation.

When excess salt or sugar is added to water, some solid remains at the bottom of the solution. The sugar or salt solution is then in equilibrium with solid sugar or salt. Such a solution is called a saturated solution.

Equilibrium is affected by temperature. For example, as the temperature increases, there will be more vapour produced from water, but at any given temperature, the pressure of the vapour over the liquid is constant.

Equilibrium situations are common in chemical reactions. This is because all reactions do not go to completion. Instead, reactants will be in equilibrium with the products. Let us look at some examples.

$$\underset{\text{clear solution}}{BiCl_3\ (aq)} \quad + \quad H_2O\ (l) \quad \rightleftharpoons \quad \underset{\substack{\text{white}\\\text{precipitate}}}{BiOCl} \quad + \quad 2HCl\ (aq)$$

If you add more acid to the white precipitate, it dissolves and gives a clear solution. If you add more water to the clear solution, it gives the white precipitate again.

$$\underset{\text{yellow}}{Fe^{3+}\ (aq)} \quad + \quad \underset{\text{colourless}}{SCN^-\ (aq)} \quad \rightleftharpoons \quad \underset{\text{deep red colour}}{(FeSCN)^{2+}\ (aq)}$$

If you add a potassium thiocyanate (KSCN) solution to a ferric nitrate solution, the solution turns deep red. To the red solution, if you add some more potassium thiocyanate or ferric nitrate solution, the colour becomes more intense. This shows that some Fe^{3+} and SCN^- are still present because of the equilibrium. That is, Fe^{3+} and SCN^- ions do not convert completely to the $(FeSCN)^{2+}$ species.

The manufacture of quicklime (CaO) by heating (900°C) calcium carbonate or limestone, $CaCO_3$, is a good example of how one exploits equilibrium reactions for preparing chemicals on a large scale.

$$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$$

If $CaCO_3$ is heated in a closed vessel, the CO_2 formed will push the reaction backward. In order to convert all the $CaCO_3$ to CaO, it is necessary to remove the CO_2 as it is formed. This is done in kilns by passing plenty of air. Note that **cement** is made by heating limestone with clay.

Many factors affect chemical reactions. These are: the concentrations of the reactants and products (as we have seen in the examples given earlier), temperature, pressure and catalysts. If a reaction is at equilibrium, and one of the conditions is changed, the position of the equilibrium will shift in such a way that the effect of change is opposed. Let us examine the role of some of the factors by taking two examples.

$$\underset{\text{brown colour}}{2NO_2\,(g)} \rightleftharpoons \underset{\text{colourless}}{N_2O_4\,(g)}$$

The reaction from left to right as written, is exothermic because bonds are formed. The forward reaction also decreases the number of moles of gas (or volume). Therefore, heat favours the reverse reaction and pressure favours forward reaction. This is because, when heat is supplied, equilibrium will shift in the direction in which heat is absorbed. Increasing pressure will shift the equilibrium to the right, that is in the direction which opposes the rise in pressure.

The industrial method (**Haber process**) for ammonia synthesis is an equilibrium reaction.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

The forward reaction is exothermic and is associated with a decrease in the number of moles (volume of the gas). Therefore, high pressure and low temperature (500°C) will favour the formation of ammonia. A catalyst is also used in this process. The biggest use of ammonia is in making fertilizers which contain NH_4NO_3 and $(NH_4)_2HPO_4$.

Sulfuric acid (H_2SO_4) is made industrially by the **contact process** which involves the catalytic oxidation of SO_2 to SO_3.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

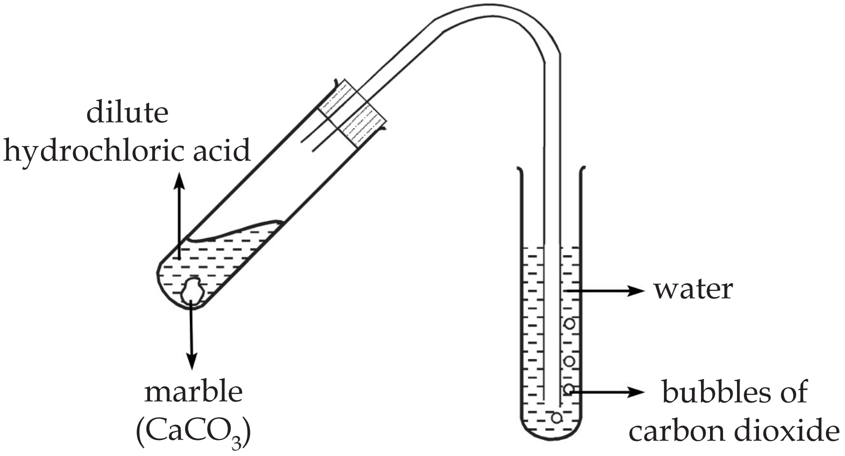
This is an exothermic process and a lower temperature (400°C) favours the reaction. SO_3 is dissolved in water to obtain H_2SO_4. To start with, SO_2 is obtained by burning sulfur or oxidizing (roasting) minerals such as ZnS.

6.3 Rates of reactions

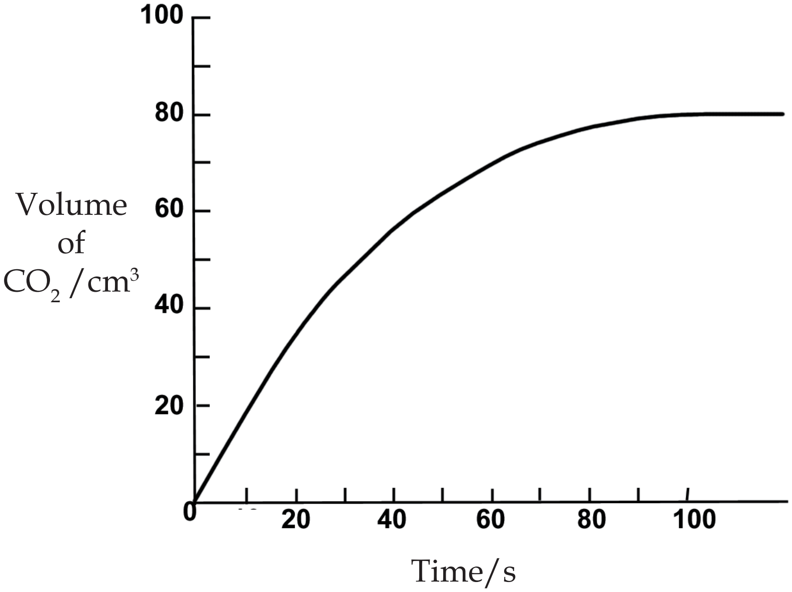
How fast or slow is a chemical reaction? The same reaction can occur at different speeds depending on the conditions. For example, hydrogen burns rapidly to form H_2O when there is lot of air. If there is little air, it does not burn that fast.

Can we measure the rate of a reaction?

Let us look at a few simple examples. In the reaction of calcium carbonate ($CaCO_3$) or marble with dilute acid, the change of rate can be followed by measuring the volume of carbon dioxide at regular intervals.

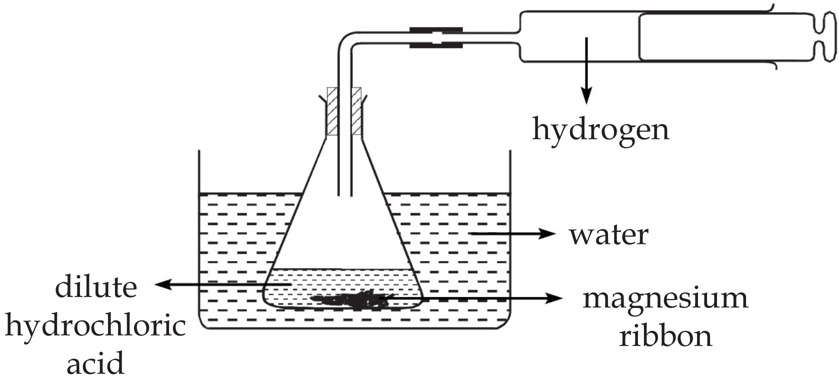


Plot the amount of CO_2 against time as follows:

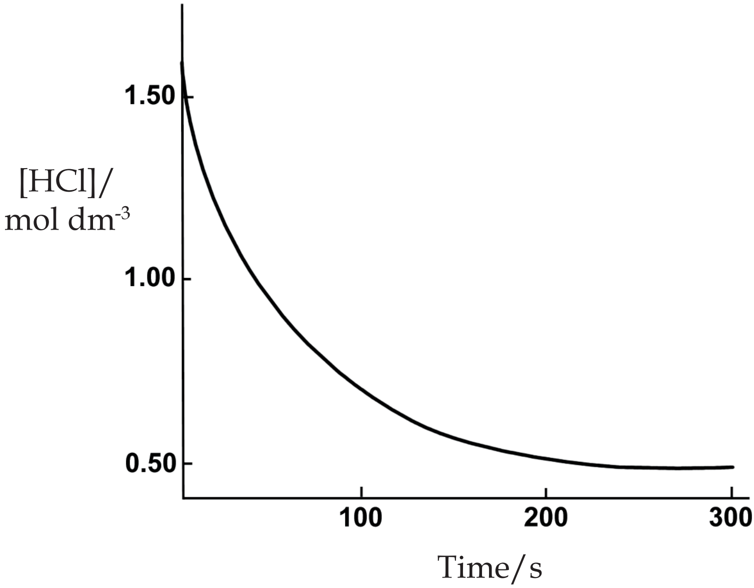


This rate curve shows the change in the amount of product formed with time.

Let us look at the reaction of magnesium with dilute acid.



Here, the hydrogen gas evolved in the reaction is measured as a function of time. The rate curve for the reaction can also be given in terms of the decrease in HCl concentration:



The rate curves (concentration versus time) are fitted into equations to classify reactions based on rate behaviour. In general, the rate of a reaction depends on the concentration of the reactants as follows:

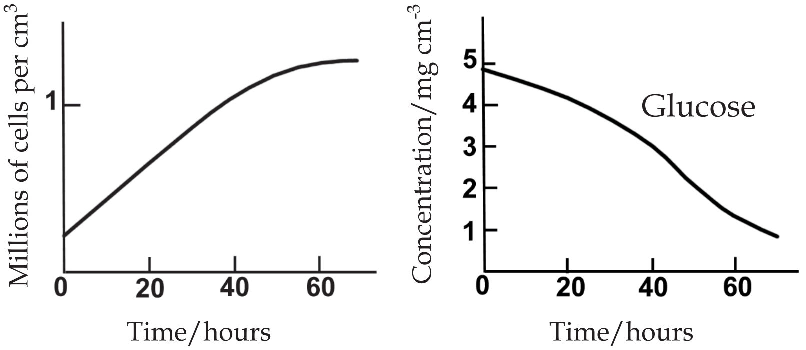
$$\text{Rate} \propto (\text{concentration})^n$$

or $$\text{rate} = \text{constant}\ (\text{concentration})^n = kc^n$$

Here, n is called the **order of the reaction**. The constant in the equation is called the **rate constant** or velocity constant.

Growth of cancer cells

Growth of cancer cells depends on the nutrient levels, temperature, pH etc. The rate of growth of cancer cells has been measured as a function of glucose (nutrient) concentration. The cells grow as the glucose concentration decreases. The data obtained on rats are shown in the plots below.



Forty years ago, we could measure the rates of reactions that occurred in a few seconds. Today, we can measure the rates of very fast reactions occurring in micro (10^{-6}), nano (10^{-9}), pico (10^{-12}) or even femto (10^{-15}) seconds. For example, the rates of electron transfer in reactions can be measured. Thus, we know the rate at which **photosynthesis** takes place in plants. Our ability to measure fast reaction rates is mainly due to the advent of **lasers**. Can you imagine how short a femto second is! Calculate the distance travelled by light in a femto second.

A clock reaction

There are some reactions whose rates can be exactly timed. Such reactions are called clock reactions. Let us look at one such reaction:

$$H_2O_2\,(aq) + 2I^-\,(aq) + 2H^+(aq) \longrightarrow I_2 + 2H_2O\,(l)$$

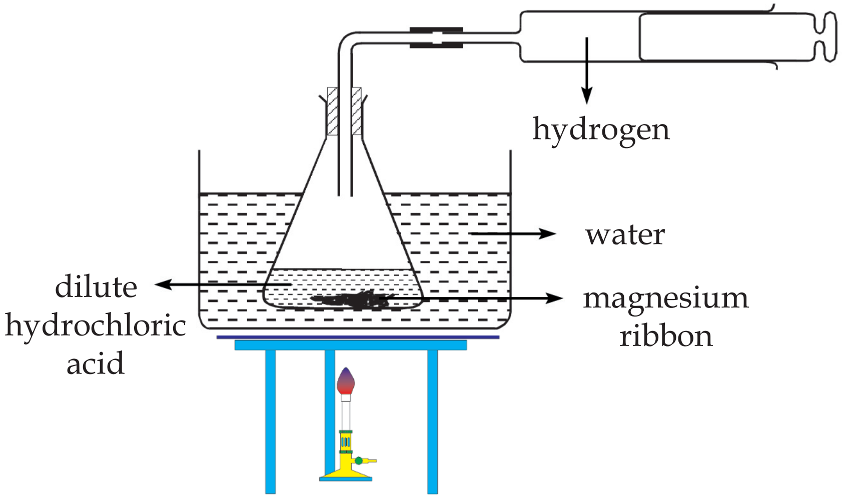
If a calculated amount of sodium thiosulfate ($Na_2S_2O_3$), (10 ml of 0.04 M solution), and 5 ml of 1% starch solution are added to a reaction mixture containing H_2O_2 (3% solution, 25 ml), H_2SO_4 (25 ml, 2.5 M), the iodine produced in the reaction reacts with the thiosulfate ions. This reaction continues until all the thiosulfate is consumed.

$$I_2 + 2S_2O_3^{2-}\,(aq) \longrightarrow S_4O_6^{2-}\,(aq) + 2I^-\,(aq)$$

Any iodine formed in the reaction later reacts with the starch and gives a blue colour to the solution. The colour appears at a fixed time (depending on the concentration of $S_2O_3^{2-}$). The larger the concentration of $S_2O_3^{2-}$, the longer is the time taken for the appearance of the blue colour.

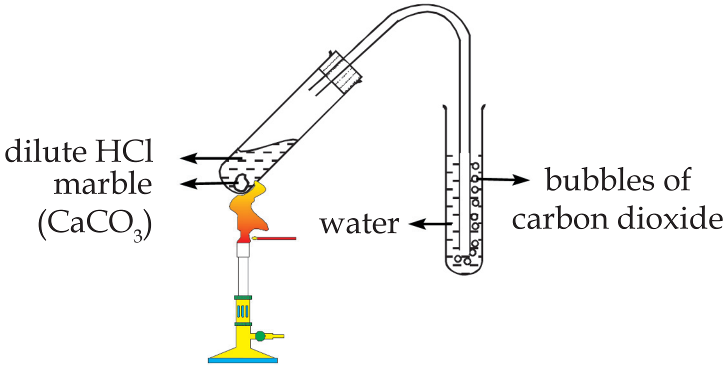
6.4 Factors that affect reaction rates

Various factors affect the rate of reactions. These are: temperature, surface area and light. In the reaction of magnesium (Mg) with an acid, if the concentration of the acid is changed, the rate of reaction changes.



If the flask is slightly warmed with a burner, the rate of the reaction increases. That is, temperature influences the rate of reaction. **The rate of a reaction increases with the increase in temperature.**

Effect of temperature: We described the reaction of calcium carbonate ($CaCO_3$) with dilute acid before. If we warm the test tube (containing marble and acid), more bubbles come out indicating the release of more carbon dioxide (CO_2).



As a thumb of rule, the rate of a reaction doubles for every 10 degree rise in temperature. The exact relation was given by Arrhenius. He showed that a plot of the logarithm of the rate constant against the inverse of temperature (log k versus 1/T) is a straight line. The slope of such line gives the **energy of activation** of the reaction.

The effect of temperature on the rate of a reaction is something we see in everyday life. We keep food in a refrigerator to slow down the rate of decomposition. During heart surgery, the body of the patient is cooled to slow down the rates of biological reactions.

Temperature not only affects the rates of reaction, but can even change the course of a reaction. Look at the following reactions of NH_4NO_3.

At 200°C, $NH_4NO_3 (s) \longrightarrow N_2O (g) + 2H_2O (g)$

At higher temperatures,

$$2NH_4NO_3 (s) \longrightarrow 2N_2 (g) + O_2 (g) + 4H_2O (g)$$

Effect of solvent: The solvent, which is the medium for carrying out a reaction, has a great effect on reaction rates. It is important to realize that molecules and ions in a solution are solvated (surrounded closely by solvent molecules). The nature of **solvation** changes with the solute and the solvent. For example, cations are solvated in water to give species like $M^{n+} (H_2O)_m$, e.g., $Na^+(H_2O)_6$. Solvents can hydrogen bond with solute molecules or solutes may affect the hydrogen bonding or association of solvent molecules.

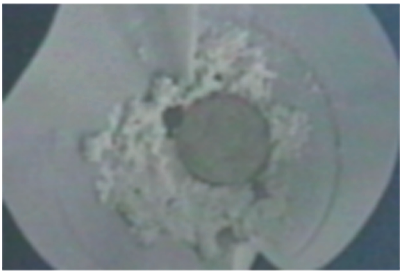
Effect of surface area: Amongst the other factors that affect the rate of reaction, the area of the surface of a solid is an important one. For example, a sugar cube takes longer to dissolve in tea or coffee than granulated or powdered sugar. Sugar powder has a larger surface area.

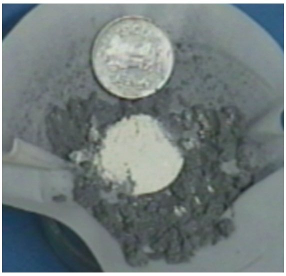
Effect of light: Light affects some chemical reactions. For example, silver chloride (AgCl) and silver bromide (AgBr) are both decomposed by light. This is the basis of **photography**.

One can do a simple experiment to demonstrate the action of light. Add hydrochloric acid (HCl) to a silver nitrate ($AgNO_3$) solution. Silver chloride (AgCl) comes down as a white precipitate.

$$AgNO_3\,(aq) + HCl\,(aq) \longrightarrow AgCl\,(s) + HNO_3\,(aq)$$

Spread the precipitate on a filter paper. Cover part of it with a coin. Expose the entire thing to sunlight. Remove the coin. What do you notice? The area covered by the coin has the light colour of silver chloride. The remaining area (not covered by the coin) would have turned black. This is because of the small particles of silver formed by the decomposition of silver chloride by light. Light-induced reactions are called **photochemical reactions**.





Photosynthesis by leaves (chlorophyll) is an important photochemical reaction. The reaction is given by:

$$6CO_2 + 6H_2O \xrightarrow{\text{light}} \underset{\text{glucose (starch)}}{C_6H_{12}O_6} + 6O_2$$

Photochemical smog: This is an example of pollution caused by the chemical reaction of primary pollutants in the presence of sunlight. Photochemical smog can either involve only nitrogen dioxide (NO_2), or nitrogen dioxide and hydrocarbons in the atmosphere. Nitrogen dioxide decomposes into nitric oxide (NO) and oxygen atom (O) in the presence of ultraviolet light from the sun.

$$NO_2 \xrightarrow{\text{ultraviolet light from the sun}} NO + O$$

The oxygen atoms thus formed combine with the atmospheric oxygen to form ozone (O_3). While ozone is beneficial at higher layers of the atmosphere, it is harmful in the troposphere (8–18 km) above the earth's surface.

$$O(g) + O_2(g) \longrightarrow O_3(g)$$

In the absence of hydrocarbons, over a period of time, ozone oxidizes nitric oxide back to nitrogen dioxide.

$$\mathrm{NO\,(g)} + \mathrm{O_3\,(g)} \longrightarrow \mathrm{NO_2\,(g)} + \mathrm{O_2\,(g)}$$

Photochemical smog caused by nitrogen dioxide and hydrocarbons: This is caused by the combined effects of primary pollutants and is more harmful than the pollution caused by each pollutant acting separately. The presence of hydrocarbons disrupts the photochemical nitrogen dioxide cycle. Hydrocarbons react chemically with the oxygen atoms and ozone molecules to produce complex pollutants.

Primary pollutants in the atmosphere (nitric oxide, nitrogen dioxide, hydrocarbons)	→	chemical reactions take place in the presence of sunlight	→	Photochemical smog containing secondary pollutants (ozone, aldehydes peroxyacetylnitrate)

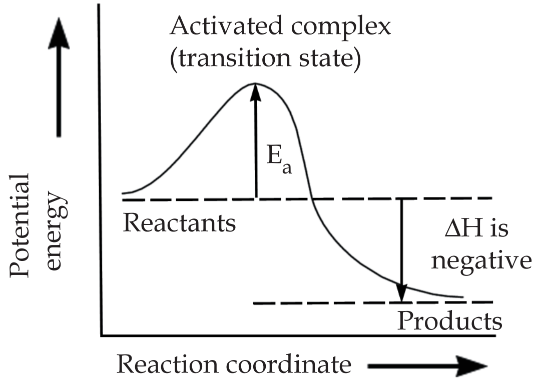
Peroxyacetylnitrate is a terribly irritating chemical.

6.5 How reactions occur

We saw earlier that chemical reactions depend upon the concentration of the reactants and temperature. This can be understood on the basis of the collisions between the species (molecules, atoms, ions etc.). The number or the frequency of collisions depends upon the concentration and the temperature.

It is necessary for the colliding species to be oriented appropriately with respect to one another if the collisions have to result in a reaction.

The manner in which the reacting molecules change to products is understood by plotting the potential energy against the reaction coordinate. The reaction coordinate represents the change in the geometrical arrangement of the atoms in the reacting molecules taken as a whole, as the reactants transform to the products. A geometrical arrangement is called **configuration**. The change from the reactant arrangement or configuration to the product configuration occurs through a critical configuration called the **transition state or activated complex**. Only molecules with sufficient energy can attain this critical configuration. As the configuration changes from the transition state to that of the products, there will be a decrease in potential energy. This is illustrated in the figure below.

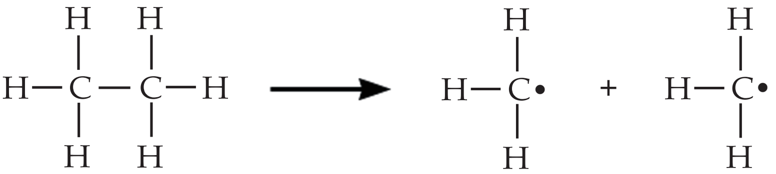


From the figure, we see that the activated complex or the transition state has a higher potential energy than the reactants or products. The products have lower potential energy than the reactants and the reaction is therefore exothermic (see Lesson 5). If the reaction is endothermic, the potential energy of the products will be higher than that of the reactants.

The transition state model explains the various factors associated with rates of chemical reaction. The difference between the potential energy of the transition state and that of the reactants gives the **activation energy**, E_a. The magnitude of E_a determines how temperature affects reaction rates.

Many of the chemical reactions involve a number of steps. A sequence of reaction steps is called **reaction mechanism**. A mechanism has to be consistent with reaction rate data and on the nature of the short-lived species that may be formed during the reaction. The short-lived species are called **reaction intermediates**. We shall describe a few of them.

Free radicals: An atom or a group of atoms possessing an odd electron (unshared electron) is called a free radical. Free radicals are produced by breaking covalent bonds.



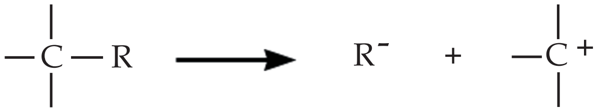
$$H_3C{-}CH_3 \longrightarrow H_3C\bullet + H_3C\bullet$$

In the above reaction, methyl free radicals are produced. We represent the odd electron in a free radical by a dot. Other examples are:

$$H_2O_2 \longrightarrow HO\bullet + HO\bullet$$

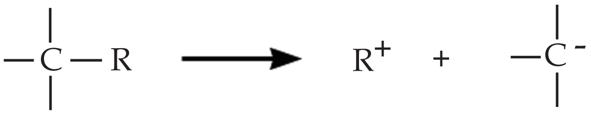
$$Cl_2 \longrightarrow Cl\bullet + Cl\bullet$$

Carbonium ions: These are positively charged ions produced when a bond is broken in such a way that one part retains both the electrons involved in forming the bond.



Carbonium ion

Carbanions: These are negatively charged ions produced in the following manner:



Carbanion

Reagents are also classified depending on whether they attack electron-rich centres or electron-deficient centres. **Electrophiles** are reagents which attack electron-rich centres (e.g., H^+, Br^+, NO_2^+, R_3C^+, BF_3^+). **Nucleophiles** are reagents which attack electron-deficient centres (e.g., H^-, OH^-, Br^-, RNH_2).

6.6 Some reactions

Hundreds of reactions are known today. One uses a combination of reactions to make new compounds. Here, we shall look at some of the simplest of reactions.

Substitution reactions:

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$

methane + chlorine → methyl chloride + hydrogen chloride

$$C_6H_6 + Br_2 \longrightarrow C_6H_5Br + HBr$$

benzene + bromine → bromo benzene + hydrogen bromide

Here, a halogen atom (Cl, Br) substitutes a hydrogen atom.

Addition reactions:

$C_6H_6 + 3H_2 \longrightarrow C_6H_{12}$
benzene + chlorine Cyclohexane

$C_6H_6 + 3Cl_2 \longrightarrow C_6H_6Cl_6$
benzene + chlorine Hexachlorocyclohexane
(gammaxene)

$C_2H_4 + H_2 \longrightarrow C_2H_6$
ethene + hydrogen ethane

$C_2H_4 + Br_2 \longrightarrow C_2H_4Br_2$
ethene + bromine dibromoethane

When hydrogen or bromine is added to ethene (ethylene), the double bond gets saturated and we get a saturated hydrocarbon (alkane) or its derivative. We right away see why alkenes decolourize bromine water (brown). Bromine adds on to double bonds.

Exchange reactions:

$KBr + NaCl \longrightarrow KCl + NaBr$
potassium bromide sodium chloride potassium chloride sodium bromide

Here, Cl and Br have exchanged places.

$H_2O + D_2O \longrightarrow 2HOD$
heavy water

Here, the two isotopes (H and D) have exchanged places.

Hydrolysis:

In hydrolysis, substances react with H_2O or hydroxyl ions (OH^-).

$FeCl_3$	+	$3H_2O$	$\longrightarrow$	$Fe(OH)_3$	+	HCl
ferric chloride		water		ferric hydroxide (precipitate)		hydrogen chloride

C_2H_5Br	+	$NaOH$	$\longrightarrow$	C_2H_5OH	+	$NaBr$
ethyl bromide		sodium hydroxide		ethanol		sodium bromide

Simple oxidations:

Mg	+	$\frac{1}{2}\,O_2$	$\longrightarrow$	MgO
magnesium		oxygen		magnesium oxide

$4Fe$	+	$3O_2$	$\longrightarrow$	$2Fe_2O_3$
iron		oxygen		ferric oxide

CH_4	+	$2O_2$	$\xrightarrow{\text{burn}}$	CO_2	+	$2H_2O$
methane		oxygen		carbon dioxide		water

$(CH_3)_2CHOH$	$\xrightarrow[500^\circ C]{\text{catalyst}}$	$(CH_3)_2C = O$	+	H_2
iso-propyl alcohol		acetone		hydrogen

C_2H_5OH	$\xrightarrow{\text{fermentation}}$	CH_3COOH
ethanol		acetic acid (vinegar)

Addition of oxygen to a substance is an oxidation reaction.

> Remember corrosion of iron is an oxidation reaction.

Removal of hydrogen is also an oxidation reaction.

$$MgH_2 \xrightarrow{\text{heat}} Mg + H_2$$

Simple reductions:

$$\begin{array}{ccccc} \mathrm{Na} & + & \tfrac{1}{2}\,\mathrm{H_2} & \longrightarrow & \mathrm{NaH} \\ \text{sodium} & & \text{hydrogen} & & \text{sodium hydride} \end{array}$$

$$\begin{array}{ccccc} \mathrm{N_2} & + & \mathrm{3H_2} & \longrightarrow & \mathrm{2NH_3} \\ \text{nitrogen} & & \text{hydrogen} & & \text{ammonia} \end{array}$$

$$\begin{array}{ccccc} \mathrm{C_2H_4} & + & \mathrm{H_2} & \longrightarrow & \mathrm{C_2H_6} \\ \text{ethene} & & \text{hydrogen} & & \text{ethane} \end{array}$$

$$\begin{array}{ccccc} \mathrm{C_6H_6} & + & \mathrm{3H_2} & \longrightarrow & \mathrm{C_6H_{12}} \\ \text{benzene} & & \text{hydrogen} & & \text{cyclohexane} \end{array}$$

Addition of hydrogen to a substance is a reduction reaction. Removal of oxygen is also a reduction reaction.

$$\mathrm{H_2O_2} \longrightarrow \mathrm{H_2O} + \tfrac{1}{2}\,\mathrm{O_2}$$

Decomposition reactions:

Some substances decompose to give simpler substances.

$$\mathrm{CaCO_3\,(s)} \xrightarrow{\text{heat}} \mathrm{CaO\,(s)} + \mathrm{CO_2\,(g)}$$

$$\mathrm{Ag_2O\,(s)} \xrightarrow{\text{heat}} \mathrm{Ag\,(s)} + \tfrac{1}{2}\,\mathrm{O_2(g)}$$

$$\mathrm{H_2O_2\,(l)} \longrightarrow \mathrm{H_2O\,(l)} + \tfrac{1}{2}\,\mathrm{O_2\,(g)}$$

$$\mathrm{N_2O_4\,(g)} \longrightarrow \mathrm{2NO_2\,(g)}$$

Dehydration reactions:

$$\mathrm{CuSO_4\,.\,5H_2O} \xrightarrow{\text{heat}} \mathrm{CuSO_4} + \mathrm{5H_2O}$$

$$\begin{array}{ccccc} \mathrm{C_2H_5OH} & \xrightarrow[\mathrm{Al_2O_3}]{\text{heat}} & \mathrm{C_2H_4} & + & \mathrm{H_2O} \\ \text{ethyl alcohol} & & \text{ethene} & & \end{array}$$

Dehydration is a decomposition reaction. Dehydration involves removal of water from a substance.

Chain reactions:

A chain reaction is one where the products obtained initially participate again in another reaction to give another product. Such reactions usually occur rapidly and can be explosive. Chain reactions occur in combustion and in reactions initiated by light (photochemical reactions). Reaction between hydrogen and chlorine in the presence of sunlight is a well-known example. In this reaction, sunlight is the initiator. The reaction takes place in three steps – **initiation, propagation and termination**.

Initiation step: $Cl_2 \longrightarrow Cl + Cl$

Propagation step: $Cl + H_2 \longrightarrow HCl + H$

$H + Cl_2 \longrightarrow HCl + Cl$

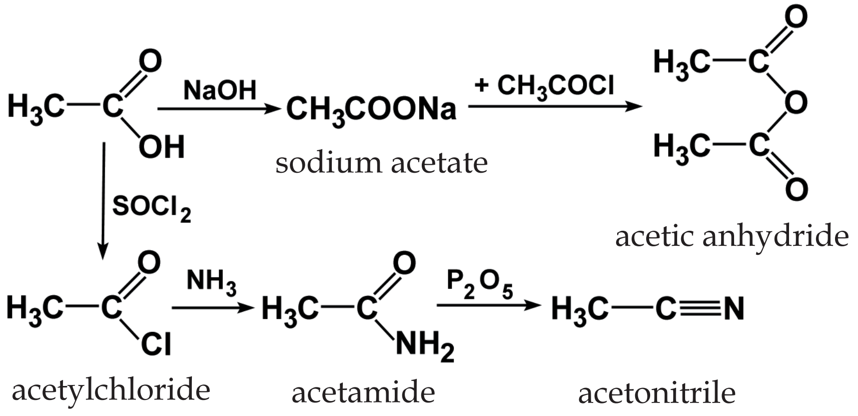
Termination step: $H + H \longrightarrow H_2$

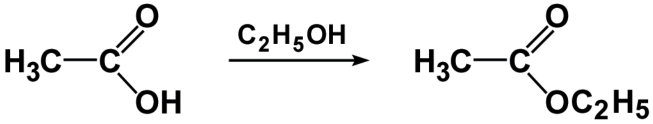
$Cl + Cl \longrightarrow Cl_2$

$H + Cl \longrightarrow HCl$

Some chemical transformations:

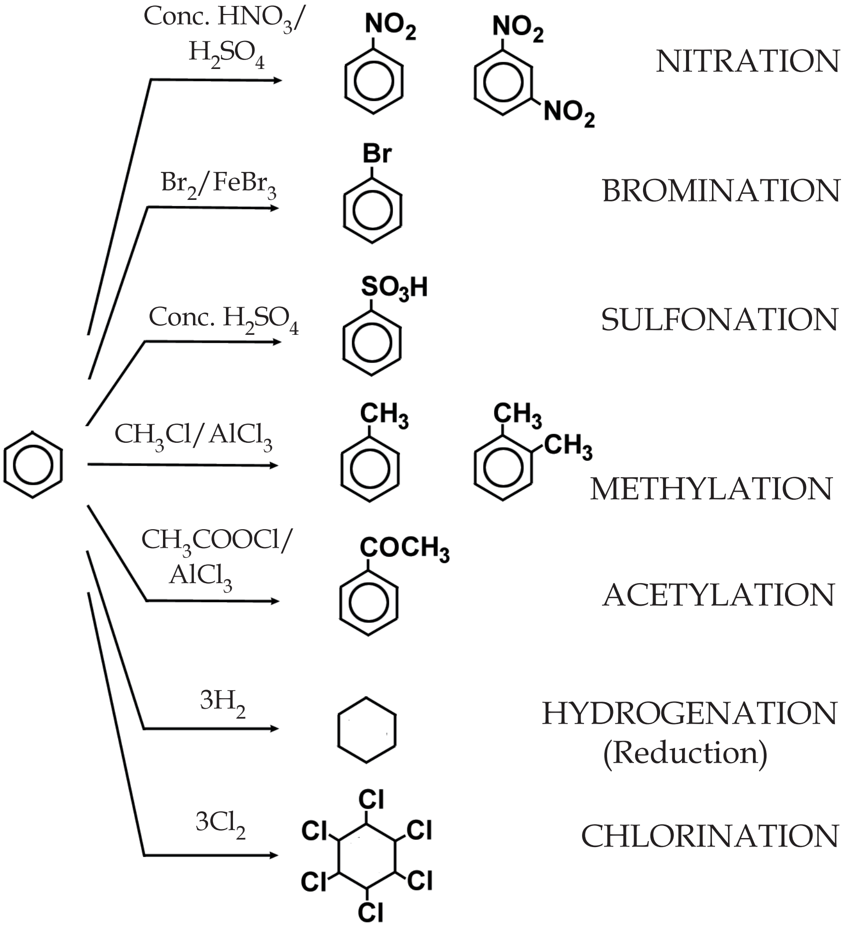
First, let us look at the reactions of a simple organic acid, acetic acid, $H_3C\ COOH$.



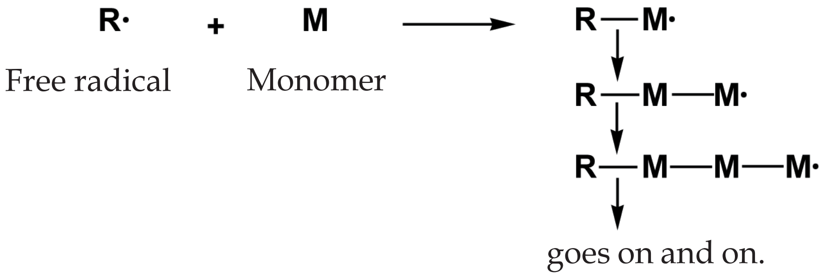


ethyl acetate

In the list below, various reactions of benzene are given. Some are substitution reactions and others are addition reactions.

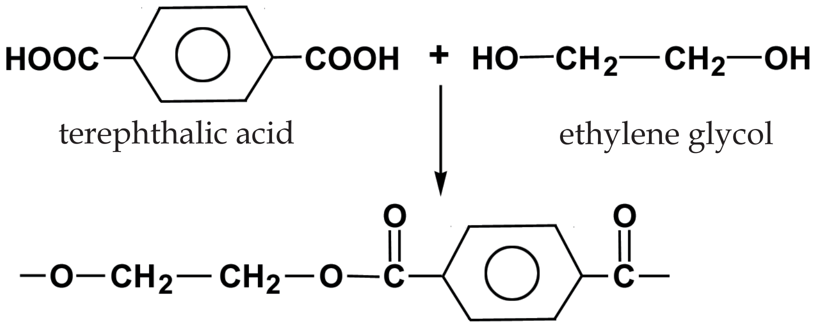


Polymerization: A reaction in which a polymer is formed from one or more types of **monomer** (small molecules) is called polymerization. There are different types of polymerization. In **chain-growth polymerization**, monomers are successively added on to a growing polymer chain (just like threading beads on a string). This type of polymerization requires an initiator, generally a free radical.



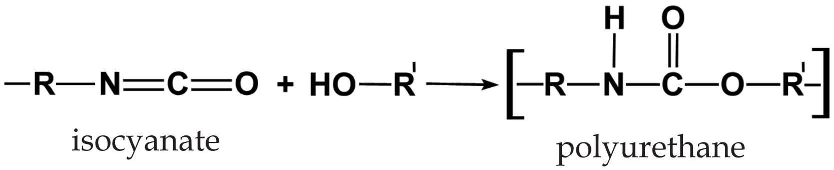
This is a chain reaction. Polyethylene (from ethylene), polypropylene (from propylene), polyvinylchloride (from vinyl chloride), polystyrene (from styrene), polyacrylonitrile (from acrylonitrile) and polymethylmethacrylate are all formed by the chain growth process.

Polymerization occurs by **step-growth** in polyesters.

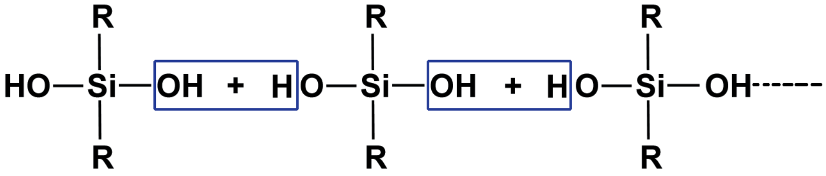


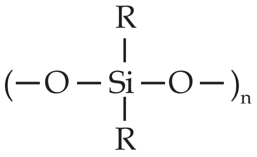
Terylene (or dacron)

Here, an acid group of one monomer reacts with the alcohol group on the other monomer to form an ester. The chain so formed has the acid and OH group at the ends and the reaction goes on. H_2O is eliminated in the reaction. Polyurethane and nylon are also formed by step growth.



Silicones are inorganic polymers. They are formed by polymerization of silanols. (H_2O is eliminated).





Silicones containing $(-O-\underset{R}{\underset{|}{\overset{R}{\overset{|}{Si}}}}-O-)_n$ units forms oils, greases, resins and rubbers.

6.7 Redox reactions (reduction-oxidation reactions)

Earlier we gave examples of simple oxidation reactions. Those examples were of addition of oxygen or removal of hydrogen. We also gave examples of reduction reactions. In those reactions, oxygen was removed from a substance or hydrogen was added.

A better definition of oxidation and reduction is based on the process of **electron transfer** occurring in a reaction. Redox reactions are those where electrons are transferred from one reactant to another. The reactant from which electrons are removed or lost gets oxidized. Oxidation involves the loss of electrons from a substance. Reduction is the gain of electrons by a substance. The substance which accepts electrons gets reduced.

Oxidation and reduction reactions occur simultaneously. One reactant gets oxidized and another is reduced. Let us consider a few examples.

$$Mg\,(s) + Cl_2\,(g) \longrightarrow MgCl_2$$

Here, Mg gets oxidized to Mg^{2+} and Cl_2 gets reduced $2Cl^-$.

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

Here, Zn is oxidized to Zn^{2+} and Cu^{2+} is reduced to Cu.

Identify which reactant is oxidized (and which is reduced) and to what, in the following reactions:

$$2Mg + O_2 \longrightarrow 2MgO$$

$$Ag_2O \longrightarrow 2Ag + \tfrac{1}{2}O_2$$

$$Fe + S \longrightarrow FeS$$

$$NiO + H_2 \longrightarrow Ni + H_2O$$

Remember, in the preparation of chlorine, Cl_2, chloride ion, Cl^-, is oxidized.

Air pollution blackens white lead (lead paint, lead carbonate). This is due to the reaction of H_2S in the atmosphere converting $PbCO_3$ to black PbS.

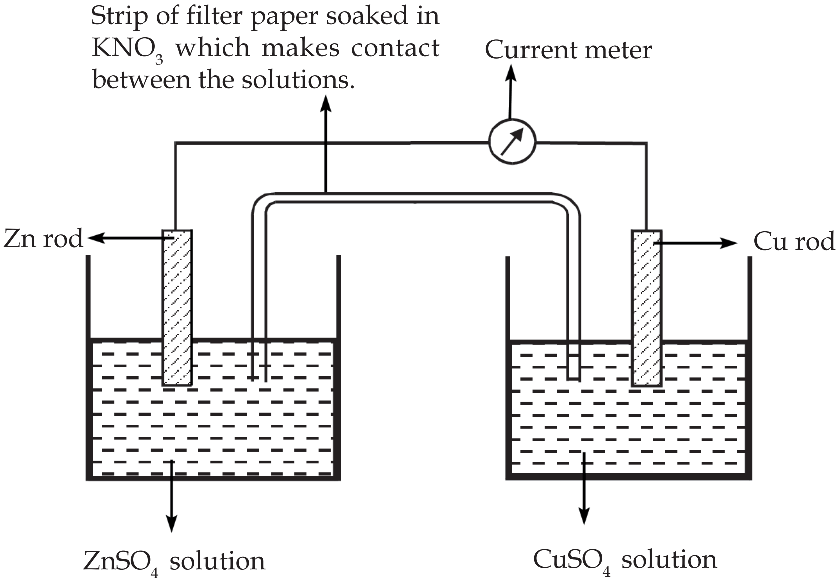
$$PbCO_3 + H_2S \longrightarrow PbS + CO_2 + H_2O$$

Treatment with hydrogen peroxide, converts PbS to $PbSO_4$.

$$PbS + 4H_2O_2 \longrightarrow PbSO_4 + 4H_2O$$

(Identify the oxidized and the reduced species in the above reactions.)

Let us make a simple cell containing a zinc rod dipped in a solution containing a zinc salt (Zn^+ ions) and a copper rod dipped in a solution containing a copper salt (Cu^{2+} ions) as follows: If we connect the two metal rods by a wire and make contact between the solutions, current will flow because of the redox reaction.



The reactions here are:

Oxidation: Zn (s) $\longrightarrow$ Zn^{2+} (aq) + $2e^-$, at the anode.

Reduction: Cu^{2+} + $2e^-$ $\longrightarrow$ Cu (s), at the cathode.

The ease with which elements can get oxidized or reduced is described by the so-called **activity series**. This series is given in terms of the **redox potentials**. We shall use these potentials without going into details of how they are obtained. The more positive the potential, the more likely it is for reduction to occur. The less positive, or more negative, the more likely it is that oxidation occurs. We list below a few potentials (in volts):

K^+ (aq)	+	e^-	$\longrightarrow$	K (s)	–2.92
Na^+ (aq)	+	e^-	$\longrightarrow$	Na (s)	–2.71
Zn^{2+} (aq)	+	$2e^-$	$\longrightarrow$	Zn (s)	–0.76
$2H^+$ (aq)	+	$2e^-$	$\longrightarrow$	H_2 (g)	0.00
Cu^{2+} (aq)	+	$2e^-$	$\longrightarrow$	Cu (s)	+0.34
Ag^+ (aq)	+	e^-	$\longrightarrow$	Ag (s)	+0.80
Br_2 (l)	+	$2e^-$	$\longrightarrow$	$2Br^-$ (aq)	+1.07

Increasing tendency ↓ for reduction

These are potentials for reduction reactions. The potentials for the opposite reactions (oxidation) will have the same values, but with the opposite signs. It is easy for bromine (Br_2) to become bromide (Br^-) ions (potential 1.07 volts), but the opposite is difficult (potential –1.07 volts). It is difficult for Na^+ to become Na (potential –2.71 volts), but it is easy for Na to become Na^+ (potential +2.71 volts). By using the the redox potentials, we can understand why Cu^{2+} + Zn gives Cu + Zn^{2+}.

When various metals are listed in the activity series as above, it is also called the **electrochemical series**. This series gives the order of reactivity of metals. In the above list, we have K, Na, Zn and Cu. This means K and Na are more reactive and electropositive than Zn, and Zn is more reactive and electropositive than Cu. The **noble metals** silver and gold come after Cu. They are least electropositive and least reactive.

The state of oxidation (or reduction) of an element is described by the **oxidation number**. It is somewhat like the valence that we read in Lesson 1. Oxidation number is the charge assigned to an atom or an ion.

Oxidation number is +1 for H, Na and K.

Oxidaton number is +2 for Ca, Mg and Zn.

Oxidation number is +3 for Al.

Oxidation number is –1 for Cl and Br (in their compounds).

Oxidation number is –2 for O (in its compounds).

Oxidation number of the elements (e.g., H_2, Br_2, O_2, Cl_2) is zero.

Some elements like Fe can have more than one oxidation number. For example, Fe_2O_3, $FeCl_3$ (+3); FeO, $FeCl_2$ (+2).

Using the above values of oxidation numbers, we can calculate the oxidation number of various elements present in compounds and ions.

CO_2: O has oxidation number of –2.
Therefore, 2 O has oxidation number of $-2 \times 2 = -4$.
Since CO_2 is neutral, the oxidation number of C in CO_2 is +4.

SO_4^{2-} : O has oxidation number of –2.
Therefore, 4 O has oxidation number of $-2 \times 4 = -8$.
SO_4^{2-} has a charge of –2.
Therfore, S in SO_4 has the oxidation number of +6.

Check the following:

Oxidation number of Cl in ClO_4^- is +7.

Oxidation number of Cr in $Cr_2O_7^{2-}$ is +6.

Oxidation number of Mn in Mn_3O_4 is +8/3.

H has an oxidation number of +1 in HCl and H_2O.
The oxidation number of H in NaH is –1!

Note that the sum of the oxidation numbers of all the elements present in a compound always comes to zero.

For example, CO_2 (C = +4; 2 O = -4),

Fe_2O_3 (2 Fe = 2 × +3 = +6, 3 O = –6)

Nice colour changes occur when some of the ions get oxidized or reduced. Such colour changes are used for tests and titrations (estimations).

$FeSO_4$ containing Fe^{2+} ions will decolourize acidified $KMnO_4$ (potassium permanganate). Fe^{2+} in $FeSO_4$ gets oxidized to Fe^{3+}; Mn^{7+} in MnO_4^- gets reduced to Mn^{2+}.

When potassium dichromate ($K_2Cr_2O_7$) is reduced, the orange colour turns to green because Cr^{6+} gets reduced to Cr^{3+}.

A simple example of an oxidation reaction is the oxidation of iodide ion (I^-) to iodine by addition of hydrogen peroxide (H_2O_2) in acidic solution.

$$H_2O_2\,(aq) + 2H^+\,(aq) + 2I^-\,(aq) \longrightarrow 2H_2O\,(l) + I_2$$

Oxidation numbers can be used to balance complex redox equations such as the one below:

$$5Fe^{2+}\,(aq) + 8H^+\,(aq) + MnO_4^-\,(aq) \longrightarrow 5Fe^{3+}\,(aq) + Mn^{2+}\,(aq) + 4H_2O\,(l)$$

6.8 Catalysis

Catalysis is a process where a substance increases the rate of a reaction without getting consumed. If you remember, in the preparation of oxygen, manganese dioxide (MnO_2) is used as the catalyst.

$$2H_2O_2\,(aq) \xrightarrow{MnO_2} 2H_2O\,(l) + O_2\,(g)$$

The action of a catalyst is specific. A catalyst that increases the rate of one chemical reaction may not do so in the case of another. The opposite of a catalyst is an **inhibitor**, which slows down the rate of a reaction. The decomposition of H_2O_2 giving O_2 is inhibited by dilute acids.

Two types of catalysis can be distinguished: **Homogeneous and heterogeneous catalysis.** In homogeneous catalysis, the catalyst and the reactants are in the same state or phase. In heterogeneous catalysis, the catalyst and the reactants are in different phases. The catalyst may be a solid and the reactants may be gases.

Million of tonnes of chemicals are made all over the world by catalytic reactions. Petrochemicals, fertilizers and a whole variety of other chemicals are produced in this way. Different reactions require different catalysts. Catalyst design , therefore, is a crucial aspect of chemistry, and catalysts constitute an important class of materials.

Examples of homogeneous catalysis: The hydrolysis of an organic ester to give an acid is catalyzed by an acid.

$$CH_3COOC_2H_5 + H_2O \xrightarrow[\text{(acid)}]{H^+} CH_3COOH + C_2H_5OH$$

Decomposition of H_2O_2 to H_2O and O_2 is catalyzed by iodide ions.

$$H_2O_2\,(aq) \xrightarrow{I^-\,(aq)} H_2O + \tfrac{1}{2}O_2$$

Heterogeneous catalysis: Heterogeneous catalysis is employed widely for the manufacture of important chemicals. To understand the important role of catalysts, we shall look at the reaction between ammonia and oxygen.

In the absence of a catalyst,

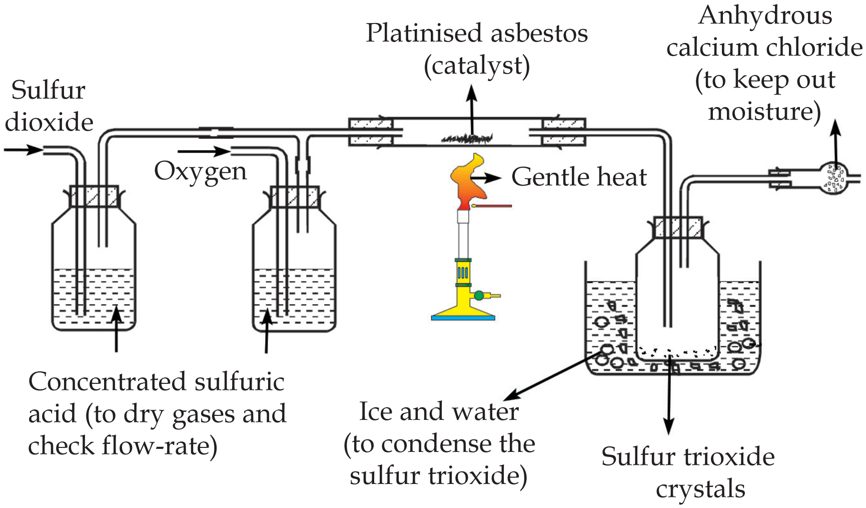
$$4NH_3\,(g) + 3O_2\,(g) \longrightarrow 2N_2\,(g) + 6H_2O\,(g)$$

In the presence of a catalyst (hot platinum wire),

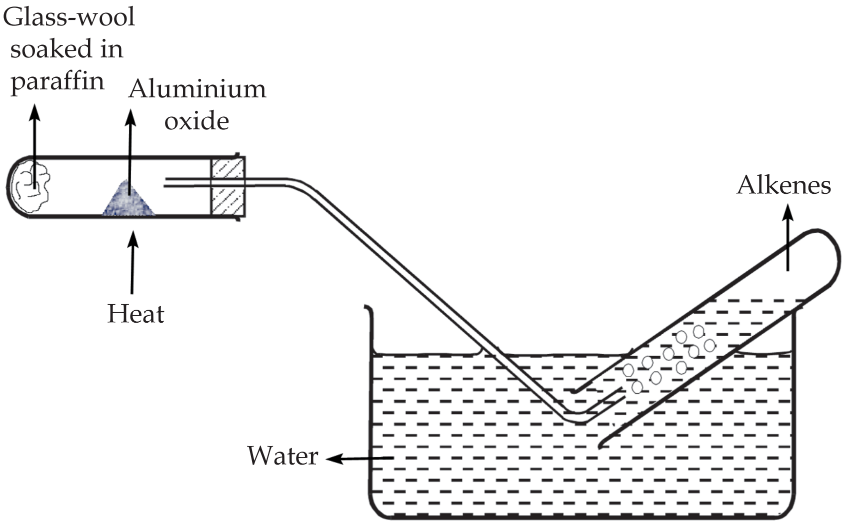
$$4NH_3\,(g) + 5O_2\,(g) \longrightarrow 4NO\,(g) + 6H_2O\,(g)$$

Nitric oxide (NO) is oxidized to NO_2 with oxygen and NO_2 is reacted with water to get HNO_3.

In the oxidation of SO_2 to SO_3 in the manufacture of sulfuric acid (by the **contact process**), we use a platinum catalyst. We can do a simple experiment in the laboratory as shown below.



Catalytic cracking is an important reaction in petrochemical industry. In this process, oil containing large hydrocarbons (alkanes) is passed over a catalyst (Al_2O_3 mixed with SiO_2 or Cr_2O_3) around 450°C to obtain smaller hydrocarbons, including alkenes. We can demonstrate this reaction by a simple apparatus shown below. The formation of alkenes is tested by shaking with bromine water.



In the **Fischer-Tropsch process**, a mixture of CO and H_2 is passed over iron or cobalt containing catalysts at high pressures and temperatures to produce hydrocarbons. Methyl alcohol (methanol) is prepared by passing a mixture of CO and H_2 over a catalyst (Cu/ZnO) at relatively high pressures at 300°C. Margarine and other types of solid edible fats are produced by the hydrogenation of vegetable oils (e.g., groundnut oil) in the presence of a nickel catalyst. In this reaction, the double bonds present in the oil get saturated or hydrogenated.

The industrial manufacture of ammonia by the **Haber process** is an outstanding example of heterogeneous catalysis. The steps involved are as follows:

$$\underset{\text{natural gas}}{CH_4\,(g)} + \underset{\text{steam}}{H_2O\,(g)} \xrightarrow{\text{Ni catalyst}} CO\,(g) + 3H_2\,(g)$$

$$CO\,(g) + \underset{\text{steam}}{H_2O\,(g)} \xrightarrow{Fe_3O_4\,/\,Cu} CO_2\,(g) + H_2\,(g)$$

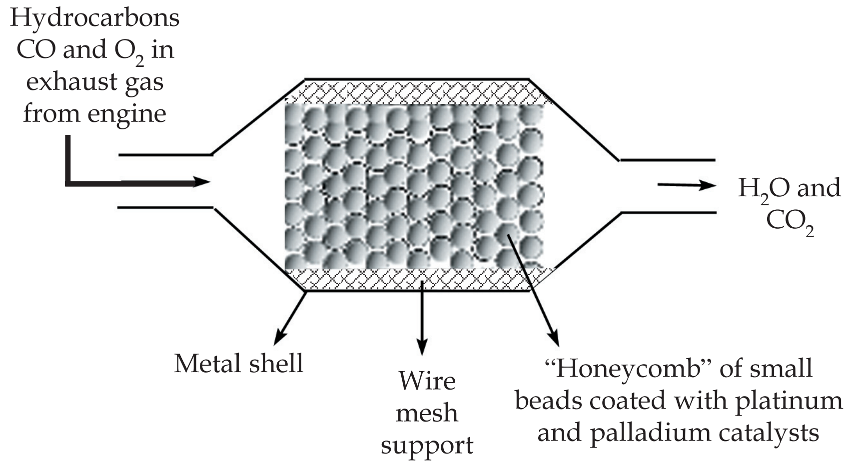
CO_2 is removed. The hydrogen so obtained is reacted with nitrogen:

$$N_2\,(g) + 3H_2\,(g) \xrightarrow{\text{Fe catalyst}} 2NH_3\,(g)$$

The reaction is carried out at 400°C and at high pressures. Millions of tonnes of fertilizers in the world are still made by this process.

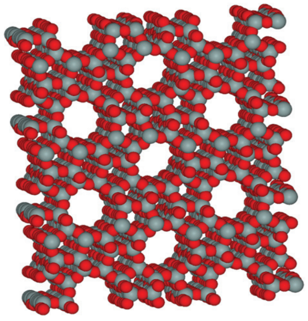
Nature, on the other hand, fixes nitrogen in the atmosphere by converting it into ammonia by making use of an enzyme (nitrogenase) under ordinary conditions. Such a conversion is carried out by certain *Rhizobium* organisms present in root nodules of legume species. Nitrogenase has an active centre containing molybdenum, iron and sulfur atoms.

Catalytic converter: Cars and lorries give out exhaust gases which pollute the atmosphere and are dangerous for health. Catalytic converters are used in vehicles to convert harmful hydrocarbons and carbon monoxide, present in the exhaust gases, to carbon dioxide and water. The catalysts used here are generally noble metals or/and metal oxides.



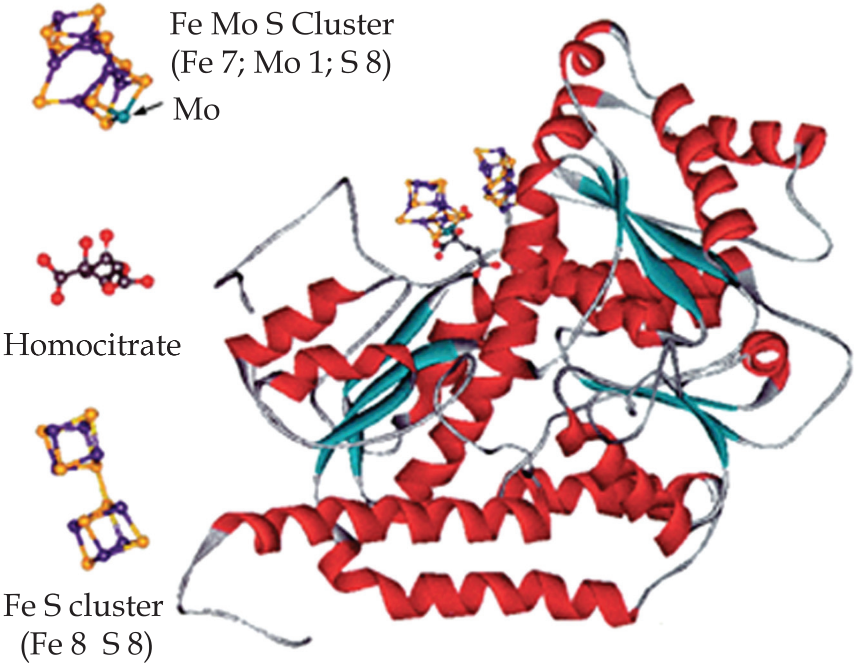
The catalytic converter consists of a "honeycomb" of small beads coated with catalysts (generally platinum and palladium catalysts). This is placed inside a metallic shell and held in place by a wire mesh support. Vehicles fitted with catalytic converters use only unleaded (lead-free) petrol. Can you think of the reason? Nitrogen oxides can be reduced to nitrogen by catalytic converters.

Zeolites as catalysts: We had encountered zeolites in an earlier lesson. Zeolites are aluminosilicates containing aluminium, silicon and oxygen. They contain cages where molecules react. The beauty of these cages is that only molecules of a certain shape and size are accommodated. A good example of a reaction carried out in zeolites is the conversion of methyl alcohol (methanol) to kerosene.



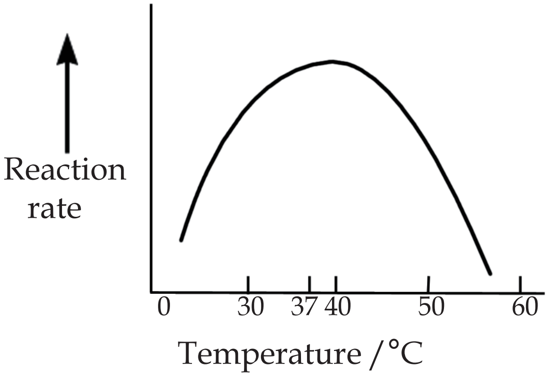
Biological catalysts: Enzymes are biological catalysts. Enzymes control biochemical reactions in living systems. **Yeast** is a common source of enzymes that we employ for various processes. Enzymes play an important role in many industrial processes.

In the figure below, we show the single subunit of **nitrogenase** which fixes nitrogen in the atmosphere to make ammonia. It contains the Fe Mo S cluster.

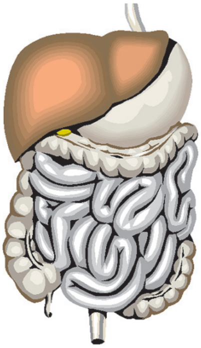


Enzymes have the following properties. The molecular mass of enzymes ranges from 10^5 to 10^7. Enzymes are specific. That is, a specific enzyme will act as a catalyst in a specific reaction. The enzyme lipase catalyses the hydrolysis of esters, whereas the enzyme urease catalyses the hydrolysis of urea.

The catalytic action of enzymes is most effective at 37°C. Enzymes get destroyed if the temperature rises above 50° C–60°C. Poisons affect enzyme action. Ethanol destroys enzymes in yeast if the ethanol concentration is more than 15.5% (for example in the fermentation process). This is why wine prepared by fermentation cannot have higher than 15.5% alcohol content.



Various enzymes in the human digestive system are responsible for breaking down carbohydrates, proteins and fats to simpler substances which can be absorbed by the body. They are amylase in saliva, pepsin and trypsin in the stomach and amylase, maltase, pepsin, trypsin, peptidases and lipase in the small intestines.



Papain is an enzyme present in papaya. It has excellent digestive properties and is used in preparing digestive remedies and as a meat tenderizer.

Enzyme deficiency as well as excess cause diseases. Phenylalanine hydroxylase deficiency causes phenyl-ketonuria.

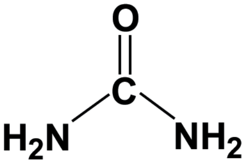
In this congenital disease, harmful compounds get accumulated in the body. This results in brain damage and mental retardation. Tyrosinase deficiency causes albinism. Some diseases are treated by administering specific enzymes. For example, the enzyme streptokinase is used to dissolve arterial clots. The enzyme is injected into the heart, through a catheter, to the blocked artery. Patients who have had heart attacks are treated by this means.

Fermentation: Fermentation is a chemical process in which yeast and certain bacteria act as catalysts on sugars to produce ethanol and other products. There are about 12 enzymes in a typical yeast. Zymase is one of the enzymes found in yeast. There are different kinds of yeast such as wine yeast, wild yeast and film yeast.

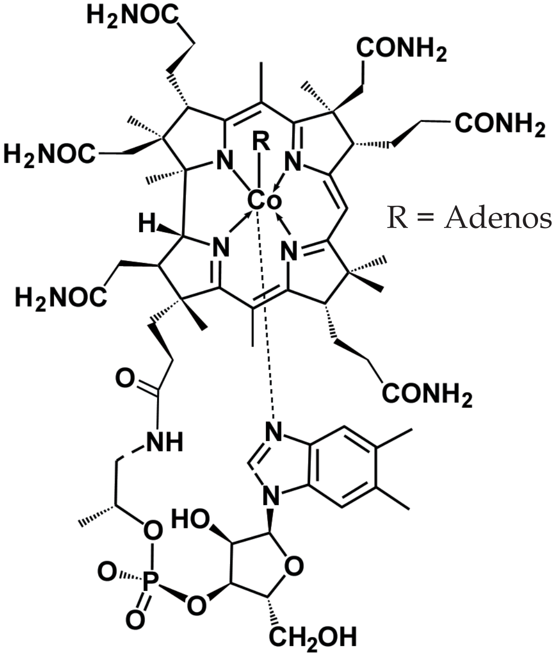
6.9 Chemical synthesis

Chemists make compounds by employing various chemical reactions. In the last few decades, several thousands of compounds have been synthesized. These include compounds that occur in Nature, such as those in plants, and also new compounds entirely designed by chemists.

The first known chemical synthesis was that of urea, NH_2CONH_2, by Wohler in 1828. In 1845, Kolbe made acetic acid, CH_3COOH, in the laboratory. Methane was made from carbon and hydrogen by Berthelot in 1856. All these are simple molecules. You must compare these with the 1972 synthesis of vitamin B_{12} by Woodward and his large group of co-workers.



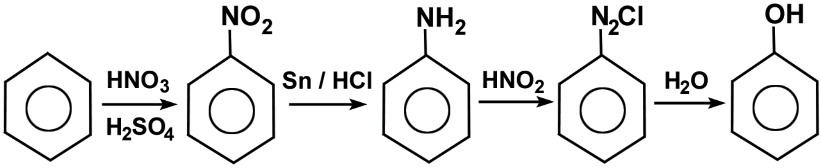
Urea



R = Adenosyl

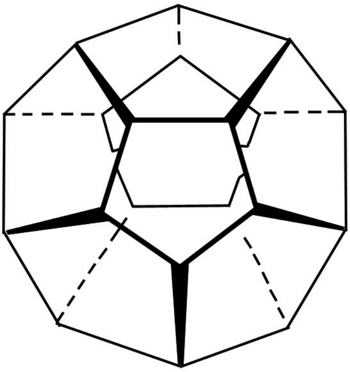
Vitamin B_{12}

Let us look at an example of the preparation of a simple organic compound, phenol from benzene. The following are the steps involved in making phenol from benzene:

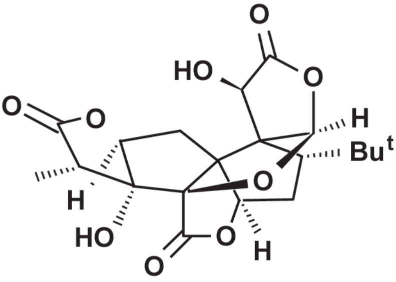


You can imagine the large number of steps (or reactions) that will be necessary to make more complex molecules.

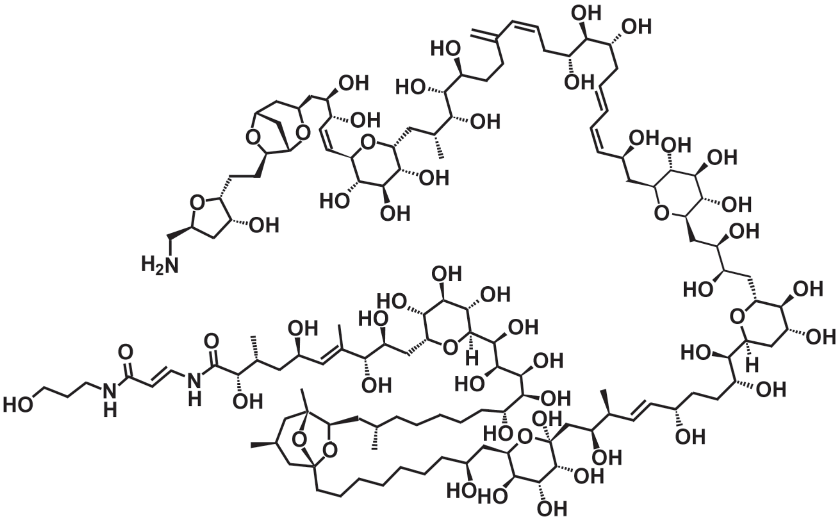
Today, chemists make highly complex compounds such as the following:



Dodecahedrane



Gingkolide A



Palytoxin

Many types of inorganic compounds, containing various elements, have also been prepared in the last few decades. Then, there are the organometallics. These are organic compounds containing metal–carbon bonds. Some of the compounds contain metal clusters. Such compounds possess metal–metal bonds as well.

R. B. WOODWARD (1917 – 1979)

Robert Burns Woodward is probably the greatest synthetic organic chemist that the world of chemistry has seen. His great knowledge of chemistry, extraordinary skill in planning synthetic strategies and unlimited enthusiasm to synthesise difficult substances are part of the folklore. He was extremely hardworking and spent most of his time doing chemistry, often with little sleep. He would give lectures lasting four to five hours on his research, writing all the structures beautifully on the blackboard.

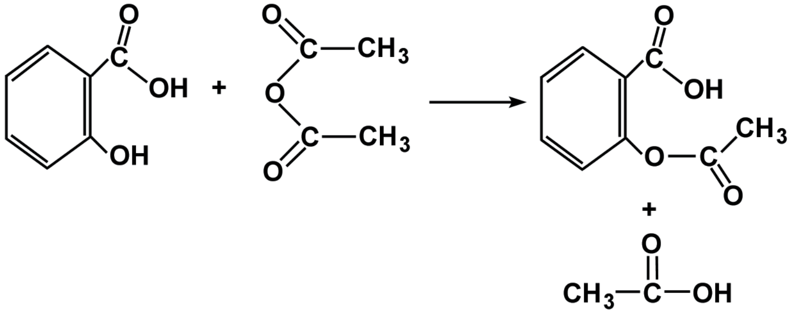
Woodward's interest in chemistry was evident even during childhood, when he did experiments using a chemistry set given to him by his mother. His college days at MIT were marked by his obsession to learn chemistry. He completed his Ph.D. degree in one year. He spent his entire career at Harvard University where he became professor at the age of 33.

A large number of students and co-workers (close to 400) from all over the world worked with him. His major synthetic achievements are quinine (1944), patulin (1950), cholesterol (1951), cortisone (1951), lanosterol (1954), lysergic acid (1954), strychnine (1954), reserpine (1956), chlorophyll (1960), tetracyclines (1962), colchicine (1963), cephalosporin (1965) and vitamin B_{12} (1972). He devised new synthetic strategies, solved the structures of many natural products and proposed many important principles of organic chemistry. He received the Nobel Prize in 1965.

The Woodward-Hoffmann orbital symmetry rules (1965) predict the ease and stereochemical outcome of concerted thermal and photochemical reactions. Woodward would have probably shared the 1981 Nobel Prize with Hoffmann for this work, but he passed away in 1979. Woodward's charisma and style made him a legend in his own lifetime. In his hands, organic chemistry took an art form. Woodward has left his indelible footprints in the field of organic chemistry.

Preparation of some chemicals:

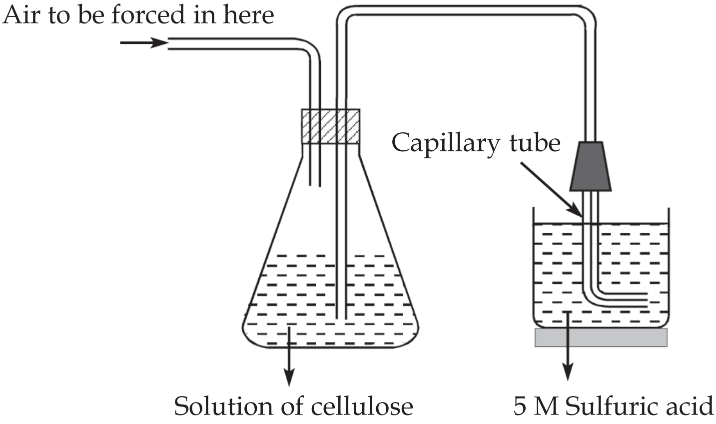
Aspirin: Aspirin is the most commonly used drug. It is acetylsalicylic acid. It is obtained by the reaction of salicylic acid with a mixture of acetic anhydride and glacial acetic acid. The equation of the reaction is:



Take 7 g of salicylic acid and 6 ml of acetic anhydride in a flask. Add 10 ml of concentrated H_2SO_4 to the above mixture. Heat the flask in a water bath for 5 min. Cool the flask and add 25 ml of distilled water to decompose remaining acetic anhydride. Pour the mixture into ice in a beaker. Crystals will appear (you may need to stir the solution or scratch the walls of the beaker). Dissolve the crystals in a minimum amount of ethanol, warm the solution and cool it. You get pure crystals of aspirin.

Rayon or artificial silk: It is obtained by chemically treating cellulose. It involves two steps: dissolving cellulose material in a solution of tetrammine cupric hydroxide and forcing the liquid through a capillary tube into a dilute sulfuric acid bath at a rapid rate. The rayon threads are then removed, washed with plenty of water and dried.

In this preparation, we first obtain a solution of tetrammine cupric hydroxide, $[Cu(NH_3)_4]$ $(OH)_2$. This is done by first obtaining a precipitate of $Cu(OH)_2$ by adding 7 ml of liquor ammonia to a solution of 15 g of $CuSO_4.5H_2O$ in 100 ml of water. The precipitate is dissolved in 40 ml of liquor ammonia to get a blue solution. Add one gram of filter paper pieces (cellulose) to the blue solution in a flask. Cover the flask and leave for two days. After the filter paper is dissolved, force the liquid through a capillary into a dilute sulfuric acid solution as shown below, to get colourless threads of rayon.



Nylon fibre: This is prepared by the reaction of sebacic acid (a dicarboxylic acid) with hexamethylene diame (a diamine). Instead of sebacic acid, sebacoyl chloride (acid chloride) can also be used.

Dissolve 3 ml of sebacoyl chloride in 100 ml of dichloromethane (CH_2Cl_2) solvent. Dissolve 4.4 g of hexamethylene diamine, 8 g of sodium carbonate in about 100 ml of water.

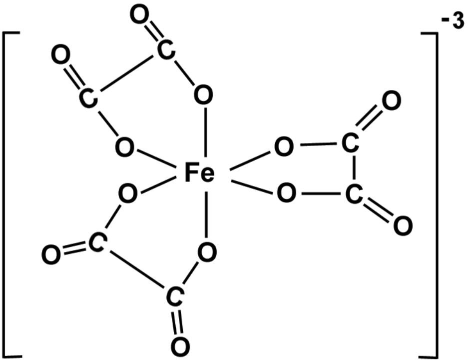
Carefully add the diamine solution to the sebacoyl chloride solution. Since the solvents (dichloromethane and water) do not dissolve in each other, two layers are formed. With a pair of tweezers, nylon thread can be pulled from the interface between the two layers. The nylon thread may be wound around a glass rod.

The reaction here is

$$\mathrm{ClOC{-}(CH_2)_8{-}COCl} + \mathrm{H_2N{-}(CH_2)_6{-}NH_2} \longrightarrow$$

$$\mathrm{({-}(CH_2)_8{-}CO{-}NH{-}(CH_2)_6{-})_n}$$

Potassium ferric oxalate: In this compound, three oxalate ions, $(C_2O_4)^{2-}$, are coordinated to Fe^{3+} ion. The compound has the formula $K_3[Fe(C_2O_4)_3].3H_2O$. The anion has the following structure.

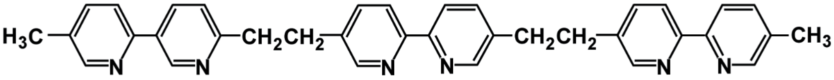


To a solution of ferrous ammonium sulfate, $Fe(NH_4)_2(SO_4)_2$ $6H_2O$ (5.5 g in 17 ml of H_2O), add a few drops of dilute H_2SO_4 (to ensure complete dissolution of the ferrous ammonium sulfate and to prevent hydrolysis of Fe^{2+}). To this solution, add a solution of oxalic acid (3 g in 30 ml of water). Heat the solution (under stirring) and cool it to get a precipitate of ferrous oxalate, $Fe(C_2O_4)$ $2H_2O$. Wash the precipitate in water thoroughly and throw away the supernatant liquid. To the precipitate, add a saturated solution (11 ml) of potassium oxalate. Heat the mixture to 40°C and add 20 ml of 3% hydrogen peroxide slowly. Add another 20 ml of 3% H_2O_2 and bring the solution to boiling. Add 10 ml of 1 M oxalic acid to the solution and continue boiling till the colour of the solution becomes green. Filter the hot green solution and add 20 ml of ethanol to it (and heat the mixture to 70°C). Add some more ethanol till the solution becomes cloudy. Cool the solution to allow the crystals of potassium ferric oxalate to settle down.

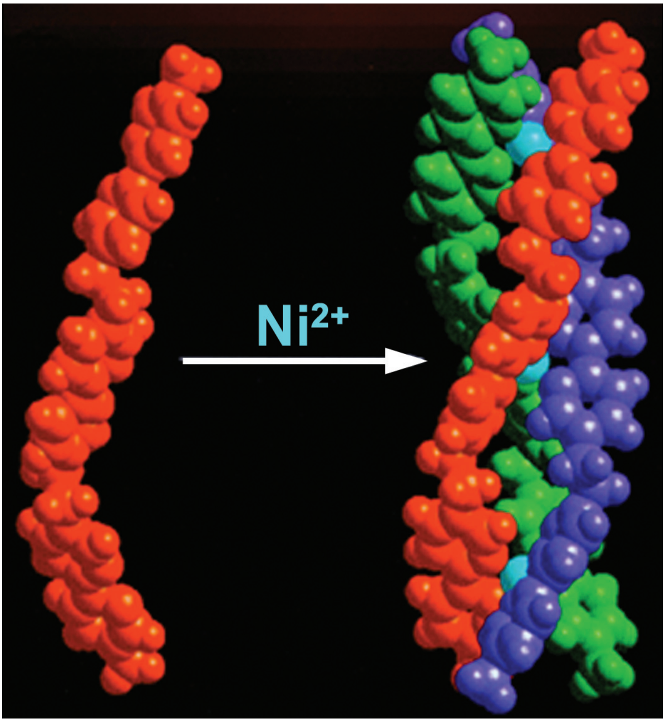
6.10 Supramolecular chemistry

In chemistry, we generally deal with molecules possessing strong covalent bonds. In the last few years, a new approach to designing molecules based on supramolecular organization is gaining ground. In supramolecular chemistry, molecular units are put together or organized in a desired fashion by making use of weak interactions between them. Examples of such weak interactions are bonding with metal ions and hydrogen bonding. Jean–Marie Lehn (France) has been the great champion in promoting the supramolecular approach to chemistry. We shall try to understand this by looking at two examples.

First, we look at an example of supramolecular organization which employs coordination of metal ions to an organic molecule. In the example below, taken from the work of Lehn, a triple helical structure is obtained by the interaction of nickel ions with a molecule containing three bipyridine units. The molecule is shown below.

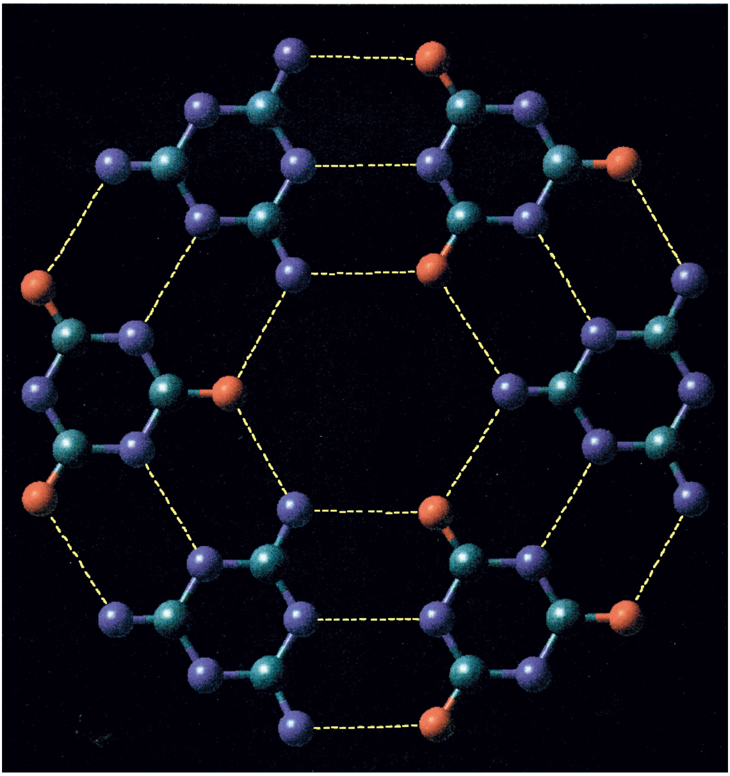


We show the three-dimensional structure of the molecule and the supramolecular assembly in the figure below.

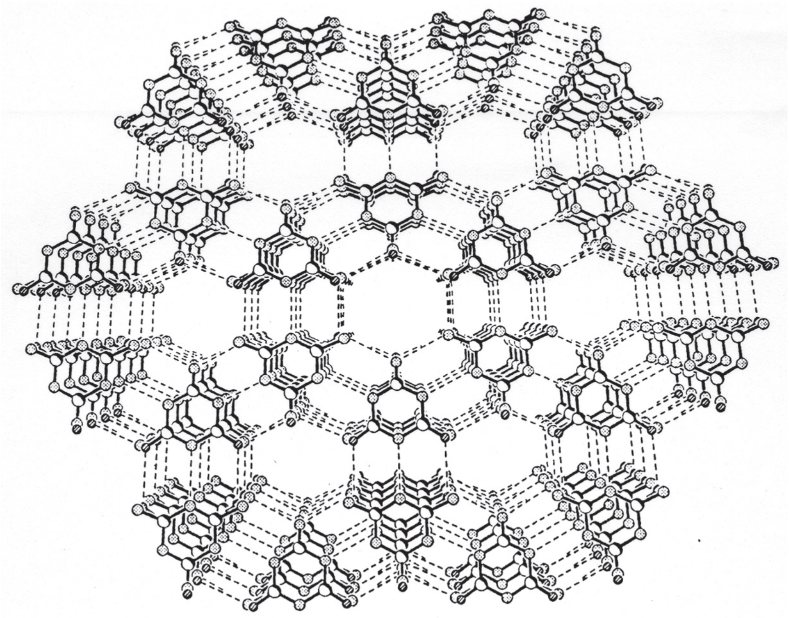


Three different colours are used to show the three helices.

In the second example, we look at the supramolecular assembly obtained through hydrogen bonding. The molecules are cyanuric acid (CA) and melamine (M). Both CA and M have their own stable structures. But if we put the two together, they form a beautiful hexagonal rossette structure shown below.



The molecule with red spheres sticking out is CA and the other is M. The dotted lines are hydrogen bonds. We see that each molecule forms three hydrogen bonds on either side. These rosettes stack themselves and the three dimensional structure, therefore, has beautiful channels.



There are any number of supramolecularly organized assemblies. Many of the beautiful things in Nature, including the sea shells, are a result of supramolecular organization of chemical species.

Conclusions

We have tried to understand the nature and causes of chemical reactivity and gone through a few types of chemical reactions. We have also examined the factors that affect chemical reactions. In particular, we have looked at catalytic reactions which play a major role in industry and biology.

The number of chemical recations and reagents is very vast indeed. By employing different reactions, chemists are able to prepare (synthesize) molecules of great complexity. Synthesis has been a great preoccupation of chemists and has yielded dividends because of the uses of the compounds so made.

Trinity or a thousand saints!

It is commonly acknowledged that Galileo, Newton and Einstein constitute the trinity in physics. In organic chemistry (synthesis), Wilstatter (Germany), Robinson (Britain) and Woodward (U.S.A.) are said to form the trinity.

Today, the ability of chemists to design and make molecules and materials of the desired structure and properties has reached a very high level, with newer accomplishments being made all the time. And, newer saints are born every so often. Some of them have many hands and heads.

If you ask chemists to make a star-shaped organic polymer, an organic molecular shuttle or an inorganic solid which has channels in them that would only allow certain molecules to pass through, they will readily oblige. If you ask them to make the channel in the inorganic solid magnetic, they will try. Then, you may want a metallic nanowire (of molecular dimensions) or small metal particles (of a few Ångstroms diameter) to be inside the channel along with a few molecules of a metal compound hanging loosely in the channel. They will certainly do that in a reasonable time. If you want the same type of channel in an organic solid, they will certainly help. It is possible that you may not want such compounds at all. Instead, you may like to have a compound which is both organic and inorganic, conducts electricity, is also magnetic, and becomes superconducting at low temperatures.

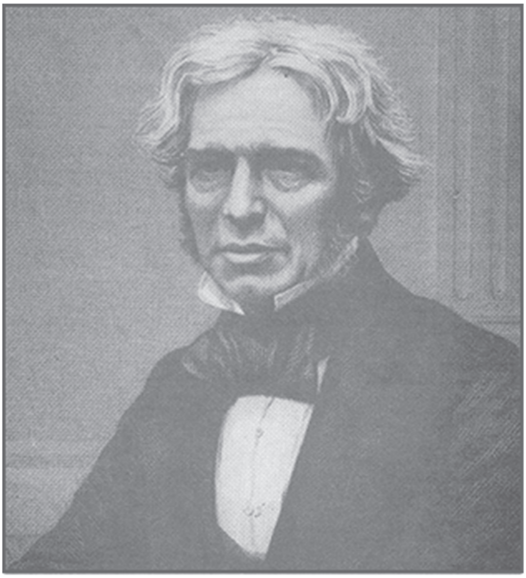
7

TWO CHEMISTS

Objectives

- The vast body of chemistry, involving hundreds of thousands of compounds with a variety of structures and properties, is the result of the efforts of a large number of chemists. We owe the traditions of chemistry to several of the pioneers.
- It is instructive and inspiring to go through the life histories and scientific work of some of those who have made major contributions to chemistry. In this lesson, we shall take a glance at the scientific biographies of two of the greatest chemists in the world – one from the 19th century and another, from the 20th century.

Michael Faraday
(1791 – 1867)



The year 1991 marked the bicentenary of the greatest experimental philosopher the world has known, Michael Faraday*. It is difficult to think of another experimental scientist besides Faraday who has left such an indelible mark of achievement in pure and applied science. His monumental contributions to science span a variety of fields, including chemistry, physics, materials science and engineering. One is left wondering whether such an individual ever lived. Faraday was a unique human being gifted with extraordinary imagination and experimental creativity. His life has elicited a romantic response from one generation after another. We

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* based on an article in *Current Science* (1991)

get some insight into the personality of Faraday through his own words:

> Do not suppose that I was a very deep thinker or was marked as a precocious person. I was a very lively, imaginative person and could believe in the *Arabian Nights* as easily as in the Encyclopaedia.

Faraday possessed a child-like awe and a great sense of purpose combined with humility. He was not spoiled by formal education; he was self-taught. He left school at the age of thirteen and started his career as an errand boy, and then as a bookbinder, and rose to become one of the greatest scientific giants. He was a prolific writer and authored about 450 research publications. There is not a single mathematical equation in any of his works, because he knew no mathematics. Yet, as Albert Einstein remarked, Faraday was responsible, along with Maxwell, for the greatest change in the theoretical basis of physics since Newton.

Faraday was born the third child of a blacksmith on 22 September 1791 in Newington Butts near London. After merely learning elementary reading, writing and arithmetic, he left school and worked first as a newspaper boy and then learnt the art of book binding. While doing so, he also took an interest in the contents of scientific books and began to do simple experiments in chemistry by spending a few pence every week. He attended some of the lectures of Sir Humphry Davy in 1812 at the Royal Institution and became so impressed by what he heard and saw that he sought an appointment under Davy. He accompanied Davy as his secretary and scientific assistant for 18 months on an European tour between 1813 and 1815. During this period, although France and Britain were at war, Napoleon had decreed that scientists were free to meet and exchange ideas. On this tour, Faraday met great scientists such as Ampère, Dumas, Gay-Lussac, Humboldt and Volta. On his return from Europe in 1815, Faraday was appointed assistant and superintendent of apparatus at the Royal Institution. He wrote his first research paper in 1816 on the analysis of native caustic lime. In 1821, he got married. In 1824, he was elected Fellow of the Royal Society.

During the mid-1820s, Faraday initiated his educational experiments and communication with the public through popularization of science. Faraday's evening discourses soon became famous. His Christmas lectures became legendary. Faraday was not a born lecturer. Yet, by consensus, he became easily one of the greatest lecturers. Faraday's most famous lecture series on "The chemical history of a candle" (first published in 1850) has become a classic.

Faraday became the first Fullerian professor of chemistry at the Royal Institution in 1834 and continued to work till his retirement. His last major publication in chemistry was in 1857 on "Experimental relations of gold and other metals to light" and dealt with colloidal metals. (Some of the metal colloids made by Faraday are still preserved.) His last major papers in physics were in 1862 on the influence of a magnetic field on the spectral lines of sodium, on the lines of force, and the concept of a field.

Faraday remained a dedicated scientist throughout his life. He refused important positions since that would get in the way of his research. He did this in all humility. Towards the end of his career when he found that he was no longer physically capable of lecturing and working in the laboratory, he voluntarily stepped down from the directorship of the Royal Institution.

In 1858, Queen Victoria granted Faraday the favour of a house at Hampton Court, where he died peacefully on 25 August 1867. He was buried in a simple grave not far from that of Karl Marx. On the grave of Karl Marx is written "Philosophers interpret the world, the task however is to change it". This statement applies more to Faraday.

Faraday's contributions to science are truly mind-boggling, considering the originality and quality and also the fact that the achievements were all accomplished by a single person. One can classify his contributions under the broad headings of physics and chemistry, although many would fall under both categories. Some would come under what in recent times is known as materials science. It is therefore not surprising that the Faraday Society, when it was established, was chartered to explore interdisciplinary areas related to different divisions of natural philosophy.

The range and number of major breakthroughs accomplished by Faraday are stupendous. If ever there were Nobel Prizes during Faraday's time, he could have won at least five (for electromagnetic induction, laws of electrolysis, magnetism and Faraday effect, discovery of benzene and the notion of a field). Many people forget that it was Faraday who coined the words diamagnetism and paramagnetism. The idea of a **field** that physicists use all too frequently was first conceived by Michael Faraday. When Faraday discovered the dynamo effect, he was asked by the Chancellor of the Exchequer, "What is the use of this discovery?" Faraday replied, "Sir, one day you will tax it."

It is Faraday's notion of a field that led to Maxwell's great discoveries at a later date. Here it would be most appropriate to recollect the providential statement of Faraday (1845) where he says,

> I have long held an opinion, almost amounting to conviction, in common, I believe with many other lovers of natural knowledge, that the various forms under which the forces of matter are made manifest have one common origin; or, in other words, are so directly related and mutually dependent that they are convertible, as it were, one into another, and possess equivalents of power in their action.

Faraday's contributions to chemistry are extraordinary. Many chemists believe that Faraday was one of their kind, which, apart from being correct, draws our attention to how this great chemist also did great physics. Some of the important chemical compounds discovered by Michael Faraday are benzene, tetrachloroethylene, isobutylene and hexachlorobenzene.

It is revealing to analyze the productivity of Faraday during the different periods. When one does so, the year 1833 particularly stands out. From his laboratory notebooks, one sees that he discovered fused-salt electrolysis in February 1833 and identified superionic conductivity in silver and other halides the same month. In early November, he did some work on catalytic activity of platinum and on 22 November, he worked on the separation of gases such as ethylene and carbon dioxide. On 25 November, Faraday carried out investigations on the wettability of solids such as quartz. In mid-December, he worked on the equivalence of electricity from various sources and later that month, carried out studies that led to the laws of electrolysis. On 24 December, he did experiments on chemical changes brought about by the passage of electricity through molten tin chloride. On 26 December, he did an important experiment on the decomposition of lead halides and other salts. There was no entry for 25 December (Christmas day).

Clearly, Faraday was a genius propelled by an urge to explore. He was painstaking, hard-working, dedicated and incorruptible and was a storehouse of energy. His creative contributions spanned a period of around 50 years since his first publication in 1816. He was a great builder of instruments and a daring experimentalist. He would demonstrate static electricity to the public by locking himself in a "Faraday cage"; he burnt diamond to show that it was nothing but carbon. His accounts of the various experiments are a marvel of thoroughness. In some of his papers, Faraday suggested how best to attack a problem (for example, in his paper "Two new compounds of chlorine and carbon"). Faraday did not have to worry about pure versus applied research (as many do now). Most of Faraday's research found application and one cannot better his record of spin-offs from fundamental research. His contribution to modern electrical industry is obvious. The laws of electrolysis govern all that has happened in electrochemical technology and industry. Faraday was the first to discover thermistor action. He liquefied gases, purified them and carried out catalytic reactions. Faraday believed that experiments provided the only way to understand Nature. As he said,

> Nothing is too wonderful to be true, if it be consistent with the laws of Nature and in such things as these, experiment is the best test of such consistency.

There is no better way of paying tribute to Michael Faraday than by recounting the words of Rutherford:

> The more we study the work of Faraday with the perspective of time, the more we are impressed by his unrivalled genius as an experimental and natural philosopher. When we consider the magnitude and the extent of his discoveries and their influence on the progress of science and of industry, there is no honour too great to pay to the memory of Michael Faraday — one of the greatest scientific discoverers of all time.

Major contributions of Michael Faraday

To Physics

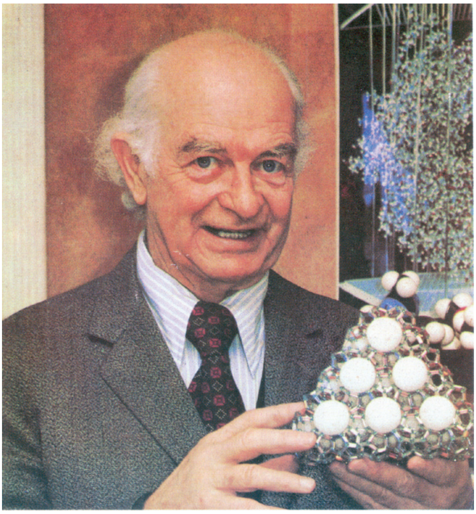
1821	Electromagnetic rotation
1831	Electromagnetic induction Acoustic vibrations
1832	Identity of electricity from various sources
1835	Discharge of electricity through evacuated gases (plasma physics)
1836	Electrostatics
1845	Relationship between light, electricity and magnetism; diamagnetism and paramagnetism, magneto-optics
1849	Gravity and electricity
1857	Time and magnetism
1862	Influence of a magnetic field on the spectrum of sodium Lines of force and the notion of a field

To Chemistry

1816	Evolution of miner's safety lamp (with Humphry Davy)
1818–1824	Preparation and properties of alloy steels
1812–1830	Purity and composition of clays, native lime, water, gun powder, rust, various gases, liquids and solids (analytical chemistry)
1820–1826	Discovery of benzene, isobutylene, tetrachloroethylene, hexachlorobenzene, isomers of naphthalenesulfonic acids (organic chemistry). Photochemical reactions
1825–1831	Production of optical grade glass
1823, 1845	Liquefication of gases (H_2S, SO_2, etc.); Existence of critical temperature and continuity of state
1833–1836	Electrochemistry; laws of electrolysis. Equivalence of various forms of electricity. Thermistor action, Fused-salt electrolytes; superionic conductors
1834	Heterogeneous catalysis; surface reactions Adsorption; wettability of solids

1835	Plasma chemistry
1836	Dielectric constant, permittivity
1845–1850	Magnetochemistry, magnetic properties of matter Faraday effect, diamagnetism, paramagnetism magnetic anisotropy
1857	Colloidal metals, sols and hydrogels

Linus Pauling
(1901 – 1994)



Linus Pauling* was born in Oswego, a small village in Oregon, U.S.A. on 28 February 1901, when the frontier spirit of the West was still prevalent. On his mother's side, he had some unconventional relatives. His father owned a small drug store. As a child, Pauling was interested in insects and minerals.

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* based on an article in *Current Science* (1994)

At school, he had one or two teachers who made science exciting. Early in his life, he lost his father and had to work during spare hours to support his family. He finished school, but did not receive the diploma since he did not complete a course in civics. (The school awarded the diploma after he received his second Nobel Prize.) He had however completed all the requirements to join the nearby Oregon Agricultural College at Corvallis as an undergraduate student. His consummate faith in his own intellect was evident even at that time. On one occasion, he seemed to have stood up in an open meeting of students during the address of the dean, to correct some of the statements. Pauling felt that he had to interject since he did not want the large assembly of students to be misinformed. Pauling had to take a break from his undergraduate studies after two years, because of financial difficulties. He could come back to the college only when he was made an assistant to teach quantitative analysis. In 1922, Pauling received a Bachelor's degree in Chemical Engineering. By that time, he had read the papers of Langmuir and Lewis on atoms and molecules. He had also taken courses in mathematics, physics and crystallography.

Although there was considerable pressure on him to take up a job to support his family, Pauling decided to pursue post-graduate studies. The choice he had was the University of California, Berkeley, where G. N. Lewis presided over a famous department or the California Institute of Technology where A. A. Noyes was the Chairman. He went to Caltech since he first obtained admission from there. Robert Millikan was then the President of Caltech. He took up crystallography for his Ph.D. thesis. He also married his long-time friend, Ava Helen, at this time.

After the Ph.D. degree, Noyes wanted Pauling to go to Europe, and even made a financial contribution towards the European tour. Pauling went to Sommerfeld in Munich and later spent some time in Copenhagen (with Bohr) and in Zurich (with Schrödinger). During his stay with Sommerfeld, Pauling came in contact with Heitler and London and wrote a classic paper on the properties of multielectron atoms as revealed by quantum mechanics. He showed how one could predict atomic properties from quantum mechanics, in agreement with the results from crystallography. Lawrence Bragg, who was an important scientist of that time, did not particularly appreciate Pauling's paper. Pauling was, however, sure that he had nothing to be ashamed of.

Pauling returned to Caltech in 1928 as an assistant professor in theoretical chemistry. At that time, Slater was making a beginning with his quantum mechanical work. One of the first things Pauling did was to reconcile the Bohr model of the atom with the Lewis model of atoms and molecules (Lewis wrote his classic paper in 1916). He wrote a series of papers under the heading "Nature of the Chemical Bond", where he described the valence bond approach, and his ideas on a variety of topics such as resonance, ionicity, hybridization and so on. In 1930, he initiated research on electron diffraction of gases and derived the structures of many important molecules of relevance to the understanding of chemical bonding. Electronegativity and hydrogen bonding are the other topics he investigated. Linus Pauling was then a fountain of knowledge that changed the direction of chemistry. This period in Pauling's life is somewhat comparable to that of Faraday, a century earlier. What is surprising is that this monumental contribution of Linus Pauling in the early 1930s did not get him the Nobel Prize.

Pauling, as a child of the golden age of physical science, became the father of modern chemistry. In 1935, he wrote the classic book entitled ***Introduction to Quantum Mechanics with Applications to Chemistry*** along with Wilson. In 1938, Pauling wrote the now immortal book, ***The Nature of the Chemical Bond***. (The book was dedicated to G. N. Lewis.) In 1947, Pauling wrote the first proper textbook of ***General Chemistry*** for fresh undergraduate students. This was a trend-setter.

Around 1935, Pauling got interested in biology. He carried out experiments on haemoglobin and protein denaturation. In the early 1940s, he started working on polypeptides and proteins. He had to deal with Dorothy Wrinch who had come out with symmetry arguments and with the cyclol model. Pauling showed that her model was wrong and was against all chemical intuition. Pauling had his own chain model for the structure of polypeptides and proteins based on the planarity of the peptide bond. By 1950, Pauling and Corey had worked out the alpha-helical structure of proteins. Apparently, the idea of the alpha-helix struck Pauling in an Oxford college where he was recovering from a cold.

Pauling was not only a person with extraordinary talent and intuition but also one with great confidence and courage. He was extremely quick in grasping a problem and worked very hard at it. If he believed in something, he would go to any length to make the other arguments meaningless. Pauling himself was subject to considerable criticism by some scientists for his unusual methods and approximations. One should remember, however, that Pauling was a phenomenon in chemistry.

Pauling's main contributions to structural biology were made between 1947 and 1952. In 1949, he wrote the famous paper on sickle-cell anemia where he showed that a change in one amino acid residue out of 146 was responsible for the disease. He called it a molecular disease. Some reservations were expressed initially by some scientists in Britain regarding the alpha-helical strucure of proteins. However, this important discovery was there to stay. He got close to solving the structure of DNA. It is during this period that Pauling met Einstein with whom he had discussions on human rights, determinism, peace and other topics.

In 1950, Pauling made a public statement on the need to avoid war. This was the time when McCarthy ruled supreme and Pauling became a victim of the wrath of the American government. He was unable to obtain a passport to attend the important meeting of the Royal Society in 1952 where he was to discuss the structure of biopolymers. Appeals from Einstein, Fermi and a number of other scientists, were of no avail. Late in 1954, Pauling received the Nobel Prize for his work on the alpha-helical structure of proteins. Shortly after the Nobel Prize, he worked on the molecular basis of mental illness and showed the importance of vitamin B_3. The saying goes that if Pauling had attended the 1952 meeting and seen the X-ray diffraction photographs of DNA presented there, he would have probably solved the structure of DNA as well.

By the middle of the 1950s, Pauling's activities in the peace movement had increased. He made fervent appeals to stop nuclear testing and warned the world community about the dangers of nuclear radiation. He had major disagreements with Libby and others who found little wrong with radiation levels caused by nuclear testing. Pauling wrote to President Eisenhower pointing out the danger of nuclear weapons, particularly its biological effects. He did not receive any response.

Instead, the press and the community at large developed tremendous antagonism towards him. At Caltech, pressures were increasing in a manner that made him resign from the chairmanship of the chemistry division in 1958. In the late 1950s, he had debates with Edward Teller about nuclear testing and the adverse effects of radiation. He visited Albert Schweitzer to obtain support for the peace movement. In 1960, Pauling sent an appeal to the United Nations with signatures of over 1500 scientists and others about nuclear test ban and disarmament. It only brought the wrath of the U.S. Senate, but this did not stop Pauling from continuing his crusade. Many universities would not allow him to lecture. There was an interesting incident in 1962. Pauling was leading a picket line in front of the White House throughout the day. The same evening there was a dinner for the American Nobel laureates hosted by President Kennedy. Pauling left the picket line in the evening and went to the White House for the dinner.

In 1962, Pauling received the Nobel Prize for peace. This created more problems for him and antagonism increased from innumerable quarters. The attitude of the American Chemical Society was not particularly pleasing. He was not even allowed to publish a rejoinder to an attack against him in its news magazine. Pauling resigned from the membership of the American Chemical Society. He decided to leave Caltech in 1964. Pauling was a harassed man from 1954 onwards, but he continued to publish papers on nuclear structure and on certain biological problems.

In the late 1960s, after receiving two Nobel Prizes, Pauling did not have a proper place to work. He first worked at the Center for the Study of Democratic Institutions in Santa Barbara and later at the University of California, San Diego. During this period, he started research on orthomolecular psychiatry and showed how mental patients were deficient in ascorbic acid, pyrodoxine and vitamin B_3. He worked for a short time at Stanford from 1969, when he wrote his paper on genetic and stomatic effects of high energy radiation. He founded the Linus Pauling Institute of Science and Medicine in 1974. Based on literature research and his own intuition, he proposed that vitamin C was good for common cold. Pauling initiated work on vitamin C and cancer. The usefulness of vitamin C in relation to cancer or heart disease has been a matter of debate. There appears to be agreement, however, that vitamin C has beneficial effects because of its role as a free radical scavenger.

In 1975, the U.S. government exonerated Linus Pauling of whatever he was accused of. He was awarded the National Medal of Science. In 1976, Caltech celebrated his 75th birthday. In 1976, the American Chemical Society (ACS) celebrated its centenary. The President of ACS then was Glenn Seaborg, the former Chairman of the U.S. Atomic Energy Commission. Pauling gave the ACS centenary lecture.

Pauling carried out research even in the 1980s. He wrote a paper on quasi-crystals in 1985 and another on superconductivity in 1988. These papers are reminiscent of the old Pauling, still interested in structure and bonding. In 1991, on the occasion of his 90th birthday, the U.S. National Academy of Sciences honoured him with a special citation.

How does one look at this great colossus? Linus Pauling was clearly the greatest chemist of the 20th century. He was the person who brought chemistry into the realm of physics and created modern physical chemistry. He was the first person who made chemical bonding his primary concern through which he changed the course of chemistry. Pauling created modern structural biology through the discovery of the alpha-helix and by showing sickle-cell anemia to be a molecular disease. Then, he was a crusader for human rights and peace. There is no scientist in this century or any other time, who took on the entire world just because he believed in something by undergoing personal suffering and harassment for long periods.

Pauling is a hero to most chemists. He was the person who created the kind of chemistry that we all love. He was way ahead of his times. He was not only the chemist of the century, but also a man for all time.

SOME CHEMICAL RECORDS

Elements

Smallest atom : Hydrogen (H)

Largest atom : Cesium (Cs)

Heaviest atom : Uranium (U); isotope 238

Element of lowest boiling point : Helium (He); –269°C (4 K)

Element of highest boiling point : Rhenium (Re); 5596°C (5869 K)

Most dense element : Osmium

Most abundant elements in the universe : H and He

Most abundant element on the earth : Oxygen

Most abundant element in the human body : Oxygen

Chemical Properties

Strongest acid : HSO_3F + 90% SbF_5 (Magic acid)

Strongest oxidizing agent : F_2O

Strongest reducing agent : Azide ion (N_3^-)

Highest oxidation state : +8 in Ru, Os and Xe

Chemical Substances

Sweetest substance : Sucronic acid (200,000 times sweeter than sugar)

Hottest compound : Capsaicin (from peppers)

Most poisonous substance : Dioxin

Most powerful explosive : Hexanitroisowurtzitane (CL 20)

Most exotic solvent : Liquid lead

Most used drug : Aspirin

Most used catalyst : Emission control catalyst (> 3 billion dollars per year)

Most used insecticides : Organophosphates (~ 3 billion dollars per year)

Most used plastic : Polyethylene

Companies and Countries

Company which has introduced the maximum number of new products in the last decade : Novartis

Biggest chemical company (based on sales) : BASF (Germany)

Biggest chemical company (based on profits) : du Pont (U.S.A.)

Largest pharmaceutical company : Merck

Country with the maximum number of chemical patents and research publications : U.S.A.

People with Two Nobel Prizes

Marie Curie : Physics (1903), Chemistry (1911)
Linus Pauling : Chemistry (1954), Peace (1962)
John Bardeen : Physics (1956), Physics (1972)
Frederick Sanger : Chemistry (1958), Chemistry (1980)

Reference: "World Records in Chemistry" ed. H. J. Quadbeck–Seeger, Wiley-VCH (1999).

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