G. C. E. (Advanced Level)

CHEMISTRY

Grade 13

Unit 14 - Industrial Chemistry and Environmental Pollution

Department of Science
Faculty of Science and Technology
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Resource Book
Grade 13

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Message from the Director General

The National Institute of Education takes opportune steps from time to time for the development of quality in education. Preparation of supplementary resource books for respective subjects is one such initiative.

Supplementary resource books have been composed by a team of curriculum developers of the National Institute of Education, subject experts from the national universities and experienced teachers from the school system. Because these resource books have been written so that they are in line with the G. C. E. (A/L) new syllabus implemented in 2017, students can broaden their understanding of the subject matter by referring these books while teachers can refer them in order to plan more effective learning teaching activities.

I wish to express my sincere gratitude to the staff members of the National Institute of Education and external subject experts who made their academic contribution to make this material available to you.

Dr. (Mrs.) T. A. R. J. Gunasekara
Director General
National Institute of Education
Maharagama.

Message from the Director

Since 2017, a rationalized curriculum, which is an updated version of the previous curriculum is in effect for the G.C.E (A/L) in the general education system of Sri Lanka. In this new curriculum cycle, revisions were made in the subject content, mode of delivery and curricular materials of the G.C.E. (A/L) Physics, Chemistry and Biology. Several alterations in the learning teaching sequence were also made. A new Teachers’ Guide was introduced in place of the previous Teacher’s Instruction Manual. In concurrence to that, certain changes in the learning teaching methodology, evaluation and assessment are expected. The newly introduced Teachers’ Guide provides learning outcomes, a guideline for teachers to mould the learning events, assessment and evaluation.

When implementing the previous curricula, the use of internationally recognized standard textbooks published in English was imperative for the Advanced Level science subjects. Due to the contradictions of facts related to the subject matter between different textbooks and inclusion of the content beyond the limits of the local curriculum, the usage of those books was not convenient for both teachers and students. This book comes to you as an attempt to overcome that issue.

As this book is available in Sinhala, Tamil, and English, the book offers students an opportunity to refer the relevant subject content in their mother tongue as well as in English within the limits of the local curriculum. It also provides both students and teachers a source of reliable information expected by the curriculum instead of various information gathered from the other sources.

This book authored by subject experts from the universities and experienced subject teachers is presented to you followed by the approval of the Academic Affairs Board and the Council of the National Institute of Education. Thus, it can be recommended as a material of high standard.

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Content

1.Industrial Chemistry and Enviornmental Pollution

Content

1.1 Industrial Chemistry

1.1.1 Chemical industries

Colossal changes occurred in the mode of production and the force of production during the periods identified as the first industrial revolution (1750-1850) and the second industrial revolution (1870-1914 or 1850-1940) in modern civilization. Along with the diversified market concepts (consumerism) based on the basic requirements of human, world scale productions and services speeds up making profits. Various types of technological tools and methods of productions were created for this. With industrialization, environmental and social problems tended to emerge. Hence more attention had to be paid to reduce the risk of environmental problems and disasters, optimize efficiency and increase productivity. Alongside the gaming of a special place by chemical industries in the process of industrial production, a field of study of which came to be known as Chemical Engineering emerged. Today it has become a well-established discipline.

Iron, ammonia, sulphuric acid, nitric acid, caustic soda and petroleum can be given as some of the main chemical products in the world. Specially medicines, monomers, polymers, lubricants and organic dyes are examples for the products manufactured using organic compounds obtained from the petroleum industry. Plastic and rubber goods, cosmetics, soap, detergents, adhesives, paper, glass, salt, sugar, used in day-to-day life are some more examples for the products of chemical industries. Production of salt using sea water is one of the chemical industries in our country.

Production of soap using major chemicals produced in the world, production of various materials and goods using natural rubber latex and production of cement, paint and glass are some of the chemical industries carried out in our country at present.

Chemical industries spread out and establish in global scale area diverse. They can be classified as chemical industries producing organic chemicals and inorganic chemicals. In addition, they can also be classified as industries which produce agrochemicals, medicine, lubricants, dyes, metals and other substances.

Only few industries are discussed as examples which are based on modern knowledge and technology. Paying attention on the enviornmental, health and social issues at present worldwide, the industries suitable to our country are considered. Management of the knowledge on such is an entrance to 'Industrial Chemistry' discussed here.

1.1.2 Requirements to be considered in establishing chemical industries

There are requirements that should be considered when establishing a chemical industry. Some of them are given below.

- Capital
- Supply of raw materials
- Labour
- Technology

- Assurance of the production process
- Assurance of continuity
- Waste products and methods of waste management.
- Strategies for preventing the addition of environmental pollutants by the industry.
- Site of installation
- Nature of power supply (fossil, solar energy, nucleic energy, bio mass) and cost
- Transport facilities and market
- Nature of probable accidents and strategies that can be adopted to prevent accidents
- Government rules, regulations and policies.

Safety of the production process and prevention of accidents are very important in chemical industry. For this some of the disasters occurred in relation to chemical industries should be investigated. On 21 September 1921, 500-600 people died at an explosion occurred in Oppau on of Germany. The explosion was caused by 4500 tons of a mixture of ammonium nitrate and ammonium sulphate meant to be used as fertilizers. Similarly, the accident at the Chernobil nuclear power station in Ukrane (26 April, 1986) claimed nearly 4000 human lives at once. Because of the Bhopal incident in India (27 December, 1984), about 8000 men and women had to lay down their lives within a period of one week. The reason for this was found to be the leakage of the highly poisonous gas methyl isocyanide. Therefore, it is very important to understand properly the real need of a chemical industry and the political, social, economic and environmental changes associated with it. Moreover, the understanding about the maintenance of the production process safely, efficiently and effectively is also great importance.

1.1.3 Use of raw materials of chemical industry

Raw materials are the substances that are supplied from outside for a chemical industry and which take part in the production process. Production of compounds such as $NaHCO_3$, H_2SO_4 can be given as examples for this. In some chemical industries, chemical components contained in raw materials exist in the product as they were. That is chemical changes do not occur; but physical changes do occur. Paint production is an example for this.

Various raw materials are used for chemical industries. Different sources are used for this. For example, nitrogen gas is used as one of the raw materials to produce ammonia. Atmospheric air is the source from which this nitrogen is obtained. Atmospheric air is first liquefied; then N_2 gas is separated by fractional distillation and used for ammonia production. But in the production of nitric acid, instead of pure oxygen gas, atmospheric air is directly used to obtain NO_2 gas by oxidizing ammonia. In ammonia production (Haber process) though atmospheric air is the source for N_2 gas, which is an essential raw material for it is obtained, in the manufacturing of nitric acid, atmospheric air itself is used as a raw material. Thus, facts such as the way the entire production process is planned, expenditure and what level of purity should be maintained are useful to decide in which form the raw materials should be used.

When using a natural resource as a raw material, it is useful to take the following into consideration.

- Occuring in large deposits for long term usage
- Easy to reach
- Purity

Specially, crude oil is the source for the production of many basic organic compounds. Hydrogen gas obtained by cracking of hydrocarbons is used as an essential raw material for the production of ammonia. Coke is a non-renewable raw material used for the production of iron.

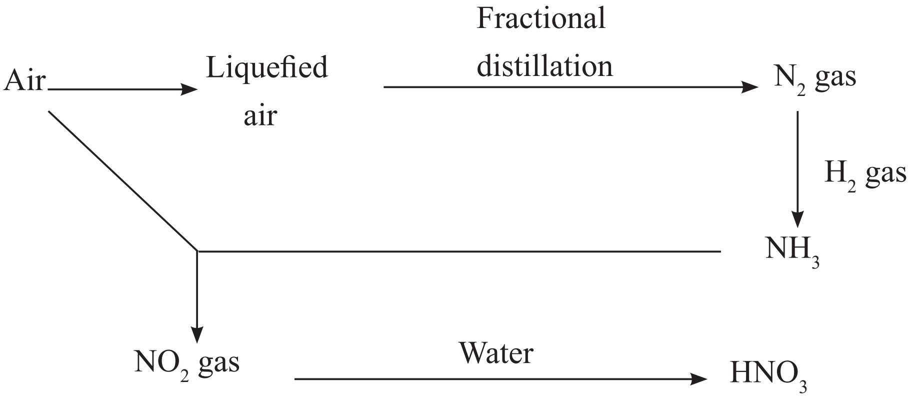
A brief account on the raw materials used for some products is given below.

Air

a) Oxygen is needed as an active component in iron extraction, production of nitric acid and sulphuric acid. Atmospheric air is used as a raw material in these productions.

b) Atmospheric air is used as a natural source of nitrogen. Nitrogen gas obtained by liquefaction of air followed by fractional distillation is used as a raw material in manufacturing ammonia. In the process of separating nitrogen gas from atmospher, atmospheric air is used as a raw material.

When using atmospheric air for chemical industries, it could be identified as a source of nitrogen or oxygen gas



Water

Water is used for the production of sodium hydroxide and, nitric acid, sulphuric acid and calcium hydroxide. Sea water is not used as a source of water in these industries. The reason for this is that various salts presents in sea water interfere with the production process and also get into the product as impurities. Hence it is very important to take care about the standards of the raw materials.

NaCl

NaCl is obtained using sea water as a raw material or from the ores of rock salt. Caustic soda is produced using NaCl as a raw material. It is also used as raw material in the extraction of Na metal. Sea water can be counted as a source for the production of NaCl. But sea water cannot be used as a raw material for the production of caustic soda.

Minerals

Minerals are non-renewable resources. For the extraction of metals such as iron, copper, nickel, aluminum and titanium, minerals containing those metals are used as raw materials. Also minerals containing phosphates are used for the production of phosphate fertilizers. As minerals are non-renewable resources, there could be a recycling process after using the products from minerals. Further, it is also important to use those products to produce useful substances that are long-lasting.

Coal

Coal is a non-renewable resource. It is mainly used as a fuel. In extraction of iron, it is used as a fuel, a direct reductant as well as a raw material essential to generate CO which is a major reducing agent.

Crude oil

Crude oil is a non-renewable resource. It is used as the main source of fuels such as petrol and diesel. Crude oil is the main source from which raw materials for the production of monomers for polymers, medicine and basic organic compounds are obtained. As this is a non-renewable resource, continuation of the productions based on it becomes a problem with its consumption. Another crisis is the increase in global warming caused by the carbon dioxide produced during the burning of fuel obtained from crude oil.

Plants

Plants are very important resources for the production of various oils, latex (rubber latex), resins and medicine. Plant materials are known as biomass and used as fuel for industries and also as raw materials for the production of various orgnic compounds. As Plants is a renewable resource, it is a source that can be managed without disturbing the natural cycles in the environment. Industries which used petroleum oil to generate power have started to use biomass as an alternative source of energy. Industries in our country too are inclined towards this.

1.2 Extraction of Mg – Dow process

Raw materials essential for extracting Mg by Dow process.

Minerals containing magnesium is abundant in the earth crust. But, extraction of Mg from sea water is more profitable.

Other than Na^+, Mg^{2+} is the most abundance cation in sea water. In sea water, about 0.13% by weight is magnesium. The solution discarded at the last stage of producing salt from sea water is called bittern. As bittern contains significant amounts of magnesium ions, it is more suitable to use bittern to extract magnesium. Either sea water or disposable brine obtained after the reverse -osmosis of sea water is suitable for this. The main steps of this process can be briefly presented as follows.

Step 1

The main aim of this step is the production of CaO, which is obtained by the thermal decomposition of limestone. Dolomite also can be used for this purpose.

$$CaCO_3(s) \overset{\Delta}{\rightleftharpoons} CaO(s) + CO_2(g)$$

$$CaCO_3\ MgCO_3(s) \overset{\Delta}{\rightleftharpoons} CaO(s) + MgO(s) + 2CO_2(g)$$

As this reaction is reversible, by designing the thermal decompostion process, carbon dioxide gas is efficiently removed. Contamination of calcium oxide with calcium carbonate is a disadvantage.

Step 2

The object of this step is to produce $Mg\ (OH)_2$ from the solution containing Mg^{2+} ions. The oxides produced in the first step (CaO or CaO and MgO) are reacted with bittern solution. Here, CaO reacts with water forming calcium hydroxide. $Ca(OH)_2$ dissolves slightly in water giving Ca^{2+} and OH^- ions. Since the solubility product of $Mg(OH)_2$ is lower than that of $Ca(OH)_2$, Mg^{2+} ions in the solution are precipitated as $Mg(OH)_2$ by OH^- ions supplied by $Ca(OH)_2$ with this, more and more $Ca(OH)_2$ goes into solution releasing OH^- ions without remaining $Ca(OH)_2$ as precipitate, it dissolves. The amount of CaO required to precipitate the Mg^2+ ions in the solution is added. Prcipitaion of $Ca(OH)_2$ with $Mg(OH)_2$ is a disadvantage.

$$CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(s) \quad \text{-------} \ (1)$$

$$Ca(OH)_2(s) \overset{\Delta}{\rightleftharpoons} Ca^{2+}(aq) + 2OH^-(aq) \quad \text{-------} \ (2)$$

$$Mg^{2+}(aq) + 2OH^-(aq) \longrightarrow Mg(OH)_2(s) \quad \text{-------} \ (3)$$

Step 3

$Mg(OH)_2$ formed is filterd and removed and reacted with concentrated HCl to get $MgCl_2$

$$Mg(OH)_2(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + 2H_2O(l)$$

If burnt dolomite (MgO.CaO) was used, CaO in it, reacts with the Mg^{2+} ions in the solution as above. But as MgO is insoluble in water, MgO is mixed with $Mg(OH)_2$ precipitaed.

Step 4

The solution is heated strongly to vaporize water. Then it is dried so that the amount of water of crystallization becomes considerably low. The dried salt contains about 16% (w/w) water.

$$MgCl_2.6H_2O(s) \longrightarrow MgCl_2.4H_2O(s) + 2H_2O(l)$$

$$MgCl_2.4H_2O(s) \longrightarrow MgCl_2.2H_2O(s) + 2H_2O(l)$$

First the solid formed is fused in the steel chambers where electrolysis is done and then it is electrolized. During heating for fusion, all the water in the salt gets completely removed by vaporization. The temperature in the cell is maintained within the range 700-800 ^{0}C. Since the melting points of $MgCl_2$ and magnesium metal are 714 ^{0}C and 650 ^{0}C respectively, the temperature of the fused salt should be maintained above those melting temperatures. As Mg metal formed during the electrolysis of the fused salt exists in the molten state, its withdrawal from the cell is easier. The density of molten Mg at its melting point is 1.584 g cm^{-3} while the density of fused $MgCl_2$ (at the melting point) is 1.68 g cm^{-3}. Thus, fused Mg metal floats on fused $MgCl_2$

Reaction at the anode (graphite) :

$$2Cl^-(l) \longrightarrow Cl_2(g) + 2e$$

Cl_2 gas liberated is used to produce HCl. HCl is reacted again with $Mg(OH)_2$ to produce $MgCl_2$

Reaction at the cathode (steel) :

$$Mg^{2+}(l) + 2e \longrightarrow Mg(l)$$

Liquid magnesium formed is taken out from the cell. From this about 99.8% yield of Mg can be obtained. As the melting point of magnesium is about 650 ^{0}C, it exists as a liquid at 700 ^{0}C.

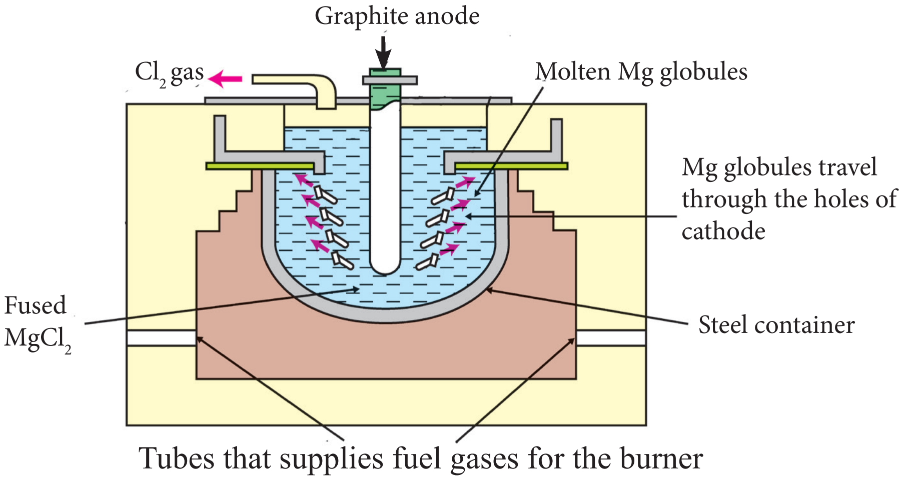


Figure 1.1 The cross sectional structure of the electro chemical cell producing magnesium

Strong and light weight metals are required for aircrafts and vehicles. Magnesium metal is very important for the production of alloys to have this kind of properties.

In this production, release of CO_2 to the atmosphere is a disadvantage. CO_2 is added to the atmosphere during the burning of limestone or dolomite and combustion of petroleum fuels to obtain a higher temperature associated with the electrolysing cell.

1.3 Production of caustic soda (NaOH)

A pure concentrated solution of sodium chloride is called brine. NaOH is produced by electrolyzing a brine solution. As the by-products hydrogen gas and chloride gas are released at the cathode and the anode respectively.

$$NaCl(s) + H_2O(l) \longrightarrow NaCl(aq)$$

$$2NaCl(s) + 2H_2O(l) \xrightarrow{\text{electrolysis}} 2NaOH(aq) + Cl_2(g) + H_2(g)$$

When 2.25 metric tons are produced from a solution containing 50% (w/w%) caustic soda, nearly I metric ton of chlorine gas and 30 kg hydrogen gas are produced. Though there is a consequence difference by mass like this, when the amounts of moles are considered, the amount of moles of chlorine and the amount of moles of hydrogen are approximately equal. In spite of the amounts of moles of chlorine and hydrogen formed are equal theoritically, the amounts of moles of chlorine and hydrogen that can be collected as gases are not equal. Since chlorine gas can slightly dissolve in the aqueous reaction medium, the amount of chlorine gas that can be collected in gaseous form is somewhat less than the amount of hydrogen.

The cells used to produce caustic soda by electrolysis are refered to as chlor-alkali cells. There are three types of cells.

a) Mercury cells

b) Diaphragm cells

c) Membrane cells

Earlier, production of NaOH was based on the mercury cell method. However, possibility of releasing mercury to the environment and contamination of NaOH with minute quantities of mercury are its main disadvantages. The basis of membrane cell and the diaphragm cell are almost identical. The major difference is that in the membrane cell, instead of a diaphragm, a membrane, permeable to Na^+ ions is used to separate the anode and the cathode. Compared to the membrane cell, in the diaphragm cell, the liquid level in the anode chamber is above the liquid level in the cathod chamber. Therefore, a hydrostatic pressure is exerted from the anode chamber solution to the cathode chamber solution across the asbestos diaphragm. This hydrostatic pressure affects the migration of Na^+ ions from the anode chamber to the cathode chamber. It also prevents the movement of OH^- ions from the cathodic solution to the anode chamber solution. But in the membrane cell, the anode is separated from the cathode by a membrane that permits only the movement of positive ions. Higher purity of NaOH produced, lesser consumption of electricity and minimal impact on the environment are the advantages of the employment of membrane cells.

In this electrolytic process, electric potential used for electrolysis and the charge released from a unit area of the electrode surface in a unit time (current density) are important factors. This information is given in the following table.

Table 1.1 The factors included in associated with the cells are used for caustic soda production

	Mercury cell	Diaphragm cell	Membrane cell
Apply cell potential / V	4.4	3.45	2.95
Current density/ A cm^{-2}	1	0.2	0.4
NaOH composition (w/w%)	50	12	35

Membrane cell method

The brine that is used in the membrane cell method should be very pure. Presence of Mg^{2+}, Ca^{2+} and SO_4^{-2} ions in brine hinders the production process. Precipitations of these cations when the solution becomes basic disturbs the cell action. Lowering of the purity of caustic soda because of the addition of these ions to the sodium hydroxide solution is also a disadvantage. Therefore, the concentration of these ionic impurities in brine that is used for the production should be at a very low level. Salt (NaCl) extracted from sea water contains Mg^{2+}, Ca^{2+} and SO_4^{2-} ions. Hence, chemical treatment to remove impurity ions in brine prepared by this salt is a very important step. Sulfate ions can be precipitated and removed as $BaSO_4$ by adding barium chloride in adequate quantities. Mg^{2+} and Ca^{2+} ions can be precipitated as $Mg(OH)_2$ and $CaCO_3$ by adding NaOH and Na_2CO_3 adequately.

$$Mg^{2+}(aq) + 2OH^-(aq) \longrightarrow Mg(OH_{)2}(s) \downarrow$$

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

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s) \downarrow$$

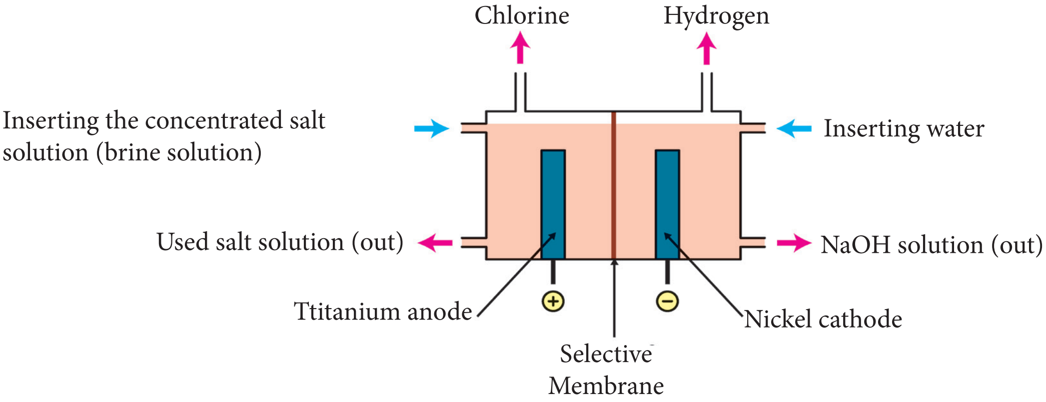


Figure 1.2 Membrane cell

At the beginning the solution in the anode chamber mainly contains Na^+ and Cl^- ions and very small amounts of H^+ and OH^- ions formed by the dissociation of water. The standard electrode potential required to oxidize OH^- ions at the anode to give O_2 is 0.4 V whereas the standard electrode potential for oxidizing Cl^- ions at the anode to liberate Cl_2 gas is 1.36 V. Hence, there is a possibility of liberating O_2 in addition to Cl_2. Several precautions have been taken to minimize releasing oxygen.

$$4OH^-(aq) \longrightarrow O_2(g) + 2H_2O(l) + 4e$$

$$2Cl^-(aq) \longrightarrow Cl_2(g) + 2e$$

NaCl concentration in the brine used to produce caustic soda is relatively high. In a situation where the OH^- concentration is very low and the Cl^- concentration is very high, the probability of forming an oxygen molecule and two water molecules by combining four OH^- ions on the electrode is relatively low. Since there is a relatively higher concentration of Cl^- ions in the anode chamber solution, the ability of forming Cl_2 gas by the oxidation of Cl^- ions is relatively greater.

With the electrolysis when the Cl^- ion concentration decreases, there is a chance for the oxidation of OH^- ions liberating O_2. Because of this, a concentrated salt solution is continuously pumped into the anodic chamber and anodic chamber solution is continuously removed. Though the Cl^- ion concentration in the system decreases, Na^+ ion concentration does not decrease. When the entire cell is considered, maintenance of electric neutrality in the system is a fundamental feature, so, when Cl^- ions are given off from the anodic chamber as Cl_2 gas, either another negative ion should come into the anodic chamber solution or Na^+ ions should migrate into the cathodic chamber solution. Reduction takes place in the cathodic chamber. H^+ ion is more easily reduced than the aqueous Na^+ ion. At the beginning the medium in the cathodic chamber has no sodium chloride, so its main component is water. Since H^+ ions resulted by the dissociation of water molecules are continuously reduced, the equilibrium maintained by the reversible dissociation of water molecules drops. Since water molecules continuously dissociate with the removal of H^+ ions formed by the dissociation of water as H_2 molecules, OH^- ion concentration in the cathodic chamber increases. When electrolysis is carried out continuously, OH^- ion concentration in the cathodic chamber rises with time.

The equilibrium brought about by the dissociation of water molecules can be shown by equation (1)

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \text{ --------- } (1)$$

The situation where the equilibrium is lost due to reduction of H^+ ions to H_2 molecules is represented by equation (2)

$$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq) \text{ --------- } (2)$$

In the cathodic chamber H^+ ions get reduced to H_2 molecules at a rate equal to the rate of oxidation of Cl^- ions to Cl_2 molecules in the anodic chamber. Because of this, the rate in which, water in the cathodic chamber continuously dissociates generating OH^- ions is equal to the rate of decreasing of Cl^- ions in the anodic chamber solution. Thus, the entire system is electrically neutral.

Along with the electrolysis, in a membrane cell, though the concentration of Cl^- ions in the anode chamber decreases, Na^+ ion concentration does not decrease. Meanwhile, in the cathodic chamber OH^- ion concentration increases because of the reduction of H^+ ions formed by the dissociation of water. This develops a potential difference across the membrane. If OH^- ions in the cathodic chamber pass into the anode chamber, they react with chlorine in it. But, in the case of a membrane cell, OH^- ions are not capable to migrate across the membrane, so this reation does not occur in the cathodic chamber solution.

In the membrane cell, the anodic and cathodic compartments are separated by a membrane permeable to positive ions (Na^+). This membrane has very tiny pores and negative ions are bound to the borders of these pores. The negative electric fields in the space around the pores attract positive ions towards the pores and repel negative ions. While water is continuously added to the cathodic chamber by an inlet tube while the solution containing NaOH is removed by an outlet.

Anode is made of titanium and cathode is made of nickel. Possibility to carry out the NaOH production process continuously is a special feature. Brine with concentration 26% is continuously pumped into the anodic chamber and as shown of the flow chart the concentration in the solution removed from the anodic solution has dropped up to 24%. In the anodic chamber, when the generation of Cl_2 by the oxidization of Cl^- ions, H_2 are formed by the reduction of H^+ ions in the cathodic chamber. Comparing to the increasing of the OH^- ion concentration in the cathodic chamber, Na^+ ions existing in the anodic chamber move to the cathodic chamber. Therefore, a concentration of sodium hydroxide builds up in the cathodic chamber. With the movement of Na^+ ions, an electrical neutrality is brought about in each chamber. These process continuously occur during electrolysis.

The Cl^- ions in the anodic chamber do not move into the cathodic chamber through the membrane. Hence, NaCl does not get mixed up as an impurity with NaOH.

Anodic reaction (Positive terminal)

$$2Cl^-(aq) \longrightarrow Cl_2(g) + 2e$$

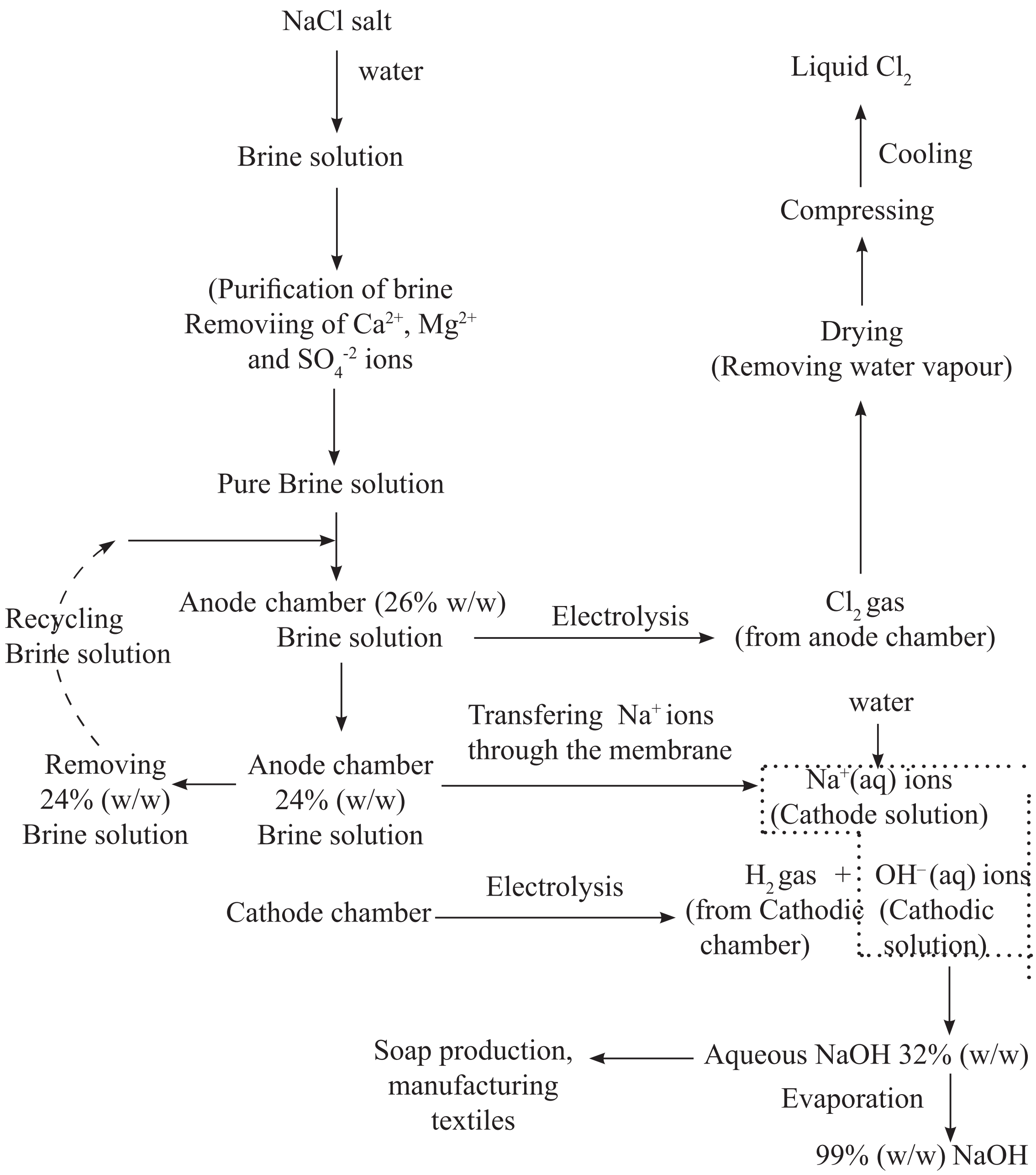
Cathodic reaction (Negative terminal)

$$2H_2O(l) + 2e \longrightarrow 2OH^-(aq) + H_2(g)$$

Overall reaction

$$2NaCl(aq) + 2H_2O(l) \longrightarrow 2NaOH(aq) + Cl_2(g) + H_2(g)$$

The flow chart for the production of NaOH by the membrane cell method.



Uses of NaOH and by-products

Uses of NaOH

1. Production of soap
2. Production of paper, artificial silk and dyes
3. Using as a strong base
4. Precipitation of heavy metal as their hydroxides in waste water treatment.

Uses of chlorine

1. Bleaching textiles, woods and paper pulp
2. Purifying the drinking water
3. Production of HC1
4. Production of chlorinated rubber, insecticides, dyes and medicine
5. Production of vinyl chloride required to produce polymers like PVC

Uses of hydrogen

1. Manufacture of HCl
2. Production of NH_3
3. Production of margarine by hydrogenation of vegetable oil
4. Using as a fuel

1.4 Production of soap

During the manufacting of soap chemically, triglycerides are subject to a hydrolysis reaction with caustic soda (saponification) forming glycerol and sodium salts of long chain carboxylic acids. These salts are known as soap. A soap molecule comprises a hydrophobic tail made of carbon and hydrogen atoms and a site with a hydrophilic head, The hydrophilic head contains Na^+ or K^+ ion and the $–COO^-$ ionic group.
Animal fat or plant oil is a one raw meterial for the production of soap. The other raw meterial is NaOH or KOH.

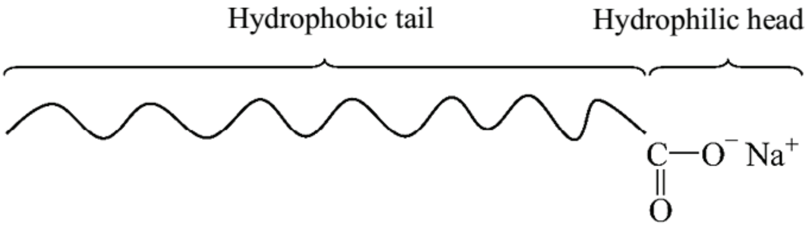


Figure 1.3 Hydrophobic tail and hydrophilic head in a soap molecule

Soap is manufactured by two processes, hot process and the cold process. In the cold process, soap and glycerol are not separated. Glycerol is deposited in soap. Here only the hot porcess and its main 4 steps are considered

1. Saponification
2. Removal of the by-product, glycerin
3. Purification
4. Finishing

The number of carbon atoms in a soap molecule varies as 12, 14, 16 and 18. In coconut oil, lauric acid, myristic acid, stearic acid and oleic acid are bound by ester bonds in the triglycerides. The amount of long chain carboxylic acids (fatty acids) present in the form of triglycerides is indicated as a percentage. In addition to this, a small amount of fatty acids occurs as free fatty acids without forming ester bonds. In coconut oil 44 – 52% of Lauric acid prercent. The number of carbon atoms in it is 12. 11 atoms out of them are in the hydrophobic tail. The percentage of myristic acid in coconut oil is 14% and it contains 14 carbon atoms. The percentages of parmitic acid (16 carbon atoms) and stearic acid (18 carbon atoms) in it are 8% and 3% respectively. Oleic acid has 18 carbon atoms and a double bond and its percentage in coconut oil is in the range of 5-8%. Soap produced using coconut oil is a mixture of sodium salts of these acids.

To remove the pigments and impurities in oil, it is sent over a special type of clay referred to as activated fuller earth. It's temperature is maintained at about 90 ^{0}C. After removing the clay particles in oil, it is used to make soap. Soap production can be conducted either as a continuous process or a Batch Process.

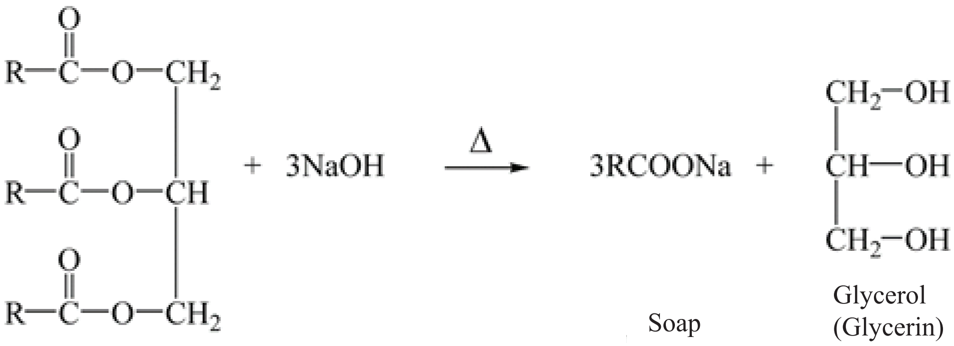
Batch Process is the traditional method. In it all the amounts of raw materials are added together to the reaction chamber and allowed to react. Afterwards the products are separated. In the continuous process, reactants are continuously supplied to the reaction chamber and products are continuously removed.

1. Saponification

Here, purified vegetable oil (coconut oil) is mixed with a solution of aqueous NaOH and heated. The purified vegetable oil (e.g. coconut oil) and the caustic soda (NaOH) solution or the caustic potash (KOH) solution are pumped into the reaction chamber. Dissolving of caustic soda in water is exothermic. Therefore dissolving of caustic soda in water is done as a separated process.

Oil and aqueous sodium hydroxide are two immiscible phases. Glycerin and soap are formed as a result of the saponification reaction taking place at the interface of these two layers. Since NaOH is neutralized here, heat is produced. The temperature of the reaction mixture is maintained at 70 ^{0}C and the mixture is mixed well. Oil divides into tiny droplets and increases the surface area. Therefore the reaction occurs uniformly throughout the entire volume of reaction mixture.

The saponification reaction can be written as follows.



$R = C_{17}H_{35} / C_{15}H_{31} / C_{11}H_{23} / C_{13}H_{27}$

2. Removal of glycerin

In the aqueous phase obtained after saponification, basicity has dropped. Glycerin and a certain amount of soap have dissolved in the aqueous phase. Soap molecules dissolved in the aqueous phase are ionized and maintain an equilibrium as follows. To decrease the solubility of soap in the aqueous phase NaCl (brine) is added. As the Na^+ ion concentration is high, the above equilibrium shifts to the left and the soap molecules separate from the aqueous phase. Glycerin dissolves in the salt solution. Density of the aqueous phase increases due to the addition of NaCl. After separating impure soap from the aqueous phase, the aqueous phase containing glycerin is pumped out.

$$\text{Water} + RCOO^-Na^+(s) \rightleftharpoons RCOO^-(aq) + Na^+(aq)$$
$$\xleftarrow[\text{When increasing } Na^+ \text{ ion concentration}]{\hspace{6cm}}$$

Pumping of crude soap is easy because the temperature is 70 ^{0}C and crude soap contains a considerable amount of wetness (water). The aqueous salt solution removed from the reaction chamber contains glycerin. Thus, it is a good source to obtain glycerin. Adequate sodium chloride is added again to the solution obtained after removing glycerin and recycled. This salt solution is used to remove glycerin in impure soap. In this salt solution, though glycerin dissolves, soap does not dissolve. Here, mixing soap well with the salt solution is very important. By this crude soap can be purified to a certain extent by removing glycerin remaining it. Then, the salt solution containing glycerin and soap partially purified and separated.

3. Purification

Water and NaCl salt are present in the soap which is purified upto a certain extent by removing glycerine. Wet soap with salt is centrifuged. Then the aqueous salt solution separates from soap. The NaCl content in soap decreases to 0.5% (w/w).

Presence of caustic soda in soap is harmful to the user. Soap with high caustic soda content can severely damage the skin and tender tissues in eyes. Therefore citric acid, phosphoric acid or free fatty acids associated with coconut oil are added to neutralize sodium hydroxide which may be present even in minute quantities in soap.

4. Finishing

It is essential to remove water in soap after removing salts. To reduce the water content in soap to 12% (w/w) soap heated to about 120 ^0C is sprayed into a low pressure zone in the form of small droplets. As heat is abosorbed for the vaporization of water, the temperature of the droplets decreases. While water vapour is removed, soap settles down in the low pressure vessel. Dry soap is then separated. Finished soap is made by mixing fillers, colouring and perfumes and moulded into required shapes.

TFM value of soap

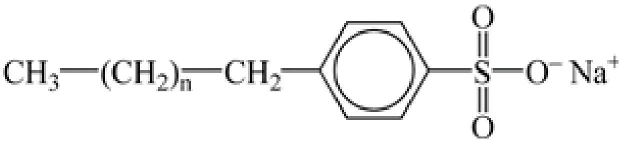
TFM (Total Fatty Matter) means the total fatty matter presents in soap. It is the percentage of RCOONa (soap) present in a cake of soap. The TFM value of a cake of washing soap is about 54-56% and the rest is fillers, colouring and substances which promote the cleaning action and colouring.

A disadventage of soap is not dissolving and not lathering in hard water. Reason for this is, reaction of soap molecules with cations caused for the hardness and get precipitated.

$$RCOO^- Na^+ + M^{2+} \longrightarrow (RCOO)_2M + 2Na^+$$

$M = Ca^{2+}, Mg^{2+}, Fe^{2+}$ etc.

Detergents do not precipitate in hard water. The main ingredients of artificial detergents is sodium alkylbenzenesulphonate.



Cleaning action of soap

Dirt is a mixture of dust particles and organic compounds gathered around on a layer of oil. As the surface tension of water is high dirt doesn't remove only with water. Soap lowers the surface tension of water and improves its cleaning action.

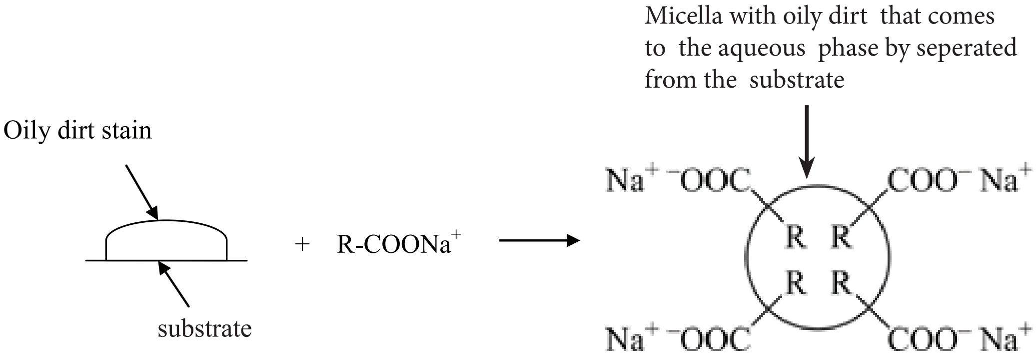


Figure 1.4 Cleaning action of soap

Since soap molecules form micella with oily droplets as shown above, dirt gets removed.

1.5 Production of Na_2CO_3 (Solvey process/ Ammonia – soda process)

Sodium carbonate is a raw material required for a number of chemical industries. Therefore Na_2CO_3 production is a major chemical industry in the world. Presently about 20 million metric tons of Na_2CO_3 are annually produced in the world.

The main chemical reactions involved in the production of Na_2CO_3 are given below.

$$NH_3 + H_2O \rightleftharpoons NH_4OH$$

$$NH_4OH + CO_2 \longrightarrow NH_4HCO_3$$

$$NaCl + NH_4HCO_3 \longrightarrow NaHCO_3 + NH_4Cl$$

$$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + CO_2 + H_2O$$

NH_3 essential for the production of Na_2CO_3 is obtained by the Haber process. CO_2 is produced by the thermal decomposition of limestone. The other main raw material is purified concentrated NaCl solution by removing Ca^{2+}, Mg^{2+} and SO_4^{2-} ions. This is refered to as brine.

$$CaCO_3 \xrightleftharpoons{\Delta} CaO + CO_2$$

The basic steps of the process occur in specially setup towers for the production of Na_2CO_3, can be briefly stated as follows.

Step 1 – Ammonification

First the brine solution is introduced from the top of the tower and ammonia gas is introduced from the bottom of the tower. Mixing reactants efficiently by sending the reactants in opposite directions is referred to as the countercurrent principle. Ammonification of brine is an exothermic process. Hence, if the temperature of brine increases, efficiency of dissolving ammonia decreases. It is important to maintain a low temperature in the tower by removing the heat in the tower through heat exchange.

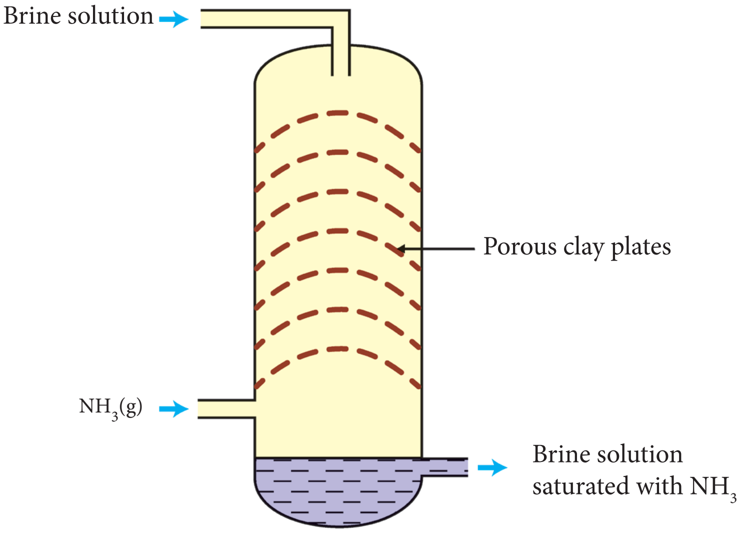


Figure 1.5 Ammonification tower

Step 2 – Carbonation

The brine solution saturated with ammonia is introduced from the top of the second tower while CO_2 is introduced from the bottom. Here, the reactants efficiently mix under the counter current method. Ammonified brine is a basic medium. CO_2 is an acidic gas. Dissolving it in water is exothermic. Hence formation of NH_4HCO_3 by reacting aqueous CO_2 with NH_4OH is also exothermic. For this also keeping the second tower cool is very important.

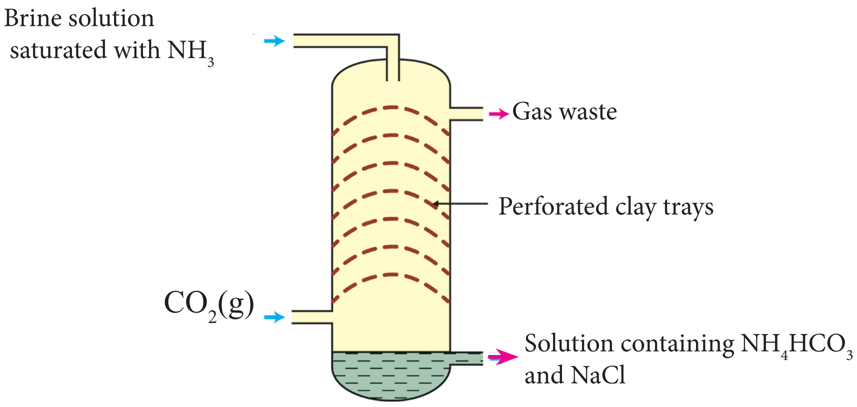


Figure 1.6 Carbonation tower

NH_3 is readily soluble in water but the solubility of CO_2 gas in water is relatively low. The concentration of HCO^-_3 ions formed by the dissolution of carbon dioxide in water is also very low. As ammonification proceedes carbonation, CO_2 gas is absorbed well into the basic $NH_3(aq)$ solution. This produces a high concentration of HCO^-_3 ions.

Step 3 – Seperation of $NaHCO_3$

As ammonification brine solution is carbonated, the concentration of NH_4HCO_3, in the solution is increased. Since this brine has a high concentration of Na^+ ions, $NaHCO_3$ Crystallizes and separates out from the solution when the concentrations of Na^+ and HCO^-_3 ions exceed the saturation limit of $NaHCO_3$. The overall reaction can be indicated as,

$$Na^+(aq) + HCO_3^-(aq) \longrightarrow NaHCO_3(s)$$

The solid $NaHCO_3$ that forms is removed from the solution.

The overall reaction of forming $NaHCO_3$ can be written as follows.

Accordingly the raw materials essential for the production of $NaHCO_3$ in theoritical point through Solvey process are NH_3, CO_2, NaCl and H_2O.

$$NH_3(g) + CO_2(g) + NaCl(aq) + H_2O(l) \longrightarrow NaHCO_3(s) + NH_4Cl(aq)$$

Step 4 – Obtaining Na_2CO_3 by heating $NaHCO_3$

Anhydrous Na_2CO_3 is obtained by heating $NaHCO_3$ which is separated. CO_2 gas formed is sent back to the carbonation tower.

$$2NaHCO_3(s) \longrightarrow Na_2CO_3(s) + CO_2(g) + H_2O(l)$$

NH_4Cl which is a by-product of this process is used to regenerate NH_3 as follows. For this NH_4Cl solution is reacted with CaO oxide obtained by the decomposition of limestone.

$$CaO(s) + 2NH_4Cl(aq) \longrightarrow 2NH_3(g) + CaCl_2(aq) + H_2O(l)$$

NH_3 formed is passed to the ammonifying tower. Accordingly the overall theroitical reaction for the entire process is as follows. However by mixing solid $CaCO_3$ and aqueous NaCl, Na_2CO_3 cannot be prepared.

$$CaCO_3(s) + 2NaCl(aq) \longrightarrow CaCl_2(aq) + Na_2CO_3(s)$$

The final by-product of this process is $CaCl_2$. It can also be used for other industries.

Due to following reasons Solvey process is economical profitable.

1) NaCl and $CaCO_3$ can be obtained easily and with low cost.
2) NH_3 is not consumed and can be used again and again by re-cycling.
3) A part of CO_2 can be re-used.

Solubility of $KHCO_3$ is higher than the solubility of $NaHCO_3$. So $KHCO_3$ is not precipitated in the tower. Therefore above method cannot be used to make $KHCO_3$.

Uses of Na_2CO_3

1) Removal of hardness of water
2) Addition to improve cleaning action when producing soap and detergents.
3) Using as washing soda
4) Mixing to the wood pulp in paper industry
5) Production of glass

1.6 Production of ammonia (Haber-Bosch process)

In modern context, manufacture of ammonia is mainly needed for the production of artificial fertilizers. At present the world population is nearly 7.3 billion and it has been estimated that it will increase to about 9 billion by 2050. With the increasing of the population, production of food is a necessity. Production of fertilizer is considered as an important field of chemical manufacture in this regard.

Of the total ammonia production 83% is used to produce fertilizer. Specially 80% of the total ammonia production is used to manufacture urea.

The chemical reaction related to the production of ammonia is given below.

$$\begin{array}{lcl} N_2(g) + 3H_2(g) & \longrightarrow & 2NH_3(g) + \text{heat} \\ 1 \quad : \quad 3 & & 2 \end{array}$$

Raw materials required to produce ammonia

N_2 gas and H_2 gas are the main raw materials. N_2 gas is separated by fractional distillation of liquefied atmospheric air. Therefore N_2 gas has a production cost.

Hydrogen gas is obtained by cracking hydrocarbons (naphtha) or using methane, which is the main component of natural gas.

Extra knowledge

Natural gas is used as a fossil fuel to generate power. Natural gas occurs in large quantities as underground ores in the Earth. Production of H_2 from natural gas is known as Steam-Methane-Reforming (SMR). A small quantities of H_2S is present in natural gas; H_2S disturbs Nickel catalytic process. Furthermore H_2 is formed by a catalytic reaction after removing H_2S in the natural gas.

The reaction related with removals of H_2S

$$H_2S\ (g) + ZnO\ (s) \rightleftharpoons ZnS\ (s) + H_2O\ (g)$$

The first step of the SMR process is reacting methane and water vapour at 700 ^0C - 800 ^0C to produce CO and H_2. This is an endothermic reaction.

$$CH_4(g) + H_2O\ (g) \longrightarrow CO(g) + 3H_2\ (g) \quad +206\ kJ\ mol^{-1} \quad \text{-------} \quad (1)$$

During the second step this gaseous mixture is further reacted with water vapour. Here, CO is converted to CO_2. This is an exothermic reaction.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \quad -41\ kJ\ mol^{-1} \quad \text{-------} \quad (2)$$

In addition to this, there is a possibility for the following reaction to occur.

$$CH_4(g) + 2H_2O(g) \longrightarrow 4H_2(g) + CO_2(g) \quad \text{-------} \quad (3)$$

The yield of H_2 can be increased by maintaining more water vapuour and shifting the total reaction to the right.

To have some understanding of the thermodynamic nature of the SMR, the relationship $\Delta G = \Delta H - T\Delta S$ can be used.

According to the above thermodynamic relationship the exothermic second reaction is spontaneous even at low temperature. Since the number of gaseous molecules does not change, pressure has no effect. Further the effect of $T\Delta S$ on ΔG is almost nil.

First and third endothermic reactions occur relatively at higher temperatures. The entropy increases because the number of gaseous molecules increases to the forward direction. So, with increase in temperature, the positive value of TΔS increases. Therefore according to $\Delta G = \Delta H - T\Delta S$, in reactions 1 and 3 ΔG becomes more negative at higher temperatures. Reaction 1 is alllowed to occur at a high temperature (1000 – 1800 ^{o}C). There even reaction 3 may occur. In order to reduce the CO concentration and increase the yield of H_2, the second reaction is allowed to occur at relatively at low temperatures (200 – 400 ^{0}C). By adding water vapour to the hot gaseous mixture of CO and H_2 its temperature can be lowered (200 – 400 ^{0}C). As the second reaction is exothermic, the heat generated by the second reaction is used to obtain the higher temperature suitable for the first reaction.

In United States, about 60% of natural gas production is used for the production of ammonia gas. Hydrogen gas can also be obtained by cracking naphtha (C_6H_{14}). It also release CO_2 to the atmosphere. The relevant reactions that occur are as follows.

$$C_6H_{14}(g) + 6H_2O(g) \longrightarrow 6CO(g) + 13H_2(g)$$

$$CO(g) + H_2O(g) \longrightarrow CO_2(g) + H_2(g)$$

Production of NH_3 from hydrogen and nitrogen gases is an exothermic reaction and it is reversible. But, under normal temperature and pressure this reaction hardly happens. The reason is the activation energy is relatively high.

Producing NH_3 by H_2 and N_2

Industrially, ammonia is manufacture by the Haber-Bosh process. The optimum industrial conditions employed for the process are a temperature in the range 450-500 ^{0}C, a pressure of 250-300 atm, iron catalyst and K_2O and Al_2O_3 as catalytic promoters.

$$N_2(g) + 3H_2(g) \underset{450\text{ - }500\ ^{\circ}\mathrm{C}}{\overset{250\text{ - }300\text{ atm}}{\rightleftharpoons}} 2NH_3(g) + \text{heat}$$

The compressed mixture of reactant gases pass over the surface of the catalyst and gets converted to NH_3. Since the reaction is reversible the gaseous mixture passing the catalyst surface contains unreacted $H_2$and N_2 gas in addition to NH_3. Therefore NH_3 gas should be seperated from this mixture. When the mixture is cooled upto - 33.34 ^{0}C, NH_3 gas liquefies. The boiling points of nitrogen and hydrogen gases are – 195.8 ^{0}C and – 252.9 ^{0}C respectively. So by cooling this mixture only ammonia can be liquefied and the mixture of H_2 and N_2 can be separated from the reaction mixture. The gaseous mixture containing H_2, N_2 and NH_3 under high pressure can be cooled by decreasing the pressure suddenly in another chamber. Then NH_3 liquefies. Remaining H_2 and N_2 gases are then pumped back into the reaction chamber. Equal amounts of H_2 and N_2 that have been used to make NH_3 are then freshly added.

This process can be depicted by Figure 1.7 in a simplified way.

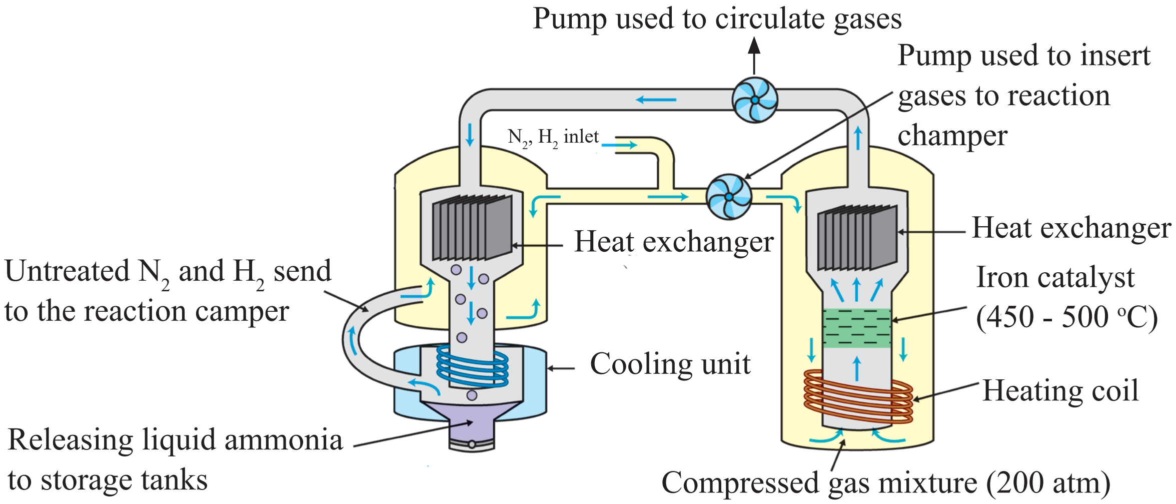


Figure 1.7 Process of ammonia production

After the removal of liquid ammonia, the gaseous mixture containing unreacted and newly added N_2 and H_2 gases (under a temperature of around -33.34 ^{0}C) is heated to 450 – 500 ^{0}C. The heat energy required to have this temperature can be supplied by the combustion of fuel also. This releases CO_2 to the atmosphere. In the Haber process CO_2-is produced at the step in which hydrogen is produced and also during the burning of fuel to gain high temperature. Due to the overall process, CO_2 which is a green house gas releases to atmosphere. Globally, when 1 tonne of ammonia is produced by overall process, about 2.9 tonnes of CO_2 is released to the atmosphere. Compared to the releasing of CO_2 to atmosphere by other processes, approximately 1.4% of it, is by ammonia production.

In ammonia production N_2 and H_2 are mixed according to their stoichiometric ratio (1:3). Since some cost has to be borne to produce nitrogen gas and hydrogen gas they are not mixed beyond their stoichiometric ratio and this prevents wastage of raw materials. Further if one gas is used in excess it would be adsorbed by the surface of the catalyst covering the surface completely. Coverage of catalyst surface by one gas reduces the chances for the reaction to occur. Both the gases need to be absorbed to the catalyst surface. Use of the catalyst decreases the time to reach the equilibrium. Based on all the factors, N_2 and H_2 gases are mixed in the optimal ratio of 1:3.

The reaction is exothermic, so it's ΔH is negative. When the reaction proceeds, entropy decreases because the number of molecules decreases. Hence ΔS of the reaction is negative. Thus $T\Delta S$ is negative and $-T\Delta S$ is positive. Therefore with the increase in temperature ΔG changes from negative to positive. The fact that high temperatures do not favour the forward reaction can also be explained by Le Chatelier's principle.

On increasing the temperature the spontaneous nature of the reaction decreases. Thermodynamically, when the spontaneity decreases, the yield decreases. To increase the yield, the temperature should be decreased. But when the temperature is decreased the rate of the reaction decreases and the efficiency of the entire process declines. A temperature of 450-500 ^{0}C is used to maintain an optimum efficiency. The NH_3 yield obtained under these conditions is relatively low. Yet, the production process has been designed so that the unreacted H_2 and N_2 gases are brought into the catalytic cycles again and again. Despite the fact that the amount of NH_3 yield by a single step is small, the process as a whole gains a high yield because it has been designed to carry out via number of catalytic cycles. According to Le Chatelier's principle, higher pressures favour the forward reaction. But the maintenance cost of the plants withstanding high pressures is high. Therefore at present, a pressure of 250-300 atm is used. Maintenance of reactant concentration at a high level and product concentration at a low level results in a higher yield of NH_3. This can be explained by the Le Chatelier's Principle. This requirement is fulfilled by introducing N_2 and H_2 into the reaction chamber from time and removal of NH_3 by cooling the gaseous mixture containing NH_3 and liquefying the gas.

Uses of ammonia

1. Production of nitric acid, fertilizers and nylon
2. Petroleum industry utilizes ammonia in neutralizing the acid constituents of crude oil
3. Used in water and waste water treatment, such as pH control, in solution form to regenerate weak anion exchange resins
4. Used as a refrigerant
5. Used in the rubber industry for the stabilization of natural and synthetic latex to prevent premature coagulation

1.7 Production of nitric acid (Ostwald method)

For this, ammonia gas, atmospheric air and water are used as raw materials. Nitrogen dioxide gas obtained by the reaction between ammonia and oxygen gas is reacted with water to produce nitric acid. The reaction involved are;

$$4NH_3(g) + 5O_2(g) \xrightarrow{\Delta} 4NO(g) + 6H_2O(l) \quad (-907\ kJ\ mol^{-1})$$

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g) \quad (-114\ kJ\ mol^{-1})$$

$$3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(aq) + NO(g)$$

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

$$4NO_2(g) + 2H_2O(g) + O_2(g) \longrightarrow 4HNO_3(aq)$$

Figure 1.8 simply illustrates this process.

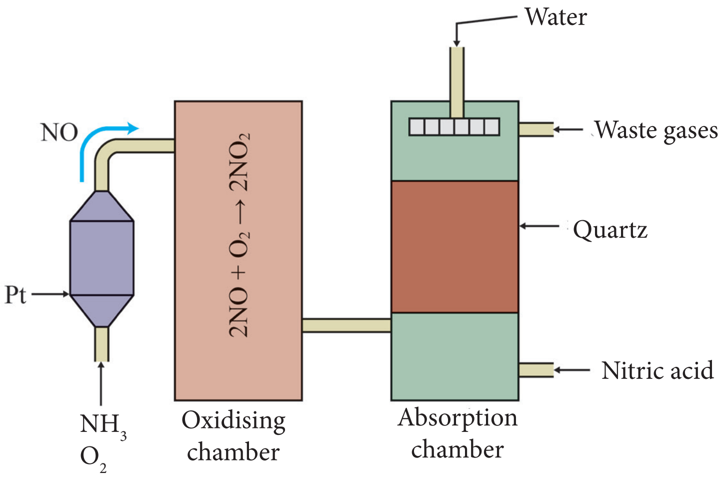


Figure 1.8 Production of nitric acid

In the first chamber ammonia is oxidized in the presence of the catalyst. In the second chamber nitrogen monoxide gas (nitric oxide) is oxidized. Nitrogen dioxide gas is reacted with water in the third chamber.

Ammonia is oxidized using atmospheric air from which dust and water vapour have been removed. Ordinary air contains 78% nitrogen gas and 21% oxygen gas by volume. A volume of atmospheric air which contains the required amount of oxygen is pumped into the reaction chamber. For a unit volume of ammonia, 9-12 units of atmospheric air by volume are required. A high temperature range (800-850 ^{0}C) is maintained. Under these conditions around 97% of NO gas can be obtained. If the ammonia concentration is high explosions may occur. Therefore maintaining the volumes of ammonia and atmospheric air in the correct proportion is important. When this gas mixture is passed through the Pt/Rh catalyst under pressure it is converted to NO gas. This NO gas is cooled to 150^{0}C. When the temperature is 150 ^{0}C, further oxidation of NO to NO_2 occurs in the oxidation chamber. In the absorption chamber NO_2 gas is allowed to react with water conforming to the counter-current principle. The gaseous mixture containing oxygen and NO_2 is pumped into the absorption chamber under a pressure of 5-10 atm. As the absorption chamber is packed with chemically inactive substances greater chance is offered for the reaction between water and NO_2. Finally a yield of around 96% is obtained.

Uses of nitric acid

1. Making fertilizer and explosives
2. Making nitrates essential for industries

   KNO_3 – to produce gun power

   $AgNO_3$ – photography

3. Making aqua regia
4. Cleaning surfaces when welding metals

1.8 Production of sulfuric acid (Contact process)

Raw materials required to produce sulphuric acid

Sulphur or ores containing shlphur and water are used in this manufacture. When extracting the metals Pb, Cu and Zn from ores containing PbS, CuS and ZnS, sulphur dioxide is obtained as a by – product. This can also be used to produce H_2SO_4. Shlphur obtained as a by – product during petroleum refining or sulphur extracted from earth can also be used for this.

In the production of sulphuric acid, sulphur dioxide is made by burning sulphur or metal sulphides. Second step is the preparing of sulphur trioxide by reacting sulphur dioxide with atmospheric oxygen. Sulphuric acid is obtained by hydrolyzing pyrosulphuric acid ($H_2S_2O_7$, oleum) made by reacting sulphur trioxide with concentrated sulphuric acid.

$$S(s) + O_2(g) \longrightarrow SO_2(g)$$

$$2SO_2(g) + O_2(g) \underset{V_2O_5(s)\ \text{catalyst}}{\overset{1\ \text{atm},\ 450\ ^0C}{\rightleftharpoons}} 2SO_3(g) + \text{heat}$$

$$SO_3(g) + H_2SO_4(aq) \longrightarrow H_2S_2O_7(aq)$$

$$H_2S_2O_7(aq) + H_2O(l) \longrightarrow 2H_2SO_4(aq)$$

Production of sulphur dioxide by burning elemental sulphur is a separate process. In the school laboratory sulpher dioxide can easily be prepared by burning a piece of sulphur with the bunsen burner. But production of sulphur dioxide industrially is not that easy. First sulphur is heated to 140 ^0C and melted. Liquid sulphur is filtered to remove various solid impurities in it.

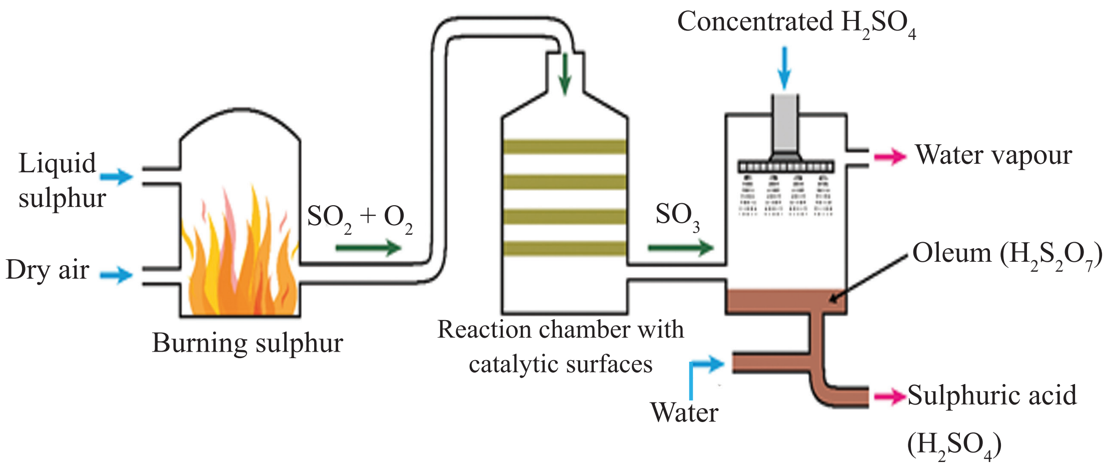
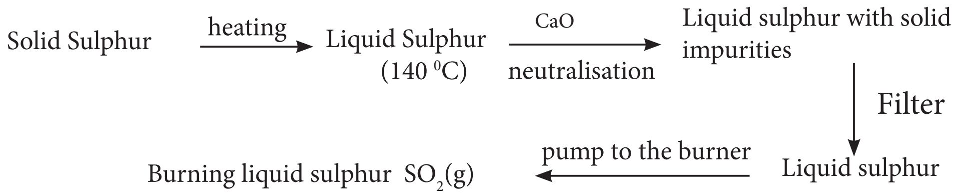


Figure 1.9 Production process of sulphuric acid



Liquid sulphur and atmospheric air should be pumped into the furnace. Liquid sulphur is pumped in the form of very small droplets which burn easily. Combution of sulphur is exothermic. In the gaseous mixture obtained after burning, the composition of sulphur dioxide is maintained between 8-9%.

The temperature around the burner is about 830 ^{0}C. In the gasous mixture of sulphur dioxide, oxygen and nitrogen in the combustion chamber, various solid particles (ash) may be present. Removal of them is crucial because the particles of dust and ash setting on the surface of V_2O_5 catalyst retards the catalytic action. Therefore, first the gaseous mixture containing SO_2 is purified. The reaction producing sulphur trioxide is reversible and exothermic. The molar ratio (or ratio by volume) between oxygen and sulphur dioxide is maintained at 1:1.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) + \text{heat}$$

For efficient progression of the reaction, an optimum temperature of 400 – 500 ^{0}C is maintained. The reaction itself generates heat. Thus, if the production plan was designed to react the whole amount of SO_2 with O_2 at once, a huge amount of heat would be liberated. This favours the backward reaction and reduces the yield. Hence the entire amount of SO_2 is converted to SO_3 in four steps. In every step the gaseous mixture is passed through the catalyst bed.

In order to increase the SO_3 yield by shifting the above reversible reaction to the right, oxygen concentration can be increased by supplying atmospheric air. As atmospheric air is a cheap raw material, this does not increase the production cost. According to the stoichiometry the ratio of SO_2: O_2 is 2:1. The amount of oxygen required for one mole of SO_2, is 0.5. But during the production the molar ratio maintained as 1:1. So 0.5 moles of O_2 is in excess for 1 mole of SO_2. Though atmospheric air is cheap, maintaining a higher oxygen concentration above the required concentration, decreases the efficiency of the process. This is because of higher the oxygen concentration, more O_2 molecules get adsorbed to the catalyst surface. This reduces the capacity of the catalyst to adsorb SO_2 molecules there by decreasing the probability for the reaction to occur.

This reaction is exothermic. Therefore increase in the yield on cooling can be predicted from Le Chaterier's Principle. But the decrease in the rate of the reaction at low temperatures brings down the efficiency of the production process. Hence, it has been decided that the optimum temperature is 400-450 ^{0}C.

Le Chaterier's Principle predicts that with increasing pressure the reversible reaction tends to move in favour of the direction in which the number of molecules in the gas phase decreases. In this reaction, increase in pressure favours the forward reaction increasing the productivity of SO_3. But in this particular reaction the yield is as higher as 99% even under 1 atm pressure. Therefore applying high pressures is unnecessary.

As this reaction is highly exothermic the production process is conducted in four steps managing heat exchange. This is illustrated in the following flow chart (Figure 1.10)

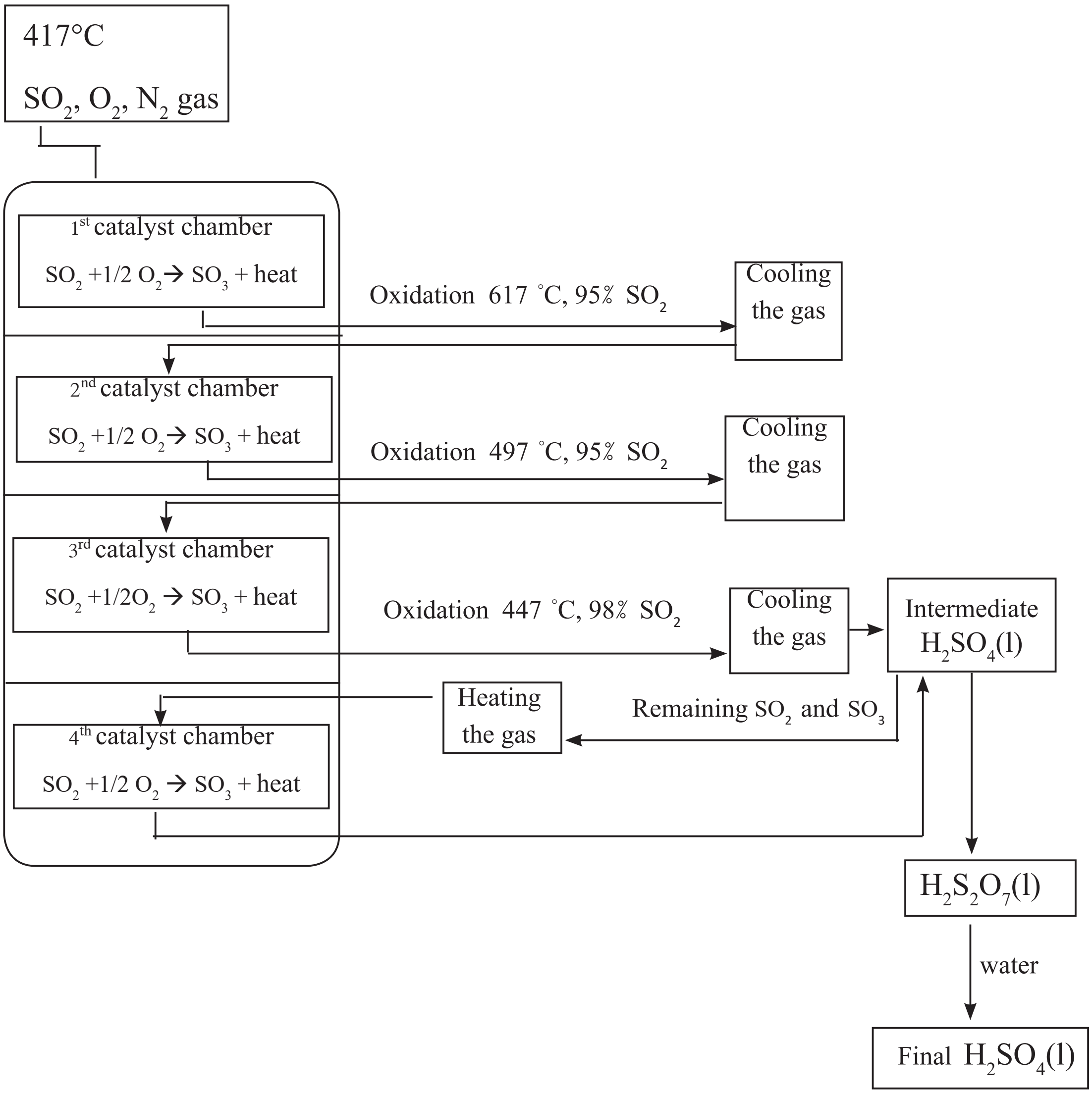


Figure 1.10 Main heat exchange steps in the production of sulfuric acid

The temperature of the gases entering the first chamber is around 690 K (417 ^{0}C). When passing through the catalyst, the temperature rises to 890 K (617 ^{0}C) and about 70% of SO_2 gets oxidized. The gases cooled to about 700 K (427 ^{0}C) is passed through the second bed of catalyst. At this stage the amount of SO_2 present is relatively low. For this reason the amount of SO_3 formed is less than that formed in the first step and the amount of heat generated is also relatively low. The second heat exchanger cools the gaseous mixture whose temperature has risen to 770 K (497 ^{0}C) to 720 K (447 ^{0}C). By that time, a considerable amount of SO_2 from its initial amount has reacted. After passing through catalyst bed in the third chamber 98% of SO_2 of its initial amount turns into SO_3.

Sulphuric acid is made by the SO_3 obtained from the third step. Here also, 100% of SO_3 is not converted to H_2SO_4. The gaseous mixture containing the remaining SO_3 and the SO_2 left due to reversibility is heated again and passed through the catalyst in the fourth chamber which converts it to SO_3. This SO_3 is also converted to H_2SO_4 again.

The reaction between SO_3 and water is violent and highly exothermic. Therefore water vaporizes and a mist of sulphuric acid fumes is made. To avoid this SO_3 gas is converted to H_2SO_4 via the steps described above. The absorption of SO_3 is maximum in concentrated (98%) sulphuric acid at 70 ^{0}C. Therefore under those conditions SO_3 is absorbed into concentrated sulphuric acid and H_2SO_4 is made by adding water to it.

Sulphur trioxide and concentrated sulphuric acid are reacted according to the counter current principle. This happens in absorption towers which are packed with ceramic materials. Because of the packing, sulphuric acid slowly trickles down the chamber from top to bottom and the surface area of liquid H_2SO_4 is increased. Sulphur trioxide moves up the chamber. Increased surface area of the acid coupled with its slow flow and the upward movement of SO_3 gas make the absorption efficient. Here, SO_3 reacts with H_2SO_4 giving oleum ($H_2S_2O_7$). Concentrated sulphuric acid is made by adding water to oleum carefully.

Uses of sulphuric acid

1. Production of phosphate fertilizers
2. Production of ammonium sulphate fertilizer
3. Production of artificial fibers including rayon and plastics
4. Production of detergents containing alkyl and aryl sulphonates
5. Production of dyes, explosives and medicines
6. Production of battery acid
7. Drying gases (e.g. Cl_2)

1.9 Production of titanium dioxide from rutile

Ilmenite and rutile are main minerals which contain titanium. The mineral in which titanium is present in abundance in the form of TiO_2 is rutile. Ilmenite is a mixture of the two oxides TiO_2 and FeO. When producing TiO_2 using Ilmenite, first FeO in it is removed. This increases its TiO_2 percentage. Removal of FeO from ilmenite is called sulphate process.

High purity TiO_2 is produced from ilmenite in which the percentage of TiO_2 is brought above 70% by removing FeO. High purity TiO_2 can be produced starting from ilmenite purified until its TiO_2 percentage is above 70% or by using rutile. The production process is referred to as the chloride process.

Chemistry of the production of titanium dioxide from rutile (Chloride process)

The aim of this process is to remove various inorganic impurities in rutile and produce high purity TiO_2. It comprises two steps.

1. Chlorination
2. Oxidation

Chlorination

Drying to remove moisture in rutile and coke is indispensable. For this they are dried well by heating to 200-300 ^0C.

For chlorination the mixture of rutile and coke is heated to about 950 ^0C and stream of chlorine is passed over it. In the presence of coke, titanium dioxide reacts with chlorine giving titanium tetrachloride gas as the product. This reaction is exothermic. The main reason for this is the oxidation of coke giving carbon dioxide. The relevant reactions are,

$$TiO_2(s) + C(s) \longrightarrow Ti(s) + CO_2(g)$$

$$Ti(s) + 2Cl_2(g) \longrightarrow TiCl_4(g)$$

The overall reaction is

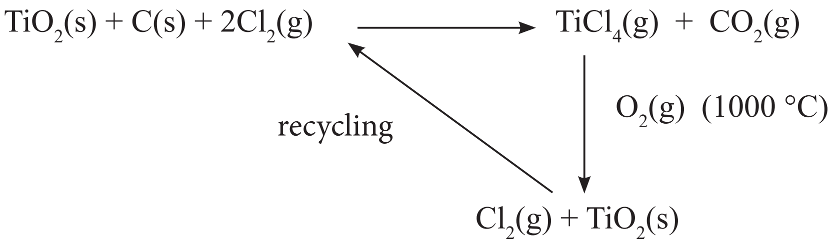
$$TiO_2(s) + C(s) + 2Cl_2(g) \xrightarrow{950\ ^0C} TiCl_4(g) + CO_2(g)$$

The boiling point of $TiCl_4$ is 134 ^0C. Therefore the exit gas mixture coming out from the reaction chamber mainly contained $TiCl_4$ and CO_2. In addition dust particles and as a result of side reactions hydrogen chloride and carbon monoxide gases may also occur. Here inorganic impurities present in TiO_2 are removed. After the removal of dust particles liquid $TiCl_4$ is separated by cooling the gaseous mixture. After further purification of separated liquid $TiCl_4$, it is oxidized.

Oxidation

Here, $TiCl_4$ produced in the first step is reacted with oxygen and TiO_2 is regenerated. This process is important for producing pure TiO_2 free of inorganic impurities present in rutile. Resulting chlorine gas is used again for chlorination. Therefore chlorine gas is re-cycled.

$$TiCl_4(g) + O_2(g) \xrightarrow{1000\ ^{0}C} TiO_2(s) + 2Cl_2(g)$$



During this process coke is oxidized and carbon dioxide is added to the atmosphere. Hence chloride process contributes to global warming. In 2006, the total amount of CO_2 released to the atmosphere by this industry was 3.6 million metric tons. Half of this was due to the burning of fuel to raise the temperature and the other half was produced by the production process.

Uses of titanium dioxide

1. TiO_2 is white in colour. Therefore it is used as a pigment to obtain bright white colour in paint, plastic goods and paper. The high refractive index if TiO_2 is also a reason for using it as a pigment.
2. TiO_2 is chemically inert. Therefore it is used as a pigment to give white colour to medicine and toothpaste.
3. TiO_2 is also used to produce substances applied to prevent sunburns in the skin due to UV radiations in solar rays. TiO_2 prevents the reach of UV rays to the skin.
4. It is used to make some solar cells.

1.10 Extraction of iron

We have an ancient history of production of iron. Archeological studies have revealed that the ancestors of this country were aware of iron extraction thousands of years ago. They have extracted iron using natural wind power and wood charcoal. Gill Juleff, an archeologist of the university of Exeter, England has confirmed the technology of iron extraction prevailed in this country by recreating an old iron extraction furnace at the wind gap of Balangoda. Her findings have been published in the periodical 'nature' under the title 'An ancient wind-power iron smelting technology'.

Raw materials essential for iron extraction

- Iron ore
- Limestone
- Coke (coal)
- Air

The furnace used to extract iron using the above raw materials is called the 'blast furnace'. Inside of the blast furnace is lined by a special type of bricks withstanding higher temperatures. The mixture of iron ore, limestone and coke is fed into the blast furnace from the inlet at the top while air is introduced near the bottom. Molten iron is tapped out from the bottom end of the furnace. The slag is removed a little above the level at which molten iron is tapped off. In the blast furnace a mass flow occurs from the top to the bottom under gravity. Simultaneously compressed air passes from the bottom to the top. Since substances flow in opposite directions (from the bottom to the top and from the top to the bottom), possibility for the reactions to occur between the solid phase and the gas phase increases. This also creates a temperature gradient.

Some facts to which attention should be drawn in the process of iron production are given below.

1. Ratio among the components of the mixture of ore, coke and limestone
2. Particle size
3. Rate at which the mixture is added to the blast furnace from the top
4. Rate of flow of the air current and its pressure

Here, the role of coke is as follows.

1. Acts as a fuel

$$C(s) + O_2(g) \longrightarrow CO_2(g) + \text{heat} \qquad \Delta H = -393.5 \text{ kJ mol}^{-1}$$

2. Acts as a direct reducing agent at high temperatures.

$$FeO(s) + C(s) \longrightarrow Fe(l) + CO(g)$$

3. Generates carbon monoxide which is the main reductant.

$$CO_2(g) + C(s) \longrightarrow 2CO(g) \quad \Delta H = 172.5\ kJ\ mol^{-1}$$

Deposition of silicates and aluminates in the ore, should be prevented as impurities in iron. Calcium oxide obtained from the thermal decomposing of calcium carbonate is useful in this regard.

$$CaCO_3(s) \xrightarrow{898\ ^\circ C} CaO(s) + CO_2(g)$$

$$CaO(s) + SiO_2(s) \longrightarrow CaSiO_3(l)$$

$$CaO(s) + Al_2O_3(s) \longrightarrow Ca(AlO_2)_2(l)$$

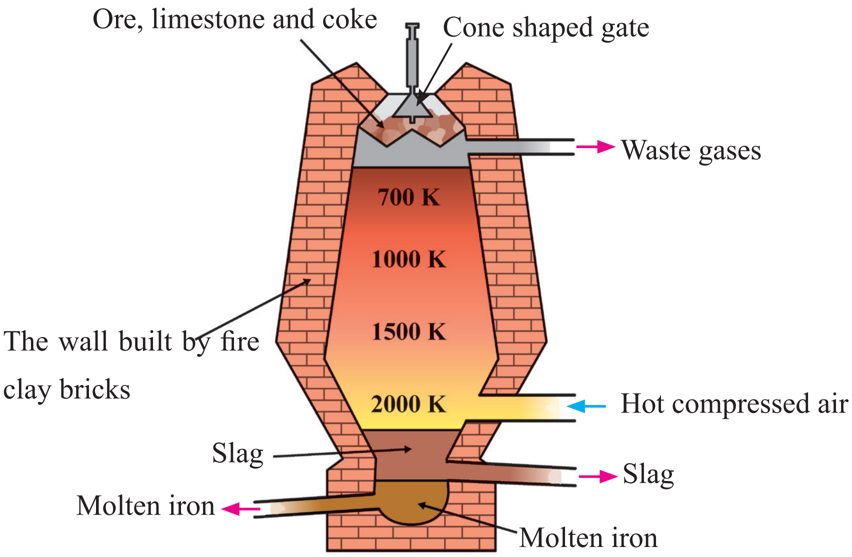


Figure 1.11 The blast furnace

Calcium silicate ($CaSiO_3$) and calcium aluminate ($Ca(AlO_2)_2$) formed are called the slag. The density of the slag is lower than that of molten iron. Therefore liquid slag layer floats on molten iron. As the slag covers the surface of molten iron, the chances for molten iron to react with oxygen are less.

From the lower part of the blast furnace hot, compressed air is injected into the furnace. Coke burns and with admission of air burning reaction is speeded up. The rate of the burning reaction is decided by the temperature of hot air, pressure and the size of coke particles.

As the combustion reaction is fast and the combustion of coke is highly exothermic large amount of heat is evolved in a short period of time. Therefore the temperature of the basal part of the furnace rises at once to about 1700 ^{0}C. The rate of the combustion reaction and the amount of coke burnt are important factors in maintaining the temperature of the basal part stable. It is important to mainain the rate of air flowing upward and the rate of mixture containing coke flowing down to maintain at optimum.

Hot carbon dioxide gas formed during combustion passes upwards through the ore. At high temperatures carbon dioxide reacts reversibly with coke forming carbon monoxide.

$$CO_2(g) + C(s) \rightleftharpoons 2CO(g)$$

$$\xrightarrow{\qquad\qquad\qquad\qquad\qquad\qquad}$$

Number of gaseous molecules increases. Therefore entropy increases.

ΔS is positive for this reaction (176.5 J). When the temperature increases, magnitude of the numerical value of $T\Delta S$ increases. At high temperatures and in the presence of coke (C), there is a tendency for reduction of carbon dioxide to carbon monoxide. Under such conditions CO gas is relatively stable thermodynamically. When the temperature is around 1000 ^{0}C nearly 100% of CO_2 is converted to CO. Figure 1.12 given below shows this variation.

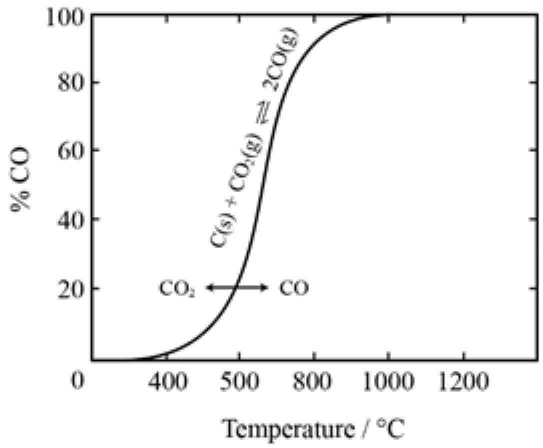


Figure 1.12 Variation of the amount of carbon monoxide against temperature

$$O_2(g) + C(s) \longrightarrow CO_2(g) + \text{heat} \text{ ---------- } (1)$$

Number of gaseous molecules does not change

$$\xrightarrow{\qquad\qquad\qquad\qquad\qquad\qquad}$$

No considerable change in entropy. Exothermic

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

Number of gaseous molecules increases

$$\xrightarrow{\hspace{6cm}}$$

Entropy increases. Exothermic

$$\Delta G = \Delta H - T\Delta S$$

Because both reactions are exothermic ΔH is negative. When the temperature increases reaction (2) has a conspicuous increase in the value of TΔS. With temperature a marked increase in the negative nature of ΔG is expected for reaction (2). When the temperature drops thermodynamic stability of CO decreases; thermodynamic stability of CO_2 increases.

Since the temperature of the bottom area is as high as 1700 ^{0}C, CO gas is formed liberating heat when CO_2 the gas interacts with red hot coke in the mixture.

When CO gas formed in the hot lower region of the furnace moves up through the mixture containing the ore, the stability of CO decreases because the temperature decreases. Hence the tendency of CO becoming CO_2 increases. As oxygen gas is not available in the region above at where coke is burnt in the furnace, CO oxidized to CO_2 by reducing Fe_2O_3. As a result of this Fe_2O_3 is gradually reduced. Going upward the furnace along with the decreasing temperature, so reduction of Fe_2O_3 in the ore continues. At temperatures below 1000 ^{0}C, reduction of Fe_2O_3 can be indicated stepwise as follows.

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

Fe_3O_4 (ferrosoferric oxide) is a mixture of FeO and Fe_2O_3 .About 33% of the iron in +3 oxidation state in Fe_2O_3 has reduced to the +2 state.

$$2Fe_3O_4(s) + 2CO(g) \longrightarrow 6FeO(s) + 2CO_2(g)$$

$$\text{or } [Fe_3O_4(s) + CO(g) \longrightarrow 3FeO(s) + CO_2(g)]$$

$$FeO(s) + CO(g) \longrightarrow Fe(l) + CO_2(g)$$

Fe_2O_3 partially reduces to Fe_3O_4 and this mixture goes down the furnance. There, it further reacts with CO gas and its Fe atoms of +3 state reduce to +2 oxidation state. FeO, which is formed as its result, reacts further with CO gas and reduces up to free iron (Fe).

Further, decomposition of $CaCO_3$ occurs at a temperature below 1000 ^{0}C (i.e. 898 ^{0}C). Carbon dioxide gas generated by it also has the ability to react with coke to produce CO.

Even this produced CO, when going upward the furnace, by reacting with Fe_2O_3 in the ore, possible to become CO_2.

Above 1000 ^{0}C, that is somewhat in the lower part of the blast furnace following reactions occur. In this region coke directly reduces FeO.

$$2FeO(g) + C(s) \longrightarrow 2Fe(s) + CO_2(g)$$

$$CO_2(g) + C(s) \longrightarrow 2CO(g)$$

$$2CO(g) + O_2(g) \longrightarrow 2CO_2(g) \qquad \Delta H= -566 \text{ kJ}$$

In the blast furnace a part of the total amount of coke participate for the combustion reaction. Another part reacts with CO_2 to produce CO. Another part reduces FeO. Air acting as an oxidant and generates heat and CO_2 by the combustion reaction. If excess air is supplied thermodynamically it is likely that in addition to the reaction with Fe_2O_3, carbon monoxide would react with oxygen to give carbon dioxide. This is a disadvantage. Therefore in the extraction of iron, it is very important to maintain the volumetric flow rate of air and the flow rate of the solid mixture containing the ore at an optimum level. In the lower part of the furnace the amount of O_2 decreases at once but, producing a proportionate amount of CO_2. For this reason there is a sudden increase in the concentration of CO_2 and production of intense heat. This CO_2 in the high temperature zone tends to move up through the solid mixture falling down. Therefore the reaction of CO_2 with the coke in the solid mixture occurs in the lower part of the furnace where the temperature is high. Because of this when the CO_2 concentration gradually decreases, CO concentration increases. Even CO generated in the lower region passes upwards through the solid mixture. Ascending the furnace the temperature decreases, so the thermodynamic stability of CO gas decreases while the tendency for the conversion to CO_2 increases. As O_2 is absent CO gas gets oxidized to CO_2 gas abstracting oxygen in Fe_2O_3. Therefore going upward the furnace, CO concentration decreases and CO_2 concentration increases again.

Because of the use of coke CO_2 is released from the furnace and this causes global warming. Thus, seeking renewable alternatives for coke is environmentally important. Avoiding unnecessary use of iron is also important.

1.11 Polymers

Polymers are formed by the chemical bonding of a very large number of relatively small molecules referred to as monomers.

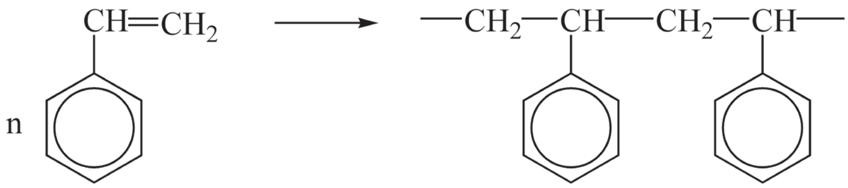
Examples :

$$nCH_2{=}CH_2 \longrightarrow -CH_2-CH_2-CH_2-CH_2-$$

Ethylene Polyethylene (PE)

$$nCH_2{=}CHCl \longrightarrow -CH_2-\underset{}{\overset{Cl}{\overset{|}{C}H}}-CH_2-\overset{Cl}{\overset{|}{C}H}-$$

Vynil chloride Polyvynil chloride (PVC)



Styrene Polystyrene (PS)

$$nCF_2{=}CF_2 \longrightarrow -CF_2-CF_2-CF_2-CF_2-$$

Tetrafluoro ethylene Polytetrafluoro ethylene (PTFE)

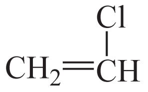
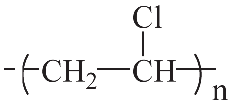
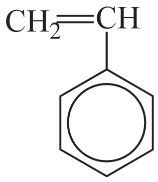
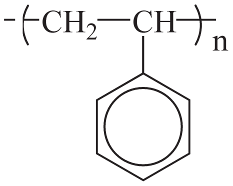
Due to the joining of a large number of monomers like this, the carbon skeleton of the monomer is repeatedly placed in the polymer. Therefore it is called the repeating unit.

$$CH_2{=}CH_2 \longrightarrow \left(CH_2-CH_2 \right)_n$$

Ethylene Polyethylene (Polythene)

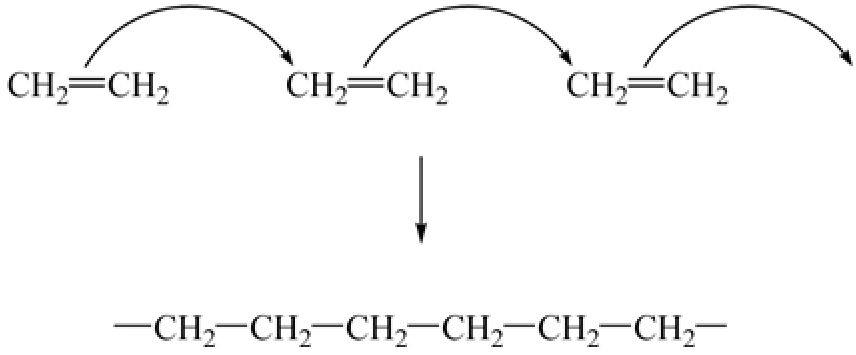
The repeating unit of polythene (polyethylene or polythene) is $-CH_2$- CH_2-. As there is a large number of repeating units in a polymer molecule. The polymer is symbolized by writing ‘n’. Some examples are given in Table 1.2.

Table 1.2 Repeating units of polymers formed by some monomers

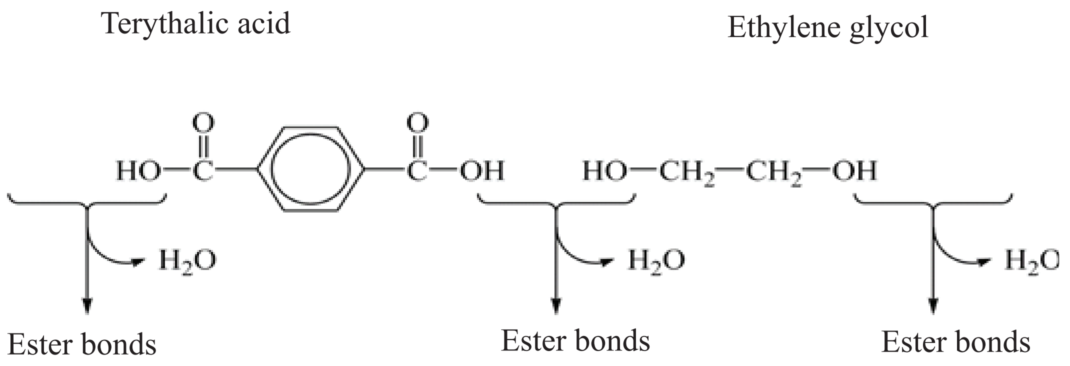
Monomer	Polymer related to the repeating unit
$CH_2{=}CH_2$	$-\!\left(CH_2-CH_2 \right)_n$
 $CH_2{=}\underset{}{\overset{Cl}{CH}}$	 $-\!\left(CH_2-\overset{Cl}{CH} \right)_n$
	
$CF_2{=}CF_2$	$-\!\left(CF_2-CF_2 \right)_n$

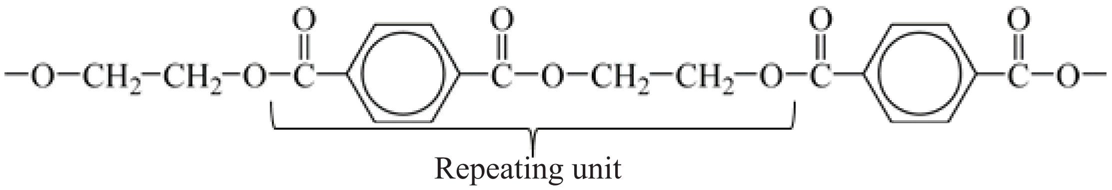
Production of polymers from monomers is called polymerization. According to the reaction occurring in polymerization polymers can be classified into two classes, addition polymers and condensation polymers.

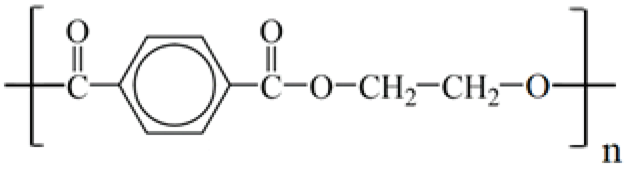
If a polymer is formed by the bonding of monomers by an addition reaction, such a polymer is known as an addition polymer. The unsaturated bonds in the monomer are important in this regard. The molar mass of the monomer is equal to the molar mass of the repeating unit of the polymer. However the three dimensional structure and the hybridization state of the carbon atom of the monomer and the repeating unit change.



During the formation of condensation polymers a condensation reaction occurs. Therefore, in addition to the polymer, small molecules of low mass are produced. For example when an ester bond is formed by the reaction between a –COOH group and a –OH group. H_2O molecule is formed. Hence in the production of polyester a condensation reaction takes place. A number of water molecules equal to the number of ester bonds formed are released. If the volume of water produced to be measured correctly, the number of ester bonds formed could be calculated using the density and molar mass of water.

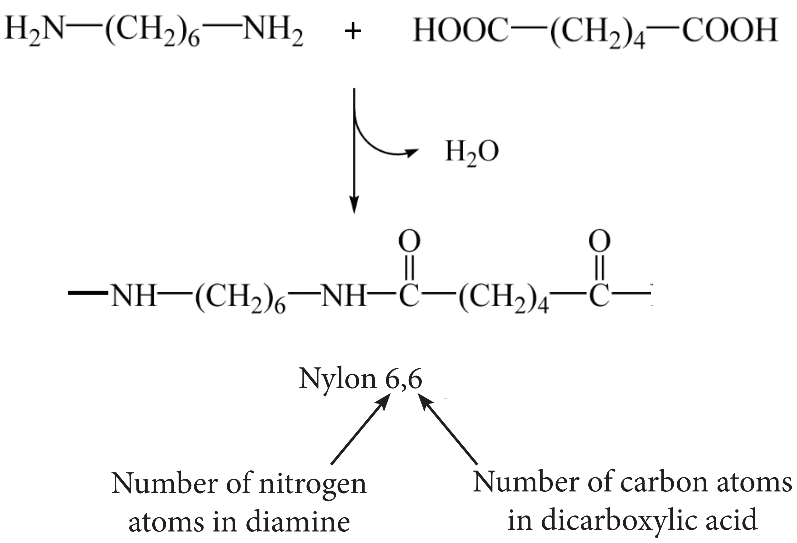






In terms of the repeating unit the structure of polyethylene terephthalate (PET) can be shown as above.

Polyamides are obtained by the polymerization reaction between a dicarboxylic acid and diamine. Nylon is such a polyamide. Production of nylon is also a condensation reaction.



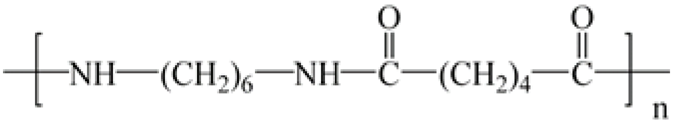
$$H_2N{-}(CH_2)_6{-}NH_2 + HOOC{-}(CH_2)_4{-}COOH \xrightarrow{-H_2O} {-}NH{-}(CH_2)_6{-}NH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}(CH_2)_4{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}$$

Nylon 6,6

Number of nitrogen atoms in diamine

Number of carbon atoms in dicarboxylic acid

The structure of nylon 6, 6 can be indicated as follows using the repeating unit. The first number here represents the number of carbon atoms of the diamine while the second number presents the number of carbon atoms in the dicaboxylic acid.



$$\left[{-}NH{-}(CH_2)_6{-}NH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}(CH_2)_4{-}\overset{\overset{\displaystyle O}{\|}}{C}{-} \right]_n$$

From the examples used thus to describe the structure of polymers, it is clear that the polymer molecule is created as a single chain. For this reason such polymers are referred to as 'linear polymers'.

Sometimes the polymers are formed as three dimensional networks. The reason for this is that the monomers have more than two reactive sites. If we consider phenol as an example, the number of sites in the benzene nucleus at which substitution can take place is three. A three dimensional network polymer is formed by the reaction between phenol and formaldehyde. The polymer is known as bakelite and the reaction is a condensation reaction.

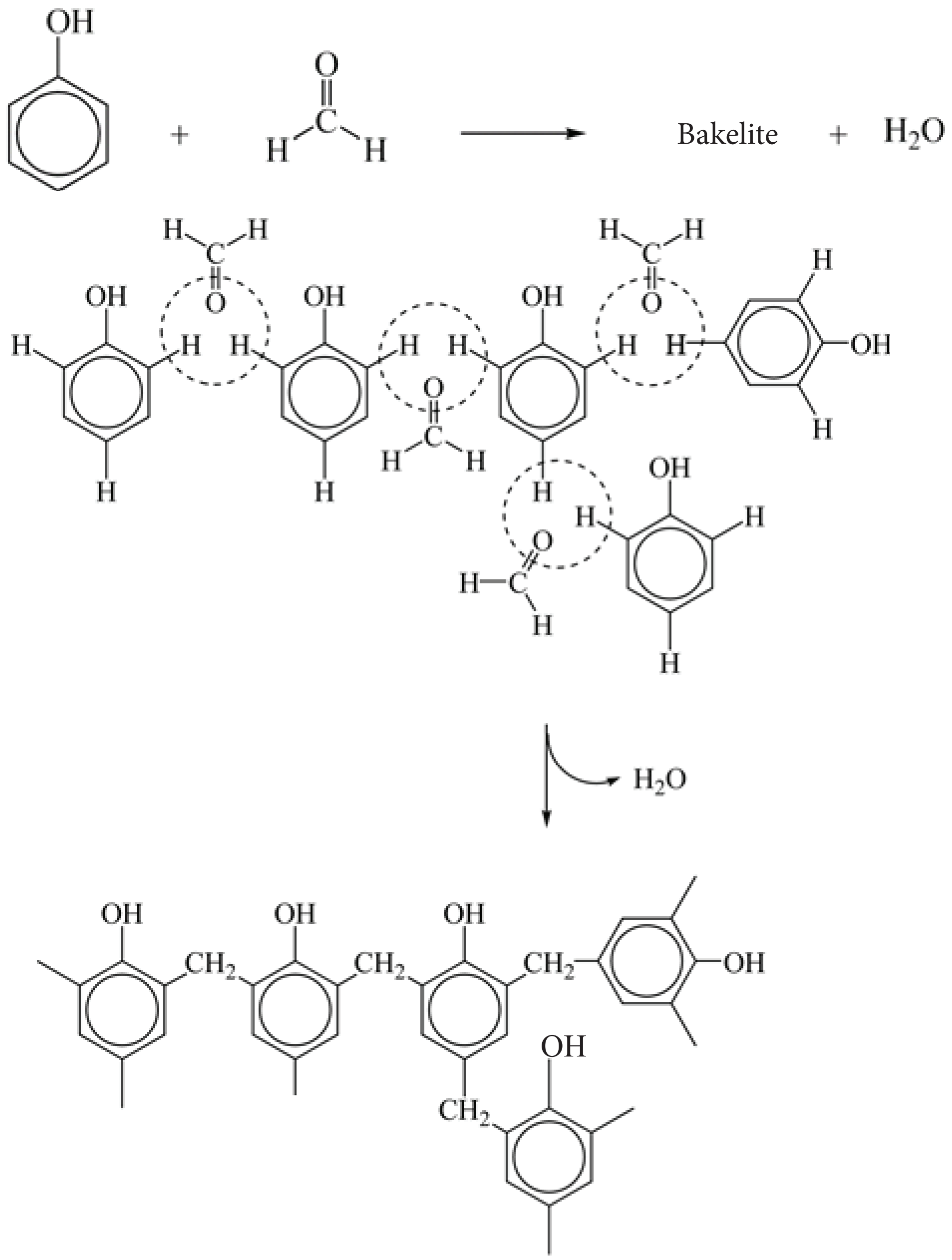
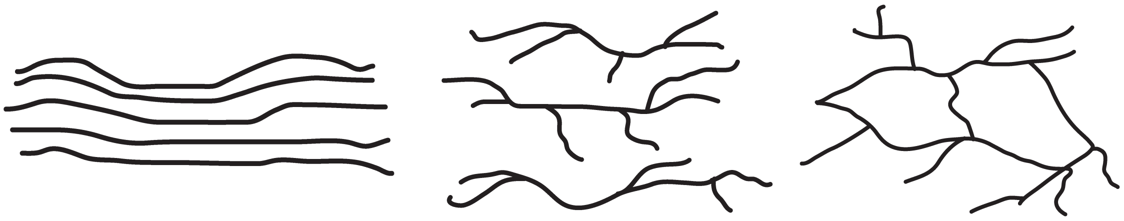


Figure 1.13 Formation of bakelite by the reaction between phenol and formaldehyde

In such instances a specific repeating unit cannot be identified.

According to the nature of the structure polymers can be classified as linear, branched and network. PS, PVC, PTFE and PET polymer molecules have a linear structure.



Linear polymer Branched polymer Network polymer

Figure 1.14 Structure of the polymers

Linear and branched polymers are packed in various ways as separate molecules. Sometimes in some regions the molecules are closely packed and orderly arranged. Such regions are called crystalline areas. In some other regions the molecules may be twisted and entwined with one another. Such regions are called amorphous regions. Some polymeric substances are totally amorphous. But some polymers have a certain amount of crystalline regions. Such substances are known as semicrystalline polymers. Polythene is an example for semicrystalline polymers. Light does not penetrate well through the membranes of semi crystalline polymers. Crystalline regions in them scatter light and reduce transparency. Light does not scatter through semicrystalline layers. Therefore they are transparent.

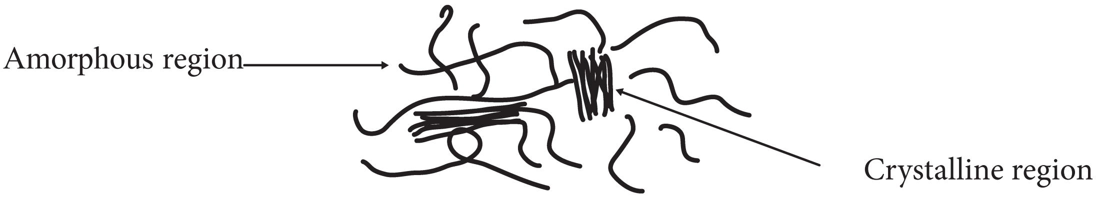


Figure 1.15 How linear and branched polymers are packed

Polyethene can be synthesized so that a branched structure is obtained. Linear polythene molecules pack closely with each other and have more high density areas. Such polyethelene are named High Density Polythene (HDPE).When branched the molecules do not pack that closely. Their density is low and have more amorphous regions. This type of polythene is referred to as Low Density Polythene (LDPE).

1.11.1 Rubber and plastic

Rubber is considered as the polymeric material which possess very high elastic properties reversibly. The elastic properties of rubber can be controlled. Starting from monomers, the polymer called rubber can be synthesized. Those are known as artificial rubber (e.g.: nitryl rubber). Highly elastic polymer can be obtained from the latex of the rubber tree too. Those are known as natural rubber (NR).

Polymers with limited elastic properties can be considered as plastics. For example; polymeric substances such as PVC, PET, PP and PE are considered as plastics. When stretched beyond the elastic limit its shape changes irreversibly. Plastic can be classified further as thermoset and thermoplastics. Thermoplastics are composed of linear polymer molecules or branched polymer molecules. Thermoset plastic have a molecular structure arranged as a network. Thermoplastic can be softened by heating. Therefore they can easily be moulded to the required shape by heating. The shape can be made permanent by cooling. PVC, PE, and PS are examples for this. Thermoset polymers cannot be softened like that. Phenol-formaldehyde (bakelite) is an example for this.

1.11.2 Natural rubber

Natural rubber (NR) is the substance with high elastic properties obtained by coagulating latex of the rubber tree (*Hevea braziliensis*). Rubber latex is collected by the systematic removal of the bark of the rubber tree. Rubber latex contains 60-65% water and 30-35% rubber. In rubber latex rubber occurs as a colloidal solution in which very small rubber particles are dispersed. Simple sugars and salts are also dissolved in this colloidal solution.

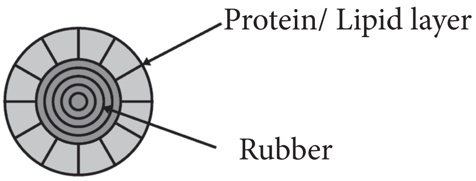


Figure 1.16 A rubber particle

There is a lipid and protein layer around a rubber particle. Inner to it lie rubber molecules. Since $-COO^-$ groups associate the outer layers of a rubber partical its outer surface is negatively charged. As electrostatic repulsion forces operate among these negatively charged particles, they are spreaded throughout the solution.

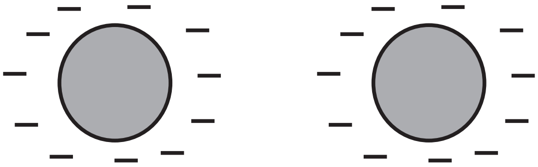


Figure 1.17 Location of negative charges on the outer surface of rubber particles

Because of the repulsive forces among the negatively charged surfaces, the particles do not combine together. In addition of acids H^+ ions neutralize the $–COO^-$ groups and the surface of the particles become electrically neutral. Then the particles combine together and settle down as a mass. This is known as ‘coagulation of latex’.

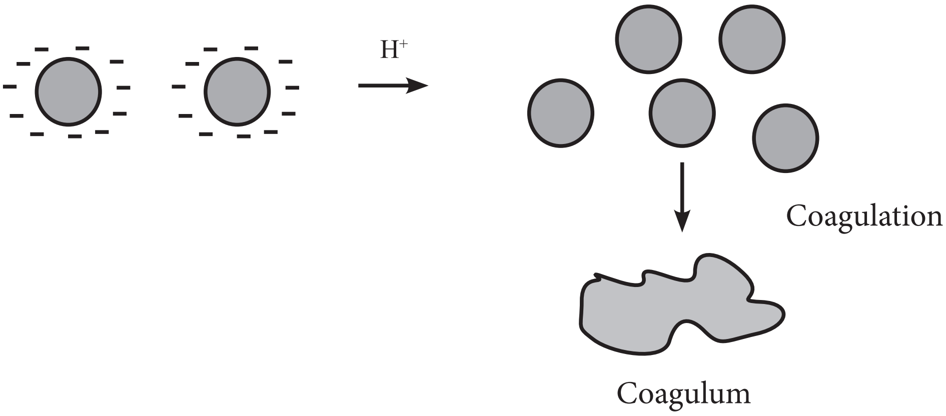
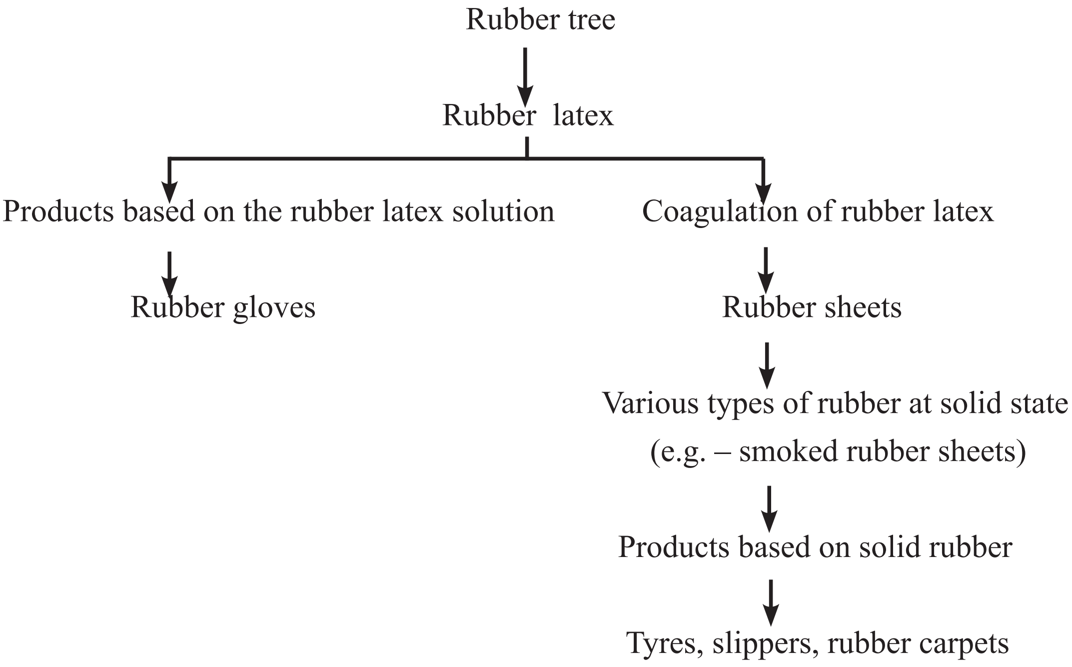
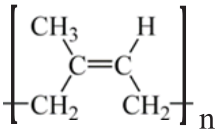


Figure 1.18 Coagulation of latex

Since the rubber latex contains salts, sugar, amino acids etc. It is a suitable medium for microbial action. Because of the acids released by the action of micro-organisms latex coagulates. Therefore, after the collection of rubber latex its coagulation can be prevented by stopping the microbial activity till it is subjected to the production process. The coagulation can be prevented by basifying the latex by adding an ammonia solution. Ammonia prevents the medium becomes acidic and stabilizes the negative charges around the rubber particles. Under these basic conditions the microbial action is suppressed.

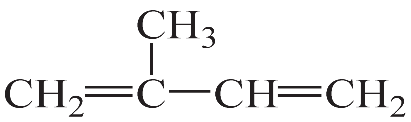


In the natural rubber molecule there are two $-CH_2$ groups and one $-CH_3$ groups joined to the doubly bonded carbon atoms in a repeating unit. It is named as cis-1,4 polyisoprene. Gutta percha has a trans structure. This natural polymer is known as trans-1,4-polyisoprene. It does not show elastic properties. There is a maximum distance between the adjacent two $-CH_2$ groups in the trans structure.



cis -1,4-polyisoprene

Polyisoprene can be made synthetically by polymerizing the monomer, isoprene. It belongs to the category of synthetic rubber. They are termed Isoprene Rubber (IR).



$$CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}CH{=}CH_2$$

Isoprene

In synthetic rubber the monomer is isoprene but we can't say that it is the monomer of natural rubber. In the rubber tree rubber molecules are produced by very complex biochemical reactions.

1.11.3 Vulcanizing of natural rubber

Existence of cis-polyisoprene chains is the reason for the elasticity of natural rubber. But to change the elastic property of rubber as required industrially and strengthen it, it is heated with 1-3% sulphur. This is called vulcanization of rubber. During vulcanization cross links are formed among the poly isoprene chains by sulphur atoms which decrease its elastic property but increase the resilience or the ability to regain its original dimensions. Ebonite is obtained when rubber is heated with 25-35% sulphur by weight. Ebonite doesn't show elastic properties. This is due to the fact that activity associated with the double bonds in rubber molecules form large number of crosslinks with sulphur atoms. Rubber vulcanized with an optimal amount of sulphur is not sticky and possess an optimum elasticity and high mechanical qualities. Figure 1.19 illustrates how rubber molecules are crosslinked by sulphur atoms.

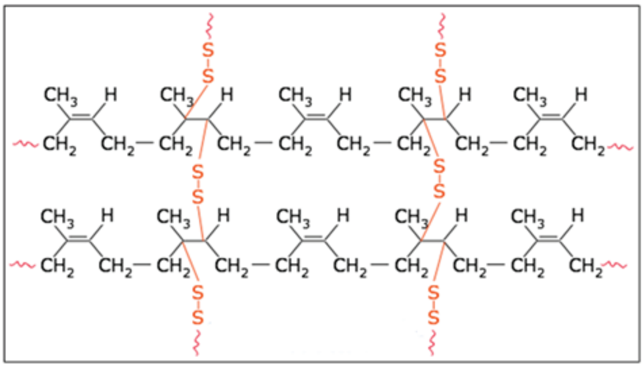


Figure 1.19 How sulphur crosslinks bind rubber molocules

1.11.4 Additives used for the polymer related products

The substances used to improve the qualities of the end product and reduce its production cost in the production of polymers are referred to as additives. Specially by using fillers, the volume required for the end product is obtained. In the production of tyres carbon black is used as the filler. Carbon back improves its physical and mechanical qualities. For example it reduces wear and increases strength. But release of these carbon black particles to the enviornment cause environmental problems. To make vulcanizing efficient various organic catalysts and catalyst promoters such as zinc oxide (ZnO) are used. Most of these organic catalysts are toxic. Various fillers are used for plastics as well. Calcium carbonate is one of them. In the production of plastics, compounds called 'plasticizers' are added to increase their flexibility. For example, PVC pipes used to supply water are hard and rigid but the outer covering of the domestic electric cables made of same material is flexible. This is because PVC of the latter is mixed with plasticizers. Therefore it gets flexibility. In addition to these, additives are added to reduce inflammability and prevent the damage caused by ultraviolet rays. Additives are added in small amounts. Most of the additives added to plastics are phthalates. It has been discovered that many additives distrupt the action of the endocrine systems. Hence much attention should be paid when plastics are used as packaging materials in food storage. Production of plastic goods using PVC is a process where additives are simply used. The reason for this is that in PVC, chlorine atoms are bonded to secondary carbon atoms. Various additives are used to prevent the breaking of C-Cl bonds easily. Because of the temperature used in the production process or when those goods are exposed to ultraviolet rays HCl (hydrogen chloride) gets removed from PVC molecules.

1.12 Chemical products related to plant sources

1.12.1 production of vinegar

Acetic acid is the active ingredients in vinegar. When toddy is subject to continued microbial activity it is oxidized to acetic acid. During this, the amount of acetic acid increases to about 48%. The vinegar so prepared is called natural vinegar. Artificial vinegar is produced by diluting appropriately, the acetic acid obtained by the oxidation of ethanol produced from raw materials turned out by petroleum industry. Natural vinegar contains salts, simple sugars, esters and alcohols in minute quantities.

1.12.2 Production of ethanol

Ethanol is used as a solvent for perfumes and scents. It is also used a medium for chemical reactions. The use of ethanol as an environmental-friendly renewable fuel is on increase. Ethanol produced from biomasses by microbial activity is referred to as bioethanol.

Industrially ethanol is produced by hydration of ethylene or fermentation of sugar or starch in the presence of yeast. Alcohol contained in alcoholic beverages is generated by various plant sources.

E.g. Grapes - vine
Barley - Beer

Various cereals, fruit juices, molasses which is a by-product of the sugar industry etc. are used to produce alcohol industrially. As yeast cannot live in a concentrated solution of ethanol, the percentage of ethanol in fermented solution is around 12%.

Products with higher alcohol content are produced by distilling the aqueous solution obtained by fermentation.

E.g. Brandy (about 40%) - by distilling vine
Arrack (about 40%) - by distilling coconut toddy

The maximum concentration of ethanol obtainable by the fractional distillation of aqueous ethanol is 96.5%. This is called rectified spirit.

As regards the current use of narcotics and drugs in the world medical specialists state that arrack is one of the most dangerous alcoholic beverage. Let's see what is arrack available in the market. Its main constitutent is ethanol. In the world today there are many methods to produce ethnol. In Sri Lanka too ethanol is produced by some of them. Legally ethanol is produced from fermented coconut toddy and molasses which is a by-product in the production of sugar form sugar cane.

Coconut toddy is produced by fermentation of sweet toddy, a sugar solution obtained by tapping the tender inflorescence of the coconut tree. The spores of yeast floating in air get deposited in the sweet toddy. During fermentation these grow in the solution using sugar as a substrate. The enzymes produced by the yeast cells gradually convert sugar into ethanol and carbon dioxide.

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{sucrase}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

(monosacaride sugars)

$$C_6H_{12}O_6 \xrightarrow{\text{yeast}} \underset{\text{ethanol}}{2C_2H_5OH} + 2CO_2$$

Within a period of about two days sweet toddy turns into fermented toddy and during this process the sugar concentration gradually decreases.

If fermented toddy is left to stay further, bacteria oxidize alcohol in the toddy converting it to acetic acid. Therefore the alcohol percentage decreases and the acid percentage increases.

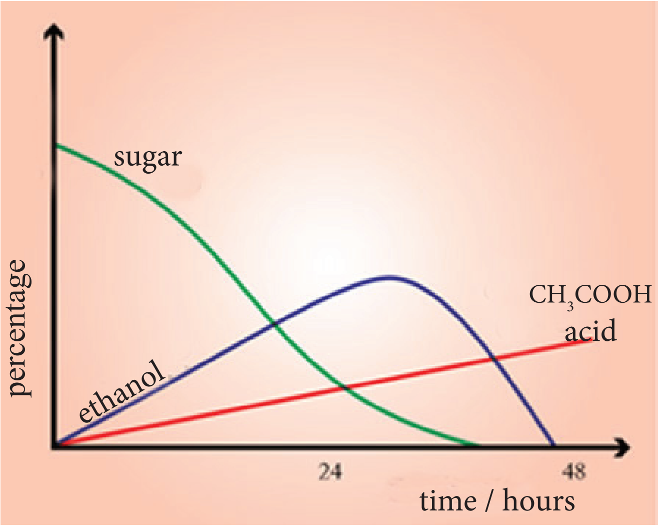


Figure 1.20 Variation of the composition of sweet toddy during fermentation

Fractional distillation

The distillation technique used to separate components which are miscible and have different boiling points from a mixture of them is called fractional distillation.

Table 1.3 Boiling point of some components

Compound	Melting point/ °C
methanol	64.6
ethanol	785
propan -1-ol	971
propan -2-ol	824
butanal	747
butanone	795
ethyl ethanoate	772

Except from coconut toddy ethanol is produced from other plant materials also containing starch Beet, potato, fruits, rice are examples. During the fermentation of these plant sources compounds like esters, aldehydes and ketones are also produced. These too add on to the aqueous mixture. If their boiling points fall within the boiling range of ethanol, they also vaporize with ethanol and pass into the distillate containing ethanol.

In this process the first distillate mainly contains methanol. This is toxic and is used as vine spirit. The second fraction of the distillation mainly contains ethanol. The third fraction obtained at higher temperatures contains higher alcohols and it is called ‘fusel oil’.

1.12.3 Essential oils

Water - insoluble volatile liquids extracted from plant materials are known as essential oils. Various essential oils have a characteristic smell of their own. They add fragrance to food and increases appetite. Essential oils are also used to make perfumes. In the commercial field of the world today, there is a huge demand for perfumes and flavours. History says that even the kings in the past used fragrances.

Essential oils are obtained from plants such as cinnamon, clove, citronella, cardamom, wintergreen. In plants there are special body parts which contain essential oils.

Table 1.4 Examples for plant parts containing essential oils.

Part that contain essential oil	Example
Root	Cinnamon, Khus-Khus (Savandara)
Stem	Sandle wood
Bark	Cinnamon
Leaf	Citroriella, lemon grass, eucaliptus, cinnamon
Bud	Clove
Flower	Jasmine, rose
Fruit	Orange, lemon
Seed	Cardomom, nutmeg

Methods of extracting essential oils

1. Steam distillation
2. Solvent extraction
3. Pressing

Stem distillation

Many essential oils are likely to decompose or polymerize under the influence of heat. Therefore heating them to high temperatures is not suitable. So, they are subjected to steam distillation and extracted under low temperatures. This phenomenon can be explained by the law of partial pressures. When the systems containing water and plant parts with essential oils are heated, those tissues are damaged and essential oils liberate. The gaseous phase of the system contains water vapour and volatile compounds. At the temperature at which the system boils the sum of the pressures exerted by water vapour and the essential oil vapour is equal to the outer atmospheric pressure. Hence at that temperature if,

Partial pressure of water vapour (saturated vapour pressure) = P_{H2O}
Partial pressure of essential oil (saturated vapour pressure) = P_A
Total pressure of the immiscible system = P
According to Dalton law of partial pressures $P = P_{H2O} + P_A$

When the total pressure (P) becomes equal to the atmospheric pressure, the mixture boils. The boiling point of this mixture is lower than the boiling point of pure water and the boiling point of the essential oil. Therefore essential oil can be distilled at a temperature below 100 ^{0}C and the boiling point of the essential oil.

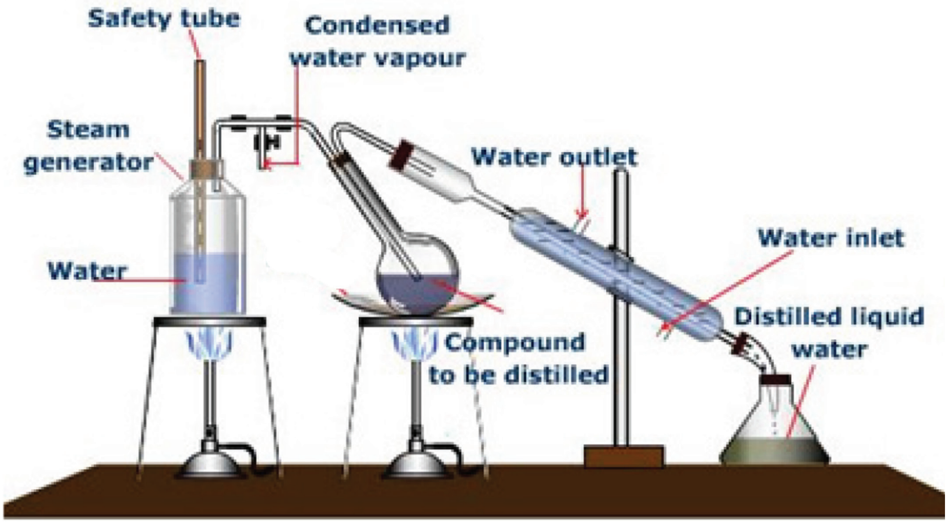


Figure 1.21 Extraction of essential oil in the laboratory by steam distillation

Steam produced by the steam generator is passed into the vessel which has plant material containing the essential oil. As steam is sent separately or from a steam generator its volumetric flow can be controlled. It is an advantage. When steam enters into the vessel containing plant parts, as plant cells destroy due to the heat of the steam, volatile compounds release. While vapour is condensed, certain amount of water vapour is accumulated in it. Water vapour and essential oil vapour exsist above the liquid water by the continuous flow of water vapour. Then the essential oil in the plant material comes into the vapour phase along with water. However, as water vapour flows continuously, the vapour coming out of the vessel contains essential oil vapour as well as water vapour. When the vapour is passed through a condenser and cooled, the distillate is obtained as two layers of water and essential oil. It can be separated easily.

Example: Main components of cinnamon oil which is obtained by the steam distillation of various parts of the cinnamon tree.

Leaf – eugenol

Bark – cinnamaldehyde

Root – camphor

Main constitution of citronella oil – geraniol

Solvent extraction

The principle of this is the dissolving of the essential oil in a solvent in which it is more soluble. The solubility of essential oils in water is very low. Nevertheless they are very soluble in organic solvents (e.g. petroleum ether, chloroform, toluene, ethanol). Plant materials are shaken with such a solvent majority of the essential oils pass into the solvent. The solvent is removed by vaporizations or by some other means thereby separating the essential oil.

Pressing

By applying a suitable pressure on plant materials, the volatile oils in them could be obtained. If pressing is done with another adsorbent, the essential oil is adsorbed into it. For example when a plant material is pressed between two glass slides coated with wax, essential oil in it is adsorbed into wax. Essential oil can then be extracted form wax using another solvent (ether) . Pressing method is rarely used because;

1. The yield is poor
2. Oil gets mixed up with other organic substances

In the extraction of oil from cardamom seeds, pressing method is also used.

Extraction of cinnamon oil is mainly done in areas like Ambalangoda, Hikkaduwa and Baddegama. First Cinnamon leaves are dried in air for 2-3 days in a shady place. Extraction of oil is easier from dried leaves than from fresh leaves. During distillation, essential oil can easily be removed when cuticles of the leaves are broken. It has been found that leaves of the middle age are most suitable than the tender or more mature leaves for oil extraction.

Earlier copper boilers were used for distillation but copper reacts with eugenol in the oil giving a dark colour to the oil. Therefore at present stainless steel or aluminum is used instead of copper.

Generally citronella is grown in Hamabantota district. There are 3 main varieties of citronella.

1. Heen pengiri (*Cymbopogon nadus*)
2. Maha pengiri (*Cumbopogon winterianus*)
3. Lenabatu pengiri

Of these the first two types are endemic to Sri Lanka. *Cymbopogon winterianus* has been introduced by Philippine. The value of citronella oil depends on the occurrence of the compound geraniol. Gereniol is an unsaturated, aliphatic alcohol. *Cymbopogon winterianus* has a greater demand because it’s gereniol content is high.

1.12.4 Biodiesel

With the production of engines which can use petroleum fuels efficiently, a rapid development in the field of transport occurred. In modern civilization, the main source of power is petroleum fuel. Easy usage and ability to use safely are their special features. Therefore extraction of petroleum widened rapidly.

Petroleum fuel is a non-renewable source of energy. Therefore in the near future all the petroleum resources in the world will be exhausted. Moreover, in the burning of petroleum fuels carbon occurred as fossils is converted to carbon dioxide. It increases the amount of carbon dioxide in the atmosphere and engenders severe environmental problems such as global warming. For this reason attention is being drawn towards the production of energy using renewable resources. Biodiesel is such a renewable fuel.

Biodiesel is produced from non-volatile plant oils. Plant oil is a renewable resource. Therefore combustion of them does not cause increase in the carbon dioxide content in the atmosphere.

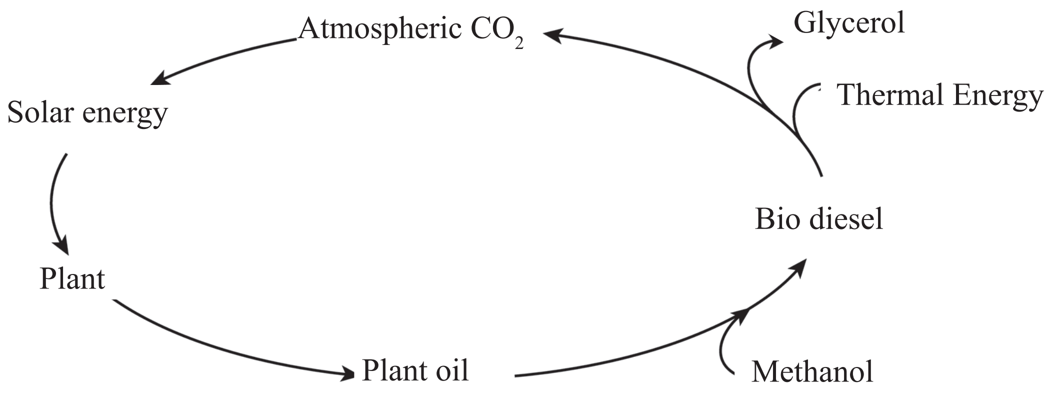


Figure 1.22 Production of biodiesel

Methanol is essential to produce biodiesel. Methanol is obtained from the products of the petroleum industry. Therefore when biodiesel is obtained using methanol is not a biodiesel product produced from 100% renewable resources. Hence attention is being focused on the production of methanol using carbohydrates and other biomasses employing micro-organisms. Methanol so produced is called bio-methanol. Biodiesel produced using bio-methanol is biodiesel 100% based on renewable raw materials.

Biodiesel is produced form the triglycerides present in plant oils. The reaction that converts the fatty acid of these triglycerides into methyl ester (FAME – Fatty acid methyl ester) is refered to as a transesterification reaction. Here, one ester is converted to another ester. A sodium hydroxide solution is used as the catalyst. Biodiesel and glycerol formed are immiscible and separate out into two layers. The main by-product of this production is glycerol. Hence biodiesel is a mixture of several methyl esters of fatty acids. Biodiesel that has low density floats on the glycerol layer.

If plant oils contain free fatty acid of the type RCOOH they may react with sodium hydroxide to give soap (RCOONa). If soap is formed, foam is also formed which inhibits the catalytic action. Thus in plant oils used for this purpose free fatty acid content should be less than 2% (w/w) and the acid value should be 0.1 mg (KOH) g^{-1}.

Production of biodiesel involves several steps.

Step 1 - Treating the plant oil taken as the raw material
Step 2 - Preparation of the catalyst mixture
Step 3 - Reacting triglycerides with methanol
Step 4 - Separating the products
Step 5 - Further purification of crude biodiesel

Step 1

Free fatty acids and non- saponifiable compounds in the plant oils are removed. This enables to have high yield by the transesterification reaction and maintain a high level of purity of the biodiesel obtained.

Step 2

Sodium hydroxide catalyst is dissolved in methanol. Afterwards the solution is mixed with triglycerides (plant oil). It is very important that the alcohol does not contain water. The amount of methanol used is also very important. Although the methanol - tryglyceride ratio is 1 : 3, methanol is added in little excess. As the reaction is reversible this makes the reaction more efficient. However methanol is not added in large excess because removal of methanol from biodiesel is difficult. In addition to sodium hydroxide compounds such as potassium hydroxide and sodium methoxide ($NaOCH_3$) are used as homogenous catalysts. Compounds like magnesium oxide and zinc oxide can be used as heterogeneous catalysts.

Step 3

Since the alcohol and plant oil are immiscible, they are mixed with continuous stirring while the temperature is maintained between 50-60 ^{0}C.

The trans esterification reaction occurring here produces biodiesel and glycerol.

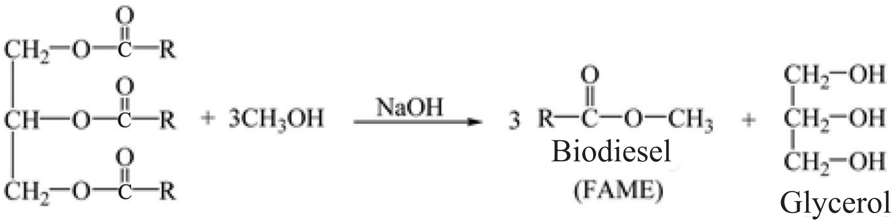
Step 4

The main products exist as two phases because they do not mix. The upper layer consists of biodiesel, unreacted triglycerides and diglycerides, and glycerol and methanol in small amounts. Lower layer contains glycerol with excess methanol and the catalyst. After the separation of the phases these layers are separated.

Step 5

When the biodiesel phase is washed with water glycerol, methanol and the catalysts dissolved in it can be removed. Finally it is possible to remove water.

Remaining methanol may occur in both the layers of biodiesel and glycerol as an impurity. By separating and heating the layers, methanol contained in them can be removed. This methanol can be re-used. Water is bubbled through biodiesel to purify it by removing sodium hydroxide and glycerol which are present in it as impurities. Then, water (moisture) sticking to biodiesel is removed.



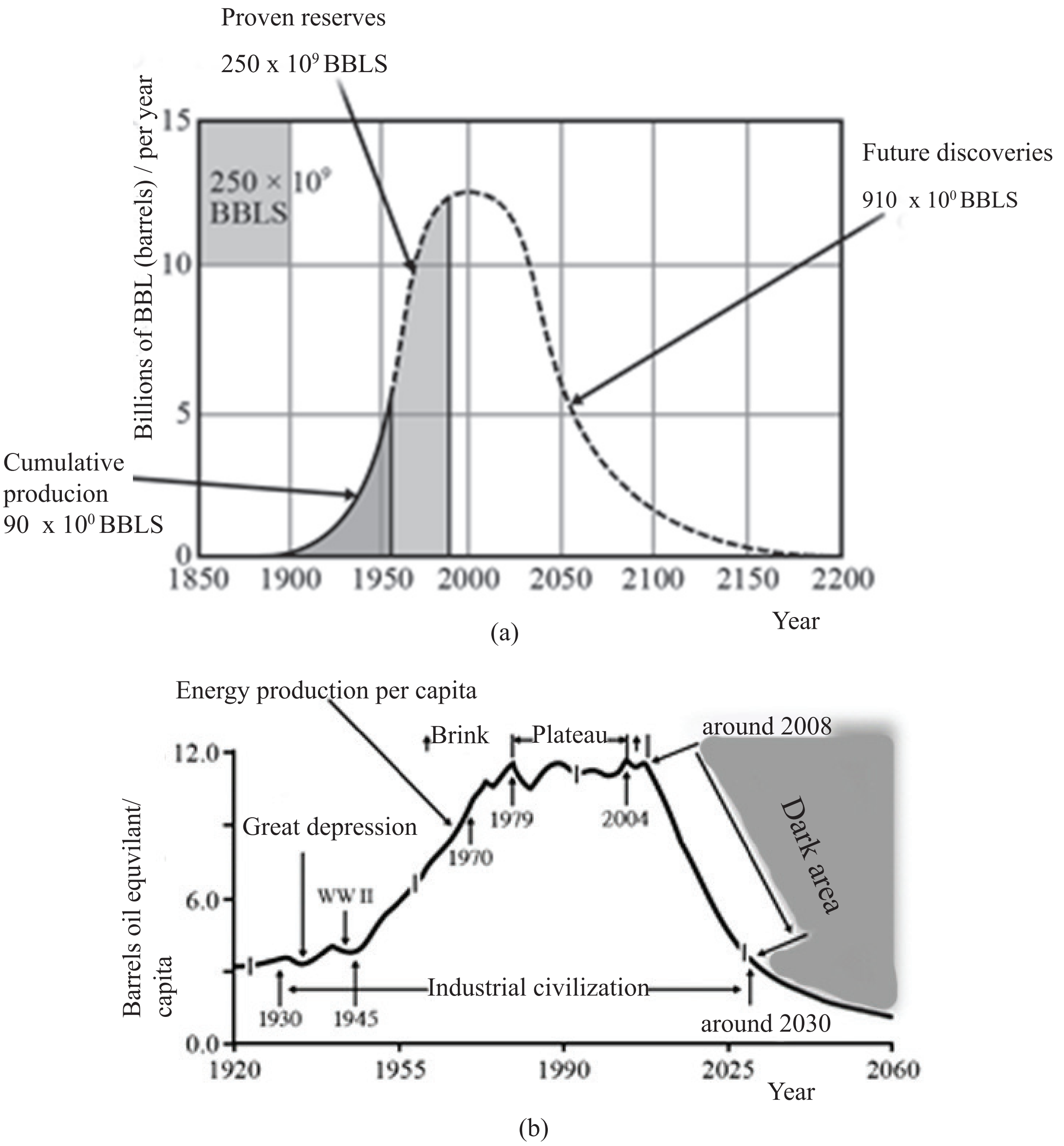
In order to prepare a sample of biodiesel, a solution prepared by dissolving 0.75 g of sodium hydroxide in 26 g of methanol and 250 g of soya oil can be used.

Petroleum fuel is a non-renewable source of energy. Petroleum which is a limited natural resource is not uniformity distributed throughout the world geographically. Therefore crude oil has become a very strong and crucial factor in international relations and international politics.As crude oil is used to produce petroleum fuel and the organic compounds obtained from the by-products are used to produce medicine and monomers required to make plastics and artificial rubber, petroleum industry has become the motive force of the modern human civilization. With the combustion of petroleum fuels obtained from the underground crude oil, the carbon dioxide content in the atmosphere rises. Increasing the global warming due to this is a booming threat for the modern human civilization.

Extra knowledge

Dr. M.K. Hubbert is a geophysicist who described the nature of exhaustion of petroleum, a non renewable resource as against the pattern of human consumption. According to the theory put forward by him (Hubbert peak theory), in a geographical area concerned, the rate of production of petroleum oil varies with time according to a bell-shaped pattern. With the increase in the demand for petroleum with the increasing population and fuel consumption, crude oil production (number of barrels of crude oil production per year) has to be increased. Yet, as the amount of crude oil in the oil wells is limited, there comes a state beyond which the rate of production cannot be increased further. Hence, the amount of barrels of crude oil produced per year comes to a maximum. Meanwhile, the rate of production cannot be maintained at a high constant level because the crude oil resources become more and more limited in spite of the demand. So, the number of barrels that can be produced yearly gradually decreases causing a decline in the production rate. In 1965, Hubbert, showed that by 1965-70 the amount of barrels of crude oil produced by United States of America reaches a peak. The validity of this prognosis was confirmed when we went past 1970. As per this theory the global production of crude oil reaches the maximum by 2000. Afterwards the yearly production of crude oil would decrease.

Despite the rate of production of crude oil after 1995 was somewhat different from the pattern predicted this theory, today we are basically passing the zone of consumption. Specially, global political factors, alternative sources of power and invention of high efficiency energies etc. have changed this rate of depletion a little. Figure 1.23 (a) depicts the curve suggested by Hubbert with regard to the production of crude oil.



(a)

(b)

Figure 1.23 Alternative sources of power and fuel efficiency

Presented in Figure 1.23 (b) is a graph based on the Oldvai theory on the spread of annual power production. In this theory, on the production of power in 1930 and prospective production 100 years afterwards (i.e. in 2030) are almost equal. For this reason attention has been focused on the global scale on the production of power using renewable raw materials and synthesizing various organic compounds using them.

1.13 Chemistry of air pollution caused by industrial emissions

1.13.1 Acid rain

Rain is one component of the water cycle. From the vapourization of water from various sources of water in the Earth's surface water enters the atmosphere. The condensation of this gaseous water due to various factors in the atmosphere and returning back to the surface of the Earth is called precipitation. There are several forms of precipitation. Rain is return as liquid water. Return in solid form occurs as snow and hails. In addition restoration also occurs by condensation into tiny droplets (aerosol) resulting in mist and fogs. Whatever is the way of return, the water coming back to the Earth from the atmosphere is the purest part of the hydrologic cycle. Except the solid particles in the atmosphere and some dissolved gases like nitrogen, oxygen and carbon dioxide there is no other substance in atmospheric water. Of the gases dissolved carbon dioxide has drawn much attention. That is because when atmospheric carbon dioxide dissolves in water, it combines with water to form a weak acid named carbonic acid.

$$CO_2(g) + H_2O(l) \longrightarrow H_2CO_3(aq)$$

Carbonic acid dissociates weakly and add H^+ ions to water.

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

Therefore pH of rain water is little less than the pH of neutral water.

Based on the present carbon dioxide composition in the air, 400 mg dm^{-3} or ppm (0.04%), the minimum pH value of rain water is 5.6. That is, rain water is slightly acidic even in the absence of any other factor affecting it. This mild acidity is not harmful to aquatic organisms, man or any other water related activity. This is the ordinary situation.

But due to various natural and human activities more acidic gases are added to the atmosphere. These are gaseous acidic oxides of nitrogen (NO_X) and gaseous acidic oxides of sulphur (SO_X). Nitric oxide (NO) and nitrogen dioxide (NO_2) can be considered as the gaseous acidic oxides of nitrogen. Sulphur dioxide (SO_2) and sulphur trioxide (SO_3) are the gaseous acidic oxides of sulphur.

Ways of gaseous acidic oxides of nitrogen enter the atmosphere

Natural process

During lightning where the temperature is high, atmospheric nitrogen reacts with atmospheric oxygen forming nitric oxide (NO) and nitrogen dioxide (NO_2).

$$N_2(g) + O_2(g) \longrightarrow 2NO(g)$$

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

NO and NO_2 are also produced by volcanic eruptions and nitrifying bacteria living in the environment. Gaseous acidic compounds of nitrogen are also produced by the oxidation of ammonia (NH_3) in the atmosphere which is produced by the microbial decomposition of nitrogenous compounds under anaerobic conditions. The amount of acidic gaseous compounds released to the atmosphere by all these natural process is very small. Thus the composition of naturally produced acidic gases of nitrogen in the atmosphere is very small and has no significant effect on making rain water acidic.

Human activities

The main anthropogenic (human) activity that emits gaseous acidic compounds of nitrogen to the atmosphere is the burning of fuel in motor vehicles. Internal combustion engines produce energy by combusting liquid fuel in air under a very high pressure and high temperature. Atmospheric nitrogen which is inert under normal condition reacts with oxygen under these conditions of high pressure and temperature mainly producing nitric oxide. Nitric oxide gets oxidized further in the atmosphere giving nitrogen dioxide.

$$N_2(g) + O_2(g) \longrightarrow 2NO(g)$$

$$2NO\ (g) + O_2(g) \longrightarrow 2NO_2(g)$$

Acidic NO_X produced by human activities makes rain water acidic.

Ways of adding oxides of sulfur to the atmosphere

Natural ways

In the volcanic eruption, ash and gases containing huge amounts of sulphur dioxide are freed and these directly enter the atmosphere. As a result of microbial activities taking place under anaerobic conditions in the sediments on the bottom of the ocean and water resources hydrogen sulphide gas is produced. Oxidation of this gas in the atmosphere gives sulphur dioxide. However the sulphur dioxide concentration in the atmosphere remains at a very low level because sulphur dioxide produced as above spread across a very large area of the atmosphere. Sulphur dioxide gas entering the atmosphere due to natural ways hardly contributes to make the rain water acidic. (Acid rains restricted to the relevant areas have been reported after volcanic eruptions.)

Human activities

Compounds of sulphur includes as impurities in less volatile fuels such as diesel and furnace oil produced during the refining of crude oil. These compounds containing sulphur turn into sulphur dioxide on combustion and enter the atmosphere.

Further, elemental sulphur and sulphur compounds (e.g. FeS) presents as impurities in coal get oxidized during the combustion of coal and enter the atmosphere as sulphur dioxide. Sulphur dioxide produced by human activities like this largely adds on to the atmosphere at certain specific regions. For this reason there could be a very high concentration of sulpher dioxide in the areas around such sites (e.g; coal power stations). Acidic oxide of sulphur (SO_x) generated by such human activities cause acidity of rain water.

How pH is lowered in rain water by acidic gases

NO is produced during the combustion in engines.

$$N_2(g) + O_2(g) \longrightarrow 2NO(g)$$

NO in vehicular emissions gets oxidezed in the atmosphere giving NO_2.

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

In the presence of air NO_2 reacts with water and produces nitric acid, a strong acid.

$$4NO_2(g) + 2H_2O(l) + O_2(g) \longrightarrow 4HNO_3(aq)$$

SO_2 gas entering the air is further oxidized to SO_3 gas.

$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$$

SO_3 reacts with water vapour to form sulphuric acid. In the presence of air SO_2 gas also reacts with water vapour giving sulphuric acid.

$$SO_3(g) + H_2O(1) \longrightarrow H_2SO_4(aq)$$

$$2SO_2(g) + O_2(g) + 2H_2O(l) \longrightarrow 2H_2SO_4(aq)$$

The compounds HNO_3 and H_2SO_4 formed above are strong acids. They completely ionize in water adding H_3O^+ ions to water in large amounts.

$$HNO_3(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + NO_3^-(aq)$$

$$H_2SO_4(aq) + 2H_2O(l) \longrightarrow 2H_3O^+(aq) + SO_4^{2-}(aq)$$

Because of the H_3O^+ ions added to water by the strong acids, the pH value of water decreases below the pH caused by carbonic acid formed by dissolving CO_2 gas.

Lowering of pH in rain water below 5.6 by adding strong acids to the rain is called acidification of air or formation of acid rain. High acidity of water leads to many problems.

Effects of the acidification of water

Aquatic organisms are very sensitive to the change of pH in water. Therefore even a small drop in pH in water is harmful to them. This causes changes in behavioural patterns, retardation of organogeny and destruction of eggs and immature organisms of fish and other aquatic organisms etc. This is detrimental to biodiversity.

Figure 1.24 Distroying of aquatic organisms

Figure 1.25 Destroying of forests

Death of coral polyps responsible for the formation of coral reefs stops their formation and bleaches the reefs.

Continuous fall of acid rains in forested areas leads to degradation of chlorophyll in plant leaves which causes gradual death of the plants. Death of plants from their top to bottom is a sign of their ruin brought about by acid rains.

Acid rains make soil acidic. Owing to the acidity, poisonous metal ions (Al^{3+}, Cd^{2+}, Cr^{2+}, Hg^{2+}) and other toxic ions strongly bound to the insoluble soil structure get detached and dissolve in water. Increased concentration of these ions is harmful to aquatic organisms and not suitable for human consumption.

Examples :

High concentration of Al^{3+}, Fe^{3+} and heavy metal ions such as is very harmful to aquatic organisms.

High acidity rain water brings about speedy dissolving of micronutrient metal ions in the soil such as Fe^{3+}, Zn^{2+} and Cu^{2+} in water which are then leached out easily. This makes soil infertile.

Acid water dissolves rocks and minerals in soil containing calcium, magnesium and aluminum. Excessive ions of these in water raises the hardness of water.

Acidity increases the rate of corrosion of metal structures in constructions. This weakens their mechanical strength and reduces the life time.

Acid rains damage statues and other artistic creations made of calcium carbonate minerals such as marble. This obliterates their fine carvings denigrating their historic value.

It decreases the mechanical strength of houses and other constructions made by mortar and cement which contain lime stone. Acid rains and acidic gases convert the less soluble corbonates in mortar and cement into more soluble sulphates and nitrates.

$$2CaCO_3 + 2SO_2 + O_2 + 2H_2O \longrightarrow 2CaSO_4.2H_2O + 2CO_2$$

Measures that could be taken to reduce acid rains and acidification of water

1. Using coal and diesel with low sulphur content in coal and diesel power plants.
2. Adopting methods to remove acidic gases like sulphur dioxide like acidic gases emitted by power plants.
   (i) Burning coal with substances ($CaCO_3$) that can react with sulphur dioxide (Fluidized bed combustion)

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

   $$CaO(s) + SO_2(g) \longrightarrow CaSO_3(s)$$

   (ii) Converting sulphur dioxide in power plant waste gases into solid substances. (reacting with calcium hydroxide (Lime slurry process))

   $$Ca(OH)_2(aq) + SO_2(g) \longrightarrow CaSO_3(s) + H_2O\ (l)$$

3. Employing environmental-friendly fuels or alternative energy sources such as solar energy, wind power, tidal energy, geothermal energy and nuclear power in place of coal and diesel.

1.13.2 Global warming

For all natural process and dynamic activities carried out by man on the Earth, energy is provided by the sun. There is an empty space between the sun and all the other plants including the Earth. Because of this reason solar energy travels to the Earth as radiations. This radiant energy comes to the Earth mainly as visible, infrared and ultraviolet radiations. Radiation energy of the Sun reaching the Earth like this are subjected to various transformation in the Earth. Finally leaves the Earth. That is to say, there is an energy equilibrium in the Earth.

Because of the transformations undergone by the radiant energy reaching the Earth, heat is generated in the Earth. As a result the earth gets heated up and reaches a certain temperature. Because of the transformation of solar energy, its return and establishment of an equilibrium, the extent to which the earth is heated remains constant. Therefore on the whole the average temperature of the Earth is assumed to be a constant value. This is about 15 ^{0}C. However due to Earth's 23.5^0 inclination to its axis's situation of latitude intensity of solar energy received by various regions is different. Because of this seasonal changes the temperature in different parts of the world in various time intervals is different.

For example, in equatorial regions the temperature is high and it is uniform throughout the year. From the equator to polar regions seasonality becomes acute and temperature within the year varies with in wide limits. The summer is extremely hot while the winter is intensely cold. In polar regions an extremely cold weather prevails throughout the year.

The average temperature of the Earth, that is 15 ^{0}C is a favorable condition for the existance of life. The reason for the prevalence of the favourabe temperature is the green house effect existing on the Earth. The potency of the green house effect on the earth helps to maintain an optimum temperature favourable for life.

Greenhouse effect

Before studying the greenhouse effect let us understand what a greenhouse is. As we all know, to grow an agricultural crop a certain optimum temperature is essential throughout the life of the crop. When we go from the equator of the Earth to mid latitude regions, the annual period of time with this optimum temperature gradually decreases. On reaching the polar regions, the time with optimal temperature necessary for plant growth becomes so short that plants do not grow in those regions. If plants grow at all, they are plants with a very short life span (e.g. The life span of plants growing in Tundra regions is about 2-3 weeks). In mountain regions a low temperature prevails year-long (e.g. Nuwara Eliya, Bandarawela etc.).

Hence, life in a particular region, if the time interval during which the optimum temperature necessary for a certain crop is less than its life span, growing that crop in the relevant, region is difficult. A greenhouse lengthens this period of optimal temperature without an external heat supply in a safe house located in that particular region. The temperature in a greenhouse is higher by 2 ^{0}C to 6 ^{0}C than the temperature outside. For this reason, even outer temperature is lower than the optimal temperature, it can be maintained that optimum temperature inside the greenhouse. In a greenhouse the time period with optimal temperature can be extended by 2-3 weeks longer than that in the normal environment. Now let's inquire into how this happens.

Action of a greenhouse

A greenhouse is an almost completely safe kept house. Its roof and walls are made of transparent material so that solar rays can penetrate them. Through these transparent materials visible and ultraviolet radiations coming from the sun, passes into the greenhouse.

Figure 1.26 A Greenhouse

Inside the greenhouse, these radiations are absorbed by the soil and other substances in it. A part of the radiant energy absorb is re-emitted as low energy ultraviolet and visible radiations while another part is re-radiated as infrared radiations. The roofing materials and materials for the walls of the greenhouse are selected in such a way that they are transparent for the visible and UV radiations but reflect IR radiations. When IR rays are reflected inside the greenhouse for a longer period of time they are absorbed by carbon dioxide and water vapour and are converted to heat. This increases the temperature inside the greenhouse. This is the process takes place inside a green house. The atmosphere of the Earth too exhibits a process somewhat equal to the action of greenhouse. This is known as the greenhouse effect of the earth.

Greenhouse effect of the earth

Solar radiations falling on the Earth are mainly belong to the ultraviolet and visible zones. Of these most of the radiations belonging to the ultraviolet zone are absorbed by the upper atmosphere and very little reaches the Earth's surface. It is UV radiations of very low energy that come like this. Visible ray and low energy UV rays reaching the Earth surface are absorbed by the Earth's surface (soil) and re-radiated as low energy radiations like in a greenhouse. In this re-radiation energy is emitted as low energy visible rays and IR rays. The emitted visible rays return to space without undergoing any significant change. But the IR radiations emitted could be absorbed by certain gases in the air. Fortunately the main gases in the air – N_2 (78%), O_2 (21%), Ar (1%), cannot absorb these IR radiations. If these gases occupying more than 99% of the Earth's atmosphere had absorbed IR radiations, the temperature of the earth could have been very high.

Greenhouse gases

The gases which can absorb infrared radiations exist stably in the atmosphere for a long period of time are referred to as greenhouse gases.

Any gas having two or more atoms can absorb IR radiations. Also a hetero diatomic gases (e.g CO) can absorb IR radiations. Homo diatomic gases (N_2, O_2) and monatomic gases (e.g. Ar) cannot absorb IR rays. Hence any gas which is not monatomic and homo diatomic can absorb IR rays. Nevertheless, if a gas is to act as a greenhouse gas in the Earth's atmosphere, it should have following characteristics.

1. Ability to absorb infrared rays
2. Ability to stay stably in the atmosphere for a long period of time.

The gases in the atmosphere which are though capable of absorbing IR rays, unstable or short-lived are not considered greenhouse gases. As per the foregoing facts the main greenhouse gases present in the atmosphere are,

1. Water vapour (H_2O)
2. Carbon dioxide (CO_2)
3. Methane (CH_4)
4. Nitrous oxide (N_2O)
5. Volatile halogenated hydrocarbons (CFC, HFC, HCFC)

Although would be present in certain amounts in the atmosphere and they are capable of absorbing IR rays, the gases such as SO_2, NO_2, NO and CO are not reckoned as greenhouse gases. This is because their life span in the atmosphere is very short. Of the above greenhouse gases, all the gases except halogenated hydrocarbons exist in nature.

The greenhouse gases aforementioned absorb IR rays emitted from the Earth and retain them long in the Earth. Therefore the Earth gets heated. The result of this heating is the maintenance of the normal temperature of the earth at around 15 ^{0}C. Thus greenhouse effect is favourable factor essential for the perpetuation of life.

Extra knowledge

The hottest planet in our solar system is not Mercury which is closest to the Sun but the second from it, Venus. Venus receives about 25% of the solar energy received by Mercury. The reason for this is the strong greenhouse effect existing in Venus. Around 95% of the atmosphere of Venus comprises carbon dioxide gas. For this reason, the atmosphere of Venus largely absorbs infrared rays and creates a strong greenhouse effect. Hence, though situated second from the sun, Venus holds the record of being the hottest planet of the solar system.

The percentages of greenhouse gases in the Earth are given in Table 1.5.

Table 1.5 Amounts of greenhouse gases in the Earth

Greenhouse gas	Quantity
Water vapor (%)	0.001 – 0.5
Carbon dioxide (ppm)	415
Methane (ppb)	1745
Nitrous oxide (ppb)	315
Volatile halogenated hydrocarbons (CFC, HFC, HCFC) (ppt)	53.3

What would happen if the percentage of greenhouse gases in the Earth increases? The outcome is production of more heat in the Earth due to absorption of more IR radiations by the increased amount of greenhouse gases. The heat so produced circulated longer in the Earth causing an increase in Earth's temperature. Along with the industrial ventures initiated by man with the industrial development the proportion of greenhouse gases is gradually increasing. It increased rapidly with the industrial awakening got under way after the second world war started with the industrial revolution.

Table 1.6 Changes in the composition of greenhouse gases before the industrial revolution and at present.

Gas	**Composition in 1750 (Volume percentage)**	**Present composition (Volume percentage)**
CO_2	0.028	0.041
CH_4	0.00007	0.00018
N_2O	0.000027	0.0000314
Halogenated hydrocarbons	0	0.00000000533

From Table 1.6 it is clear that the amount of all greenhouse gases has drastically increased. Though the amount of water vapour in the earth atmosphere changes with geographical factors and some weather factors on short-term, the total amount of water vapour in the Earth remains unchanged on long-term. Because of this, although water vapour is a greenhouse gas it does not contribute to global warming. Owing to the increase in greenhouse gases the temperature of the Earth has risen by about 0.95 ^{0}C from 1750. This increase is 0.65 ^{0}C from 1950. This shows that global warming has rapidly increased during the few decades in the recent past.

Figure 1.27 Impact of the increase in the temperature of the Earth

Human activities leading to the increase in greenhouse gas concentration

Carbon dioxide (CO_2)

To meet the energy requirement of man, coal and petroleum are being burnt in excessive amounts. The carbon reserves which occurred inertly inside the Earth for millions of years were burnt in a very short time adding the resulting CO_2 to the atmosphere. When the rate of addition of CO_2 to the atmosphere exceed the rate of the mechanisms which remove CO_2 from it, CO_2 gas accumulates in the atmosphere.

Because of excessive deforestation, trees are felled indiscriminately. The debris contain carbon reserves collected over hundred of years. When these are decomposed by the microbial activity CO_2 is added to the atmosphere. This causes the carbon dioxide content in the atmosphere to rise.

Methane

When the indiscriminately disposed organic wastes decay in the environment they are acted upon by anaerobic bacteria. When those bacteria decompose organic substances methane is produced. Disposal of urban wastes as heaps of garbage is also a reason for the production of methane in large amounts. Agricultural practices (paddy cultivation) undertaken in marshy and water-logged areas favour anaerobic decomposition of organic substances producing methane.

Methane is also produced in the guts of the ruminants like cattle, sheep and goats due to bacterial decomposition of plant material under anaerobic conditions. Therefore rearing such animals in commercial scale is a reason to release methane in large amounts to atmosphere. Crude oil mining too increases the methane content in the atmosphere. During the mining process methane gas occurring as natural gas in crude oil deposits is freed to the atmosphere.

Nitrous oxide

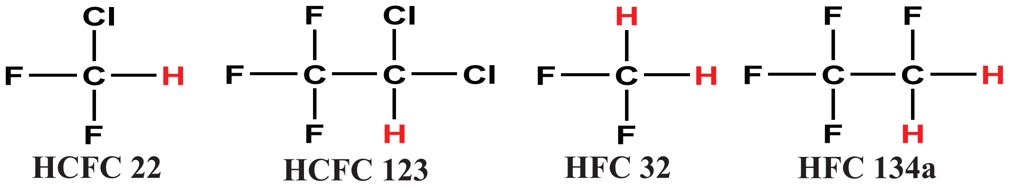
Oxides of nitrogen are mainly added to the atmosphere by the bacterial action on nitrogenous compounds. Action of denitrifying bacteria on the nitrogen compounds added to the soil as fertilizers in agriculture produces nitrous oxide (N_2O).

Gaseous halogenated hydrocarbons

Halogenated hydrocarbons are very powerful greenhouse gases. These are ten thousand times as strong as carbon dioxide. For this reason, presence of these gases in the atmosphere even in small quantities contributes significantly to global warming.

Halogenated hydrocarbons are scare in nature. Halogenated hydrocarbons responsible for increasing the global warming are,

1. Chlorofluorocarbon (CFC)
2. Hydrochlorofluorocarbon (HCFC)
3. Hydrofluorocarbon (HFC)



HCFC 22 HCFC 123 HFC 32 HFC 134a

Figure 1.28 Some halogenated hydrocarbon molecules

All these three types are compounds synthesized by man and are used as cooling gases in air conditioners and refrigerators. They are also used as a blowing agent in the production of perforated plastics and in aerosols, for example in deodorant sprays and pesticides. In repair and disposal of the above equipment these compounds enter the atmosphere. The atmospheric lifetime of these are hundreds of years.

Adverse effects of global warming

- With the global warming polar ice caps and glaciers in high mountains areas tend to melt while the oceanic waters expand. This entails in inundation of costal lowlands. (e.g. Ganges river in Bangladesh, the delta of river Brahmaputra, Mekong delta in Vietnam). Loss of settlements, destruction of costal ecosystems, infertility of soil caused by the sea water swamping inland and devastation of crops are the other outcomes of this. Moreover it may obliterate Maldives and many other small island states in the pacific ocean completely from the world map.

Figure 1.29 Melting of ice caps in polar regions

- Because of the high temperature epidemics (e.g; dengue, Ebola) spread fast.
- Increase in the number of hot days and decrease in the number of cold days per year, occurrence of strong heat waves more frequently and lasting for a longer period of time (rapid increase in the temperature in regions within a small time interval).
- Frequent emergence of hurricanes, tornadoes etc. of greater violence.
- Rapid spread if invasive plants and animals. Such plants and animals may encroach new areas (cold blooded animals like snakes and other reptiles would migrate to cooler areas).
- Excessive drying of some regions (South Asia, Central Africa) while some other regions (e.g. Europe) receive heavy rainfall.
- Frequent long-standing droughts and flash floods due to heavy rainfall in a short period of time.

Global climatic changes

Many human activities in the world are connected with the climate of the relevant region. For examples, agriculture, animal husbandry, tourism and pottery are strongly linked to climatic patterns. These climatic patterns are created by the differences in solar energy received by various parts of the world. The shift of energy circulation caused by global warming brings about changes in the climatic patterns.

Not receiving rain on time, untimely rains, droughts and occurrence of whirl winds and tornadoes in regions where they have not been experienced before are examples. Prolonged droughts causing desertification in some regions forcing people to leave those areas. Climatic changes may indirectly engender political crises among nations and even battles.

For example, when the citizens of a certain country are displaced they migrate to neighbouring countries and a need arises to provide political asylum for them. Political crisis and wars may erupts for sharing water in rivers common to several countries (e.g. Nile, Brahmaputra, Mekong) specially when water goes scarce.

Global warming and climatic changes caused by it, is a problem common to the entire world. The most affected by this are the underdeveloped and developing countries which contribute least to global warming. So, in order to control global warming all the countries in the world should get together and have to adopt measures that minimize the emission gases which cause it.

The following solutions could be suggested in this regard.

- Limited the burning of fossil fuels and inclining to use alternative fuels. The best option is sloar energy. In addition nuclear power and wind power be used. Updating the machinery of current use and increasing their fuel efficiency could also be done.
- Instead of fossil fuels it is suitable to use renewable sources of energy such as ethanol and biodiesel. The amount of pure carbon added to the atmosphere by the combustion of bio-fuels is nil.
- By getting used to a simple lifestyle, high energy demand essential for a luxurious life can be minimized.
- Minimizing deforestation. To make furniture and paper and obtain firewood, fast-growing plants can be used without destroying forests.
- Avoiding indiscriminate waste disposal and adopting systematic method of waste disposal with proper management of waste. This minimize the emission of methane to the atmosphere.
- Refraining from the consumption of meat as much as possible getting used to vegetarian diet. By this rearing of animals such as cattle, goats and sheep for meat can be minimized.

- Use of compost in place of chemical fertilizers. This helps minimize the emission of nitrous oxide (N_2O) to the atmosphere.
- Restricting the use of refrigerators and air conditioners and using in such machines with less powerful gases such as hydrofluroolefines (HFO), isobutene (R600a) and coolant gas like ammonia in place of more stronger greenhouse gases like CFC and HCFC.

1.13.3 Depletion of the ozone layer

Energy for all the process taking place in our planet Earth is provided by the sun. Energy is transmitted from one place to another by three methods, conduction, convention and radiation. Of these, conduction and convention need a medium for the transmission of energy. Radiation does not require a medium for energy transmission. In our planetary system an empty space (vacuum) occurs between the sun and the planets. Therefore there is no possibility at all to transmit energy from the Sun to the Earth by conduction and convention. Hence the solar energy reaches the Earth by radiation which does not need a medium. The radiation that carry energy from the Sun to the Earth are known as electromagnetic radiations.

Electromagnetic radiations are classified according to the energy in them. That is as X-rays, ultraviolet rays, visible rays, infrared rays, micro waves and radio waves. Table 1.7 indicates the properties of various electromagnetic waves.

Table 1.7 Properties of electromagnetic waves

Electromagnetic waves	Mean wave length	Mean frequency/ s^{-1}	Mean energy/ kJ mol^{-1}
Radio waves	1 cm	3×10^{10}	1.2×10^{-2}
Micro waves	1 mm	3×10^{11}	1.2×10^{-1}
Infared waves	10 µm	3×10^{13}	12
Visible waves	500 nm	6×10^{14}	240
Ultraviolet waves	250 nm	1.2×10^{15}	479
X ray	1 nm	6×10^{17}	1.2×10^{5}

Of these X-rays and ultraviolet rays are highly energetic. Therefore when exposed to them they cause chemical changes in the bio-molecules in our body. The structural changes in the active bio-molecules in our body namely DNA, RNA and proteins (enzymes) obstruct their functions causing various complication in our bodies. We discuss these complications at length under the sections to come.

Energy is transmitted from the Sun to our planet Earth mainly in the form of ultraviolet rays, visible rays and infrared rays. Of these visual rays and infrared rays are low in energy and we are not harmed by the exposure to them. In the electromagnetic spectrum the only ray type sensitive to our eyes are visible rays and they help to give us the sense of vision. We become sensitive to infrared by sensing heat.

Figure 1.30 illustrates the nature of the solar rays reaching the Earth and their intensity. From it we see that a considerable portion of the solar energy reaching the upper limit of the Earth’s atmosphere are lost before reaching the earth’s surface. Further examination of the figure, reveals that most of the UV rays have been eliminate before they reach the Earth's surface. Why does it happen so? It is because the absorption of those rays by the gas molecules in the upper strata of the atmosphere while the solar rays travel to the Earth’s surface across the atmosphere.

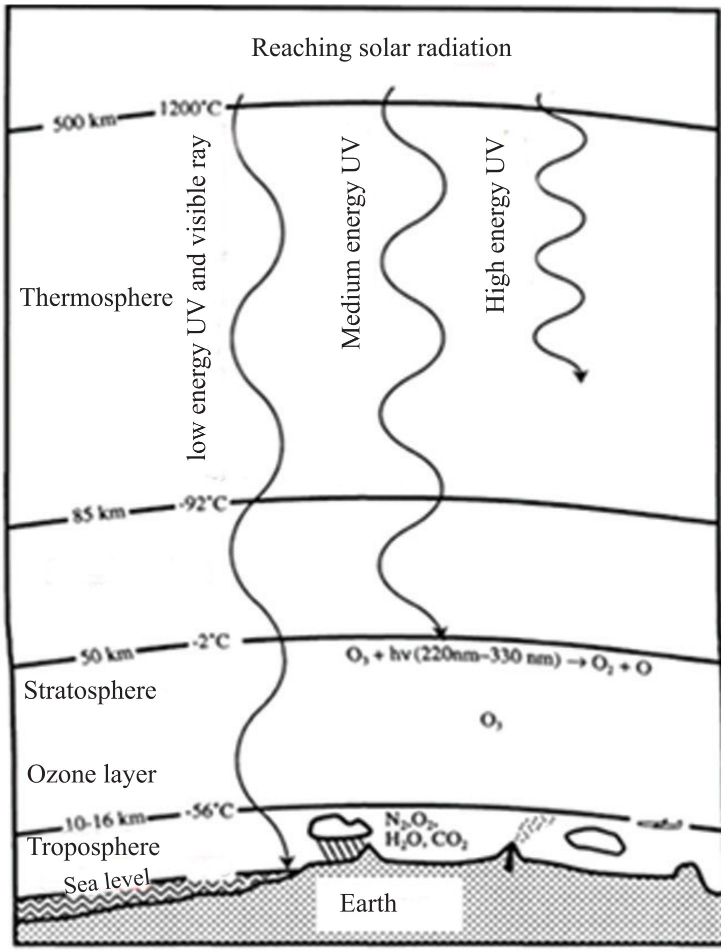


Figure 1.30 Stratification of Earth’s atmosphere and penetration of strata by solar radiations

Stratification of the atmosphere

For the convenience of studying the atmosphere is divided into several layers. This stratification is based on the variation of temperature and the density of the gases in respective regions.

Troposphere This stretches from the Earths surface to about 15 km upwards. A greater percent (about 99%) of the atmospheric gases is found in this region.

Ascending from the Earth's surface, the temperature decreases.

Stratosphere	The region from 15 km to 50 km from the Earth's surface is stratosphere. The percentage of gases here is very low and ascending the layer, the temperature increases.
Thermosphere	It is the region above 50 km from the Earth's surface. Amount of gases in this region is extremely small and the temperature is very high.
Ozone layer	A sub-zone in the stratosphere is referred to as the ozone layer. This extends from 20 km to about 35 km from the Earth's surface. This is called ozone layer because most of the naturally occurring ozone gas in the Earth (around 95%) is found in this region. However it should be remembered that this is not composed only of ozone.

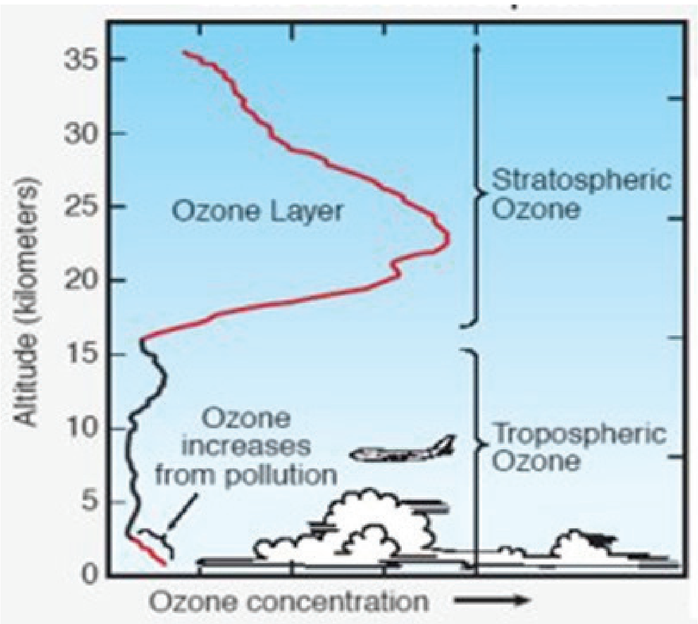


Figure 1.31 Ozone layer and the stratification of Earth's atmosphere

A greater part of the UV rays received from the Sun is spent to maintain the ozone gas in the ozone layer in the stratosphere. Therefore most of the harmful UV radiations coming from the Sun does not reach the Earth's surface. In other words, the ozone layer protects us from being exposed to higher energy UV rays by acting as a filter to them. This phenomenon is vital for the survival of life on the Earth. It is important for the maintenance of the life as much as the existence of water and an optimum temperature.

Functioning of the ozone layer

When higher energy UV rays coming from the Sun reach the stratosphere, they decompose oxygen gas and produce atomic oxygen.

$$O_2(g) \xrightarrow{hv} O(g) + O(g) \quad \Delta H > 0 \quad \text{-----------} (1)$$

As this atomic oxygen is very reactive it reacts with another oxygen molecule forming ozone.

$$O_2(g) + O(g) \longrightarrow O_3(g) \quad \Delta H < 0 \quad \text{-----------} (2)$$

Ozone is an unstable gas. In the presence of UV rays it decomposes giving oxygen.

$$O_3(g) \xrightarrow{hv} O_2(g) + O(g) \quad \Delta H > 0 \quad \text{-----------} (3)$$

$$O_3(g) + O(g) \longrightarrow 2O_2(g) \quad \Delta H < 0 \quad \text{-----------} (4)$$

$$(1) + (2)\times 2 \text{ , } 3O_2(g) \longrightarrow 2O_3(g) \text{ ; } O_3 \text{ formation}$$

$$(3) + (4) \text{ , } 2O_3(g) \longrightarrow 3O_2(g) \text{ ; breaking of } O_3$$

In the ozone layer when the rates of breaking and making of ozone like this become a dynamic equilibrium sets in maintaining a fixed amount of ozone in this region. i.e. the following equilibrium exists in the ozone layer.

$$2O_3(g) \rightleftharpoons 3O_2(g)$$

As UV rays coming from the Sun are absorbed in maintaining this equilibrium, the entry of those harmful rays to the Earth's surface is prevented.

Depletion of the ozone layer

The ozone level in the ozone layer was continuously measured from 1950 with the aid of weather balloons. During making this measurement an amount of the ozone level in the ozone layer was observed decreasing annually from mid-seventies.

Generally the ozone level in the ozone layer does not remain constant every day. It changes to some extent with the temperature of the environment, seasonal changes and geographical factors. But annually it drops gradually. This continuous decrease in the ozone level in the ozone layer is, called ozone layer depletion. Depletion of ozone layer is a serious environmental problem.

The ozone layer prevents the entry of harmful UV rays to the Earths' surface. Because of the depletion of ozone layer in upper levels more harmful UV rays reach the Earth's surface. Exposure of the Earth's inhabitants more to the harmful UV rays causes various complications in them.

Causes for ozone layer depletion

Both natural factors and human activities cause ozone layer depletion. Of these the natural causes are temporary and the damage made is recovered in a short period of time. Sulphur containg compounds added to the upper atmosphere during powerful volcanic eruptions is one natural factor damaging the ozone layer.

The most severe and non-reversible damages to the ozone layer are brought by the human. This is caused by the volatile compounds released to the atmosphere by man.

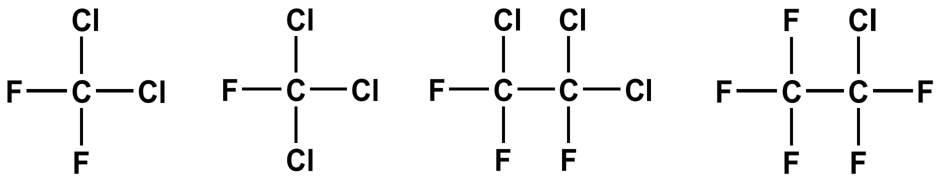
Examples are,

1. Chlorofluorocarbon

   In addition to this, volatile organic compounds containing bromine (bromofluorocarbon) indirectly contribute to ozone layer depletion.

2. Nitric oxide (NO) gas emitted by the aircrafts flying close to the upper atmosphere also depletes the ozone layer.

The main class of compounds which contributes to ozone layer depletion is chlorofluorocarbons. These are derivatives of hydrocarbons with one or two carbon atoms. Of these, all the hydrogen atoms are replaced by chlorine or fluorine.



Freon 12 **Freon 11** **Freon 113** **Freon 115**

Figure 1.32 Some CFC molecules and their industrial names

All CFCs are synthetic compounds and not found in nature. Mainly they have the following industrial applications.

1. Used as the coolant gas in air conditioners and refrigerators
2. Used as an aerosol spray under high pressure in perfumes
3. Used as a blowing agent in the production of foam plastic (e.g.: polystyrene, cushions, mattresses, thermal insulating porous walls) to give porosity to them
4. Bromofluorocarbons are used in fumigation and in fire extinguishers.

How CFCs and other compounds damage the ozone layer

We should remember that none of the above compounds react directly with ozone. The CFCs describe above are very stable compounds. They are not thermally decomposed and are resistant to bio-degradation. For this reason these compounds can stay long in the atmosphere. However, these compounds are very volatile. Hence, they can evaporate rapidly and reach the stratosphere which accommodates the ozone layer where they are exposed to high energy UV rays in upper atmosphere which do not found in lower atmosphere. Under the influence of these C-Cl bonds undergo fission producing $^{\cdot}\mathrm{Cl}$ free radicals. These free radicals react with ozone. They catalyze the breakdown reaction of ozone speeding it up and adding another process of breakdown other than to the natrual breakdown of ozone. Because of this the ozone-breaking process outstrips the ozone making process and the ozone layer is subjected to degradation. This can be illustrated by the following equations.

$^{\cdot}Cl$ free radicals react with ozone

$$^{\cdot}Cl(g) + O_3(g) \longrightarrow O_2(g) + {}^{\cdot}OCl(g) \quad \text{----------------} (1)$$

$^{\cdot}OC1$ free radicals formed react with oxygen atoms formed by the natural breakdown of ozone and regenerates free radical.

$$O_3(g) \longrightarrow O_2(g) + {}^{\cdot}O(g) \quad \text{----------------} (2)$$

$$^{\cdot}OC1(g) + {}^{\cdot}O(g) \longrightarrow O_2(g) + {}^{\cdot}Cl(g) \quad \text{----------------} (3)$$

(1) + (2) + (3),

$$2O_3(g) \longrightarrow 3O_2(g)$$

This shows that after the decomposition of an O_3 molecule by a $^{\cdot}C1$ free radical the $^{\cdot}C1$ free radical is regenerated without being destroyed. That means, until getting destroyed by another reaction a $^{\cdot}C1$ free radical can decompose a large number of O_3 molecules. Hence $^{\cdot}C1$ free radicals have acted as a catalyst in the breakdown of O_3 molecules.

Adverse effects of ozone layer depletion

The main adverse effect of ozone layer depletion is the entrance of high energy, harmful UV rays in high intensity to the Earth's surface. A grater amount of such UV rays gains admission to the Earth's surface after the degradation of the ozone layer than that reached to the Earth's surface before its degradation. Then Earth's creatures expose more to the harmful, high enegy UV rays and become victims to their injurious effects.

Listed below are such unfavourable effects.

1. Skin cancer
   Due to high energy in UV rays, exposure to them brings about structural changes in the molecules like DNA in the skin cells. In the presence of UV radiations, hydrogen bonds in these large molecules break and rearrange in another way. These molecular deforemations give birth to cancer cells which spread fast in the skin ultimately causing cancer.
2. Cataract in eyes
   DNA molecules as well as proteins maintain their structure through hydrogen bonds. Under the influence of the UV rays these bonds break and rearrange changing the

structure of proteins. The eye lens which is essential for vision is made up of a transparent, semi-solid protein. Owing to UV rays, the structure of the proteins in the eye lens changes and its transparency gradually decreases. This is called cataract (e.g.:when transparent egg white is heated it becomes white. This is because the structure of the protein albumin in egg white changes on heating). Cataract in the eye happens not only in humans but also in animals like cattle and goats which live mostly outdoor.

3. Mutations

   Plants with gene mutations would arise when they are excessively exposed to UV rays (e.g.: dwarf plants, plants with deformities in leaves)

4. Bleaching

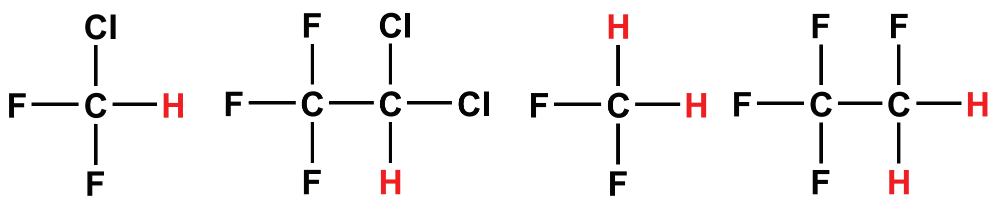
   UV rays bleach pigments in cloths and degrade their quality.

Measures to be taken to protect the ozone layer

If the ozone layer goes on degrading at the rate it is happening at present, the Earth will become a place unsuitable for the perpetuation of life; or it would be a place where eye cataract and skin cancer patients are omnipresent.

Therefore immediate action should be taken to reduce the rate of ozone layer depletion. As CFC is the main destroyer of the ozone canopy its production and usage should be stopped. Action has already been taken in this regard and the Montreal Convention ended the production of CFCs from about 1996. At present alternative gases are being used for the industrial applications for which CFCs were used.

HCFC (Hydrochlorofluorocarbon) was the first alternative gas used for CFCs. This molecule is very much similar to CFC and the only difference was presence of a hydrogen atom in addition to chlorine and fluorine atoms.



HCFC 22 (a) HCFC 123 (b) HFC 32 (c) HFC 134 a (d)

Figure 1.33 (a) and (b) some HCFC molecules and (c) and (d) some HFC molecules

The C-H bond is this molecules is disassociated by solar rays carrying relatively lower energy than the energy in the lower atmosphere. For this reason a considerable part of this compound is decomposed before it reaches the ozone layer. But due to high volatility this gas also can reach the stratosphere. If it reaches the ozone layer like this it has the potential to damage the of ozone layer by cleavage of the C-Cl bond under the influence of high energy UV rays and formation of $^{\cdot}$Cl free radicals. The other alternative used to protect the ozone layer is the use of hydrofluorocarbon (HFC) gas as the coolant in refrigerators. HFCs lack chloride atoms and have only fluorine and hydrogen atoms. Their stability is also low due to the existence of hydrogen atoms (as in HCFC) but they do not form $^{\cdot}$Cl free radicals in the upper atmosphere for they do not contain chlorine atoms. Therefore they do not damage the ozone layer. Hence the coolant use in the airconditions and refrigerators in the world today is HFC (HFC 134a).

Note : Though HFC gas does not harm the ozone layer HFC, CFC and HCFC all are very powerful greenhouse gases. The global warming potential (GWP) of these gases is thousand times the GWP of carbon dioxide.

Table 1.8 Greenhouse gases and their GWP values

Gas	GWP value
CO_2	1
CH_4	22
N_2O	310
HFC 23	11700
HFC 134a	1300
CFC 12	10600
HCFC 22	1700

Despite the fact that the above gases occur in the atmosphere in very small concentrations (ppt), they can contribute considerably to increase global warming because of their very high GWP values. HFC is a good alternative for the ozone layer depletion. But its use is questionable because it contribute to another global environmental issue, the global warming. This has prompted the global community to use cooling gases that do not damage the ozone layer and contribute little to global warming.

Use of volatile hydrocarbons (e.g. R600a) and unsaturated hydrofluorocarbon compounds (Hydrofluoroolefin) (e.g. HFO-1234a) which are less stable in the atmosphere has been already started as alternatives. Isobutene (industrially labeled R600a) is being used as a volatile hydrocarbon. Usage of hydrofluoroolefin (HFO) have been prescribed as an unsaturated hydrofluorocarbon. HFO is structurally similar to HFC and has a double bond. As compounds with double bonds are more reactive, HFO compounds decompose faster in the lower atmosphere and get removed. Thus their contribution to global warming is very low.

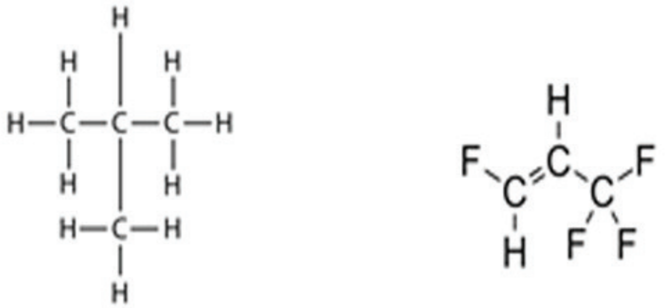


Figure 1.34 (a) Isobutene (R600a) (b) hydrofluoroolefin (HFO - 1234a)

1.13.4 Photochemical smog

Are you a person living in a town congested traffic jams? If so, have a look over the town form a fairly tall building in an afternoon. You will able to see a less transparent, brown coloured mist above the relevant buildings. On less windy days with a clear sky this could be seen in areas close to towns like Pettah, Borella, Kaduwelan and Kandy. Though somewhat rare in Sri Lanka this is a dreadful common in towns like New Dilhi, Mumbai, Culcata, Shanhai, Bejing and Kuala Lumpur.

What is the reason that gives rise to this kind of a less transparent, browny haze in afternoons? The complex photochemical process leading to this phenomenon is called photochemical smog. Photochemical smog means the lowering of the transparency of the atmosphere due to scattering of solar rays by chemical substances formed by the interaction of several environmental pollutants, fine particles and droplets of water.

Chemical pollutants causing photochemical smog and their sources

Two types of chemical pollutants contribute to the photochemical smog. They are nitric oxide gas (NO) and volatile hydrocarbons (unburnt fuel). In addition to these sunlight and a temperature above 15 ^{0}C are requirements.

Chemical pollutants causing photochemical smog are **NO, $CH_3(CH_2)_nCH_3$ (n = 1- 4)**

Both these chemical substances are added to the air almost totally by the transportation by automobiles. Hydrocarbons are the main component of liquid petroleum fuels. The transportation of vehicles totally depends on liquid petroleum. These fuels filled into vehicles enter the environment as unburnt fuel in various ways. Because of the high volatility of gasoline fuel, they vaporize from the fuel tank of vehicles and the volatile hydrocarbons release to the enviornment. A considerable amount of hydrocarbons vaporizes from the carburetor as well. Yet, the largest amount of them enters the air through the exhaust system of the vehicle. Although fuel is burnt in the engine of the vehicle under high temperature and pressure, all the fuel molecules entering the piston do not burn. Especially the hydrocarbon molecules lying closer to the outer wall of the piston do not burn. These unburnt fuel molecules are released to the atmosphere via the exhaust system.

Inside the engine, fuel is burnt by mixing fuel and air in an optimum ratio and igniting under high pressure. Due to the heat evolved by the combustion a high temperature and pressure are created in the engine. Under this high temperature and pressure nitrogen which is considered as an inert gas under normal conditions, reacts with oxygen to produce nitric oxide. This nitric oxide gas escapes into the air through the exhaust system of the vehicle. Accordingly both the pollutants causing the photochemical smog are added to the air by the transportaion of vehicles. This is the reason why the photochemical smog is intense in urban areas with lot of traffic jams.

Chemistry of the photochemical smog

The photochemical smog is a result of a series of complex chemical reactions happening in the lower atmosphere under the influence of sunlight. But to make the study facile, the reactions occurring in the photochemical smog can be simplified as follows.

Nitric oxide gas released from internal combustion engines is subjected to further oxidation in the atmosphere producing nitrogen dioxide. This NO_2 when exposed to solar rays, get decomposed forming atomic oxygen.

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

$$NO_2(g) \xrightarrow{hv} NO(g) + O(g)$$

Atomic oxygen reacts again with molecular oxygen (O_2) forming ozone (O_3) which is a main pollutant in the photochemical smog.

$$O(g) + O_2(g) \longrightarrow O_3(g)$$

Formation of $^{\cdot}OH$ free radicals: $O(g) + H_2O(g) \longrightarrow {}^{\cdot}OH(g)$

In addition to these, $^{\cdot}OH$ free radicals and ozone which is formed by atomic oxygen react with volatile hydrocarbon forming alkyl and proxyalkyl free radicals. These alkyl ($R^{\cdot}$) and proxialkyl ($ROO^{\cdot}$) free radicals react with NO_2 and O_2 producing harmful volatile short chain aldehydes, preoxyactyle nitrate (PAN) and peroxybenzyl nitrate (PBN). Aldehydes produced are subjected to polymerization forming small particles suspended in air. Large particles are formed by these small particles by the deposition of dust, water vapour etc. on them. These particles scatter sunlight reducing the transparency and it appear like a mist in the lower atmospere. Photochemical smog is the only state of pollution visible to our naked eye.

Adverse effects of the photochemical smog

- Ozone is produced as a main product of the photochemical smog. Ozone is a toxic gas. When inhaled it causes respiratory complaints destruction of mucous membranes in the respiratory tract, cough etc.
- Ozone is an unstable and very reactive gas. Therefore when plants are exposed to ozone yellow spots appear especially in tender leaves due to destruction of chlorophyll. This cuts down food production resulting in retardation of growth and decrease in the yield of agricultural crops.
- Ozone spilts the double bonds in rubber molecules (ozonolysis). This shortens the chains of rubber molecules reducing the mechanical strength of rubber-based products. It also causes reduction in the elasticity of rubber and splits in rubber tyres.
- Many volatile aldehydes are produced by the photochemical smog. Inhalation of these compounds causes respiratory diseases and the people who are suffering from asthma, wheezing, bronchitis etc., their ailing conditions get worst and exacerbate. Inhalation of these compounds, also can cause allergic conditions.
- Peroxyacetyl compounds (PAN and PBN) produced by photochemical smogs are carcinogenic and cause gene mutations. They bring about chemical changes in active proteins and enzymes in the body and disrupt the action of enzymes.
- Ozone bleaches colourings. Therefore they deteriorate the quality of textiles.

1.14 Chemistry of the water pollution caused by industrial emissions

Water is one factor indispensable for the survival of life on the Earth. That is for the reason that water contributes to biochemical reactions and acts as the solvent for those reactions. Further, water also acts as the solvent for the natural environmental reactions. Water acts as the solvent for the bio-environmental reactions like this because of the exceptional properties of the water molecule. As regards the geometrical shape of water molecule is angular (Figure 1.35).

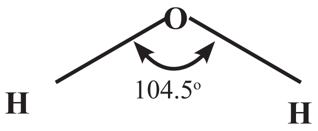


Figure 1.35 Geometrical shape of the water molecule

The value of its HOH angle is 104.5^0. Due to the difference in the electronegativities of the elements H and O of O-H bond in the water molecule, is polar. Since the two polar O-H bonds are angularly situated in space, the water molecule has a resultant polarity. This polarity is around 1.85 D (Debye). This has made the water molecule a strongly polar molecule. Because of this high polarity, strong hydrogen bonds form among the water molecules. Therefore bulk water occurs as a liquid at room temperature. That is, water is a strongly polar liquid and because of this high polarity many polar compounds dissolve in water. Water is a good solvent for polar compounds. Many natural compounds as well as the compounds taking part in biochemical processes too are polar. For this reason water acts as a solvent for biochemical and environmental process. Hence water is named environmental polar solvent in environmental chemistry.

In the property of being a good solvent for polar compounds, there are demerits in water also. Many unwanted polar compounds readily dissolve in water and pollute it. Dissolving of various substances in water making it unsuitable for the relevant task, is called water pollution. Water pollution differs according to the task for which it is meant. For example there are occasions where water considered polluted for the drinking purpose, is reckoned unpolluted as far as agriculture is concerned. Water polluted by micro-organisms making it unsuitable for food processing is suitable to obtain steam.

Although the water is a strong polar solvent non-polar compounds also dissolve slightly in it. Some such non-polar compounds are highly toxic and even if dissolved in traces it would be at a harmful level. For example the solubility of benzene which is a very strong carcinogen, in water is about 1780 parts per million (1780 ppm). But for the drinking water parameters the maximum permissible value for benzene is 5 parts per billion (5 ppb). That is to say solubility of benzene in water is 350,000 times higher the permissible level. From this we can conclude that water is polluted by dissolving of polar as well as non-polar compounds in it. Oxygen is a completely non-polar molecule, yet oxygen is slightly soluble in water (8 ppm). This oxygen which is slightly soluble in water, is a vital factor for all the aquatic organism for their living processes. All the biological processes in the aquatic organisms occur because of this slightly dissolved oxygen in water.

1.14.1 Water cycle and water pollution

Figure 1.36 shows an environmental water (hydrological) cycle. This indicates the exchange of water among various sectors of the environment. Water is liable to get contaminated in every stage in this cycle. The least polluted water in the cycle is atmospheric water (clouds, water vapour, fog, frost and rain water). Water enters the atmosphere by evaporation of ground water. Since the boiling point of most of the polar compounds (salts etc.) dissolved in water is high, those compounds do not enter the atmosphere with the evaporation of water. For this reason water entering the atmosphere by evaporation is the purest and least polluted water in the environment. However, volatile polar compounds (H_2S, NH_3, NO_2) dissolve in water in the atmosphere. Besides, various chemical compounds produced by photochemical process (NO_2, SO_2, H_2SO_4, HNO_3, NH_4NO_3 etc.) in the atmosphere also dissolve in atmospheric water. Further, very small suspended particles (dust, pollen, bacteria etc.) found in the atmosphere blend with atmospheric water and pollute it.

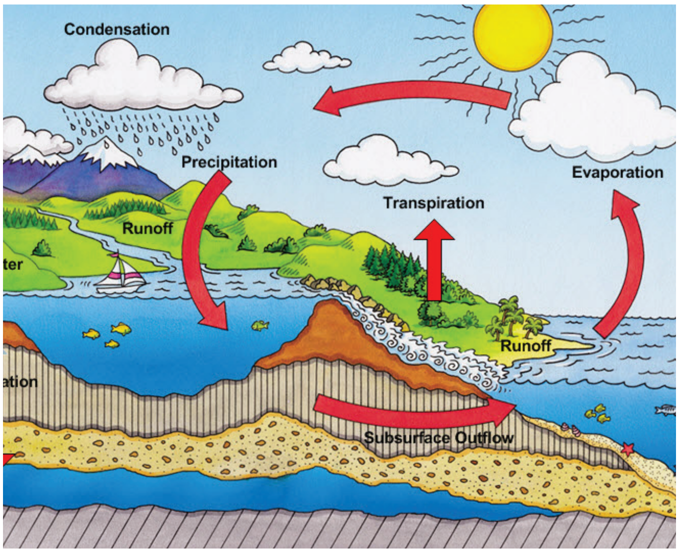


Figure 1.36 Water cycle

This atmospheric water reaches the Earth's surface by way of precipitation in the form of rain, snow, frost, fog and hales. Because of the runoff across the Earth's surface a portion of water reach the Earth's surface, is polluted further. It is also contaminated by the dissolving of salts formed by the weathering of minerals (heavy metal salts), various salts in the soil and various chemicals produced and added to the environment by man (fertilizers, industrial chemicals, agrochemicals). A part of water reaching the Earth's surface by rain percolates to the interior of the Earth (ground water) through the layers of rocks. When water passes through the layers of rocks and minerals, these layers decay. As a result, various mineral salts dissolve in water polluting the ground water as well.

1.14.2 Water quality parameters

As we have mentioned before, many polar as well as non-polar substances dissolve more or less in water. Since, though dissolve in large amounts, are not harmful (e.g. NaCl) Some are very toxic even when dissolved in minute quantities (e.g. heavy metal ions). For this reason it is essential to measure the suitability of water for the task in which it is used. For this, maximum and minimum thresholds or ranges with regard to the dissolved and undissolved substances have been stipulated. These pre-determined standards are called water quality parameters. Various countries and international institutions have published parameters for drinking water and parameters for releasing waste water. When the indicators fall outside the limits of these parameters, water is considered not suitable for the particular task.

Table 1.9 indicates the maximum level or the range of constituents published by the Sri Lanka Standards Institute for water suitable for domestic use.

Table 1.9 Domestic water quality parameters published by the Sri Lanka Standards Institute, Sri Lanka

Parameter	Unit	Maximum value or range
Colour	Hazen Units	15
Turbidity	NTU (Nephelometric Turbidity Unit)	2
pH	-	6.5 - 8.5
Chemical oxygen demand (COD)	mg L^{-1}	10
Total dissolved solids	mg L^{-1}	500
Hardness (as $CaCO_3$)	mg L^{-1}	250
Total phosphate (as PO_4^{3-})	mg L^{-1}	2.0
Arsenic (as As^{3+})	mg L^{-1}	0.01
Cadmium (as Cd^{2+})	mg L^{-1}	0.003
Lead (as Pb^{2+})	mg L^{-1}	0.01
Mercury (as Hg^0 and Hg^{2+})	mg L^{-1}	0.001

1.14.3 Waste Water quality parameters

Let us consider some waste water quality parameters very briefly.

pH value

Here, pH stands for the 'potential of hydrogen'. The pH scale means a scale that expresses the magnitude of acidity or alkalinity of a solution. pH value is the negative logarithm of the hydrogen ion concentration given in mol dm^{-3}.

There are several methods to determine the pH value of a solution.

1. By a titration or some other method: H^+ ion concentration of the solution is determined. By taking its negative logarithm, pH value can be found very accurately.
2. Using pH indicators (pH papers change colour according to the H^+ ion concentration in the solution): An approximate value for pH can be obtained by soaking a pH paper in the relevant solution and comparing the colour with a standard pH colour scale.
3. Using a pH meter: The potential of a special electrode (glass electrode) which changes with the H^+ ion concentration of the solution is measured relative to a standard electrode (Ag/AgCl electrode) and the pH value is read directly.

Figure 1.37 presents pH values of some common aqueous solution which we come across in our day to day life. It has been decided that the pH range of drinking water in Sri Lanka should be 6.5 – 8.5.

Figure 1.37 pH value of some aqueous solutions met in day to day life

Conductivity

The conductivity of an aqueous solution is a measure of the ability of the respective solution to conduct electricity. For this there must be free ions in water. The conductivity of pure water is very low. Pure water contains a very small amount of H^+ and OH^- ions formed by the self-ionization of water (1.0×10^{-7} mol dm^{-3}). The major cause for the conductivity of water is the amount of salts dissolved in water. When salts get dissolved in water they separate into cations and anions which occur as hydrated ions. As these ions are movable in water, they move towards the electrodes when a potential difference is applied, giving rise to conductivity. Water-soluble inorganic salts and organic compounds which can dissociate into ions (organic acids and bases) contribute to conductivity. The organic compounds like glucose and sucrose which dissolve in water but do not dissociate into ions, have very small contribution to the conductivity of water. The conductivity meter is used to measure the conductivity. The unit of measuring conductivity is siemens per centimeter (S cm^{-1}). But in many aqueous solutions which we often come across the conductivity expressed in S cm^{-1} takes a very small value, so microsiemens per centimeter (μS cm^{-1}) is used as the unit.

The conductivities of some aqueous solutions which we find in our day to day life are given in Table 1.10.

Table 1.10 Conductivities of some aqueous solutions which we find in our day to day

Solution	**Conductivity/** μS cm^{-1}
Deionized water	0.1- 5
Distilled water	1-10
Drinking water	50-1000
Milk	1000
0.01 M KCl solution (standard solution for conductivity measurements)	1410
Ground water	100-8000
Sea water	2000-60000
Apple juice	10000
Concentrated acids	60000-900000

Turbidity

Clean water is fully transparent; i,e, light passes through it without any obstruction. But due to addition of various foreign substances, water loses its transparency and appears cloudy. The loss of transparency in water like this is referred to as turbidity. The turbidity is caused by the presence of undissolved, suspended particles, that is fine particles which do not settle under the gravity in water. Because of these small particles light passing through water is scattered. Then, the sample of water appears cloudy or foggy. Presence of suspended particles is one visible instance in water pollution.

Existence of fine colloidal particles in water also leads to its turbidity. Fine clay particles, very small organic and inorganic particles, colonies of small unicellular organism and fine polymer particles are the suspended particles causing turbidity in water.

In order to gauge the turbidity in water, how much of a beam of light is scattered or transmitted by water is measured. The measurement is done by comparing the amount of light scattered by the solution concerned with the amount of light scattered by a solution of known turbidity. The unit of measuring turbidity is Nephlometric Turbidity Unit (NTU). Figure 1.38 shows the NTU values of some solutions with standard turbidity.

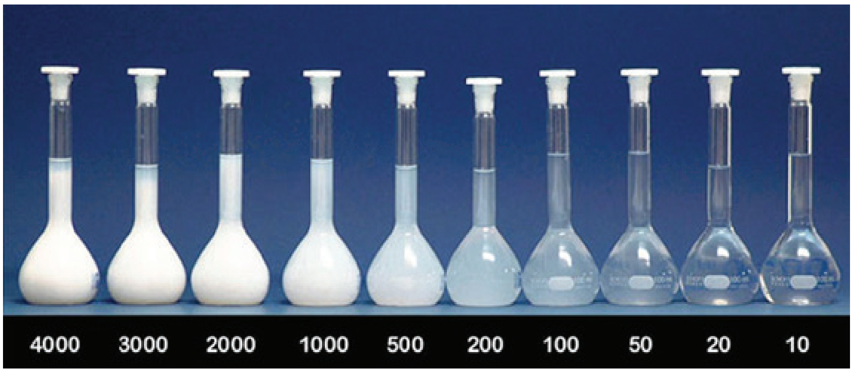


Figure 1.38 NTU values of a solution series with standard turbidity

Hardness of water

Are you living in the dry zone of Sri Lanka? Or have you ever drunk water drawn from a well or taken from any other source when you have visited such an area? Recall the taste of water you consumed. You would remember that the water is brackish in taste. Perhaps you would have observed that your hair becomes sticky and rough after bathing in that water. Why does it happen so? The brackish taste and roughness in hair were due to the high level of hardness in water.

The hardness of water is defined the capacity of water to precipitate soap. The chemical species causing the hardness in water are the polyvalent metal cations dissolved in water. It is the total concentration of Ca^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+}, Al^{3+} and any other polyvalent metal cations. In natural water, the most abundant polyvalent metal cations are Ca^{2+} and Mg^{2+} ions. Therefore Mg^{2+} and Ca^{2+} are the two cations almost contribute to the hardness of natural water. But very rarely there are instances where ions like Mn^{2+}, Fe^{2+} and Al^{3+} also contribute to hardness. Soap is sodium or potassium salts of fatty acids. The carboxylate groups of these salts combine with polyvalent metal cations to form polyvalent metal cation slats of fatty acids. As these salts are less soluble in water they get precipitated. Since the density of this precipitate is less than that of water it floats on water as a soap scum. Hence soap does not function as a cleaning agent until all these polyvalent metal cations are removed. Also, these polyvalent metal cations neutralize the naturally occurring negative charges on the surface of hairs. Then, the hair which repelled one another due to the surface charges on them before come together making them sticky due to the loss of charges.

The permanent hardness in water has no relationship with the anions (e.g. Cl^-, SO_4^{2-}) present in water. The unit of expressing the hardness in water is parts per million calcium carbonate (ppm $CaCO_3$). The hardness level of water are classified approximately as follows (Table 1.11).

Table 1.11 The hardness level of water

Calcium carbonate/ mg L^{-1}	The quality of water
0 -50	Soft
50 -100	Moderately soft
100 - 200	Slightly hard
200 - 300	Moderately hard
300 - 450	Hard
450 +	Very hard

Temporary hardness

The presence of hydrogen carbonate (bicarbonate) ions and carbonate ions at a concentration above the total concentration of the polyvalent metal cations is temporary hardness. This is called temporary hardness because it can be removed by boiling of water. On boiling, the relevant metal cations are precipitated as their carbonates.

$$Ca^{2+} + 2HCO_3^- \xrightarrow{\Delta} CaCO_3 + CO_2 + H_2O$$

$$Mg^{2+} + 2HCO_3^- \xrightarrow{\Delta} MgCO_3 + CO_2 + H_2O$$

Permanent hardness

The presence of carbonate ions and hydrogen carbonate (bicarbonate) ions at a concentration very much below the total concentration of polyvalent metal cations is known as the permanent hardness.

This is termed permanent hardness because here, the metal ions existing in a concentration above the equivalent concentration of carbonate and bicarbonate ions cannot be precipitated by boiling. Permanent hardness can be removed by adding water-soluble carbonates (e.g. Na_2CO_3) from outside.

$$Ca^{2+} + 2Cl^- + Na_2CO_3 \longrightarrow CaCO_3 + 2Na^+ + 2Cl^-$$

Chemical oxygen demand (COD)

The chemical oxygen demand in water is the amount of oxygen required to oxidize the oxidizable substances dissolved in water. The most abundant oxydizable substances present in water are the various organic compounds. These occur in different oxidation states and can finally be oxidized to carbon dioxide or carbonates. Fatty acids, ammonia acids, sugars like glucose and fructose, starch and proteins are among these compounds.

Inorganic species like Fe^{2+} and Mn^{2+} ions also contribute to the chemical oxygen demand of water. COD of water is determined by a titration. The sample is distilled with a known amount of acidified potassium dichromate solution, a strong oxidant. The remaining amount of dichromate ions is titrated with a standard Fe^{2+} solution and the value of COD value is determined.

Mostly the COD value is measured in the waste water discharged by industries. That is because when waster water with high COD is added to water bodies they get polluted.

Maximum COD values of waste water prescribed by the Central Environmental Authority of Sri Lanka for release into different water bodies are given in Table 1.12.

Table 1.12 Maximum COD values recommended by the Central Environmental Authority of Sri Lanka for release into different water bodies

Effluent	Maximum COD value/ mg L^{-1}
Industrial effluents to surface water	250
Industrial effluents to irrigation	400
Industrial effluents to marine water	250
Effluents from rubber factories	400
Effluents from textile factories	250

Disisolved oxygen level

The dissolved oxygen level (DO) is defined as the amount of molecular oxygen (O_2) dissolved in a unit volume of water. The dissolved oxygen comprised the oxygen gas directly dissolved from the 21% of oxygen present on the atmosphere and dissolving of oxygen gas produced by the photosynthetic aquatic plants and organisams (e.g.: algae, cyanobacteria) in the presence of sunlight. Because water molecule is polar and oxygen molecule is non-polar, solubility of oxygen in water is very low. For example at $21^{o}C$ temperature and 1 atm atmospheric pressure at sea level the dissolved oxygen level in water is nearly 9 mg L^{-1} (9 ppm). Owing to various chemical and biological process occurring in water, the dissolved oxygen level in water decreases. When the dissolved oxygen level in water goes below 5 ppm, aquatic organisms are subjected to stress. In a situation like this, stress symptoms such as fish swimming to the water surface and keeping their mouths open to the atmosphere can be observed. When this value drops to 1-2 ppm fish start to die. Sometimes we have heard about sudden deaths of thousands of fish in reservoirs of different parts of the country. The main reason for such an incident is the slump of DO to a very low value.

When the DO decreases to a very low level (close to 0 ppm) anaerobic conditions set in water. This occurs in the bottom of deep lakes and tanks. There are several methods to determine the DO level in water.

1. Direct measurement using an oxygen meter/ probe sensitive to dissolved oxygen

2. By a titration (Winkler method) In this the DO level is determined by a back titration.

In this method, first dissolved oxygen is reacted with manganese ion Mn^{2+} in the basic media to form manganese dioxide.

$$\underset{}{2Mn(OH)_2} + \underset{1\ \text{mol}}{O_2} \xrightarrow{\text{In water}} \underset{2\ \text{mol}}{2MnO_2} + 2H_2O \qquad \text{-------------}\ (1)$$

The manganese oxide formed is reacted with iodide ions in an acid medium.

$$\underset{1\ \text{mol}}{MnO_2} + 4H^+ + 2I^- \longrightarrow Mn^{2+} + \underset{1\ \text{mol}}{I_2} + 3H_2O \qquad \text{-------------}\ (2)$$

The liberated iodine is then titrated with a standard thiosulphate solution.

$$\underset{1\ \text{mol}}{I_2} + \underset{2\ \text{mol}}{2S_2O_3^{2-}} \longrightarrow 2I^- + S_4O_6^{2-} \qquad \text{-------------}\ (3)$$

Four moles of thiosulphate are used up for one mole of oxygen. In the laboratory you can determine the DO level of various water samples by this method.

according to (1), (2), (3)

$$\underset{1\ \text{mol}}{O_2} = \underset{2\ \text{mol}}{MnO_2} = \underset{2\ \text{mol}}{I_2} = \underset{4\ \text{mol}}{S_2O^{2-}_3}$$

Eutrophication

The excessive growth of algae due to addition of nutrients to the water is defined as eutrophication.

When algae grow in abundance they form a thick blanket of their colonies on the water surface. This cuts down the penetration of sunlight to the lower layers of water bodies and prevents photosynthesis happening in them. This reduces the level of dissolved oxygen close to the bottom resulting in the death of aquatic plants and animals. When the dead bodies of these plants and animals are decomposed by aerobic bacteria, the DO level goes down further creating anaerobic conditions. Under anaerobic conditions gases like hydrogen sulphide are produced which make the area foul-smelling. Various nutrients are essential for algae growth but in many instances the limiting nutrient seems to be phosphate ions (PO_4^{3-}). Sometimes it could be nitrate ions (NO_3^-) as well. Because of these two ions becomes the limiting factor, the growth of algae in water bodies is controlled naturally. But by various human activities such as agriculture, disposal of industrial waste and addition of domestic detergents phosphate ions enter the water bodies. This eliminates the limiting conditions of the nutrient concerned ensuring rapid algae growth. This is eutrophication. If the algae growth has to be stopped, the phosphate level of the relevant water body should be maintained below 0.05 ppm. But in many urban wastes this phosphate level is high as 25 ppm.

Figure 1.39 Death of fish due to eutrophication

Occurrence of heavy metal ions in water

Absence of a strict definition for a heavy metal not with standing, the following denotations are in use.

1. In metallurgy a heavy metal is described as a metal whose density is greater than 5 g cm^{-3} or a metal whose relative density stands above 5.
2. In physics heavy metal defined as metal with the atomic number greater than 20.
3. In chemistry they are metals producing cations which give insoluble precipitates with sulphide ions (S^{2-}) and hydroxide ions (OH^-).

In some occasions these heavy metal ions are micronutrients (e.g. Zn^{2+}, Fe^{2+}). In many instances they are harmful and toxic (e.g. Hg^{2+}, Cd^{2+}, Pb^{2+}). Some are indispensable element at low concentrations but are harmful at high concentrations (e.g. Cu^{2+}). Some heavy metal ions do not contribute to any biological process. Heavy metals occur as sediments, deposits in soil, water and on the bottom of water bodies.

Heavy metals occurring as rocks, minerals and their debris in the Earth's crust enter the soil and water after the weathering of rocks. In natural water, heavy metals occur as hydrated ions and complex compounds. Table 1.13 lists the sources of few toxic heavy metals in water and their effects.

Table 1.13 Sources of a few toxic heavy metals in water and their effects

Heavy metal	**Source to water**	**Effect**
As (as As_2O_3)	Industrial waste water, waste of phosphate fertilizers, ground water, fungicides, ectronic items	Carcinogenic, arsenicosis
Cadmium (Cd^{2+})	Industrial emissions, mining waste, metal refining, rechargable batteries	Enzyme deactivation, high blood pressure, kidney damage
Lead (Pb^{2+})	Industrial emissions, mining waste, leaded gasoline, leaded paints, metal pipe welding materials	Kidney and reproductive disfunction, mental retardation of children, anaemia , inhibition of haemoglobin
Mercury (Hg, Hg^{2+})	Industrial waste, traces in many minerals, coal burning, equipment containing mercury (CFL bulbs, thermometers , vacuum apparatus)	Brain damage, insomnia, kidney damage, minamata disease

Arsenicosis

Minamata disease

Figure 1.40 Effects of toxic heavy metals

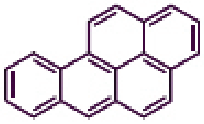
Dissoloved organic compounds

Dissolved organic compounds are compounds which are non – toxic but contribute to biochemical oxygen demand (BOD) or chemical oxygen demand (COD). Sugars, carbohydrates, lipids, fatty acids, amino acids, proteins, soluble hydrocarbons, primary and secondary metabolic products of plants and metabolic wastes products belong to this category. When these substances occur in water they are decomposed by bacteria. This increases the oxygen demand of water and decreases the dissolved oxygen level (DO). This impedes the biological processes in water.

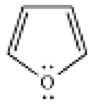
Toxic or hazardous organic compounds

Presence of these compound in water even in trace amount makes water unsuitable for use. Mostly persistent organic compounds belong to this class. Some pesticides, industrial chemicals, halogenated organic compounds, dioxin, furan, polychlorinated biphenyls (PCB), polyaromatic hydrocarbons (PAH) and disinfected by-products are examples for persistent organic compounds.

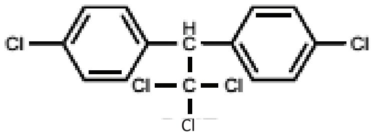
Given below are some organic compounds which are highly toxic or hazardous if present even in trace amounts in water.



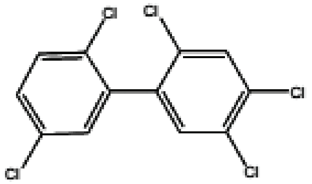
Benzo(a)pyrene(PAH)



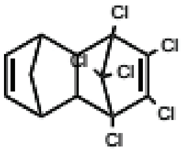
Furan



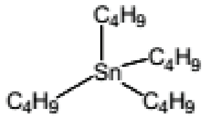
DDT



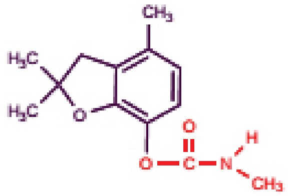
2,2',4,5,5' –pentachlorobiphenyl
(PCB)



Aldrin

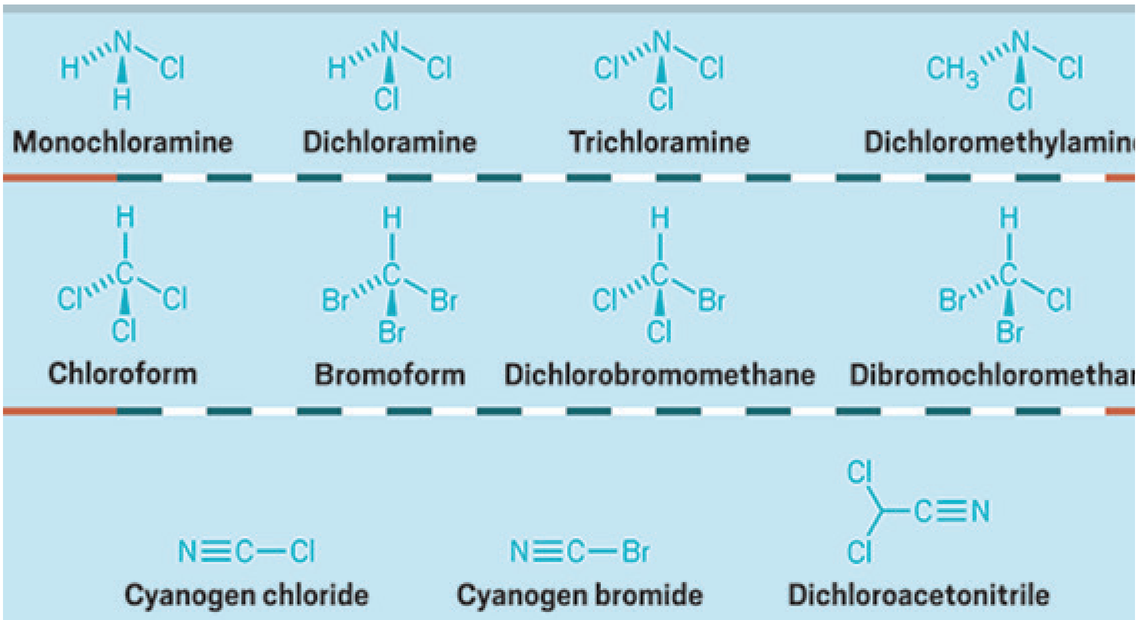


Tetra-n-butyltin



Carbofuran

Water disinfection by-product are the chlorine containing compounds formed by the reaction between hypochlorite ions (OCl^-) and some organic compounds dissolved in water. Hypochlorite ions are produced by chlorine (Cl_2) or hypochlorite salts (e.g. $NaOCl$, $Ca(OCl)_2$) added for disinfecting water. These compounds are poisonous. Some water disinfection by-products are given below.



Plastic additives

At present, virtually there is no consumer product devoid of plastic. Even if it is a food item, many plastic materials are connected with it. Few polymers are used to make all these consumer goods made of plastic. But do you know that many other additives are added when making plastic goods from these polymers? These additives are used to facilitate production, minimize cost, import various mechanical and workable properties and to get consumer attraction. These additives are ordinary chemical substances. During incorrect usage and when disposed to soil or water after use, there is a possibility of releasing these chemicals slowly from the plastic item. Some of these additives are hazardous. There are additives which cause cancer, affect the endocrine system and damage kidneys and various glands in the body. Escape of hazardous catalysts and monomers used in the synthesis of plastics from the finished product is also possible as traces. During the manufacture of plastic various additives are added to facilitate manipulation and mechanization. These also enter our bodies. Hazards additives also enter our bodies due to misuse of plastic items. A common example is the use of empty plastic water bottles to store liquids like coconut oil. Some additives in plastic bottels are insoluble in water but enter into non-polar liquids like coconut oil and enters our body.

Uses of some chemical substances commonly used as plastic additives and their effects are given in Table 1.14.

Table 1.14 Uses of some chemical substances commonly used as plastic additives and their effects

Additive	Uses	Effects
Pthalates Dioctyl phthalate Dimethyl phthalate Di (2-ethylhexyl) phthalate	Make plastics less rigid More flexible	Decrease the hormone secretion of endocrine system Carcinogen
Leaded pigments $PbCrO_4$(yellow) Pb_3O_4 (red) $PbCO_3$ (white)	To get vivid colours to plastic	Central nervous system damage, slow mental growth in children, kidney damage, delayed growth, likely carcinogen, decrease the hormone secretion of endocrine system
Brominated flame retardants Decabromodiphenyl ether Tetrabromobisphenol A	Used as a flame retardant in plastic covers, electrical cables, carpets and in plastic layers	Accumilate in the lipophilic and bio membranes and affect the nervous system. Decrease the endocrine hormone secretion of endocrine system
Bisphenol A	Used as a monomer in polycarbonate plastics item (school water bottles, baby feeding bottles) Used as an antioxdiant in the prduction of PVC. Polymers of bisphenol A is used as a protective coating for corrosion on the inner walls of metallic tin vessels.	Decrease the endocrine hormone secretion of endocrine system Mimics the action of estrogen hormone and disturbs its action Organ development issues in small children

Additive	**Uses**	**Effects**
Monomers and catalytic residues in plastic products Styrene, vinyl chloride, Bisphenol A as monomers Cr, Pb, Cd compounds as catalytic trace residues	Used to make polymers and accelerate polymer resin synthesis	Highly toxic, carcinogenic and mutagenic (monomer residues) Neurological damage and carcinogenic (catalytic residues)
Organotin compounds Dibutyl tin and tributyl tin compounds	Used as stabilizer in PVC and as a catalyst in Polyurethane production	Disturb the action of endocrine hormones in organisms Carcinogenic and mutagenic
Polyaromatic hydrocarbons Pyrene, benzopyrene	Fillers in plastics, processing oil in plastic manufacture	Some compounds are strongly carcinogenic

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