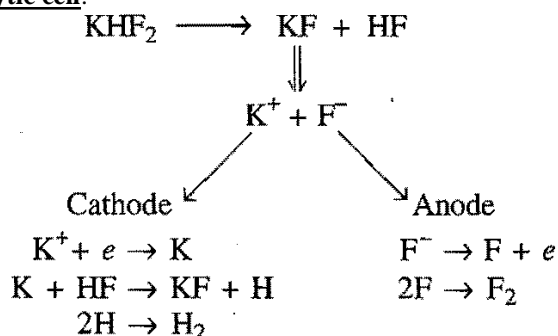


Fluorine

- ❖ **Occurrence:** Fluorine is extremely reactive and, hence does not occur in free state. It is widely found in the combined state as fluorides. The important minerals are:
 - ❖ Fluorspar (Fluorite) CaF_2
 - ❖ Cryolite Na_3AlF_6
 - ❖ Fluorapatite $\text{CaF}_2 \cdot 3\text{Ca}_3(\text{PO}_4)_2$
 - ❖ It is present in small amount as fluorides in plant-ashes, soil, sea water, bones and teeth of animals. It constitutes nearly 0.054% of earth's crust.
- ❖ **Isolation:** Fluorine presented many difficulties in its isolation. It remained a difficult problem in chemistry for many years and after a hard labour of many chemists for about 75 years it could be isolated finally by Moissan in 1886. The reason for its late discovery were its high reactivity and non-conducting nature of hydrofluoric acid. Fluorine attacked the material of the vessels used for its isolation. Carbon vessel was attacked with formation of CF_4 and platinum vessel was reduced to chocolate powder. The vessels of other metals were also affected. The platinum and carbon could not be used as electrodes. Another difficulty experienced was that when the electrolysis of aqueous hydrofluoric acid was carried out, hydrogen and oxygen (ozone) were obtained and when anhydrous hydrofluoric acid was tried it was found to be a bad conductor of electricity.
- ❖ Moissan finally solved the problem and isolated the fluorine by the electrolysis of anhydrous hydrofluoric acid in the presence of potassium hydrogen fluoride using Pt-Ir alloy vessel at -23°C , The electrodes used were also of Pt-Ir alloy.
- ❖ **Modern methods of isolation:** In modern methods fluorine is prepared by electrolysis of a fused fluoride (usually potassium hydrogen fluoride, KHF_2). The electrolytic cells are made of copper, nickel or monel metal. The anode is generally of graphite and the fluorine set free contains some carbon tetrafluoride.

❖ **Reactions in the electrolytic cell:**



Precautions:

- ❖ The electrolyte must be completely dry. In presence of moisture, the evolved fluorine reacts with moisture to form O_2 and O_3 .
- ❖ The parts of the apparatus which come in contact with fluorine must be free from oil and grease.
- ❖ The vessel in which fluorine is collected should also be absolutely dry.
- ❖ The gas must be made free from HF before storing by passing through sodium fluoride (NaF) otherwise HF will attack vessel.
- ❖ The electrolytic cells used are :
 - ❖ (a) Dennis-cells-and-(b)Whytlaw Gray-cell.

Properties:

- ❖ The gas is pale greenish yellow in colour. It can be condensed to yellow liquid at -188°C and pale yellow solid at -223°C .
- ❖ It has pungent odour resembling that of a mixture of ozone and chlorine.
- ❖ It is a poisonous gas but less poisonous than HF gas.

Uses:

- ❖ It is used as an insecticide.
- ❖ It is extensively used for the preparation of various fluorine compounds which have wide applications.
- ❖ Freon, CCl_2F_2 (dichloro-difluoro-methane), is used in refrigerators and cold storage plants.
- ❖ Teflon (C_2F_4)_x, a new plastic, has a very high electrical resistance and is used as insulating material in cables. Teflon is not affected by acids, alkalis and strong oxidising agents.

- ❖ H_2F_2 is used for etching of glass and for removing silica from iron castings.
- ❖ UF_6 is used in the separation of U^{235} from natural uranium by diffusion method.
- ❖ SF_6 has insulating properties. It is used in X-ray and high voltage machines.
- ❖ Sodium fluoroacetate is used as a rat poison.
- ❖ NaF and Na_3AlF_6 (cryolite) are used as insecticides.
- ❖ CuF_2 is used in the ceramic industry and as a flux in soldering, welding and glazing.

❖ **Fluorine storage:**

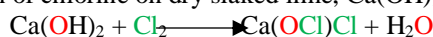
- ❖ The reaction between metals and **fluorine** is relatively slow at room temperature, but becomes vigorous and self-sustaining if the temperature is elevated. Store and use only in vented gas **storage** cabinets or fume hoods.

Bleaching powder ($\text{CaOCl}_2 \cdot \text{H}_2\text{O}$)

- ❖ Bleaching powder is also called calcium chlorohypochlorite because it is considered as a mixed salt of hydrochloric acid and hypochlorous acid.

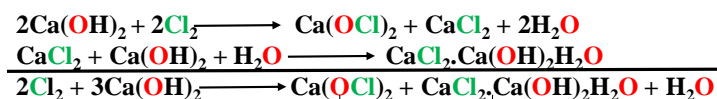


- ❖ It is manufactured by the action of chlorine on dry slaked lime, $\text{Ca}(\text{OH})_2$, at 40°C .



- ❖ This is the Odling view about its formation.

- ❖ There is another view proposed by Clifford according to which bleaching powder is a mixture of calcium hypochlorite and basic calcium chloride.

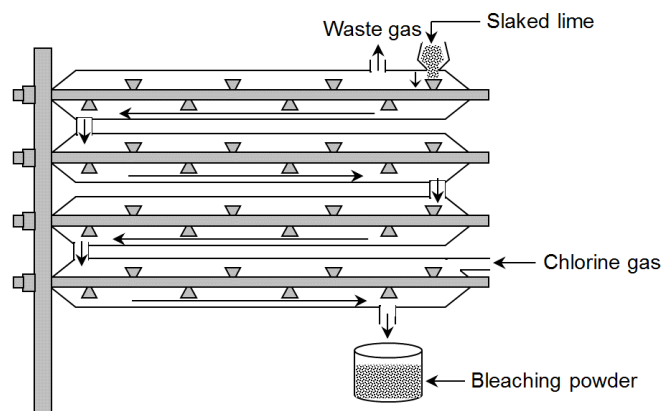


Bleaching Powder

- ❖ The manufacture of bleaching powder is carried out in any one of the following plants:
 - Hasenclever's plant (Old process),
 - Beckmann's plant (Modern process).

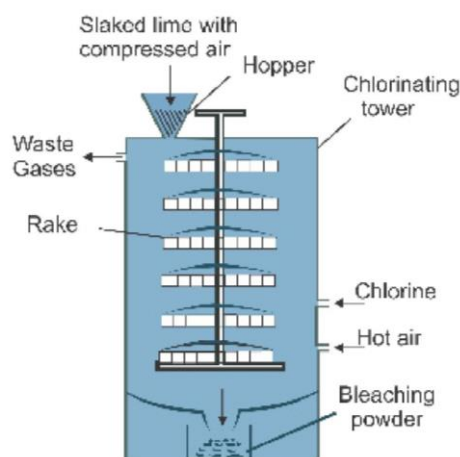
- ❖ **Hasenclever's plant:** It consists of a number of cast-iron horizontal cylinders, each provided with a rotating shaft fitted with blades and arranged as shown in Fig.

- ❖ The dry slaked lime is introduced through the hopper in the uppermost cylinder. It is pushed onwards with the help of the blades when the shaft rotates. A stream of chlorine is admitted from the bottom and passes upwards. The chlorine is completely absorbed by the time till it reaches the top cylinder. Bleaching powder is collected in a barrel placed below an outlet in the lowermost cylinder while the waste gases escape from the top.



Hasenclever plant

- ❖ **Beckmann's plant (Modern process):** It consists of a vertical cast-iron tower. The tower is provided with a hopper at the top, two inlets near the base (one for chlorine and other for hot air) and an exit for waste gases near the top (Fig.)



- ❖ The tower is fitted with eight shelves at different heights each equipped with rotating rakes. The slaked lime is introduced through the hopper and it comes in contact with chlorine which slowly moves upwards. Bleaching powder is collected in a barrel at the base.
- ❖ The chlorine used in the manufacture of bleaching powder should be dilute and the temperature should be maintained below 40°C.

Properties

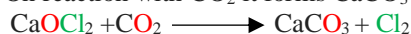
- ❖ It is a pale yellow powder. It has a strong smell of chlorine. It is soluble in water but a clear solution is never formed due to the presence of impurities.
- ❖ On long standing, it undergoes auto-oxidation into calcium chlorate and calcium chloride.
- ❖ In presence of cobalt chloride, CoCl_2 , it loses its oxygen.
- ❖ In presence of a slight amount of a dilute acid, it loses oxygen. On account of the formation of nascent oxygen, it shows oxidising and bleaching properties.
- ❖ The amount of chlorine obtained from a sample of bleaching powder by treatment with excess of dilute acids or carbon dioxide is called available chlorine. A good sample of bleaching powder contains 35-38% of available chlorine.
- ❖ Bleaching powder converts acetone or ethyl alcohol into chloroform.

Uses of Bleaching Powder

- ❖ It is used
- ❖ As a disinfectant and germicide especially in the sterilisation of drinking water.
- ❖ For manufacture of chloroform.
- ❖ For making wool unshrinkable.
- ❖ As an oxidising agent in industry.
- ❖ Mainly as bleaching agent for cotton, linen and wood pulp. However, delicate articles like straw, silk, ivory, etc. are not bleached by bleaching powder.

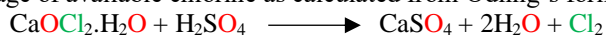
Storage of Bleaching Powder:

Bleaching powder also known as Calcium oxychloride, is kept in air tight container so that it doesn't come under the influence of air. On reaction with CO_2 it forms CaCO_3 and Chlorine.



Estimation of Available Chlorine:

- ❖ The maximum percentage of available chlorine as calculated from Odling's formula comes to 49%.



M. mass = 145

71

145 g of bleaching powder contains = 71 g chlorine

100 g = $71/145 \times 100$

= 49 g Chlorine

The estimation of available chlorine in a given sample of bleaching powder is done volumetrically by:

- ❖ **Iodometric** method or **Arsenite** method.

Phosgene

- ❖ Phosgene is the organic chemical compound with the formula COCl_2 .
- ❖ It is a colorless gas; in low concentrations, its odor resembles freshly cut hay or grass.
- ❖ Phosgene is a valued industrial building block, especially for the production of urethanes and polycarbonate plastics.

- ❖ However, it is very poisonous and was used as a chemical weapon during World War I where it was responsible for 85,000 deaths.
- ❖ In addition to its industrial production, small amounts occur from the breakdown and the combustion of organochlorine compounds

Structure and Basic Properties:

- ❖ Phosgene is a planar molecule as predicted by VSEPR theory. The C=O distance is 1.18 Å, the C–Cl distance is 1.74 Å and the Cl–C–Cl angle is 111.8°.
- ❖ It is one of the simplest acyl chlorides, being formally derived from carbonic acid.

Production:

- ❖ Industrially, phosgene is produced by passing purified carbon monoxide and chlorine gas through a bed of porous activated carbon, which serves as a catalyst:

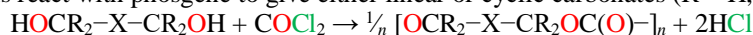
$$\text{CO} + \text{Cl}_2 \rightarrow \text{COCl}_2 \quad (\Delta H_{\text{rxn}} = -107.6 \text{ kJ/mol})$$
- ❖ The reaction is exothermic, therefore the reactor must be cooled. Typically, the reaction is conducted between 50 and 150 °C. Above 200 °C, phosgene reverts to carbon monoxide and chlorine, $K_{\text{eq}}(300 \text{ K}) = 0.05$. World production of this compound was estimated to be 2.74 million tonnes in 1989.
- ❖ Because of safety issues, phosgene is often produced and consumed within the same plant, and extraordinary measures are made to contain it.

Uses:

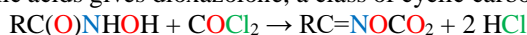
The great majority of phosgene is used in the production of isocyanates, the most important being toluene diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI). These two isocyanates are precursors to polyurethanes. The reaction of an organic substrate with phosgene is called phosgenation.

Synthesis of carbonates:

- ❖ Significant amounts are also used in the production of polycarbonates by its reaction with bisphenol A. Polycarbonates are an important class of engineering thermoplastic found, for example, in lenses in eyeglasses. Diols react with phosgene to give either linear or cyclic carbonates (R = H, alkyl, aryl):

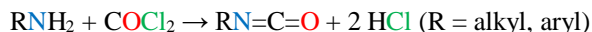


- ❖ Phosgenation of hydroxamic acids gives dioxazolone, a class of cyclic carbonate esters:



Synthesis of isocyanates:

- ❖ The synthesis of isocyanates from amines illustrates the electrophilic character of this reagent and its use in introducing the equivalent of CO²⁺.



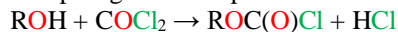
- ❖ Such reactions are conducted in the presence of a base such as pyridine that absorbs the hydrogen chloride.

Laboratory uses:

- ❖ In the research laboratory phosgene still finds limited use in organic synthesis. A variety of substitutes have been developed, notably trichloromethyl chloroformate (diphosgene), a liquid at room temperature, and bis(trichloromethyl) carbonate (triphosgene), a crystalline substance. Aside from the above reactions that are widely practiced industrially, phosgene is also used to produce acyl chlorides and carbon dioxide from carboxylic acids:



- ❖ Such acid chlorides react with amines and alcohols to give, respectively, amides and esters, which are commonly used intermediates. Thionyl chloride is more commonly and more safely employed for this application. A specific application for phosgene is the production of chloroformic esters:



- ❖ Phosgene is stored in metal cylinders. The outlet is always standard, a tapered thread that is known as CGA 160.

Safety:

- ❖ Phosgene is an insidious poison as the odour may not be noticed and symptoms may be slow to appear.
- ❖ The odour detection threshold for phosgene is 0.4 ppm, four times the threshold limit value. Its high toxicity arises from the action of the phosgene on the proteins in the pulmonary alveoli, the site of gas exchange: their damage disrupts the blood–air barrier, causing suffocation. It reacts with the amines of the proteins, causing crosslinking by formation of urea-like linkages, in accord with the reactions discussed above. Phosgene detection badges are worn by those at risk of exposure.
- ❖ Sodium bicarbonate may be used to neutralise liquid spills of phosgene. Gaseous spills may be mitigated with ammonia.

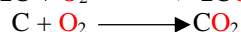
Phosgene Storage:

At room temperature (70°F), **phosgene** is a poisonous gas. With cooling and pressure, **phosgene** gas can be converted into a liquid so that it can be shipped and **stored**. When liquid **phosgene** is released, it quickly turns into a gas that stays close to the ground and spreads rapidly.

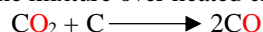
Carbon Monoxide

Manufacture:

- ❖ Carbon monoxide is obtained in the form of water gas and producer gas when air (moist) is passed over a bed of white hot coke. The following reactions may occur.



- ❖ Carbon dioxide is reduced by passing the mixture over heated charcoal.



The CO produced, always consists of N₂, H₂, CO₂, etc.

Properties:

- ❖ It is a colourless and odourless gas.
- ❖ It is slightly soluble in water.
- ❖ It is a combustible gas but does not support combustion.
- ❖ Its density is nearly equal to the density of air.
- ❖ It is highly poisonous in nature. One part in 100 parts of air causes death in few minutes. The poisonous nature of CO is due to the fact that it combines with haemoglobin.
- ❖ It is not decomposed by heat.
- ❖ It is neutral to litmus.
- ❖ It burns with blue flame to form CO₂. This is an exothermic process.
- ❖ It is a good reducing agent as it takes up oxygen and converted into CO₂, This property is utilised for the extraction of metals from their oxides.

Uses:

- ❖ It is used as a fuel in the form of water gas (CO + H₂) and producer gas (CO + N₂).
- ❖ CO is used in the manufacture of methanol, synthetic petrol, formic acid and phosgene gas (highly poisonous gas).
- ❖ It is used as a reducing agent in the extraction of iron.
- ❖ It is used in the extraction of nickel (Mond's process).

Storage of CO:

- ❖ Carbon monoxide is shipped and stored in high-pressure cylinders, tube trailers or ISO modules, depending on the quantity required by the consumer.
- ❖ These containers are manufactured according to applicable codes and specifications for the temperatures and pressures involved.

CO Hazards:

- ❖ Breathing **CO** can cause headache, dizziness, vomiting, and nausea. If **CO** levels are high enough, you may become unconscious or die. Exposure to moderate and high levels of **CO** over long periods of time has also been linked with increased risk of heart disease.

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