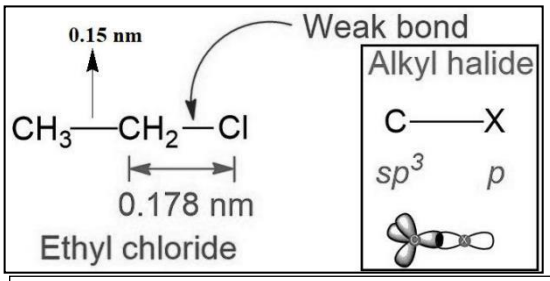
UNIT-III: Structure and Uses of Alkyl halides

Structure and uses of ethylchloride, Chloroform, trichloroethylene, tetrachlorethylene, dichloromethane, tetra chloromethane and iodoform.

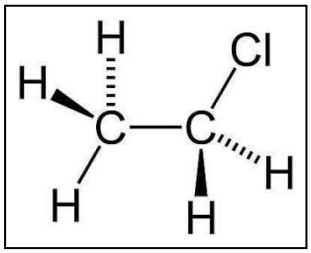
❖ Ethylchloride

- Chloroethane or monochloroethane, commonly known by its old name ethylchloride, is a chemical compound with chemical formula C_2H_5Cl, once widely used in producing tetraethyllead, a gasoline additive.

Chemical formula	C_2H_5Cl
Molar mass	64.51 g/mol
Appearance	Colorless gas
Odor	Pungent
Density	0.8898 g/cm^3 (25° C)
Melting point	−138.7 °C
Boiling point	12.27 °C decomposes at 510° C
Solubility in water	0.574 g/100 mL (20 °C)
Solubility	Soluble in alcohol, ether
Refractive index (n_D)	1.3676 (20 °C); 1.001 (25 °C)
Viscosity	0.279 cP
Dipole moment	2.06 D



10 Ångström is equal to 0.1 nanometers (nm).



- Chloroethane is produced by hydrochlorination of ethene: $\mathbf{C_2H_4 + HCl \rightarrow C_2H_5Cl}$

- **Uses:**

- The major use of Chloroethane was to produce tetraethyllead (TEL: It is a petro-fuel additive), an anti-knock

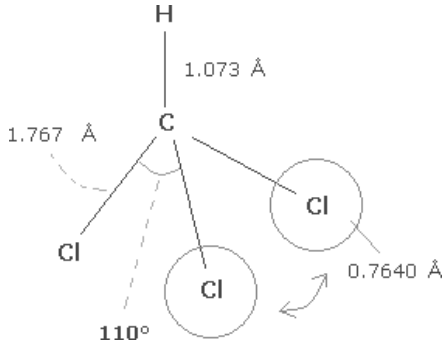
Gasoline or gas for short (American English), or petrol (British English), is a transparent, petroleum-derived liquid that is used primarily as a fuel in internal combustion engines.

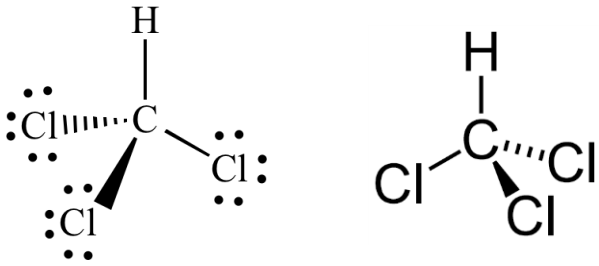
additive for gasoline.

- Chloroethane has been used as a refrigerant, an aerosol spray propellant, an anesthetic, and a blowing agent for foam packaging.
- In dentistry, Chloroethane is used as one of the means of diagnosing a 'dead tooth', i.e. one in which the pulp has died. A small amount of the substance is placed on the suspect tooth using a cotton wad. Chloroethane's low boiling point creates a localized chilling effect. If the tooth is still alive this should be sensed by the patient as mild discomfort that subsides when the wad is removed.
- Chloroethane is not classifiable as to its carcinogenicity to humans, but toxic over-exposure starts at 9% to 12% concentrations, the heart rate drops.

❖ Chloroform

- Chloroform, or trichloromethane, is an organic compound with formula $CHCl_3$. It is a colorless, sweet-smelling, dense liquid that is produced on a large scale as a precursor to **PTFE (Polytetrafluoroethylene)**. It is also a precursor to various **refrigerants**.
- The molecule adopts tetrahedral molecular geometry.



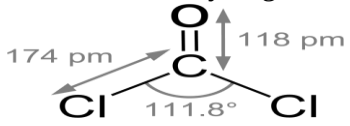


Lewis structure of Chloroform

Chemical formula	$CHCl_3$
IUPAC name	Trichloromethane
Other names	Methane trichloride; Methyl trichloride; TCM; Methenyl trichloride; Freon 20; Refrigerant-20
Molar mass	119.38 g/mol
Appearance	Colorless liquid
Odor	ethereal odor
Density	1.48 g/cm^3 (25° C)
Boiling point	61.2 °C
Solubility in water	8.09 g/L (20 °C)
Solubility	Soluble in benzene; Miscible in diethyl ether
Molecular shape	Tetrahedral

- Chloroform volatilizes readily from soil and surface water and undergoes degradation in air to produce phosgene, dichloromethane, formyl chloride, carbon monoxide, carbon dioxide, and hydrogen chloride. Its half-life in air ranges from 55 to 620 days.

$$\mathbf{2\ CHCl_3 + O_2 \rightarrow 2\ COCl_2 + 2\ HCl}$$



Phosgene

- In industry, chloroform is produced by heating a mixture of chlorine and either chloromethane or methane. At 400 – 500°C, a free radical halogenation occurs, converting these precursors to progressively more chlorinated compounds:

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

$$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$$
$$CH_2Cl_2 + Cl_2 \rightarrow CHCl_3 + HCl$$

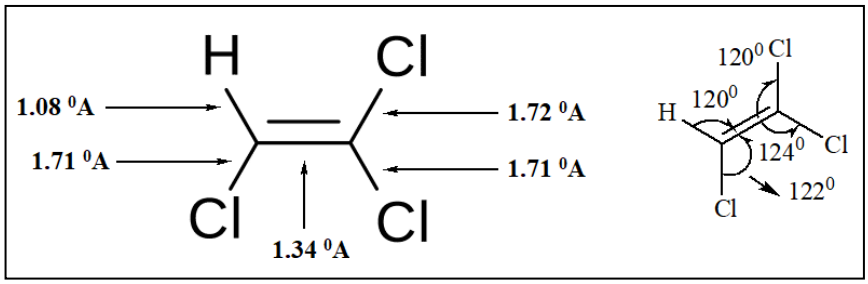
- **Uses:**

- The hydrogen attached to carbon in chloroform participates in hydrogen bonding. Worldwide, chloroform is also used in pesticide formulations, as a solvent for fats, oils, rubber, waxes, gutta-percha, and resins, as a cleansing agent, grain fumigant, in fire extinguishers, and in the rubber industry..
- Chloroform is also used to extract and purify penicillin.
- Chloroform used for extraction and purification of Alkaloids.
- Chloroform was popular as an **anesthetic** from the mid-1800s to around 1900, but it was found to cause death from paralysis. It also depresses most of the body's other organs, including the blood vessels, liver, pancreas, and kidneys. It is toxic to the liver. Oxygen-gas mixtures (oxygen with nitrous oxide, for example) regained use in anesthesia after 1900, and chloroform was replaced by safer compounds after about 1940.
- Chloroform gives relieve the pain of childbirth.
- Although chloroform did carry some risk of heart failure, it was more pleasant to take and more powerful than ether. Queen Victoria's anesthetist, an inhaler to regulate the amount of chloroform administered to a patient so that patient felt no pain but remained conscious.

❖ Trichloroethylene

- The chemical compound trichloroethylene is a halocarbon commonly used as an industrial solvent. It is a clear non-flammable liquid with a sweet smell.
- Trichloroethylene is not a persistent chemical in the atmosphere; its half-life in air is about 7 days.

Chemical formula	C_2HCl_3
IUPAC name	trichloroethene
Other names	1,1,2-Trichloroethene; 1,1-Dichloro-2-Chloroethylene; Acetylene; 1-Chloro-2,2-Dichloroethylene
Molar mass	131.4 g/mol
Appearance	Colorless liquid
Odor	chloroform-like
Density	1.46 g/cm^3 (25° C)
Boiling point	87.2 °C
Solubility in water	1.28 g/L (20 °C)
Solubility	Soluble in benzene, ether, ethanol, chloroform



- When1,2-dichloroethane heated to around 400°C is converted to trichloroethylene:

$$ClCH_2CH_2Cl + 2Cl_2 \rightarrow ClCH{=}CCl_2 + 3HCl$$

• Uses

- The main use of trichloroethylene is in the vapor degreasing of metal parts.
- Trichloroethylene is also used as an extraction solvent for greases, oils, fats, waxes, and tars, a chemical intermediate in the production of other chemicals, and as a refrigerant.
- Trichloroethylene is used in consumer products such as typewriter correction fluids, paint removers/strippers, adhesives, spot removers, and rug-cleaning fluids.
- Trichloroethylene was used in the past as a general anesthetic.

• Acute Effects:

- Central nervous system effects are the primary effects noted from acute inhalation exposure to trichloroethylene in humans, with symptoms including sleepiness, fatigue, headache, confusion, and feelings of euphoria. Effects on the liver, kidneys, gastrointestinal system, and skin have also been noted.

Dichloromethane

- Dichloromethane (DCM, or methylene chloride) is an organic compound with the formula CH_2Cl_2. This colorless, volatile liquid with a moderately sweet aroma is widely used as a solvent. Although it is not miscible with water, it is miscible with many organic solvents.
- Natural sources of dichloromethane include oceanic sources, ***macroalgae, wetlands***, and **volcanoes.** However, the majority of dichloromethane in the environment is the result of industrial emissions.

Macroalgae are Seaweed refers to several species of macroscopic, multicellular, marine algae

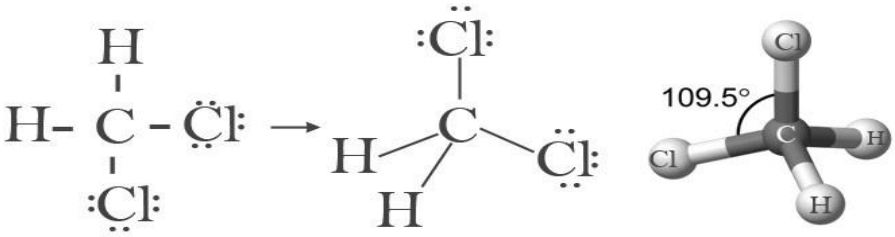
- DCM is produced by treating either chloromethane or methane with chlorine gas at 400–500 °C.

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

$$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$$

Chemical formula	CH_2Cl_2
IUPAC name	Dichloromethane
Other names	Methylene chloride, methylene dichloride
Molar mass	84.93 g/mol
Appearance	Colorless liquid
Odor	chloroform-like
Density	1.32 g/cm^3 (25° C)
Boiling point	39.6 °C
Solubility in water	25.6 g/L (20 °C)
Solubility	Miscible in ethyl acetate, alcohol, hexanes, benzene, CCl_4, diethyl ether, $CHCl_3$

Molecule	Average carbon–chlorine bond length
 Chloromethane	1.783 Å
 Dichloromethane	1.772 Å
 Trichloromethane	1.767 Å
 Tetrachloromethane	1.766 Å



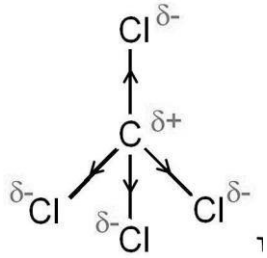
Lewis structure 3-D structure

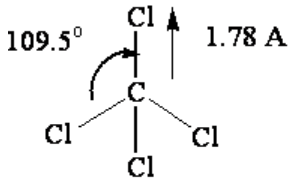
- **Uses:**

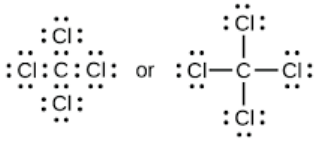
- DCM's volatility and ability to dissolve a wide range of organic compounds makes it a useful solvent for many chemical processes.
- It is widely used as a paint stripper and a degreaser.
- In the food industry, it has been used to decaffeinate coffee and tea as well as to prepare extracts of hops and other flavorings. Its volatility has led to its use as an aerosol spray propellant and as a blowing agent for polyurethane foams.

❖ Tetrachloromethane

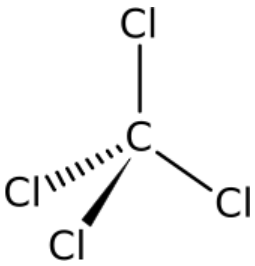
- Tetrachloromethane also known by many other names Carbon tetrachloride.
- It was formerly widely used in fire extinguishers, as a precursor to refrigerants and as a cleaning agent. It is a colourless liquid with a "sweet" smell that can be detected at low levels.
- It has practically no flammability at lower temperatures.





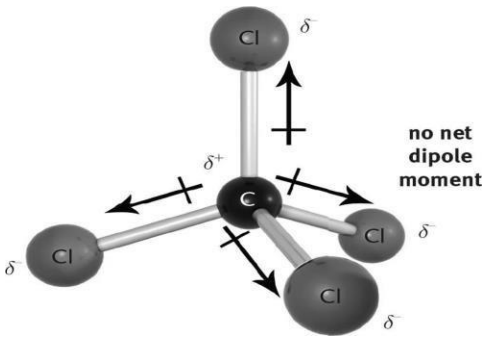


Lewis Structure



Carbon tetrachloride

- Why is the carbon tetrachloride molecule nonpolar and yet the bonds in it are polar?
  - Carbon tetrachloride molecule nonpolar and yet the bonds in it are polar because of its molecular geometry. In order for a molecule to be polar, it must have a net dipole moment. In the case of carbon tetrachloride, that net dipole moment is equal to zero.
  - The **C−Cl** bond is indeed quite polar. Chlorine is more *electronegative* than carbon, which means that it will attract the **bonding electrons** more.
  - Consequently, a *partial negative charge*, (**δ-**) will appear on the chlorine atom and a *partial positive charge*, (**δ+**) will appear on the carbon atom.
  - A **bond dipole moment** will thus appear for each of the four C−Cl bonds that exist in a molecule of carbon tetrachloride. Because these four bonds are **identical**, theese dipole moments will also be **identical** in magnitude.
  - Now, carbon tetrachloride has a **tetrahedral** molecular geometry. This means that the *resultant* of any three **C−Cl** bonds will always
    - ✓ *be **equal in magnitude***
    - ✓ *have an **opposite direction***
  - In other words, no **net dipole moment** will exist because the four bond dipole moments that arise from the polar **C−Cl** bonds will **cancel each other out**.



Chemical formula	CCl_4
Molecular shape	Tetrahedral
IUPAC name	Carbon tetrachloride, Tetrachloromethane
Other names	Carbon chloride, Methane tetrachloride, Methyl tetrachloride, Perchloromethane,
Molar mass	153.81 g/mol
Appearance	Colorless liquid
Odor	ether-like
Density	1.58 g/cm^3 (25° C)
Boiling point	76.7 °C
Solubility in water	0.097 g/L (20 °C)
Solubility	Soluble in alcohol, ether, chloroform, benzene, naphtha, CS2, formic acid

- It is mainly produced from methane: $\mathbf{CH_4 + 4\ Cl_2 \rightarrow CCl_4 + 4\ HCl}$

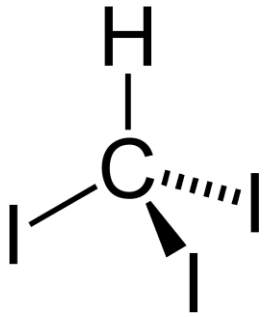
- **Uses**

- Carbon tetrachloride was used to produce the chlorofluorocarbon refrigerants **R-11** (trichlorofluoromethane) and **R-12** (dichlorodifluoromethane).
- Carbon tetrachloride has also been used in the detection of neutrinos.
- Use of carbon tetrachloride in determination of oil has been replaced by various other solvents, such as tetrachloroethylene. Because it has no **C-H** bonds, carbon tetrachloride does not easily undergo free-radical reactions. It is a useful solvent for halogenations.
- Carbon tetrachloride was widely used as a dry cleaning solvent, as a refrigerant, and in lava lamps.
- Carbon tetrachloride is one of the most potent hepatotoxins (toxic to the liver), so much so that it is widely used in scientific research to evaluate Hepatoprotective agents.
- Under high temperatures in air, it forms poisonous phosgene

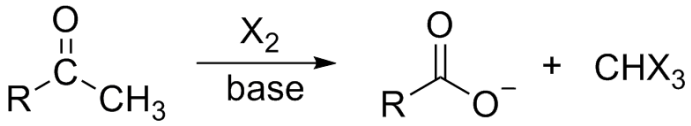
❖ Iodoform

- Iodoform is the organoiodine compound with the formula **CHI_3**. A pale yellow, crystalline, volatile substance, it has a penetrating and distinctive odor and, analogous to chloroform, sweetish taste.
- It is occasionally used as a disinfectant. It is also known as tri-iodomethane, carbon triiodide, and methyl triiodide.

Chemical formula	CHI_3
IUPAC name	Triiodomethane
Other names	Iodoform
Molar mass	393.73 g/mol
Appearance	Pale, light yellow, opaque crystals
Odor	Saffron-like
Density	1.32 g/cm^3 (25° C)
Melting point	119° C
Solubility in water	100 mg/L (20 °C)
Solubility	Miscible in diethyl ether, acetone, ethanol.



- Iodoform can produced by the exhaustive halogenationof a methyl ketone**.**



R = H, alkyl, aryl
X = Cl, Br, I

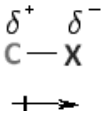
- **Uses:**

- The compound finds small-scale use as a disinfectant.
- It was used in medicine as a healing and antiseptic dressing for wounds and sores.
- It is the active ingredient in many ear powders for dogs and cats, along with zinc oxide and propanoic acid, which are used to prevent infection and facilitate removal of ear hair.

- ***Halogens and the Character of the Carbon-Halogen Bond***

- With respect to electronegativity, halogens are more electronegative than carbons. This results in a carbon-halogen bond that is polarized. As shown in the image below, carbon atom has a partial positive charge, while the halogen has a partial negative charge.

The Polar C-X Bond



- The relationship between the halogens and electronegativity. As we move up the periodic table from iodine to fluorine, electronegativity increases. Electronegativity I < Br < Cl < F

- The relationships between bond length, bond strength, and molecular size. As we progress down the periodic table from fluorine to iodine, molecular size increases. As a result, we also see an increase in bond length. Conversely, as molecular size increases and we get longer bonds, the strength of those bonds decreases.

Bond length	C-F	<	C-Cl	<	C-Br	< C-I
Bond strength	C-I	<	C-Br	<	C-Cl	< C-F
Molecular size	F	<	Cl	<	Br	< I

- ***The influence of bond polarity***

- Of the four halogens, fluorine is the most electronegative and iodine the least. That means that the electron pair in the carbon-fluorine bond will be dragged most towards the halogen end. Looking at the methyl halides as simple examples:

- The electro negativities of carbon and iodine are equal and so there will be no separation of charge on the bond.