Tetra-halides (Carbon tetrachloride or tetrachloromethane, CCl_4).

It is the most important tetrahalogen derivative of methane.

(1) **Manufacture**

(i) **From methane**: Chlorination of methane with excess of chlorine at 400°C yields impure carbon tetrachloride.

$$CH_4 + 4Cl_2 \xrightarrow{400^\circ C} CCl_4 + 4HCl$$

Methane used in this process is obtained from natural gas.

(ii) **From carbon disulphide**: Chlorine reacts with carbon disulphide in presence of catalysts like iron, iodine, aluminium chloride or antimony pentachloride.

$$CS_2 + 3Cl_2 \longrightarrow CCl_4 + \underset{\text{Sulphur monochlori de}}{S_2Cl_2}$$

S_2Cl_2 further reacts with CS_2 to form more of carbon tetrachloride.

$$CS_2 + 2S_2Cl_2 \longrightarrow CCl_4 + 6S$$

Carbon tetrachloride is obtained by fractional distillation. It is washed with sodium hydroxide and then distilled to get a pure sample.

(iii) **From propane**: Propane is reacted with chlorine at about 400°C and at a pressure of 70-100 atmosphere.

$$C_3H_8 + 9Cl_2 \xrightarrow[\text{Pressure}]{\text{Heat}} \underset{\substack{\text{Carbon tetrachlor ide}\\(\text{Liquid})}}{CCl_4} + \underset{\substack{\text{Hexachloro ethane}\\(\text{Solid})}}{C_2Cl_6} + 8HCl$$

(2) **Physical properties**

(i) It is a colorless liquid having characteristic smell.

(ii) It is non-inflammable and poisonous. It has boiling point 77°C.

(iii) It is insoluble in water but soluble in organic solvents.

(iv) It is an excellent solvent for oils, fats, waxes and greases.

(3) **Chemical properties:** Carbon tetrachloride is less reactive and inert to most organic reagents. However, the following reactions are observed.

(i) **Reaction with steam** (Oxidation**):**Carbon tetrachloride vapours react with steam above 500°C to form phosgene, a poisonous gas.

$$CCl_4 + H_2O \xrightarrow{500\,^\circ C} \underset{\text{Phosgene (Carbonyl chloride)}}{COCl_2} + 2HCl$$

(ii) **Reduction**: It is reduced by moist iron filling into chloroform.

$$CCl_4 + 2H \xrightarrow{Fe/H_2O} CHCl_3 + HCl$$

(iii) **Hydrolysis**: On heating with aqueous potassium hydroxide it forms carbon dioxide which combines with potassium hydroxide to give KCl and potassium carbonate (Inorganic salts).

$$CCl_4 + 4KOH \xrightarrow{-4KCl} \underset{\text{Unstable}}{[C(OH)_4]} \xrightarrow{-2H_2O} CO_2 \xrightarrow{2KOH} K_2CO_3 + H_2O$$

(iv) **Reaction with phenol** (Reimer-tiemann reaction**)** : It combines with phenol in presence of sodium hydroxide to form salicylic acid.

$$C_6H_5OH + CCl_4 \xrightarrow{+4NaOH} \underset{\text{Salicylic acid}}{C_6H_4\begin{matrix}OH\\COOH\end{matrix}} + 4NaCl + 2H_2O$$

(4) **Uses**

(i) It is used as a fire extinguisher under the name **pyrene**. The dense vapours form a protective layer on the burning objects and prevent the oxygen or air to come in contact with the burning objects.

(ii) It is used as a solvent for fats, oils, waxes and greases, resins, iodine etc.

(iii) It finds use in medicine as **helmenthicide** for elimination of hook worms.