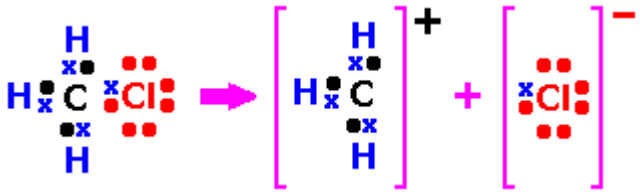
CFCs, Ozone and Free Radicals

- **If enough energy** is supplied by heat or by visible/uv electromagnetic radiation, or the is weak enough, a **covalent bond can break in two ways**. This illustrated with the molecule **chloromethane CH_3Cl**.

- **Unevenly** where the electron bond pair can stick with one fragment and a positive and negative ion form.

e.g. **CH_3Cl ==> CH_3^+ + Cl^-** (at AS-A2 level this is called **heterolytic bond fission**)

-  shows what happens to the molecule

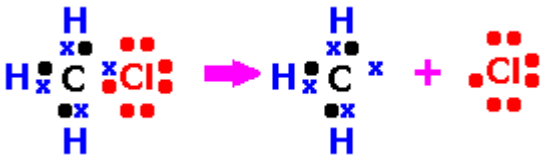
or

- **Evenly**, where the bonding pair of electrons are equally divided between two highly reactive fragments called **free radicals**.

- Free radicals are characterised by having **an unpaired electron** not involved in a chemical bond.

- The · means the 'lone' electron on the free radical, which is not part of a bond anymore, and wants to pair up with another electron to form a stable bond - that's why free radicals are so reactive!

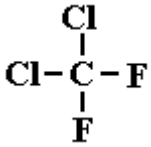
e.g. **CH_3Cl ==> $CH_3\cdot$ + $\cdot Cl$** (this is called **homolytic bond fission**)

-  shows what happens to the molecule

- In the stratosphere small amounts of unstable **ozone O_3** (**trioxygen**) are formed by free radical reactions.
- The **chemistry of free radicals** is important in the current environmental issue of **ozone layer depletion**.

Chlorofluorocarbons (**CFC**'s) are organic molecules containing carbon, fluorine and chlorine

e.g. dichlorodifluoromethane has the formula CCl_2F_2 .



- They are very useful low boiling organic liquids or gases, until recently, extensively used in **refrigerators** and **aerosol sprays** e.g. repellents.
- They are **relatively unreactive, non-toxic and have low flammability**, so in many ways they are 'ideal' for the job they do.
- However it is their chemical stability in the environment that eventually causes the ozone problem but first we need to look at **how ozone is formed and destroyed** in a '**natural cycle**'. This presumably has been in balance for millions of years and explains the uv ozone protection in the upper atmosphere.

- **Ozone is formed in the stratosphere by free radical reactions**.
  - 'ordinary' stable **oxygen O_2** (**dioxygen**) is split (dissociates) into two by high energy **ultraviolet radiation** (**uv photon energy 'wave packets**) into two oxygen atoms (which are themselves radicals) and then a 'free' oxygen atom combines with an oxygen molecule to form ozone.

  - **O_2 + uv ==> $2O^{\cdot}$** then **$O^{\cdot}$ + O_2 ==> O_3**

  - The ozone is a highly reactive and unstable molecule and decomposes into dioxygen when hit by other uv light photons. The oxygen atom radical can do several things including ...
  - **O_3 + uv ==> O_2 + $O^{\cdot}$**
  - This last reaction is the main **uv screening effect** of the upper atmosphere and the ozone absorbs a lot of the harmful incoming uv radiation from the Sun.

  - **If the ozone levels are reduced more harmful uv radiation reaches the Earth's surface and can lead to medical problems such as increased risk of sunburn and skin cancer and it also accelerates skin aging processes.**
  - **There is strong evidence to show there are 'holes' in the ozone layer with potentially harmful effects, so back to the CFC problem!**

- The **chemically very stable CFCs diffuse up into the stratosphere** and decompose when hit by ultraviolet light (uv) to produce free radicals, including free chlorine atoms, which themselves are highly reactive free radicals.
  - e.g. **CCl_2CF_2 ==> $CClF_2^{\cdot}$ + $Cl^{\cdot}$** (note the C-Cl bond is weaker than the C-F bond)

- The **formation of chlorine atom radicals is the root of the problem** because they readily react with ozone and change it back to much more stable ordinary oxygen.
  - **O_3 + $Cl^{\cdot}$ ==> O_2 + $ClO^{\cdot}$** bye bye ozone! and no uv removed in the process!
  - and then: **ClO + O ==> Cl + O_2** , which means the 'destructive' Cl is still around!
  - The two reactions above involving chlorine atoms are known as a **catalytic cycle** because the chlorine atoms from CFC's etc. act as a catalyst in the destruction of ozone.
- Therefore **many countries are banning the use of CFCs**, but not all despite the fact that scientists predict it will take many years for the depleted ozone layer to return to its 'original' O_3 concentration and alternatives to CDC's are already being marketed.