**NOTES**

# Ozone and CFC's

### The Chronology of the Ozone/CFC Saga

1970/1 Fears are voiced about the threat to the ozone layer posed by SST's such as the Anglo–French Concorde and the proposed Boeing SST.

1974 F. S. Rowland and M. Molina warn of the dangers of ozone depletion from the CFC's in aerosols etc.

1978 US bans CFC's as propellants for aerosols.

1979 EC adopts precautionary policy—voluntary agreement to limit CFC production.

1981 UNEP sets up working group to draft framework convention for protection of the ozone layer.

1985 Measurements from the British Antarctic Survey reported by Joe Farman and colleagues. Vienna Convention for the Protection of the Ozone Layer signed March 1985 by 20 nations, to come into force by September 1989.

1987 Evidence of an enlarged Ozone Hole over the Antarctic by U.S. airborne investigation using NASA's ER-2 (modified U2 spy plane). Montreal Protocol signed 16th September 1987.

1990 Revised protocol with phase-out by 2000.

### The Chemistry of the Ozone Cycle

(i) Ozone production occurs most abundantly in the stratosphere through the photo-disassociation of oxygen molecules into the constituent atoms caused by ultraviolet radiation (1). Free radicals of oxygen then combine with oxygen molecules to form ozone (2).

$$O_2 \longrightarrow O + O. \tag{1}$$

$$O + O_2 \longrightarrow O_3. \tag{2}$$

(ii) Ozone is repeatedly destroyed and reformed (3) until it is destroyed finally (4) by the collision with an oxygen radical.

$$\mathrm{O_3} \rightleftharpoons \mathrm{O_2} + \mathrm{O} \tag{3}$$

$$\mathrm{O} + \mathrm{O_3} \longrightarrow 2\mathrm{O_2} \tag{4}$$

(iii) The destruction of ozone is catalysed by free radials of nitric oxide (NO), chlorine (Cl), bromine (Br) and hydrogen (H). The two stages in the case of the chlorine radical are illustrated as follows:

$$\begin{aligned} \mathrm{O_3} + \mathrm{Cl} &\longrightarrow \mathrm{O_2} + \mathrm{ClO}, \\ \mathrm{O} + \mathrm{ClO} &\longrightarrow \mathrm{O_2} + \mathrm{Cl}. \end{aligned} \tag{5}$$

Here the intermediate compound is a molecule of chlorine monoxide (ClO). The catalysed reaction may be denoted alternatively as follows:

$$\big\{\mathrm{O_3} + \mathrm{Cl}\big\} + \mathrm{O} \to \mathrm{O_2} + \big\{\mathrm{O} + \mathrm{ClO}\big\} \to 2\mathrm{O_2} + \mathrm{Cl}. \tag{6}$$

The net effect is the same as that of (4).

The general case is conveyed by the equation

$$\begin{aligned} \mathrm{O_3} + \mathrm{X} &\longrightarrow \mathrm{O_2} + \mathrm{XO}, \\ \mathrm{O} + \mathrm{XO} &\longrightarrow \mathrm{O_2} + \mathrm{X}, \end{aligned} \tag{7}$$

where X is Cl, Br, NO or H and where XO is chlorine monoxide (ClO), bromine monoxide (ClO), nitrogen dioxide ($\mathrm{NO_2}$) or the hydroxide radical (OH).

(iv) The sources of the free radicals are a variety of gasses which percolate upwards from the troposphere into the stratosphere where they are disassociated by ultraviolet radiation. The natural source gasses are nitrous oxide ($\mathrm{NO_2}$), methane ($\mathrm{CH_4}$) and chloromethane ($\mathrm{CH_3Cl}$). It is the chemical stability of these gases which allows them to reach the stratosphere where most of the ozone is created and where they can assist in its destruction once they have been disassociated into their constituent radicals. The destruction of ozone is now being accelerated by the release into the atmosphere of several artificial chlorine-containing source gasses:

$$\begin{aligned} &\mathrm{CFC} - 11 \quad (\mathrm{CFCl_3}) \\ &\mathrm{CFC} - 12 \quad (\mathrm{CF_2Cl_2}) \\ &\mathrm{CFC} - 113 \quad (\mathrm{C_2F_3Cl_3}) \\ &\mathrm{CFC} - 114 \quad (\mathrm{C_2F_4Cl_2}) \\ &\mathrm{CFC} - 115 \quad (\mathrm{C_2F_5Cl_)} \\ &\text{carbontetrachloride} \quad (\mathrm{CCl_4}) \\ &\text{methylchloroform} \quad (\mathrm{C_2H_3Cl_3}) \\ &\mathrm{HCFC} - 22 \quad (\mathrm{CHF_2Cl_)} \end{aligned}$$

## The Antarctic Ozone Hole

The weather system of the Antarctic represents a self-contained entity throughout the winter of the southern hemisphere. In involves a spiral vortex of cold westerly winds which circulate in the mid to low stratosphere. Only in spring, does this weather system break down when it is penetrated by warm air travelling southward from the equator.

During the Antarctic winter, ice crystals form in the cold air of the polar vortex which absorb the molecules of hydrogen chloride (HCl) and chlorine nitrate ($NO_3Cl$) which represent a sink and a reservoir for the chlorine radicals (Cl), (ClO). In the spring, these molecules are rapidly broken down by reactions which take place on the surface of the icy particles and which are energised by the sunlight. Once liberated, the chlorine radicals assist in the rapid destruction of ozone which is replenished only when the ozone-bearing air currents from the equatorial regions penetrate the Antarctic weather system.

## Ozone Screen Shrinks

Online: *The Guardian,* Thursday 16th February 1995

The World Meteorological Organisation reports that, over the past two weeks, the stratospheric ozone levels over Siberia have fallen to 35 per cent of normal. In the previous months, levels have hovered around 25 percent below average. Over Europe, the thinning was less severe, with a 10 to 15 percent drop, with a similar 10 percent drop over the west coast of North America. The Ozone layer is the natural protective screen against dangerous ultra-violet radiation, and any drop in it is expected to be followed by increases in skin cancer and in cataracts of the eye. Although CFC's, the main man-made chemicals that have been damaging the ozone layer, are being phased out, frequent dramatic drops in the ozone cover are expected for the next decade or two.

**Tim Radford**