

[CFCs] [CFCs]

a specific chemical to the impact from an equivalent mass of CFC-11, the standard by which all others are calculated. The ODP takes into consideration,

(a) The reactivity of the species. (b) Atmospheric lifetime of species, and (c) Molar mass of species.

In addition, the amount of chlorine species is also very important. For example, CFC-114 ($\text{CF}_2\text{Cl.CF}_2\text{Cl}$) contains 2 chlorine atoms and has an ODP of 1.0, while CFC-115 (CF_2ClCF_3) has only 1 chlorine atom and has an ODP of 0.6. Similarly, CCl_4 has four chlorine atoms, but has a high ODP of 1.1 – 1.2. *It should be noted that,*

(a) Most CFCs have ODP values between 0.1 and 1.0. (b) Most hydrochloro fluoro carbons (HCFCs) have ODP values which are about 10 times smaller (0.01 to 0.1). (c) Hydrofluorocarbons (HFCs) have no chlorine and have an ODP value of zero.

In halons, the first digit indicates the number of carbon atoms, the second, the number of fluorine atoms, the third, the number of chlorine atoms, and the fourth the number of bromine atoms. Additional atoms required for a saturated carbon are assigned to hydrogen atoms. For example,

CF_2ClBr (H-1211)	Bromochlorodifluoromethane.
CF_3Br (H-1301)	Bromotrifluoromethane
$\text{CBrF}_2\text{CBrF}_2$ (H-2402)	Dibromotetrafluoroethane.

The main cause of ozone depletion is the widespread use of chlorofluorocarbons (CFCs). About 30% of world CFC production is used in fridges, freezers and air conditioners, about 25% in sprays, another 25% in blowing foams and the remaining 20% for cleaning and other purposes. Besides, some halons are used primarily as fire extinguishers. They do 10 times greater damage to the ozone, compared to the CFCs. According to an estimate, the concentration of the halons in the atmosphere is doubling every 5 years.

Table (1) Properties of common CFCs

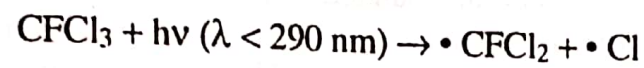
CFC	Formula	Atmospheric lifetime	ODP
CFC - 11	CFCl_3	60 years	1.0
CFC - 12	CF_2Cl_2	195 years	1.0
CFC - 113	$\text{CF}_2\text{ClCFCl}_2$	101 years	0.8
CFC - 114	$\text{CF}_2\text{ClCF}_2\text{Cl}$	236 years	1.0
CFC - 115	CF_2ClCF_3	522 years	0.6

Burning coal and oil and the increasing use of nitrogenous fertilizers are also contributing to the destruction of ozone layer. Ozone is destroyed by its reaction with nitric oxide (NO) and nitrogen dioxide (NO_2). These oxides are formed in the stratosphere from NO_2 that originates in silts, sediments and water. Aerobic nitrification is one of the potential sources by which NO_2 is emitted. Supersonic flights and space shuttles release nitrogen oxides and chlorine respectively.

Chlorofluorocarbons, which are used as propellants in pressurised aerosol cans, as coolants in air conditioners and refrigerators, in foam insulation, cleaning solvents, extinguishing equipments etc, escape into the atmosphere and reach stratosphere, where they get accumulated. Here, these CFCs, under the influence of ultraviolet radiation release chlorine atoms each of which reacts more than 1,00,000 molecules of ozone, converting them into oxygen. The protective ozone layer of the stratosphere is thus depleted and UV radiation gets intensified. One percent

reduction of O₃ in the stratosphere increases UV radiation on earth by 2%. The super sonic jets which fly at high altitudes in the stratosphere release nitrogen oxide (NO_x) which also destroy ozone molecules catalytically. The CFCs are very stable on the earth. But when they slowly drift upto the stratosphere, intense UV-C radiation acts on their chemical bonds releasing chlorine which strips an atom from the molecule of ozone turning it into ordinary oxygen. The chlorine goes on to repeat the process, and in this way one CFC molecule can destroy thousands of molecules of ozone. There are about 200 processes by which CFCs can destroy the ozone.

We have seen that CFC molecules are much heavier than those of air. However, they tend to mix homogeneously and get distributed throughout the troposphere in the gas phase because of strong convective mixing. CFCs are almost completely unreactive biologically and chemically in the earth environment, including the troposphere. While unreactive in the troposphere, they are capable of undergoing UV photolytic decomposition into the stratosphere because of being exposed to intense flux of energetic UV radiation.

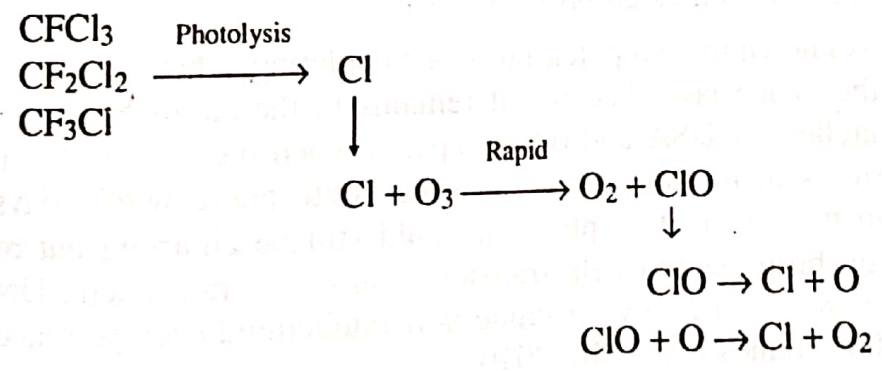


The Cl• so released takes part in catalytic processes described earlier.

GENERAL MECHANISM OF OZONE DEPLETION BY CFCs

(a) Freons are very much more effective greenhouse gases in the atmosphere than is CO₂, though the amount of freons present is extremely small.

(b) In the upper atmosphere freons undergo a photolytic reaction and produce free chlorine atoms, which are radicals. These react readily with ozone. The ClO radicals formed decompose slowly, reforming chlorine radicals, which react with ozone and the process goes on. The chlorine radicals do not recombine to form Cl₂, because they require a three body collision to dissipate the energy, and such collisions are extremely rare in the upper atmosphere. There is no effective sink for chlorine radicals. Once formed they are used again and again. So, even a small number of radicals make a very effective scavenger for ozone.



The overall reaction is 2O₃ → 3O₂.

(c) Several less harmful aerosol propellants are now in use. Hydrofluorocarbons (HFCs) such as CH₂FCF₃ and hydrochlorofluorocarbons (HCFCs) such as CHCl₂CF₃ are being used as substitutes. They are also greenhouse gases, and may damage the ozone layer, but they do less damage than CFCs as they do not remain in the atmosphere for so long.

(d) The H atoms are attacked by hydroxyl radicals in the upper atmosphere, forming trifluoroacetic acid, which is not very toxic, and is eventually decomposed by bacteria in the soil.

(e) CO₂ is an alternative propellant, but when cold it has a low vapour pressure and is therefore, no use for windscreen deicers. Butane also gives difficulties because it is flammable and can not be used with food.