

**EE/GG510 Physical Principles of the Eenvt
Oct 6, 2004**

**Atmospheric chemistry and non-CO₂ greenhouse
gases:**

Halocarbons, CFC's, the ozone hole

**What you need to know about each of these
chemicals**

- 1. CH₄ methane**
- 2. O₃ ozone**
- 3. N₂O nitrous oxide**
- 4. Halocarbons**

Reactive gases (influence GHGs):

- 5. OH- Hydroxyl radical**
- 6. Nox Nitrogen oxides ("knox")**
- 7. CO Carbon monoxide**

Halocarbons ('halogen-carbons')

• Halogens (fluorine, chlorine, bromine, etc.). Alone, these are very reactive elements (why?)

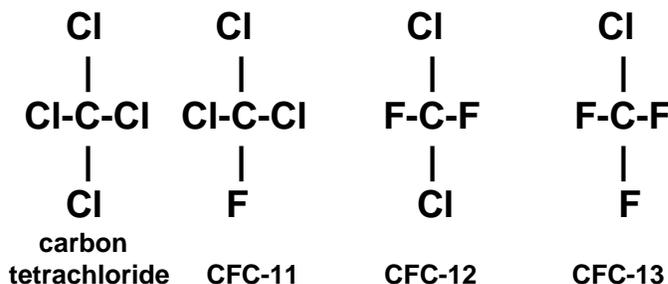
Unpaired electrons and the octet rule

Periodic Table of the Elements*

* Data adapted from Lide, D.R., Editor (1995) CRC Handbook of Chemistry and Physics, 76th Edition, CRC Press, Boca Raton, Florida.
 ** Atomic mass values in parentheses denote the atomic mass of the most stable isotope of those elements too unstable for the determination of a standard atomic mass.

Halocarbons ('halogen-carbons')

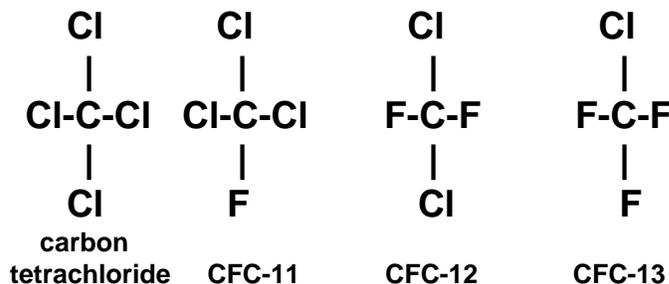
• When combined with carbon, they become extremely stable
 Some examples:



(carbon as legos vs. halogens as superglue)

Halocarbons ('halogen-carbons')

•Nomenclature



$$90 + X = C + H + F$$

e.g. $90 + (\text{CFC})13 = 103 = 1 \text{ carbon}, 0 \text{ hydrogen}, 3 \text{ fluorine}$

e.g. $90 + (\text{HFC})23 = 113 = 1 \text{ carbon}, 1 \text{ hydrogen}, 3 \text{ fluorine}$

e.g. $90 + (\text{CFC})113 = 203 = 2 \text{ carbon}, 0 \text{ hydrogen}, 3 \text{ fluorine}$

Halocarbons ('halogen-carbons')

•Hydrofluorocarbons are generally less stable than CFC's
(see lifetimes in Table 4.1)

•This is good for the ozone layer, not so good for applications like refrigeration etc.

•Most halocarbons are very strong greenhouse gases

•The key benefit of HFC's are that they don't contain chlorine.

•Why is this lack of chlorine so important for the ozone layer?
We need to look at a bit of chemistry in the stratosphere...

CFC's and the ozone hole: the role of Cl

•Cl participates in a *Catalytic Reaction Cycle*, which has the crucial property of regenerating the original catalytic agent (Cl) to facilitate further stratospheric ozone destruction.

•Here's a generalized ozone destruction reaction:



Where $\text{X}\cdot$ and $\text{XO}\cdot$ are highly reactive chemicals (" \cdot ") indicates a 'free' (unpaired) electron that is highly unstable)
Bottom line: Cl helps destroy O₃ and is regenerated to do it again!

CFC's and the ozone hole: the role of Cl

A question: how do we get $\text{Cl}\cdot$ from CFC's?

UV light in the stratosphere is strong enough, and abundant enough, to break up CFC's

An example with CFC-11:

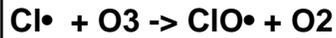


A single CFC molecule can release 3 (or even up to 4, with CCl_4) $\text{Cl}\cdot$'s!!

Note we also have $\text{F}\cdot$ released – why isn't it important? It is quickly consumed to form HF, and slow to regenerate.

An interesting, and important, aside:

Here again is the ozone destruction by Cl:



It turns out that we can plug in NO• or NO2• as well:



But where does the NO• or NO2• in the stratosphere come from?

Largely from N2O (nitrous oxide)!!

Example:



Thus, by increasing nitrous oxide emissions, humans still impact stratospheric ozone. The montreal protocol doesn't cover N2O.

In fact, the initial studies of stratospheric ozone depletion focused on N2O (Crutzen) before Molina/Rowland considered Cl.

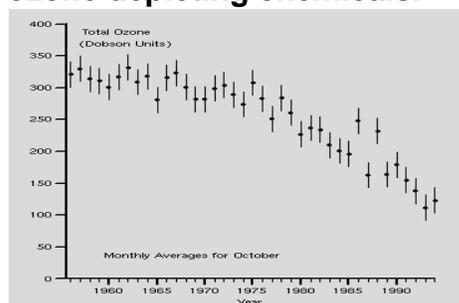
Further thoughts on the ozone hole:

•It occurs largely over antarctica and to a lesser degree, the arctic (see Farman paper). Why?

Answer: Cold temperatures and large seasonality in light
We'll explain why those factors matter later...

**Why we usually hear about the ozone hole over antarctica.
(and in the antarctic spring)**

1. Cold temperatures mean ice clouds
2. Ice cloud particles provide focal surfaces for ozone depleting chemical reactions to occur ('heterogeneous reactions').
3. Polar night allows ozone depleting chemicals to build up on cloud ice particles, polar day allows light to release and react these ozone depleting chemicals.



Strat. Ozone depletion occurs in the polar spring over antarctica, moreso the farther south one goes.

Empirical findings of Farman et al. validated the predictions of Molina and Rowland

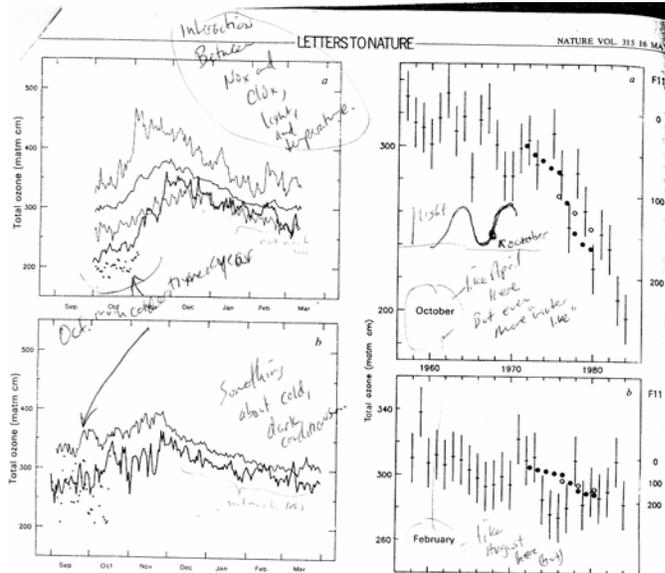
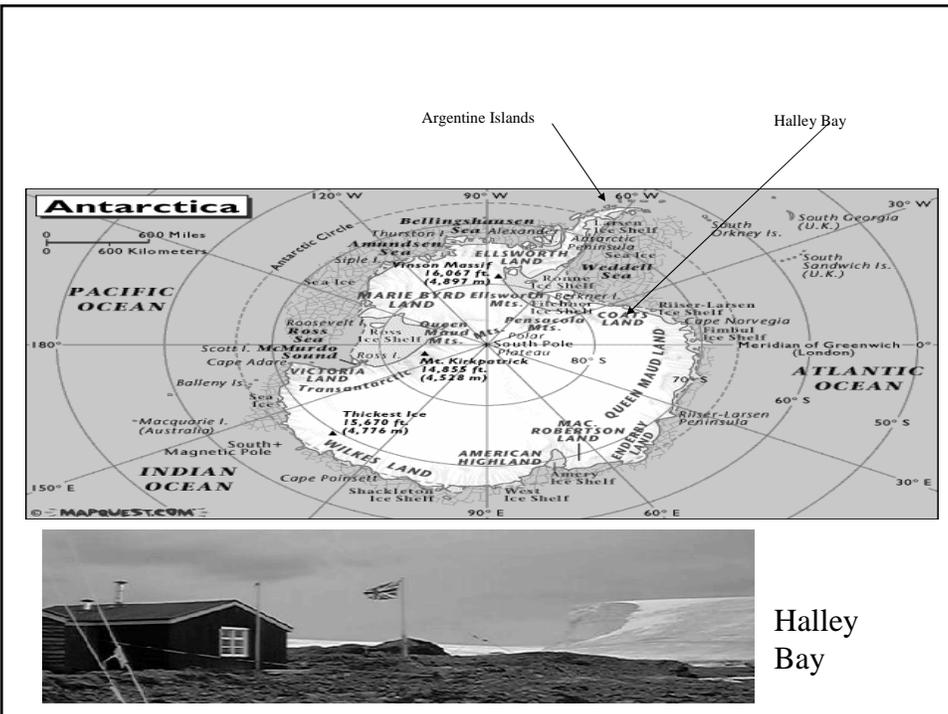


Fig 1 Daily values of total O₃. a, Halley Bay: thin lines, mean and extreme values for 16 seasons, 1957-73; thick line, mean values for four seasons, 1980-84; +, values for October 1984. Observing season: 1 October to 13 March. h, Argentine Islands: as for Halley

Fig 2 Monthly means of total O₃ at Halley Bay, and Southern Hemisphere measurements of F-11 (●), ppb.v. (parts per thousand by volume, CFC-11) and F-12 (○), ppb.v. (parts per thousand by volume, CFC-12)



Key steps in stratospheric ozone depletion:

- 1. Winter buildup of ozone destroying 'reservoir' molecules: a latent atmospheric 'poison':**

Everywhere in stratosphere, a natural feedback on ozone depletion is locking up of N and Cl catalysts:



M is a mediator molecule that absorbs excess rxn energy.

But these products are temporary and can photodissociate back to the initial reactants:



But in polar winter, no light for this process, so the reactants build up

Key steps in stratospheric ozone depletion:

- 2. Chemical breakup of reservoir molecules is enhanced with freezing stratospheric temperatures:**



(here HCl is a harmless reservoir molecules with renders Cl harmless to ozone).

The Cl₂ can photodissociate to form damaging Cl:



However, in the gas phase, the reaction at the top of this page is so slow as to be negligible. Must be another way to release Cl• In stratospheric ice clouds, the reaction occurs very fast – both ClONO₂ and HCl attach readily to ice crystals.

Summary:

The timing of seasonal ozone loss found by Farman et al. makes sense with this mechanism.

ClONO₂ builds up over the long winter because there is little light for dissociating it.

In spring, temperatures still cold, but light increases, allowing for dissociation of Cl₂ into Cl, and rapid depletion of ozone.

Question: why not as strong over the arctic?

Some concluding thoughts:

“The issues of ozone depletion and climate change are inter-connected; hence, so are the Montreal and Kyoto Protocols. Changes in ozone affect the earth’s climate, and changes in climate and meteorological conditions affect the ozone layer...”

Hence, decisions taken (or not taken) under one Protocol have an impact on the aims of the other Protocol. For example, decisions made under the Kyoto Protocol with respect to methane, nitrous oxide, and carbon dioxide will affect the rate of recovery of ozone, while decisions regarding controlling HFC’s may affect decisions regarding the ability to phase out ozone-depleting substances.

WMO Scientific Assessment of Ozone depletion: 1998