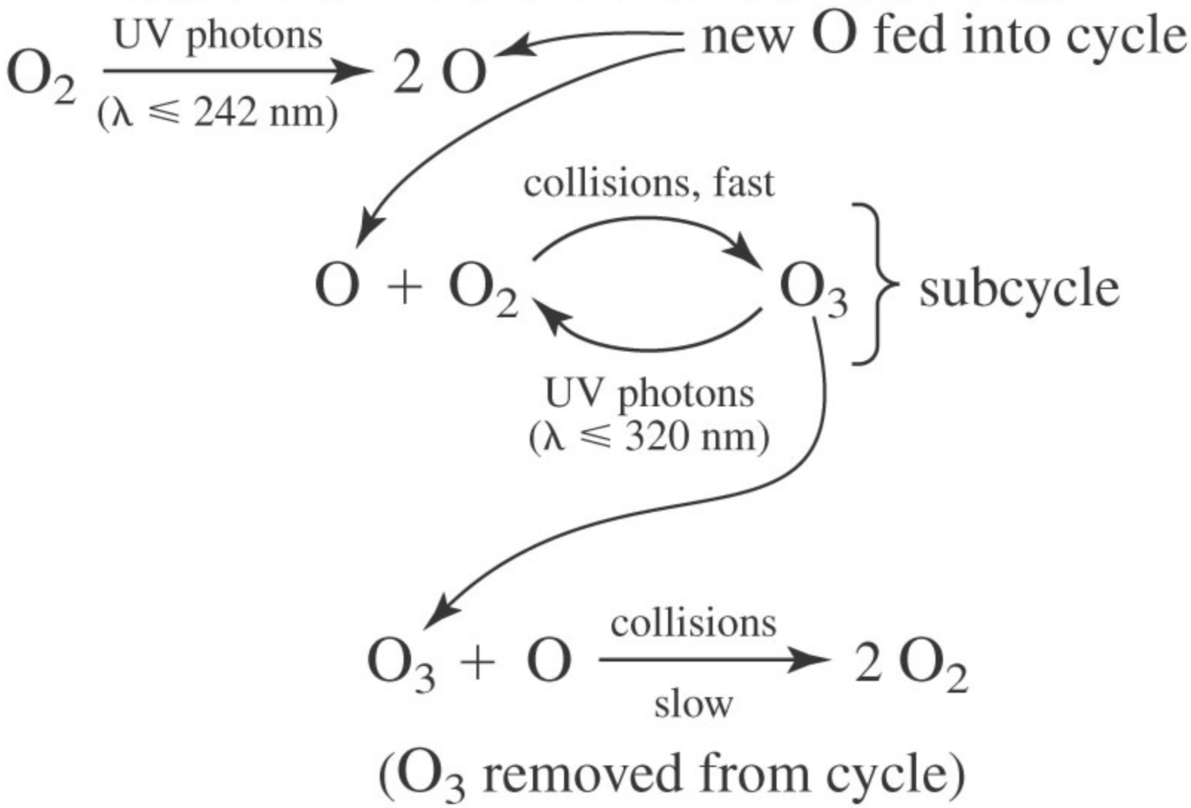
Chapman Cycle

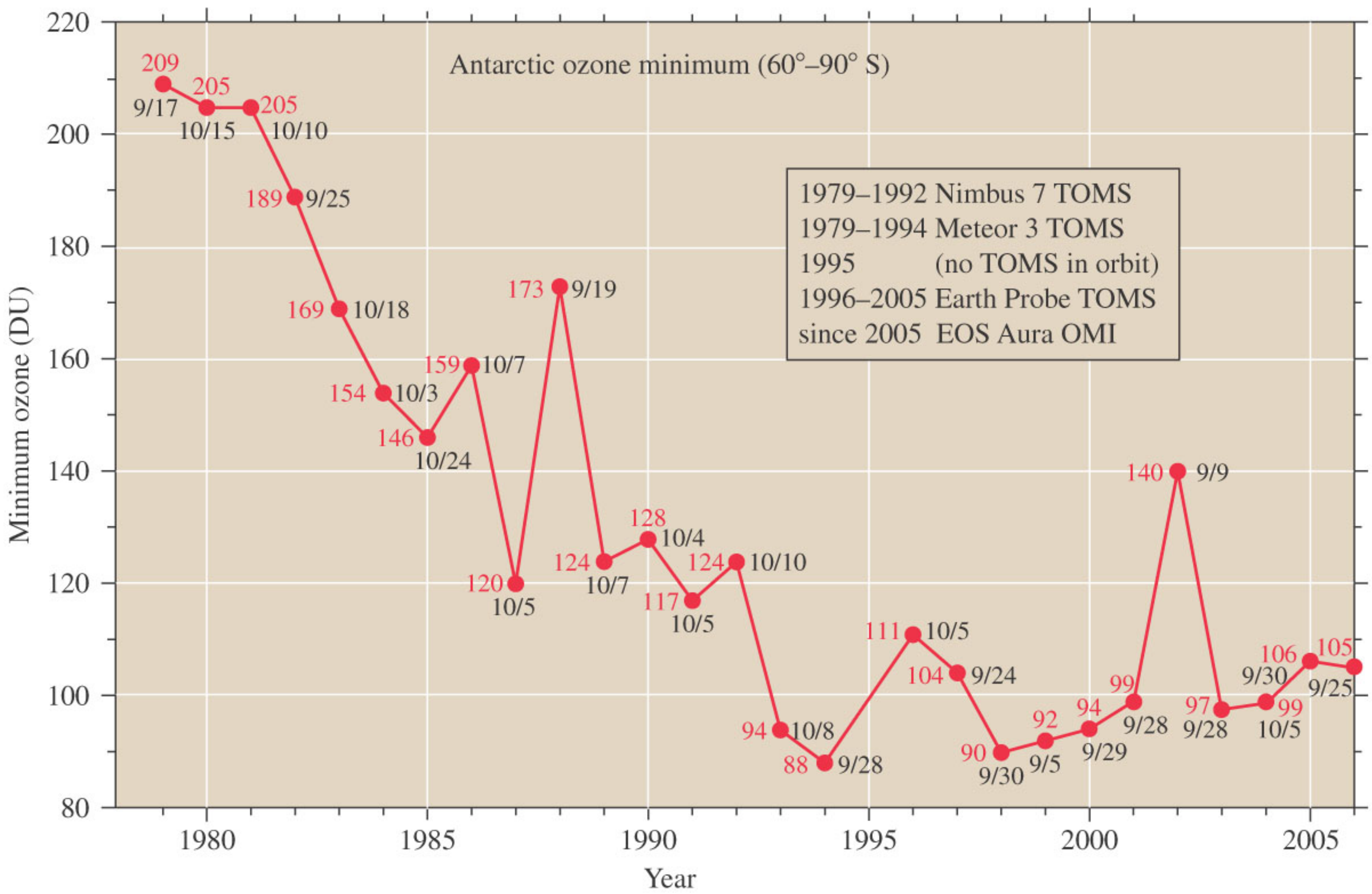
The cycle describes reactions of O_2 and O_3 in stratosphere

Even though reactions are happening, the concentration of O_3 remains constant
This is an example of a **dynamic equilibrium** or **steady state condition** (UV light is being consumed)



Ozone Depletion in Antarctica

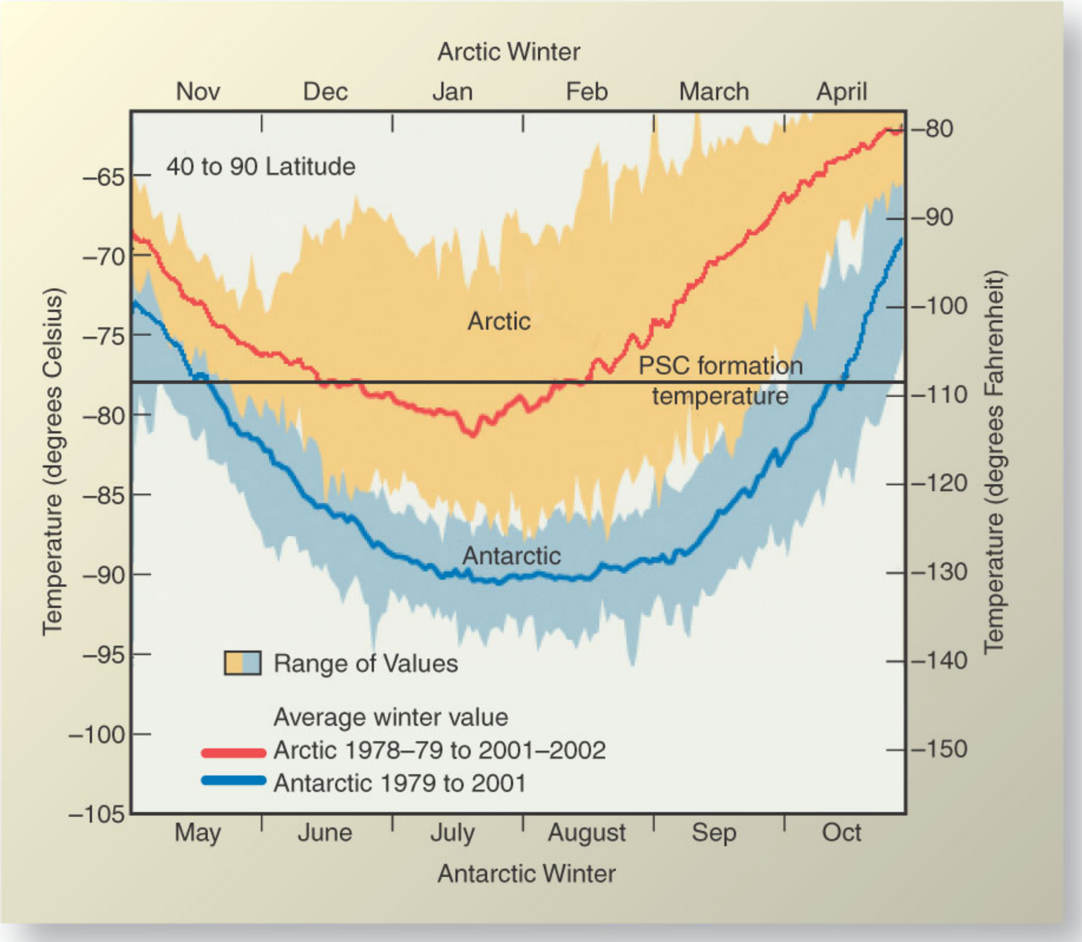
Minimum spring stratospheric ozone concentration over Antarctica:



Why Does Antarctica Get the Worst of It?

Dude, it's cold there:
Cl-containing molecules condense on Polar Stratospheric Clouds (PSCs)

When the sun comes out, PSCs provide surfaces for reactions to occur

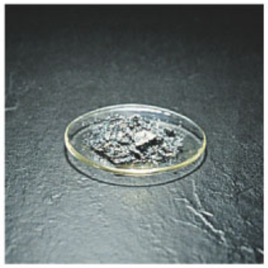


Halogens

Group to the left of the noble gases, including F, Cl, Br, I, At:

Cl_2 (gas)

Br_2 (liquid)



I_2 (solid)

Table 2.2 Total and Outer Electrons for Atoms of the First 18 Elements

Group 1A	2A	3A	4A	5A	6A	7A	Noble Gases 8A
1 H 1							2 He 2
3 Li 1	4 Be 2	5 B 3	6 C 4	7 N 5	8 O 6	9 F 7	10 Ne 8
11 Na 1	12 Mg 2	13 Al 3	14 Si 4	15 P 5	16 S 6	17 Cl 7	18 Ar 8

• Number *above* the atomic symbol is the atomic number, the total number of protons. It also gives the total number of electrons in a neutral atom.

• Number *below* the atomic symbol is the number of **outer** electrons in a neutral atom.

24 Cr 52.00 — Atomic number — Atomic mass

1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 H 1.008																	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (269)	109 Mt (268)	110 Ds (271)	111 Rg (280)	112	113	114	115	116	117	118

58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

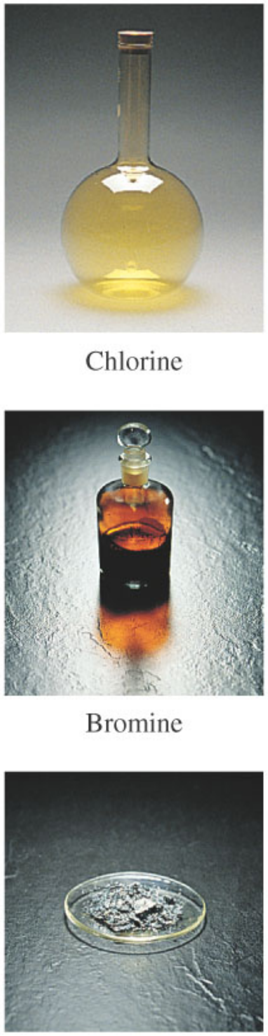
Metals

Metalloids

Nonmetals

The 1–18 group designation has been recommended by the International Union of Pure and Applied Chemistry (IUPAC) but is not yet in wide use. In this text we use the standard U.S. notation for group numbers (1A–8A and 1B–8B). No name has been assigned for element 112. Elements 113–118 have not yet been synthesized.

A Link Between Atmospheric Halogens and Ozone Depletion



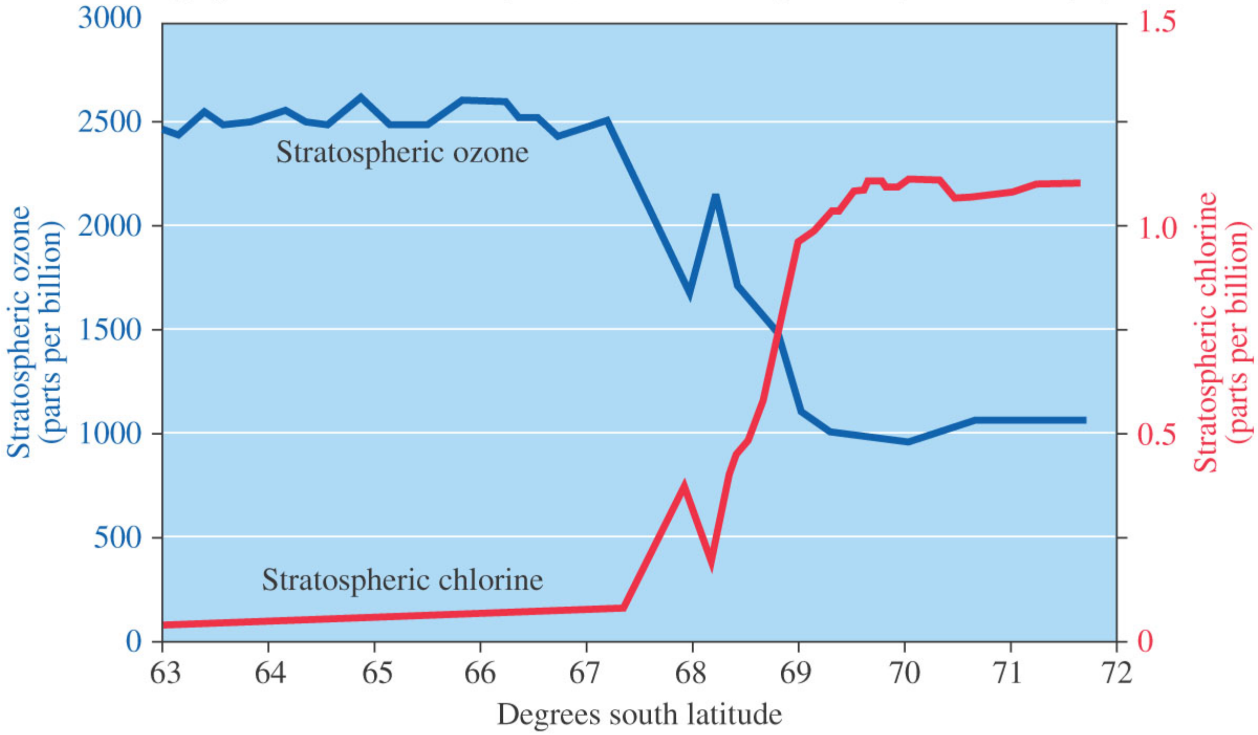
Chlorine

Bromine

Iodine

Flight through the Antarctic ozone hole, 1987:

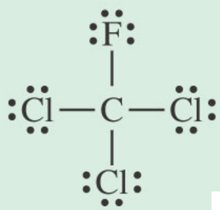
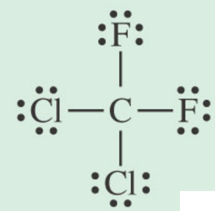
Fig. 2.15

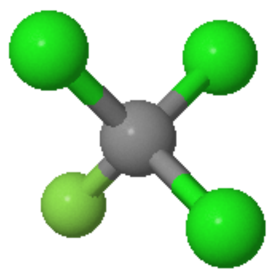


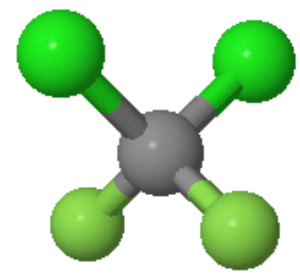
correlated

The Promise of Chlorofluorocarbons (CFCs)

Table 2.6 Two Important Chlorofluorocarbons

Freon 11 (CFC-11)	Freon 12 (CFC-12)
CCl_3F	CCl_2F_2
trichlorofluoromethane	dichlorodifluoromethane
	





Pros:

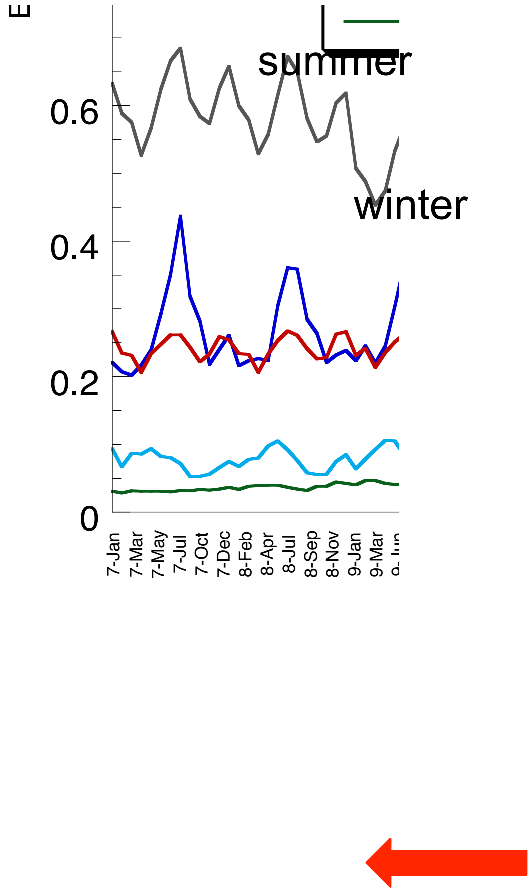
Inert
Non-toxic
Cheap
Excellent refrigerant : replaced NH_3 & SO_2, which are toxic & corrosive
Helped growth in humid, hot American south

Uses:

Refrigerant
Fire suppressant
Solvents (for electronics and surgical instruments)

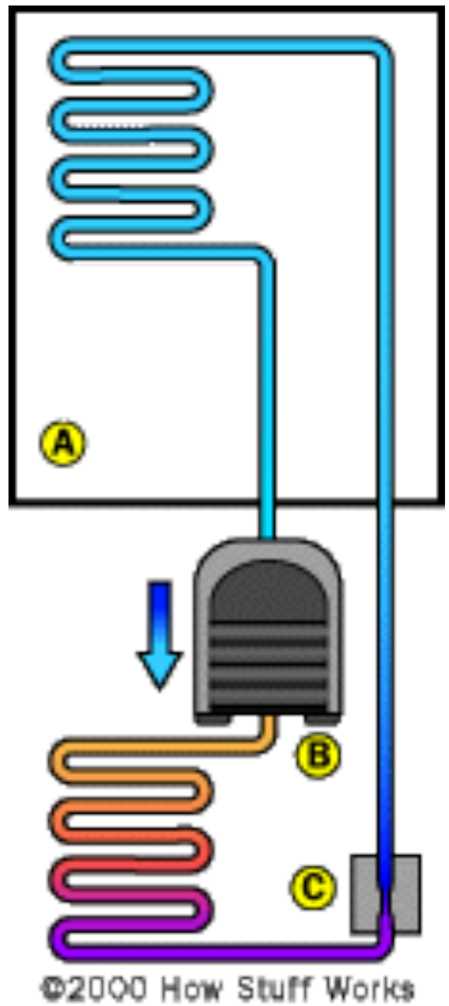
Discovered in late 1920's

Electricity Seasonal uses & sources



Refrigeration

5. Cold HFC gas is sucked up by the compressor, and the cycle repeats



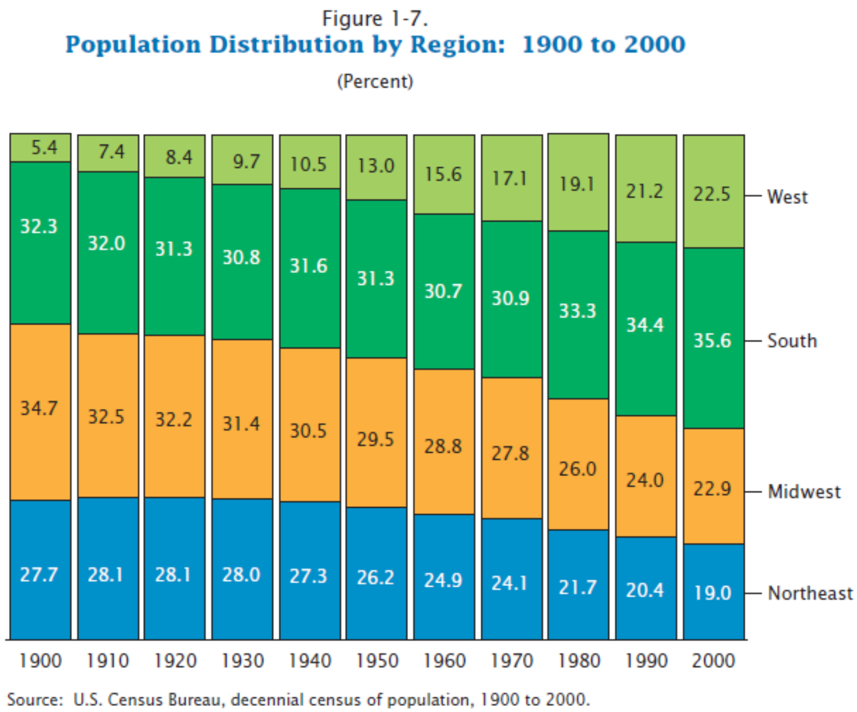
4. Liquid HFC vaporizes (light blue), its temperature dropping to -27 F. This makes the inside of the refrigerator cold (A)

1. Compressor (B) compresses HFC gas. (compressed gas heats up as it is pressurized (orange))

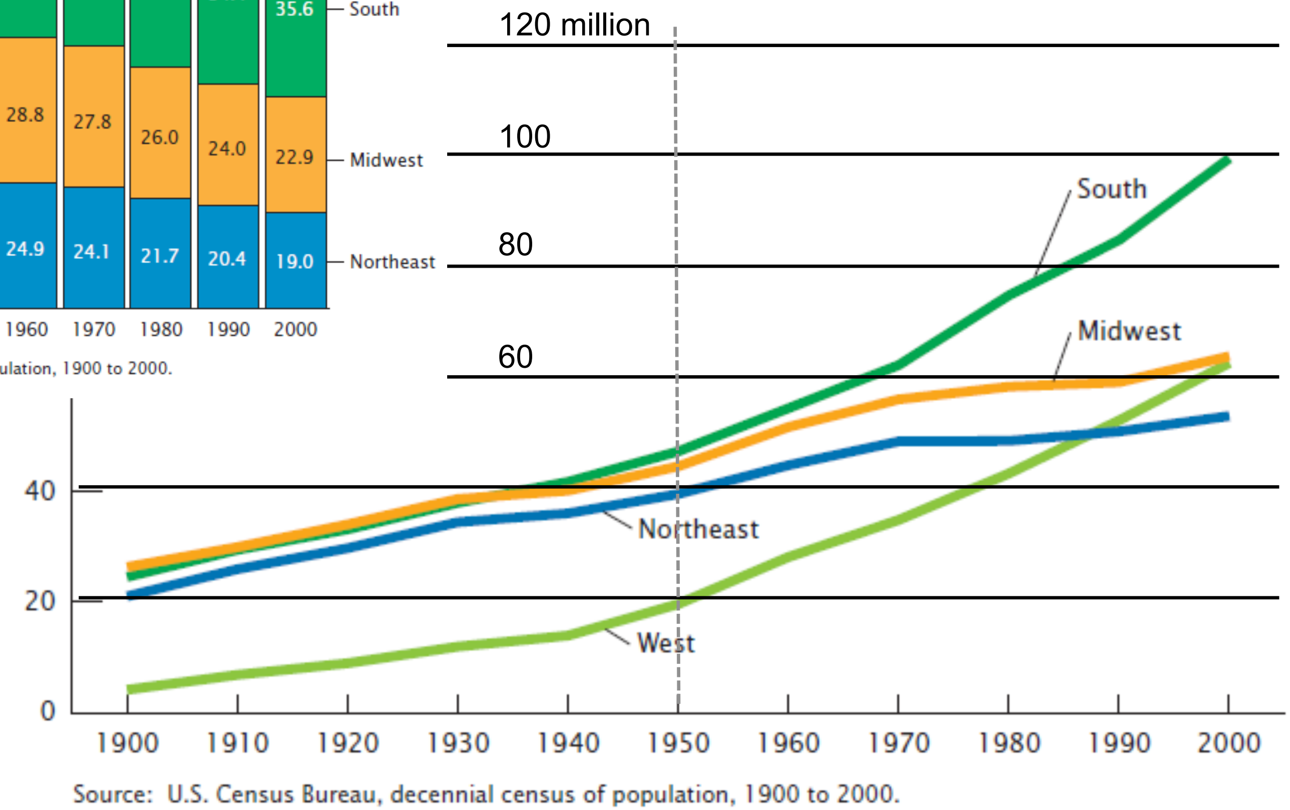
2. Coils on the back of the refrigerator dissipate HFC gas heat. The HFC gas condenses into HFC liquid (purple) at high pressure

3. High-pressure HFC liquid flows through the expansion valve (C).
(a small hole). On one side of the hole is high-pressure HFC liquid. On the other side of the hole is a low-pressure area (the compressor is pumping gas out of that side).

US Population by Region in the 20th Century



The South and West accounted for nearly two-thirds of the U.S. population increase from 1900 to 2000.



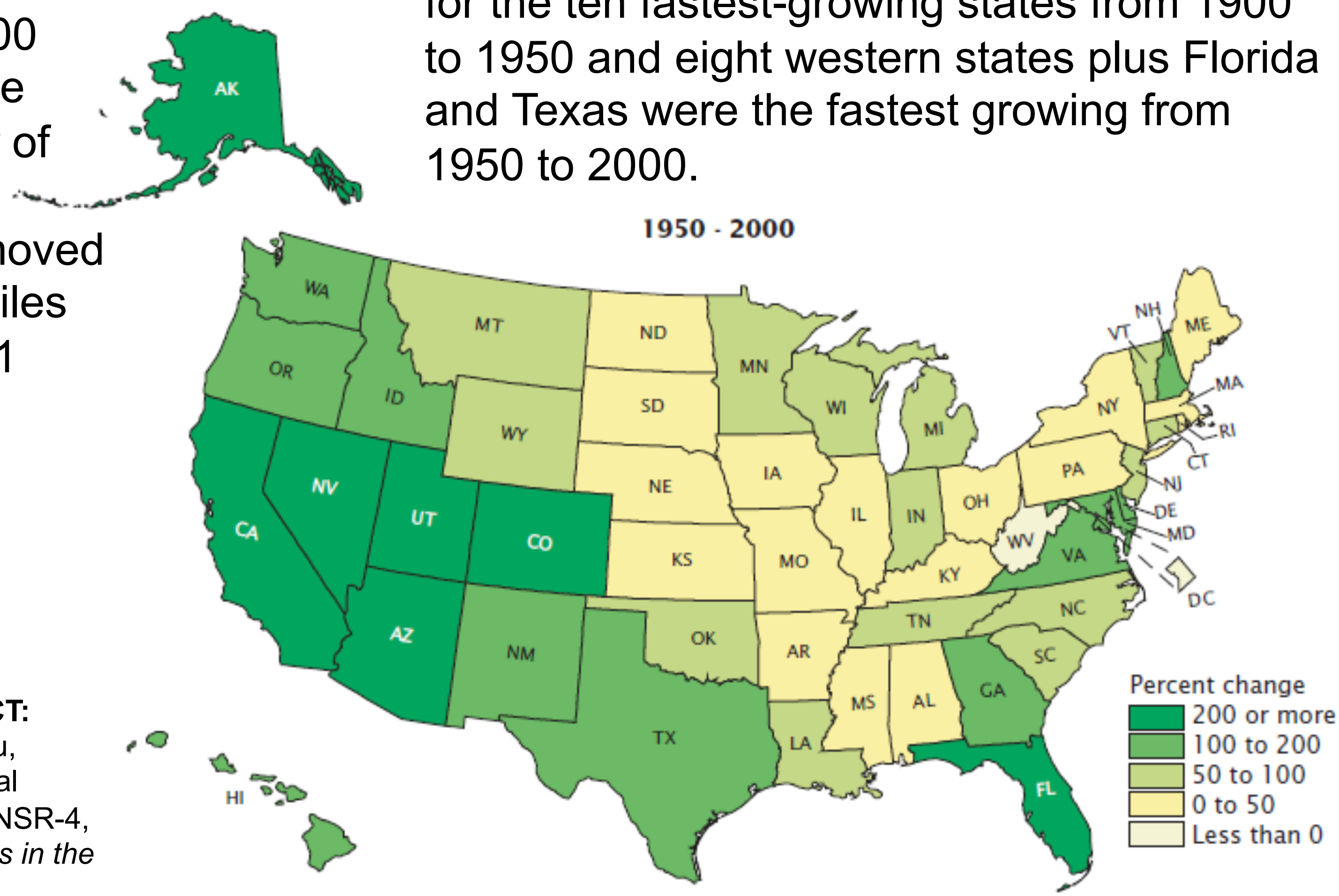
Available on RamCT:
U.S. Census Bureau, Census 2000 Special Reports, Series CENSR-4, *Demographic Trends in the 20th Century*

Freons discovered in late 1920's

US Population Growth by Region in the 20th Century

Nine western states and Florida accounted for the ten fastest-growing states from 1900 to 1950 and eight western states plus Florida and Texas were the fastest growing from 1950 to 2000.

Between 1900 and 2000, the mean center of the U.S. population moved about 324 miles west and 101 miles south.



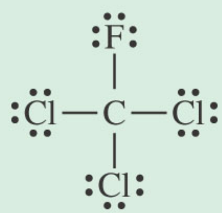
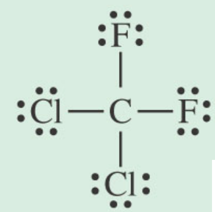
Source: U.S. Census Bureau, decennial census of population, 1900, 1950, and 2000.

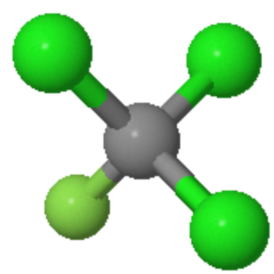
Available on RamCT:
U.S. Census Bureau, Census 2000 Special Reports, Series CENSR-4, *Demographic Trends in the 20th Century*

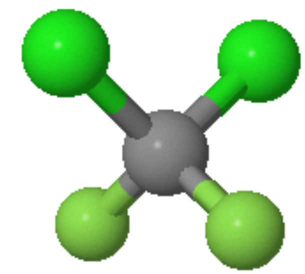
Air conditioning w/ cheap CFCs helped make this population growth possible.

CFCs: Inertness is a Double Edged Sword

Table 2.6 Two Important Chlorofluorocarbons

Freon 11 (CFC-11)	Freon 12 (CFC-12)
CCl_3F	CCl_2F_2
trichlorofluoromethane	dichlorodifluoromethane
	





Cons:

Inert
- remain intact in atmosphere for a long time
- survive up 120 years
- & drift into stratosphere in 5 years

React with UV-radiation to form stable radicals in the stratosphere

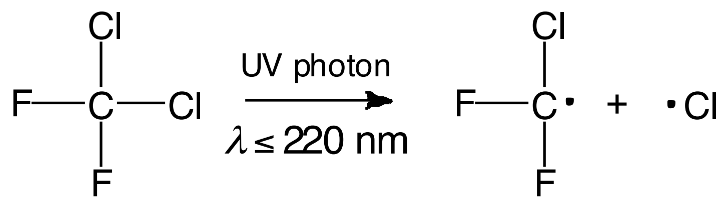
CFCs represent the major source of anthropogenic halogen in the atmosphere… with adverse consequences…

Ozone Depletion Chemistry

Natural: $H_2O \rightarrow$ (<240 nm) H• + •OH (above 50 km)

500 kJ/mol

Anthropogenic:



$$2Cl\bullet + 2O_3 \longrightarrow 2ClO\bullet + 2O_2$$

$$2ClO\bullet \longrightarrow ClOOCl$$

$$ClOOCl \xrightarrow{\text{UV photon}} ClOO\bullet + \bullet Cl$$

$$ClOO\bullet \longrightarrow Cl\bullet + O_2$$

Cl• is both a reactant & a product, it's a catalyst (just like catalytic converter)

Adding all the equations together:

$$2Cl\bullet + 2O_3 + 2ClO\bullet + ClOOCl + ClOO\bullet \longrightarrow 2ClO\bullet + 2O_2 + ClOOCl + ClOO\bullet + \bullet Cl + Cl\bullet + O_2$$

Cancelling common terms:

$$2\cancel{Cl}\bullet + 2O_3 + 2\cancel{ClO}\bullet + Cl\cancel{OO}Cl + Cl\cancel{OO}\bullet \longrightarrow 2\cancel{ClO}\bullet + 2O_2 + Cl\cancel{OO}Cl + Cl\cancel{OO}\bullet + \bullet\cancel{Cl} + \cancel{Cl}\bullet + O_2$$

$$2O_3 \longrightarrow 3O_2$$

Natural and Human: •NO as another source of radicals

Moving Past CFCs

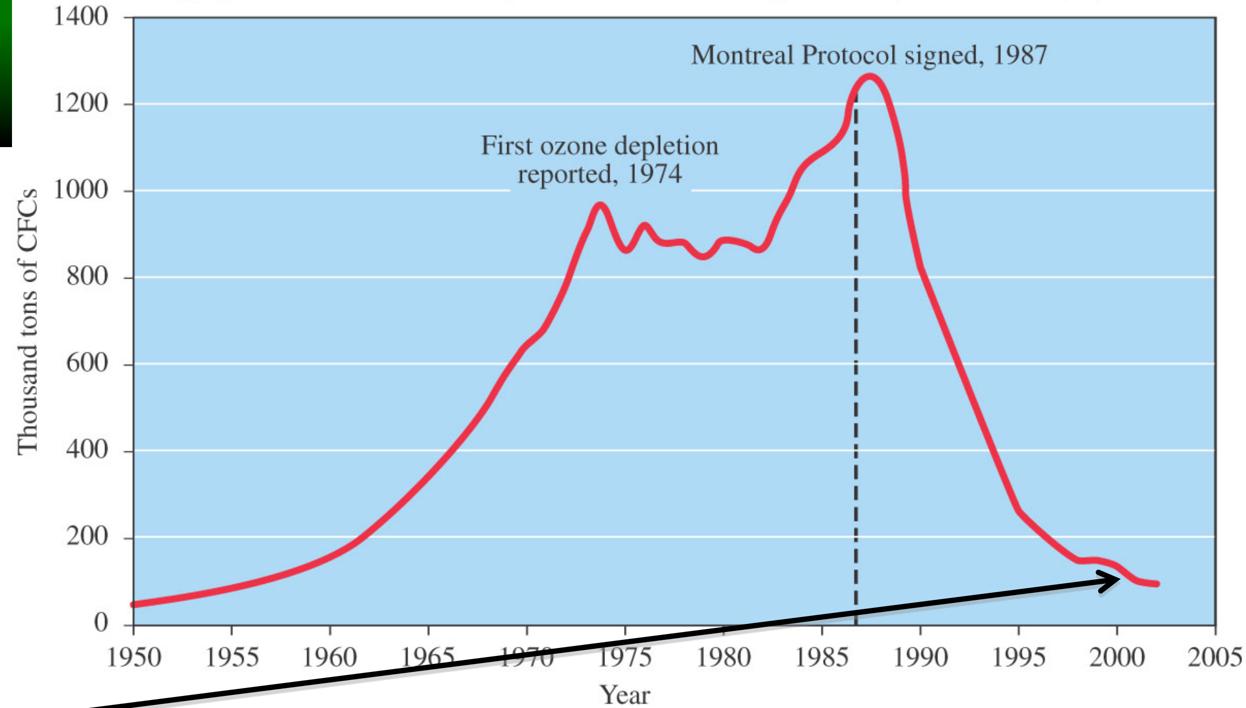
1987: signing of Montreal Protocol on Substances that Deplete the Ozone Layer

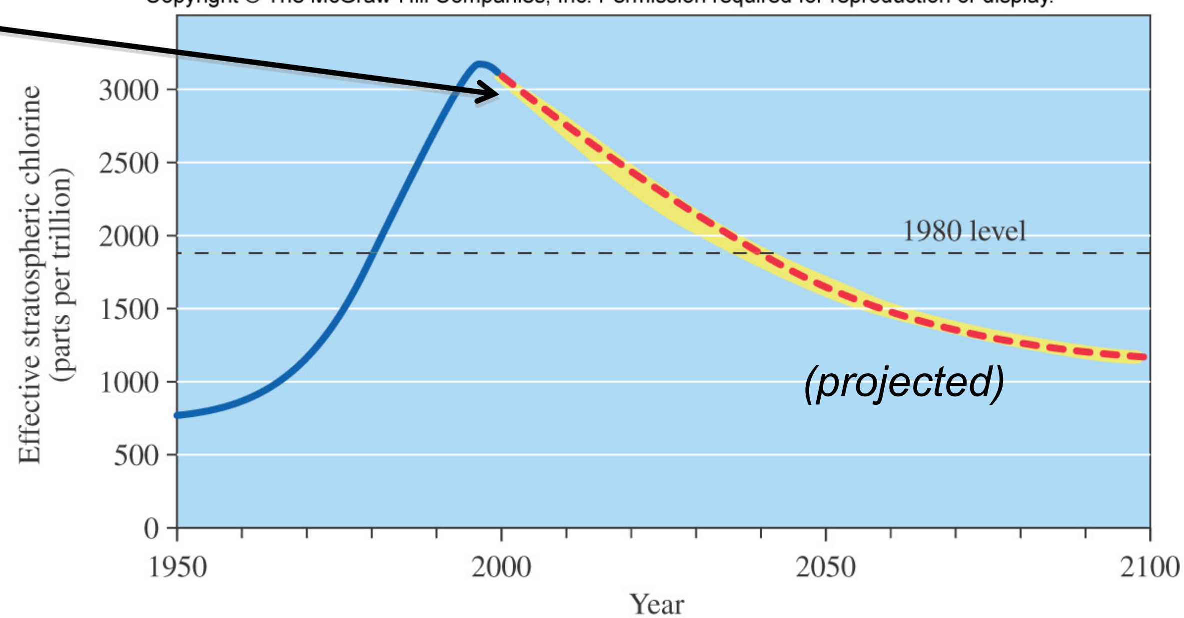
Eliminates the production and (eventually) the use of CFCs

The protocol is working as intended:
- -fewer CFCs in atmosphere
- -lower [Cl•] in atmosphere

Economic consequences:
- -cost of alternatives
- -developing nations

Remember: CFCs can exist for ~100 years in the atmosphere





Replacements for CFCs

A. HCFCs
More reactive (decompose in troposphere) but still have ozone-depleting potential

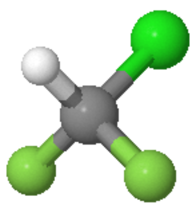
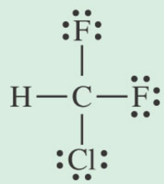
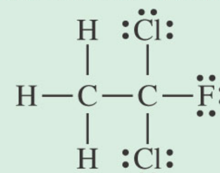
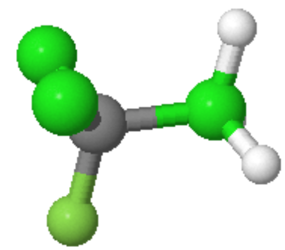


Table 2.7 Two Important Hydrochlorofluorocarbons

HCFC-22	HCFC-141b
$CHClF_2$	$C_2H_3Cl_2F$
chlorodifluoromethane	dichlorofluoroethane







B. HFCs
Contain no chlorine
but are more reactive

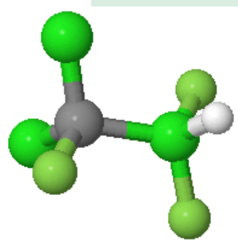
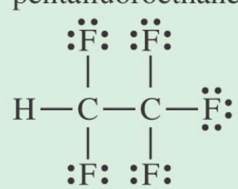
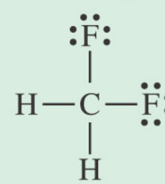
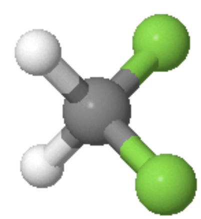


Table 2.8 Two Important Hydrofluorocarbons

HFC-125	HFC-32
C_2HF_5	CH_2F_2
pentafluoroethane	difluoromethane







Unit 4.1 Summary

- interaction of light and matter
  - need to understand the relationships between wavelength, frequency and energy
  - need to understand how light can break chemical bonds
- reactivity of ozone
  - Chapman cycle (establishment of steady state concentrations)
  - production of persistent radicals and their interactions with ozone
  - understand the function of catalysts
  - role of CFCs and related materials in ozone depletion
- environmental, biological and political effects of ozone depletion