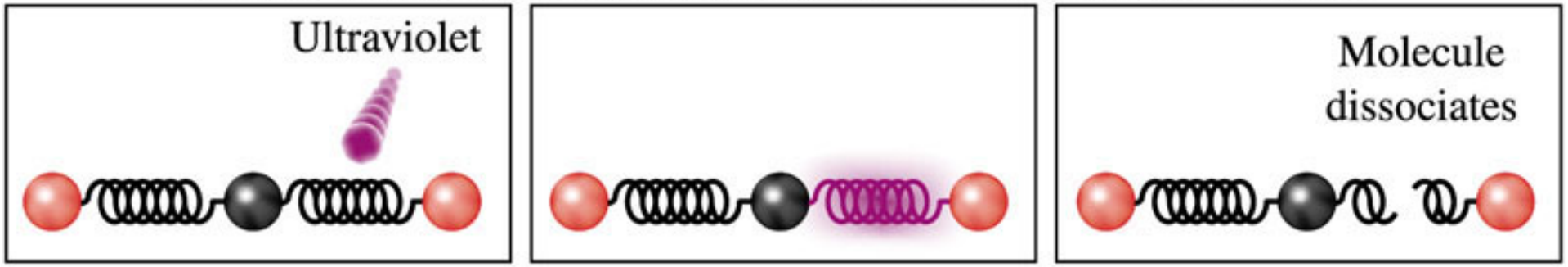
EXAM 1 THURSDAY

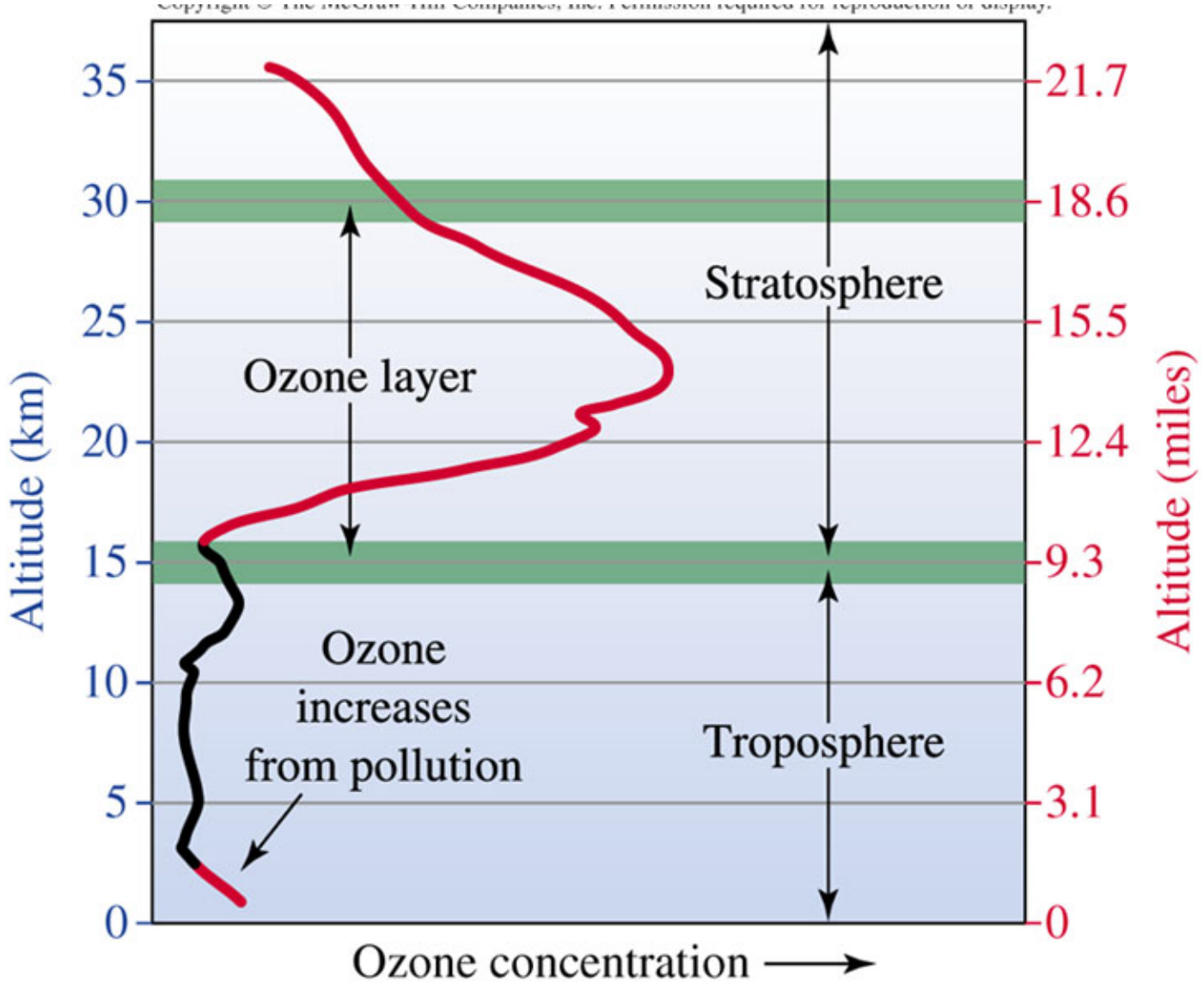
The Interaction of Light with Molecules

•It turns out that the energy in one photon of ultraviolet light has approximately the same energy as a molecular bond!

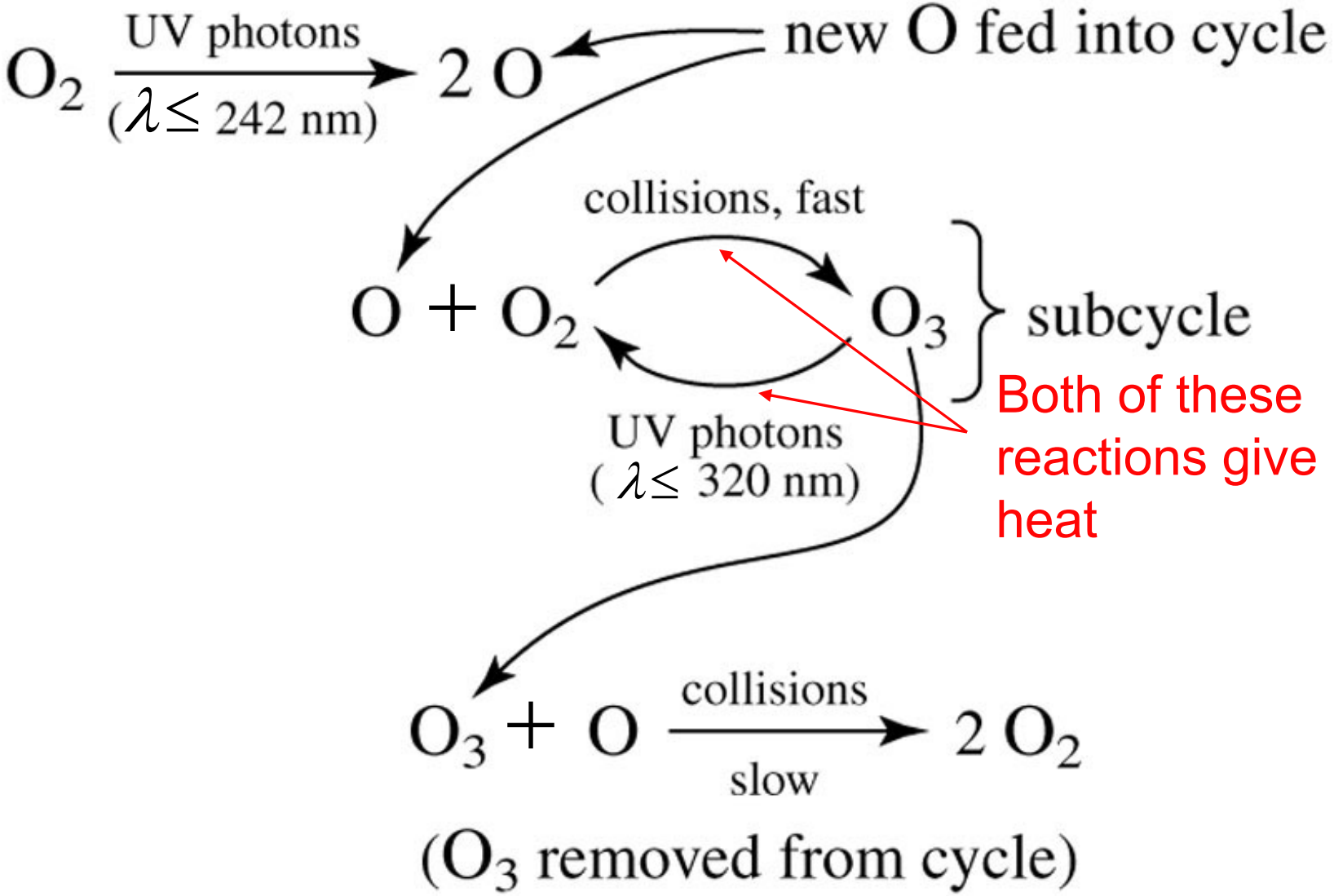
•If a molecule is struck by a photon of the right energy – that is, of the right frequency! – the molecular bonds will break



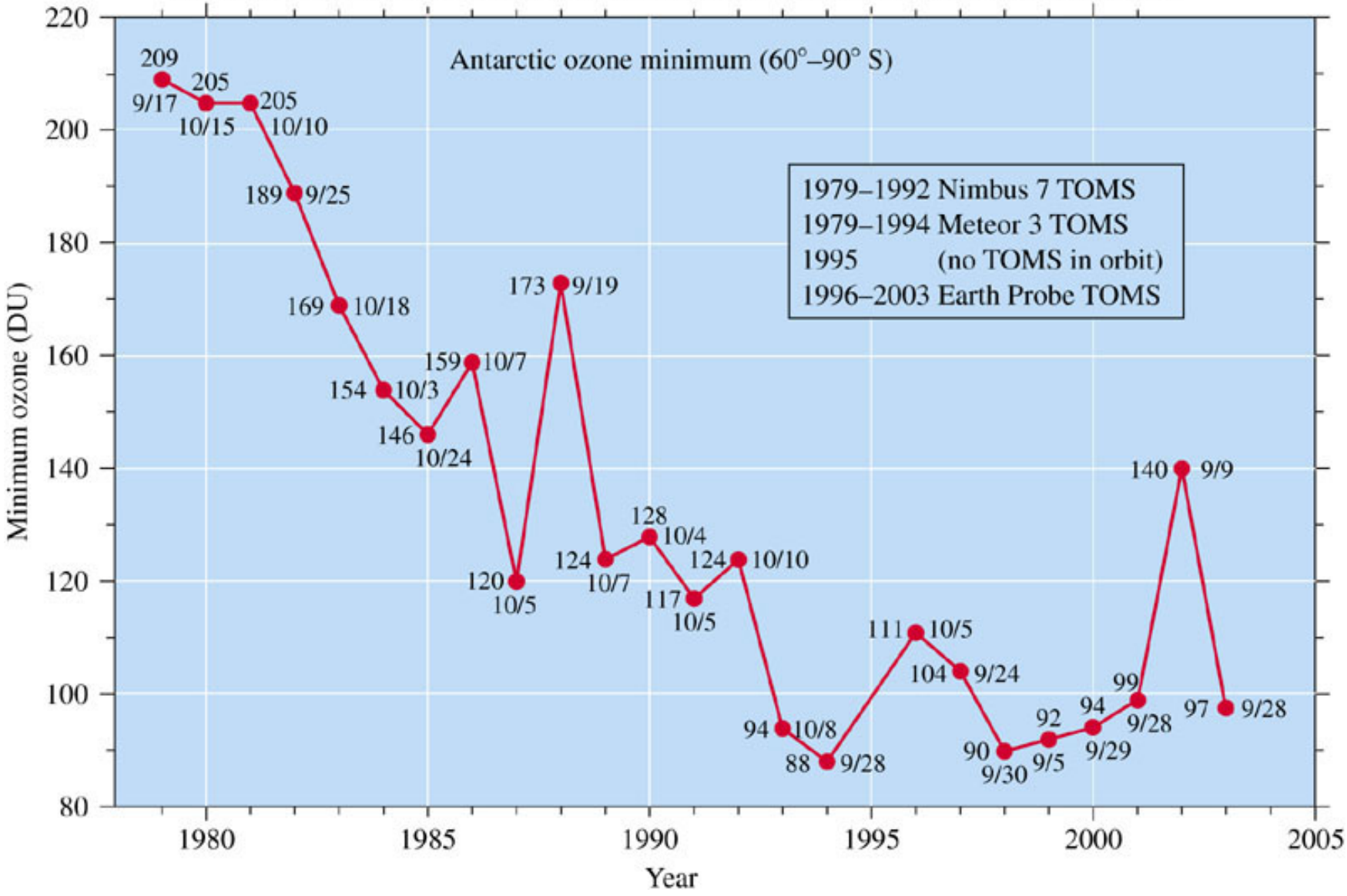
Ozone: What and Where Is It?



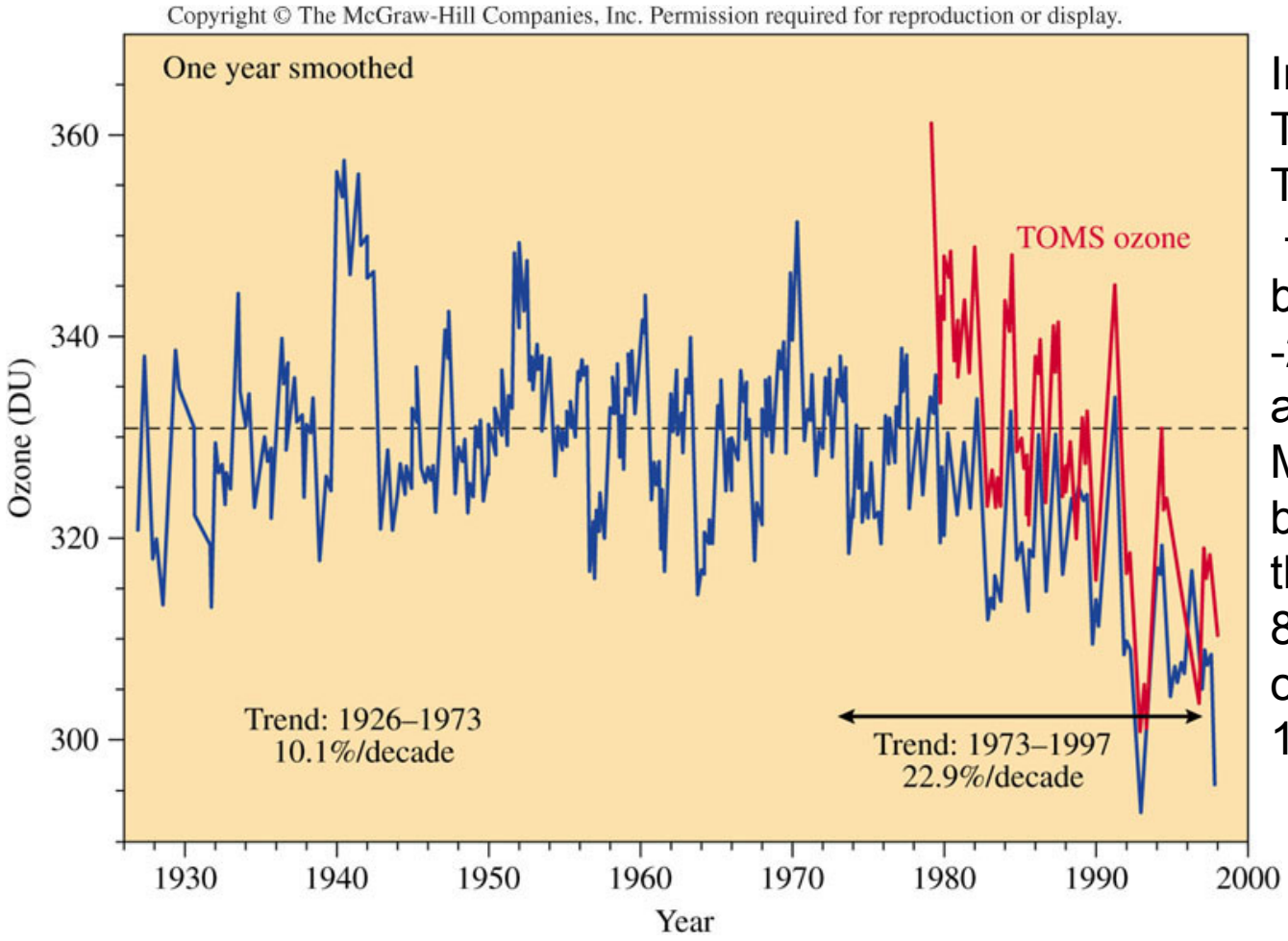
The Chapman Cycle



Stratospheric Ozone Destruction – A Polar Phenomenon

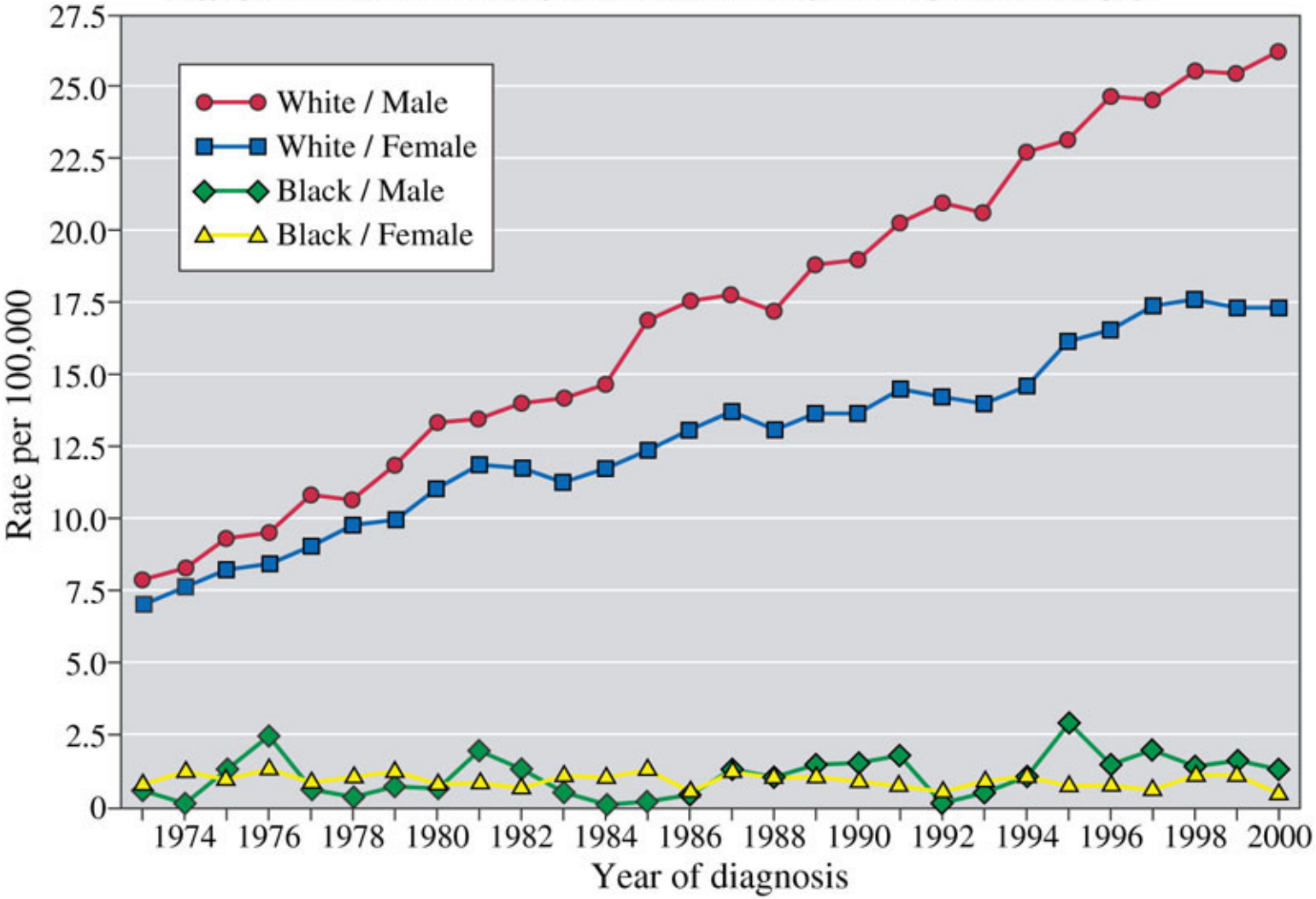


Stratospheric Ozone Destruction – Also A Global Phenomenon



Important correction:
These numbers are typos.
The **actual** trends were a +0.1%/decade increase before 1973 and a -2.9%/decade decrease after 1973.
Much smaller, obviously, but still real. Overall, there is approximately an 8% decrease in strat. ozone at midlatitudes since 1973.

Biological Effects of Ultraviolet Radiation



Scientists have determined that a given % reduction in O_3 concentration will produce twice that % increase in skin cancer

Stratospheric Ozone Destruction – A Global Phenomenon

- Natural Causes of Ozone Depletion
  - Water (5ppm) in Stratosphere

$$H_2O + photon \rightarrow \bullet OH + \bullet H$$

    •OH is the hydroxyl radical, also common in troposphere
  - Nitrogen monoxide, NO

    NO is **also** produced in the stratosphere from anthropogenic sources – particularly from the engines of high-flying aircraft

These natural "sinks" of ozone can **not** describe the depletion that has been observed

Chlorofluorocarbons: Properties, Uses and Interactions with Ozone

- CFCs
  - Made up of carbon, fluorine, and chlorine
  - Halogens – group 7A
    - Diatomics in their standard state

Chlorine

F_2 (g) and Cl_2 (g)

Bromine

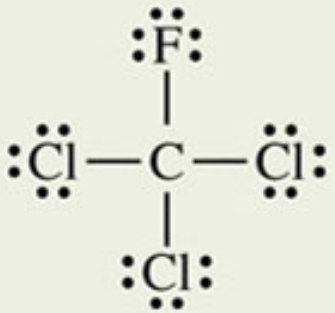
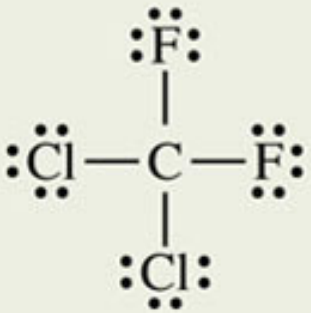
Br_2 (l)

Iodine

I_2 (s)

Chlorofluorocarbons: Properties, Uses and Interactions with Ozone

Table 2.6 Two Important Chlorofluorocarbons

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

Chlorofluorocarbons: Properties, Uses and Interactions with Ozone

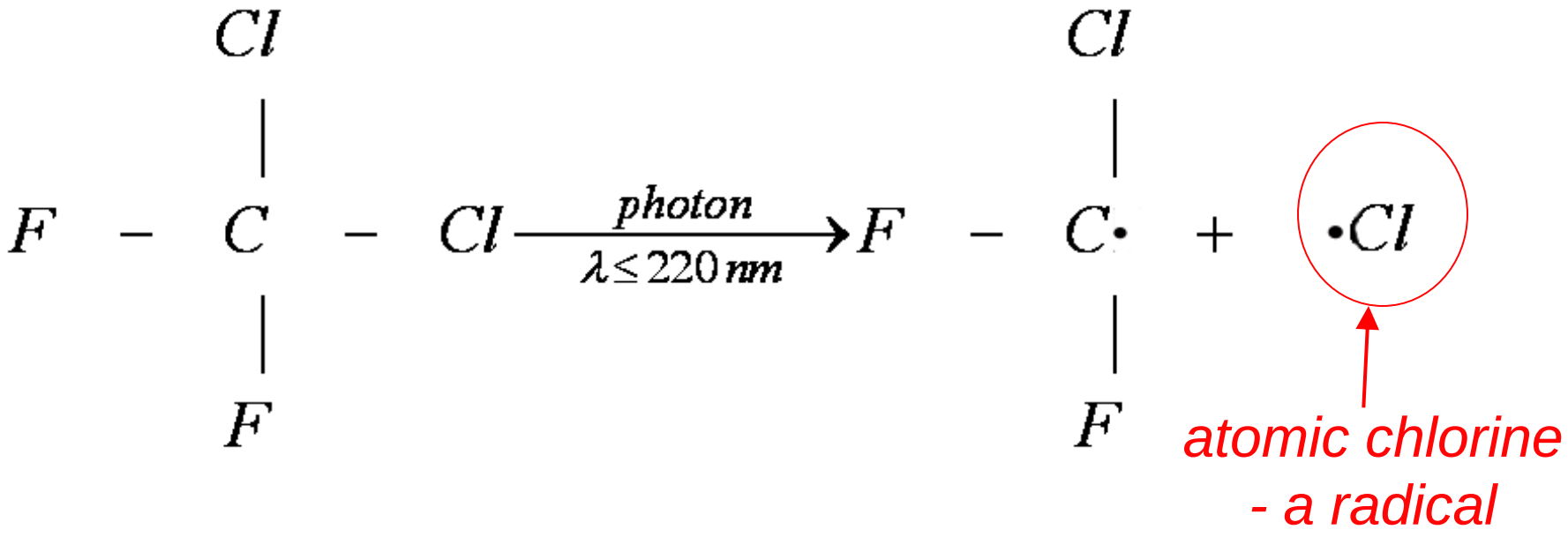
- Completely synthetic – invented in the 1930s by DuPont (“Freon”)
- Nontoxic, nonflammable, nonreactive
- Replaced NH_3 and SO_2 as refrigerants
- Allowed for widespread introduction of Air Conditioning in the 1960s
- Used to create bubbles in plastic foams
- Used as propellants in aerosol spray cans
- Used as residue cleaners in electronic fabrication

Chlorofluorocarbons: Properties, Uses and Interactions with Ozone

- Revolutionized Western civilization!
- So… what's the problem?

Chlorofluorocarbons: Properties, Uses and Interactions with Ozone

- CFCs very stable (Freon-12 has lifetime of 120 years)
- CFCs do not react in the troposphere, but drift up into the stratosphere where they are exposed to the same UV light that breaks bonds in oxygen and ozone



Chlorofluorocarbons: Properties, Uses and Interactions with Ozone

- Reaction of atomic chlorine in stratosphere

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

$$ClO\bullet + ClO\bullet \rightarrow ClOOCl$$

$$ClOOCl \xrightarrow{UVLight} ClOO\bullet + Cl\bullet$$

$$ClOO\bullet \rightarrow Cl\bullet + O_2$$

$$2\ O_3 \rightarrow 3\ O_2$$

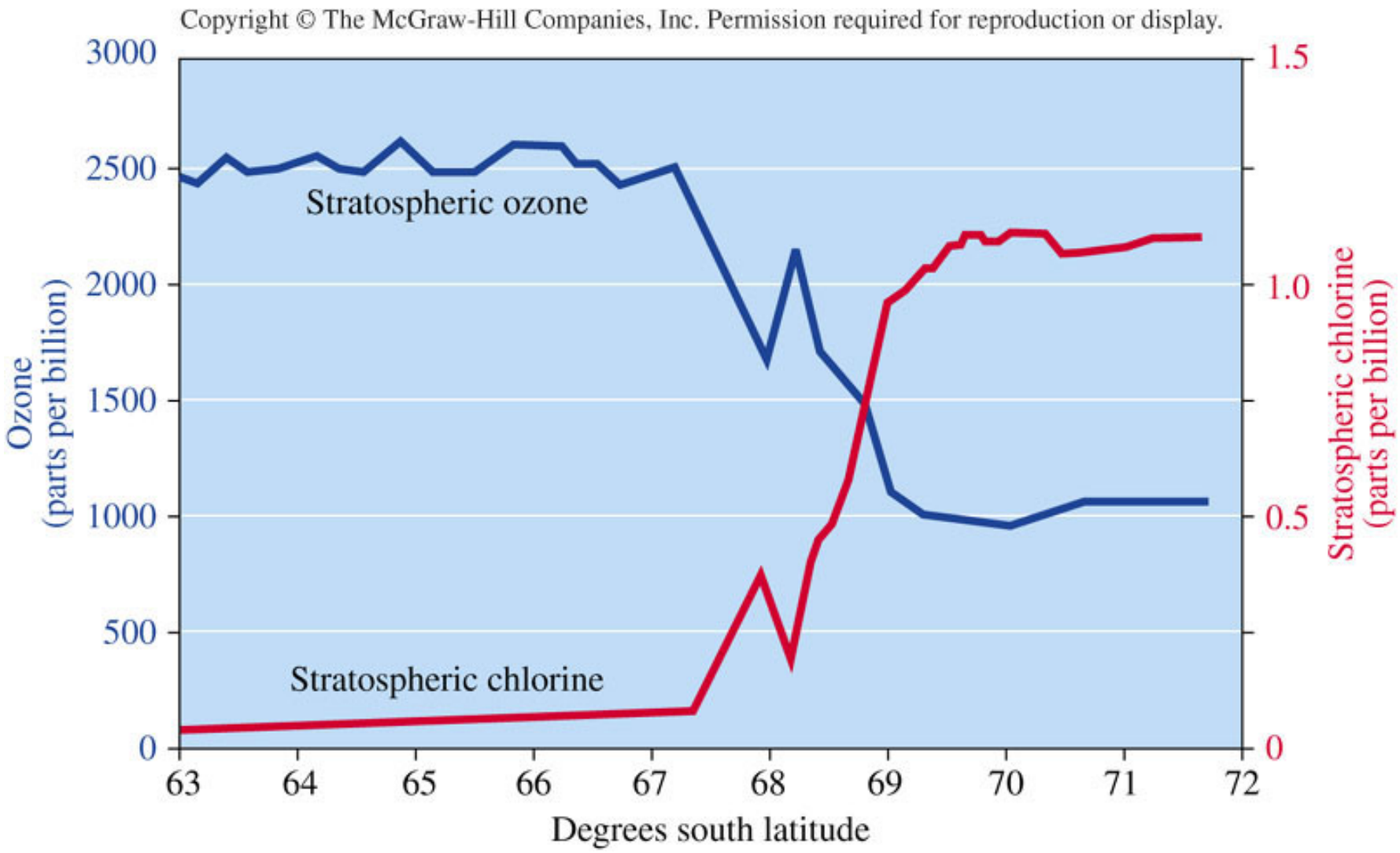
Chlorofluorocarbons: Properties, Uses and Interactions with Ozone

- Atomic chlorine acts as a **catalyst**
  - A chemical substance that participates in a chemical reaction and influences its speed without undergoing permanent change
- A single chlorine atom can catalyze the destruction of as many as 100,000 O_3 molecules.

Other ozone-depleting compounds

- “CFC”s which don’t actually contain Cl (i.e., CF_4) produce similar effects with F radicals
- As do brominated species (CH_3Br, one of the world’s most widely used pesticides)
- “Halons” – C, B, and F – are widely used as firefighting foams

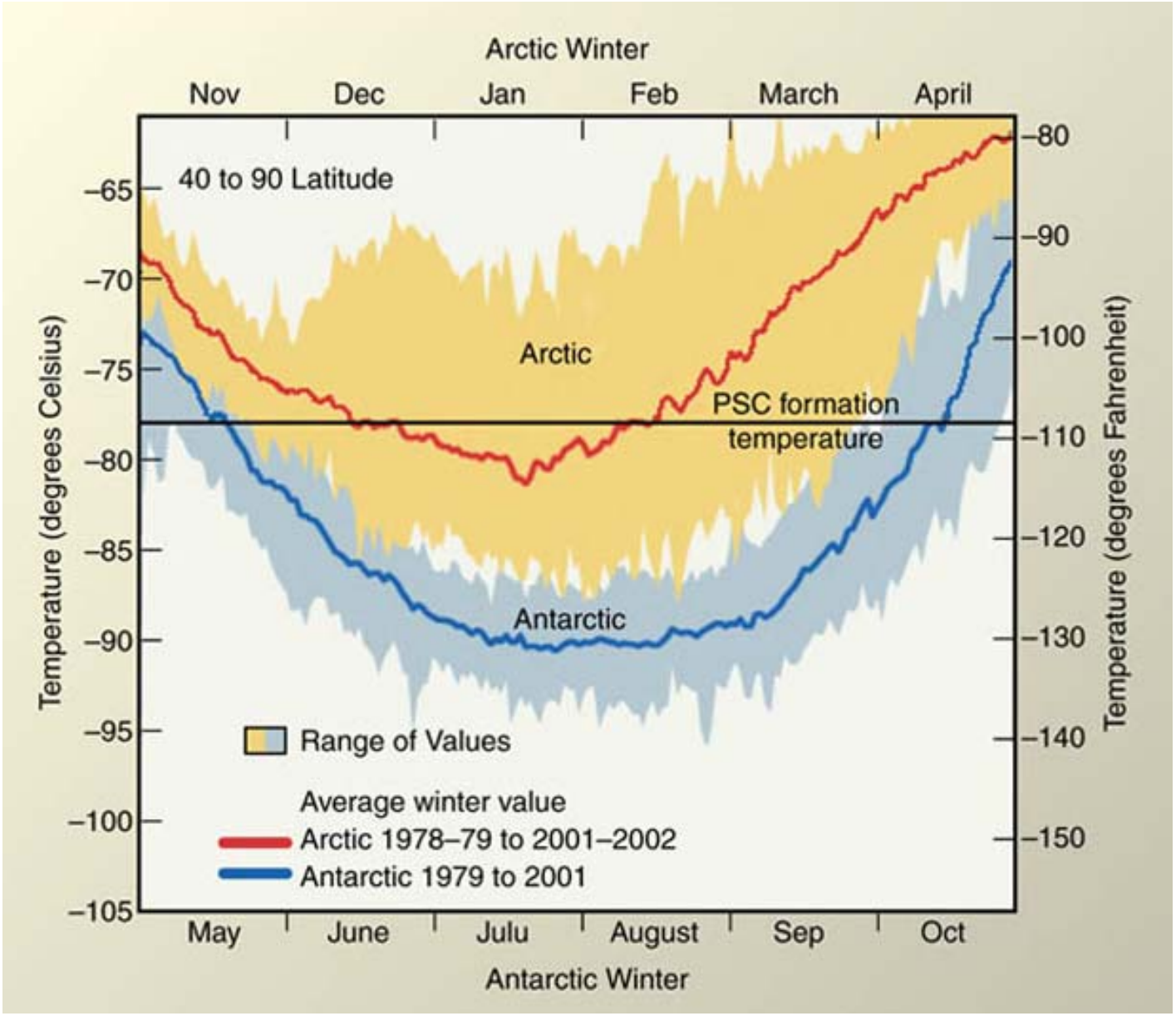
Chlorofluorocarbons: Properties, Uses and Interactions with Ozone

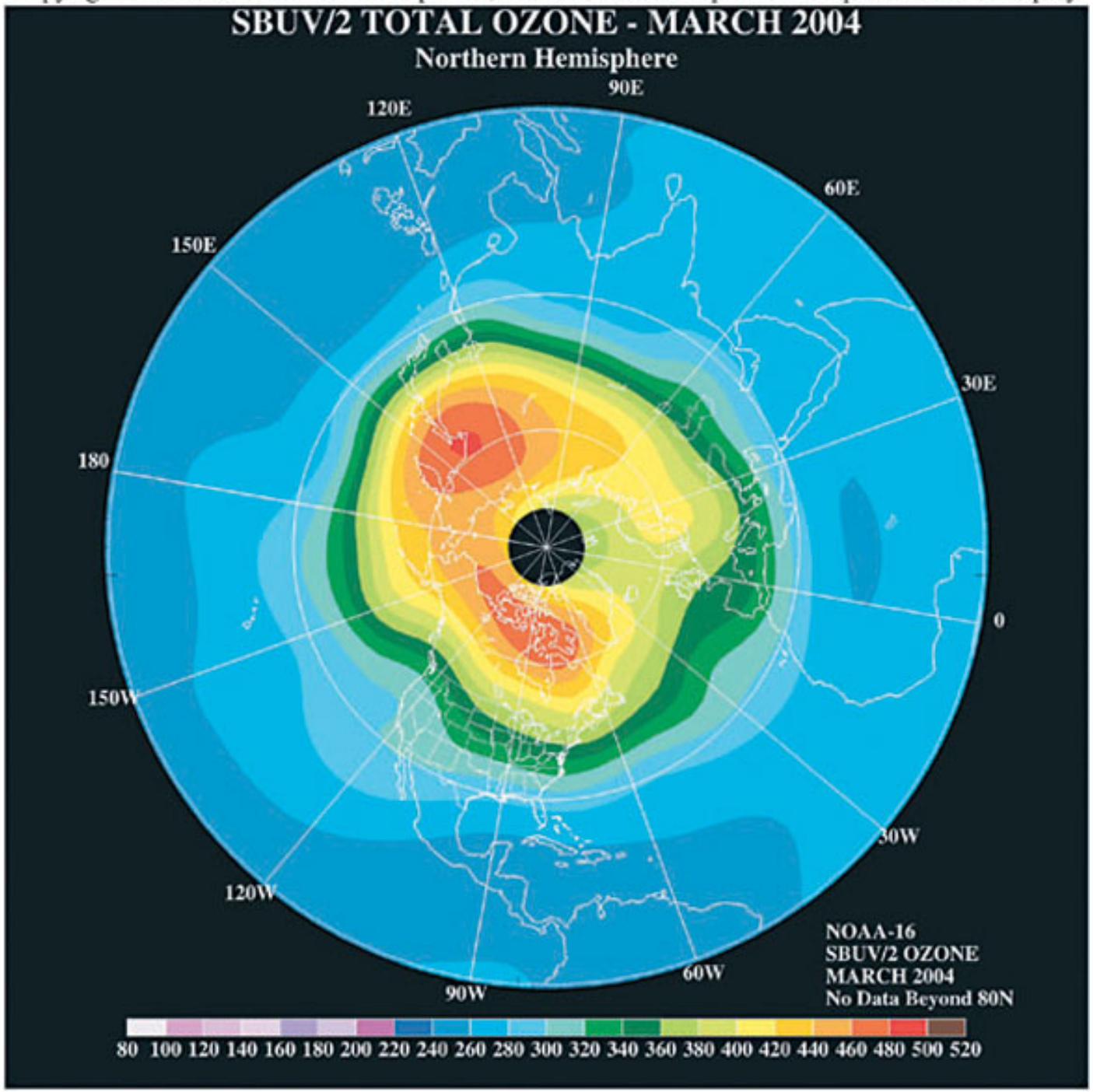


The Antarctic Ozone Hole: A Closer Look

- Vortex winds blow around the South Pole
- Temperatures as low as -90°C
- Polar Stratospheric Clouds (PSCs) form
- Perpetual darkness during winter
- Reservoir molecules adsorb ("stick") to clouds
  - React to form active molecules (HOCl & Cl_2)
- Spring comes
  - Warmer weather
  - Sunshine

The Antarctic Ozone Hole: A Closer Look





Regulation of CFCs

The U.S. banned CFCs in spray aerosols in 1978, but international regulation was required

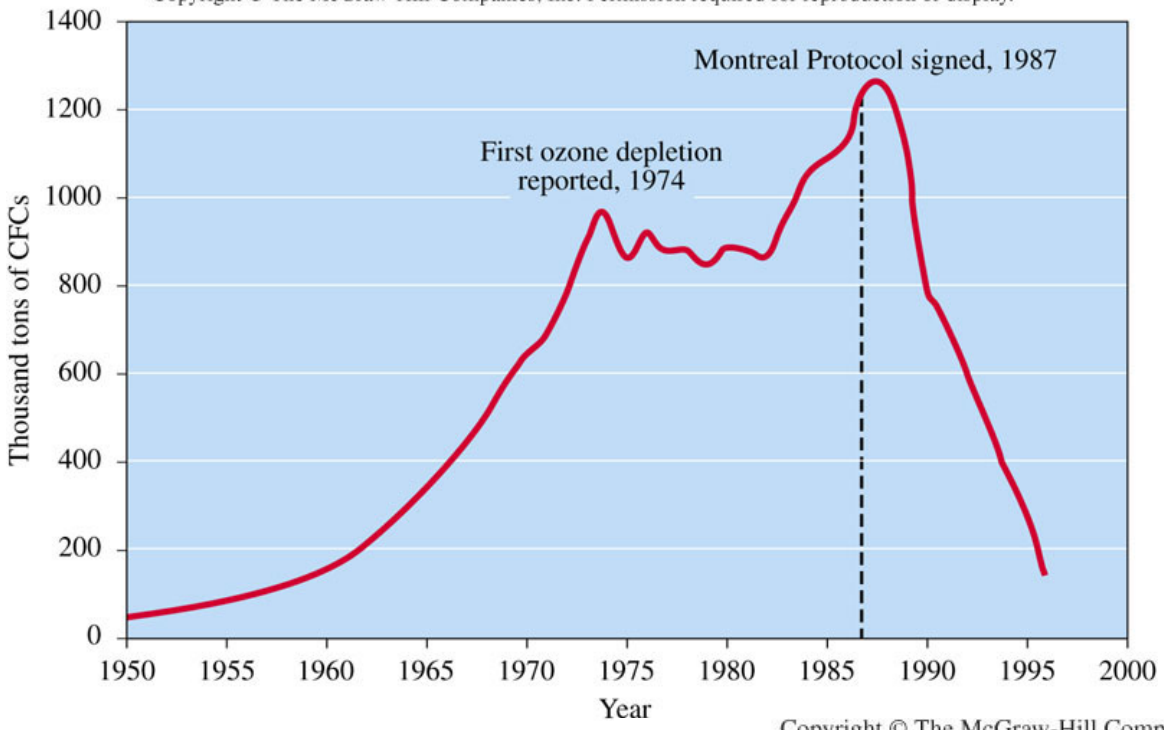
1985 saw the Vienna Convention on the Protection of the Ozone Layer, which led to scientific discussion, but the science wasn't well understood

The Montreal Protocol was signed in 1987, and made sweeping changes

Kofi Annan: "[It is] perhaps the single most successful international agreement to date..."

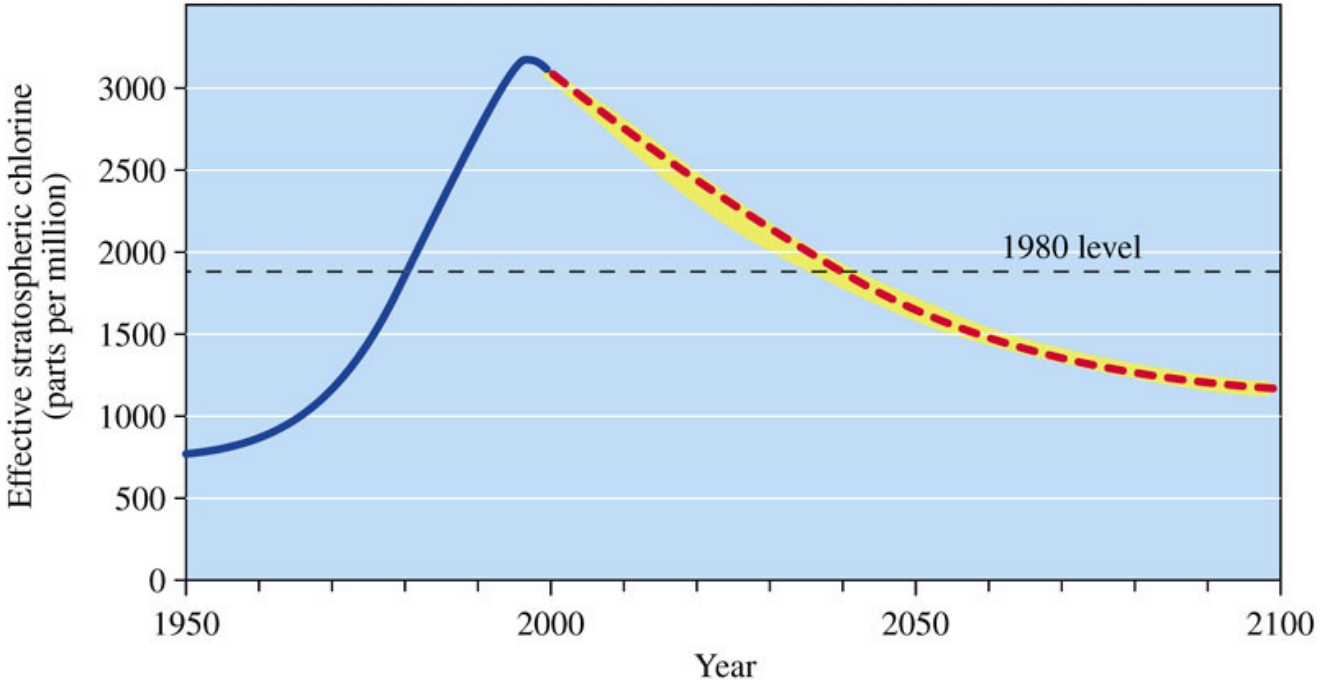
Regulation of CFCs – The Montreal Protocol

- Bound nations to reduce their CFC output to one half of 1986 levels by 1998
- Required future meetings to revise standards
- In 1990, 100+ nations agreed to halt CFC production altogether by 2000, and this phase-out was accelerated further at later meetings
- The Beijing Amendment of 1999 added bromine-containing “halons” …
- … AND required the regulation of the short-term replacement HCFCs
- Important provisions were made for developing nations whose economies couldn’t sustain the mandated changes



Global Production of CFCs

Stratospheric concentrations of chlorine



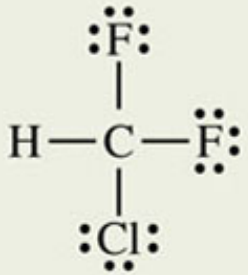
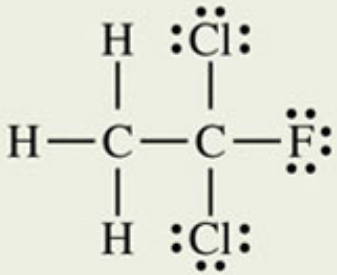
Looking to the Future

- *What can be done?*
  - *–Wait it out?*
  - *–Chemically remove the chlorine?*
  - *–Replace lost ozone?*

Looking to the Future

- Find **replacement** molecules – make CFCs obsolete
  - Hydrochlorofluorocarbons (HCFCs)
  - Hydrofluorocarbons (HFCs)

Table 2.7 Two Important Hydrochlorofluorocarbons

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

Looking to the Future

Find **replacement** molecules – make CFCs obsolete

- Hydrochlorofluorocarbons (HCFCs)
- Hydrofluorocarbons (HFCs)

Why are they "better"?

$$\bullet OH + HCFCl_2 \rightarrow H_2O + \bullet CFCl_2$$

Since hydroxyl radical is prevalent in the troposphere, this reaction may take place **before** the species has the opportunity to reach the stratosphere

The radical fragment that's left behind will react with **something** to ensure that it is destroyed

Looking to the Future

- Find **replacement** molecules – make CFCs obsolete
  - Hydrochlorofluorocarbons (HCFCs)
  - Hydrofluorocarbons (HFCs)
- Requires a balancing act:
  - Using H makes the molecule more reactive, more flammable and lighter
  - Using Cl makes the molecule heavier, but more toxic
  - Eventually, we'd like to eliminate Cl entirely – this is where HFCs come in

Pyrocool FEF being applied to subterranean fires at Ground Zero, North Tower at West Street, September 30, 2001.
Pyrocol FEF is environmentally benign and yet more effective than the halons (molecules containing carbon, fluorine, and bromine) traditionally used to fight fires.

Looking to the Future – CFC Regulation and Use World Wide

- Your text asks you to investigate the planned 2005 phase-out of methyl bromide
- In 2005 and 2006, the US successfully obtained a “critical use exemption”, fearing that US agriculture would be unable to compete with developing nations who are not required to eliminate CH_3Br until 2015

Looking to the Future – CFC Regulation and Use World Wide

- Some developing nations – particularly China and India – initially refused to sign the Montreal Protocol due to economic concerns
- They and other reluctant countries were convinced to sign because of the Multilateral Fund, which disburses money to help modernize industry in poorer nations

Looking to the Future – CFC Regulation and Use World Wide

"Our development strategies cannot be sacrificed for the destruction of the environment caused by the West"

– Ashis Kithari, a member of an Indian environmental group

- CFC consumption by the **developing** world has increased from 1986 - 2002

Looking to the Future

Perhaps most pressing… we have since learned that HFCs and HCFCs are "greenhouse gases", and contribute to global warming…

Which is the subject of Chapter 3.