Chapter 18

Environmental Chemistry

I) Earth's Atmosphere

A) 4 regions based on temperature

1) Troposphere

Temp. dec. w. inc. altitude

- min. of ~ 215 K at 10 km (at tropopause)

2) Stratosphere

Temp. inc. w. inc. altitude

- max. of ~ 275 K at 50 km (at stratopause)

3) Meso<u>sphere</u>

Temp. dec. w. inc. altitude

- min. of ~ 180 K at 85 km (at mesopause)

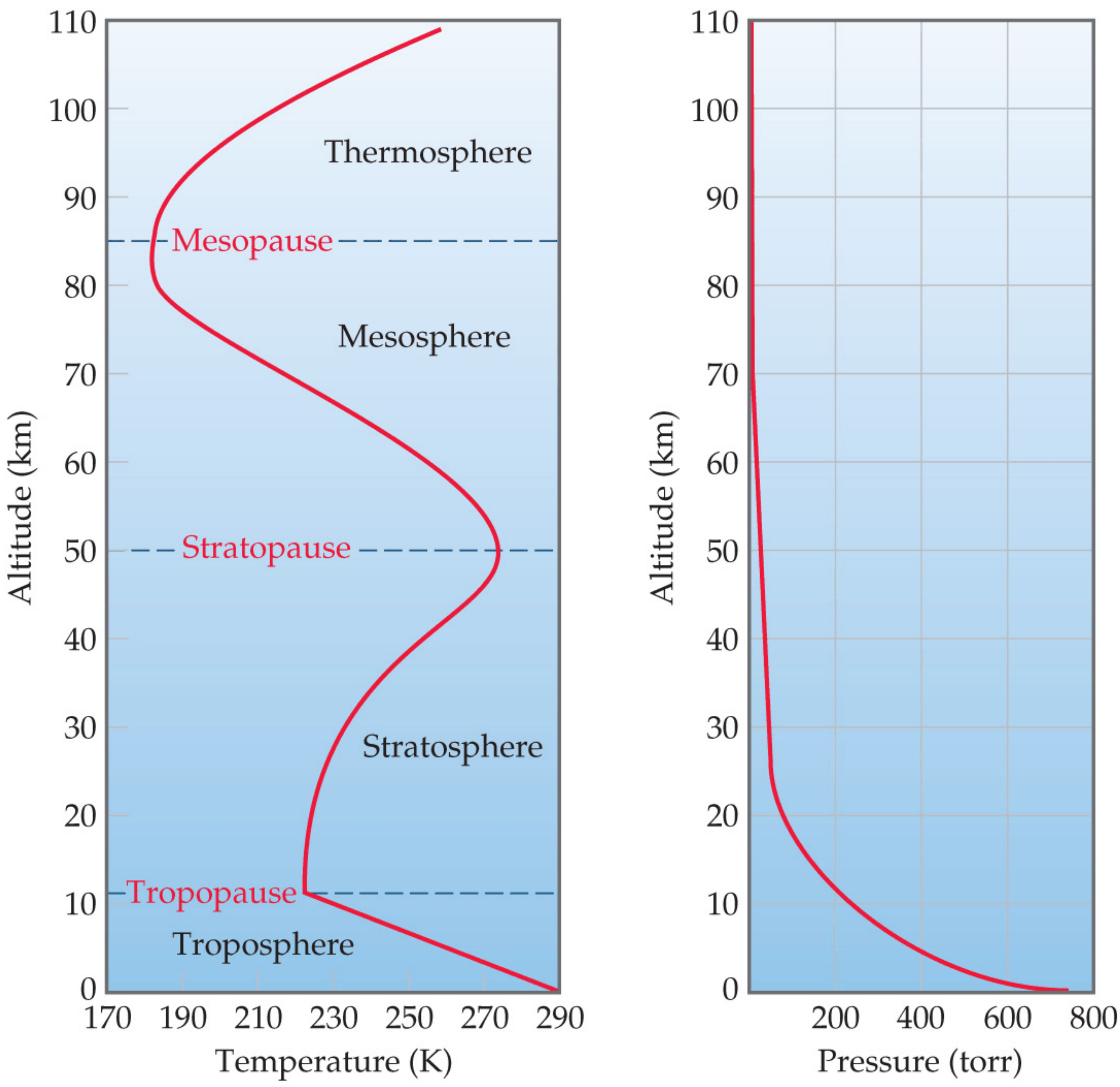
4) Thermosphere

Temp. inc. w. inc. altitude

- max. of ~ 260 K at 110 km

Mixing across boundaries (indicated with suffix "-pause") is slow

- pollutants don't move quickly from one region to another


110
100
90
80
70
60
50
40
30
20
10
0
Altitude (km)
Thermosphere
Mesopause
Mesosphere
Stratopause
Stratosphere
Tropopause
Troposphere
170
190
210
230
250
270
290
Temperature (K)
Pressure (torr)
200
400
600
800

B) Pressure

Dec. in regular way w. inc. in altitude

- drops more rapidly
  at lower elevations

  - due to compressibility of
    atmosphere (amount of material
    at various elevations)

troposphere & stratosphere

- 99.9% of mass (75% in tropo.)

C) Composition

Lighter particles rise to top

- comp. not uniform

N_2 & O_2: ~ 99% of atmosphere at sea level

CO_2 & noble gases
- most of other 1%

1) Conc

Mole Fraction

$$P_g = \boldsymbol{X}_g P_{tot}$$

Vol Fraction ≡ Mole Fraction

TABLE 18.1 • The Major Components of Dry Air Near Sea Level

Component*	Content (mole fraction)	Molar Mass (g/mol)
Nitrogen	0.78084	28.013
Oxygen	0.20948	31.998
Argon	0.00934	39.948
Carbon dioxide	0.000382	44.0099
Neon	0.00001818	20.183
Helium	0.00000524	4.003
Methane	0.000002	16.043
Krypton	0.00000114	83.80
Hydrogen	0.0000005	2.0159
Nitrous oxide	0.0000005	44.0128
Xenon	0.000000087	131.30

*Ozone, sulfur dioxide, nitrogen dioxide, ammonia, and carbon monoxide are present as trace gases in variable amounts.

Often use ppm - Vol ppm

1 ppm = 1 part vol/10^6 parts vol

= 1 mol cmpd/10^6 mol air

= $X_g * 10^6$

a) Ex : The partial pressure of CO in an area is 6.02×10^{-3} torr when the total pressure is 755 torr. What is its conc. in ppm?

1) Reactivity

N_2 - very low reactivity

O_2 - very reactive

- forms acidic oxides w. nonmetals

  CO_2 SO_2 SO_3

  react w. H_2O to form acids

  H_2CO_3 H_2SO_3 H_2SO_4

- forms basic oxides w. metals

  Na_2O CaO

  react w. H_2O to form bases

  NaOH $Ca(OH)_2$

D) Photochemistry of the Atmosphere

Radiation passing through upper atmosphere causes two kinds of chemical changes:

photodissociation

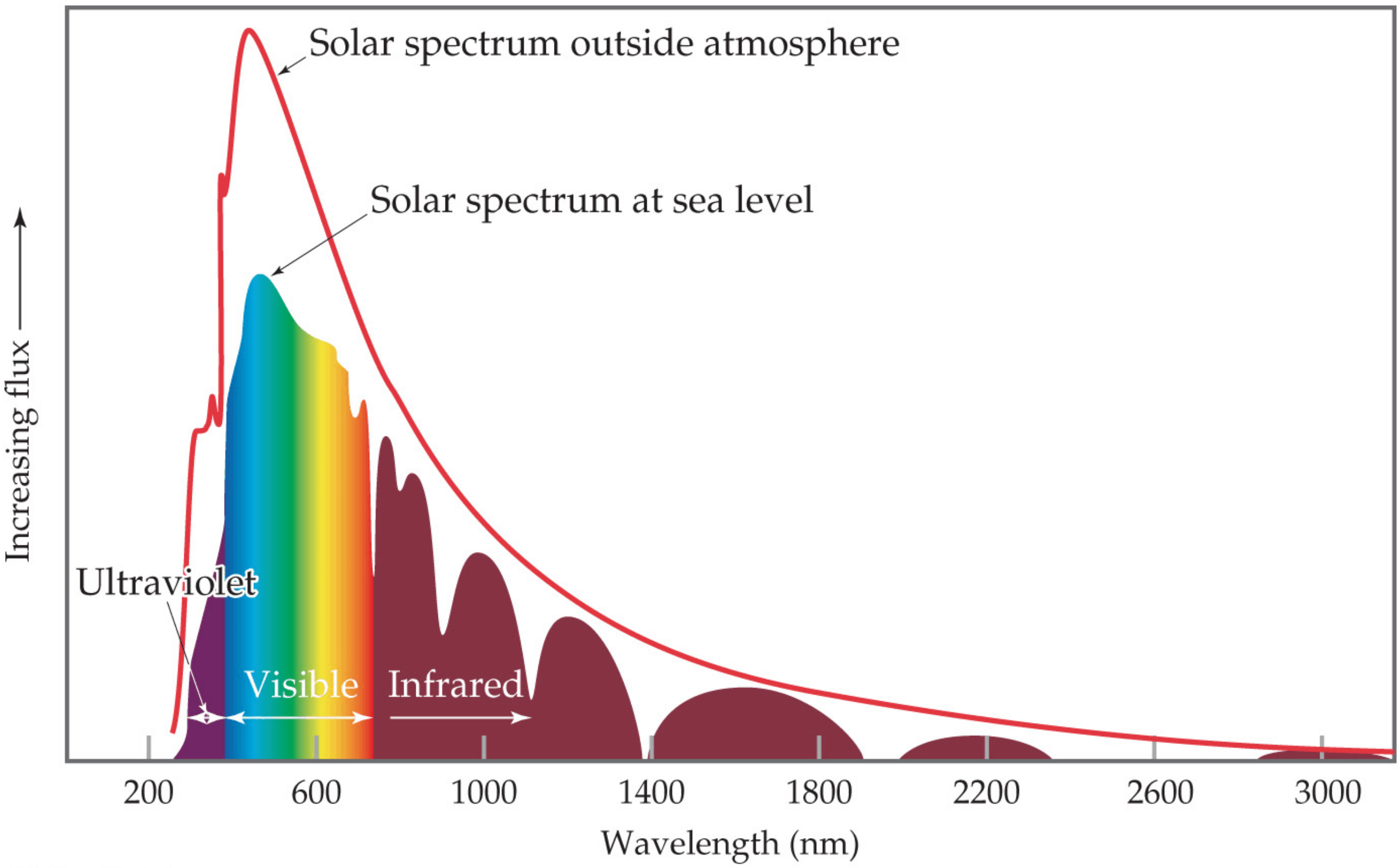
&

photoionization

Remember:

$$E_{photon} = h\,\nu = \frac{h\,c}{\lambda}$$

$h = 6.63 \times 10^{-34}$ J•s (Planck's const.)


Solar spectrum outside atmosphere
Solar spectrum at sea level
Increasing flux
Ultraviolet
Visible
Infrared
200
600
1000
1400
1800
2200
2600
3000
Wavelength (nm)

1) Photodissociation

Chemical bond breakage due to absorption of a photon

$$O_2\,(g) \xrightarrow{h\nu} 2\ \cdot\ddot{\underset{\cdot\cdot}{O}}\cdot\ (g)$$

Occurs mostly above 130 km

a) Ex : The bond energy of O_2 is 495 kJ/mol. Will a photon with a wavelength of 425 nm cause dissociation?

2) Photoionization

Absorption of a photon by a molecule (or atom) resulting in the ejection of an e^-

Cation

Occurs for N_2, O_2, O & NO at altitudes above 90 km

- high-energy uv radiation

$\lambda < 135$ nm

- these wavelengths are completely filtered out

E) Ozone in the Stratosphere

O_3 key absorber of photons w.

$240 \text{ nm} \leq \lambda \leq 310 \text{ nm}$

~ 90% of ozone in stratosphere

- occurs mostly near stratopause

1) Formation of Ozone

$$O (g) + O_2 (g) \longrightarrow O_3^* (g)$$

rxn. releases 105 kJ/mol

O_3^* contains excess energy

O_3^* decomposes easily if energy not dissipated

collide w. another particle, M,
& transfer energy to it

$$O\,(g) + O_2\,(g) \rightleftharpoons O_3^*\,(g)$$

$$O_3^*\,(g) + M\,(g) \rightarrow O_3\,(g) + M^*\,(g)$$

$$O\,(g) + O_2\,(g) + M\,(g) \rightleftharpoons O_3\,(g) + M^*\,(g)$$

M : usually N_2 or O_2

Highest rate of formation of O_3 occurs at ~ 50 km

- balance between stabilizing collisions & radiation energetic enough to dissociate O_2

2) Photodissociation of Ozone

O_3 dissociates by absorption of photons w. $\lambda < 1140$ nm

- strongest absorption is:

$$240 \text{ nm} \leq \lambda \leq 310 \text{ nm}$$

Have cyclic process of O_3 formation & decomposition

$$O_2 (g) + h\nu \rightarrow O (g) + O (g)$$

$$O (g) + O_2 (g) + M (g) \rightarrow O_3 (g) + M^* (g)$$

(heat released)

$$O_3 (g) + h\nu \rightarrow O_2 (g) + O (g)$$

$$O (g) + O (g) + M (g) \rightarrow O_2 (g) + M^* (g)$$

(heat released)

Radiant energy => thermal energy

Temp rise in stratosphere

II) Human Activities & Atmosphere

A) Chlorofluorocarbons (CFCs) & Ozone

$CFCl_3$ (Freon 11)

CF_2Cl_2 (Freon 12)

Unreactive in lower atmosphere

- insoluble in H_2O
  - not removed by rain or dissolution in oceans

Cause ozone depeletion

Photolysis of CFCs

light-induced rupture of C-Cl bond

$190\ nm \leq \lambda \leq 225\ nm$

Occurs at greatest rate at ~ 30 km

$CF_2Cl_2\ (g) + h\nu \rightarrow CF_2Cl\ (g) + Cl\ (g)$

$Cl\ (g) + O_3\ (g) \rightarrow ClO\ (g) + O_2\ (g)$

rate = k [Cl][O_3] $k = 7.2 \times 10^9\ M^{-1}s^{-1}$
(at 298 K)

$ClO\ (g) + h\nu \rightarrow O\ (g) + Cl\ (g)$

Sequence of steps resulting in:

$$2\ Cl\ (g) + 2\ O_3\ (g) \rightarrow 3\ ClO\ (g) + 2\ O_2\ (g)$$

$$2\ ClO\ (g) + h\nu \rightarrow 2\ O\ (g) + 2\ Cl\ (g)$$

$$O\ (g) + O\ (g) \rightarrow O_2\ (g)$$

$$2\ O_3\ (g) \xrightarrow{Cl} 3\ O_2\ (g)$$

Cl acts as a catalyst

each Cl atom destroys ~ 10^5 O_3 molec. before being destroyed itself

Ozone Hole - Oct. 1989 O_3 levels over South Pole dropped to ~ 60% of Aug. levels

- since 1996 leveled off

B) Sulfur Cmpds and Acid Rain

S_8 (s) + 8 O_2 (g) ⟶ 8 SO_2 (g)

SO_2 most serious health hazard

~ 87 million tons (7.9 x 10^{13} g) SO_2
released worldwide every year

China produces 22 million tons/year

combustion of coal accounts for 65%
of SO_2 released annually in US

EPA's new standard (2010)
for SO_2 emissions:

75 ppb/hr (about ½ previous)

SO_2 major contributor to acid rain

1) Combustion rxns of Hydrocarbons, Alcohols and Sulfur Cmpds

$CH_4 + O_2 \longrightarrow$

$CH_3OH + O_2 \longrightarrow$

$CH_3SH + O_2 \longrightarrow$

3) Natural Rainwater

Naturally Acidic

pH ~ 5.6

due mainly to CO_2

$$CO_2\,(g) + H_2O\,(\ell) \longrightarrow H_2CO_3\,(aq)$$

$$K_{a1} = 4.3 \times 10^{-7}$$

$$K_{a2} = 5.6 \times 10^{-11}$$

Can usually be neutralized by CO_3^{2-} (and other basic anions) in soil & HCO_3^- in waterways (acts as buffer)

4) Acid Rain

$$2\ SO_2\ (g)\ +\ 8\ O_2\ (g) \longrightarrow 2\ SO_3\ (g)$$

$$SO_2\ (g)\ +\ H_2O\ (\ell) \longrightarrow H_2SO_3\ (aq)$$

For H_2SO_3

$K_{a1}\ =\ 1.7 \times 10^{-2}$

$K_{a2}\ =\ 6.4 \times 10^{-8}$

$$SO_3\ (g)\ +\ H_2O\ (\ell) \longrightarrow H_2SO_4\ (aq)$$

For H_2SO_4

K_{a1} Very Large (strong acid)

$K_{a2}\ =\ 1.2 \times 10^{-2}$

a) <u>Ex</u> : What is the pH of a soln. containing 1.0 g SO_2 in 1.0 L of soln.?

Natural Waterways

pH : 6.5 – 8.5

Most organisms die at

pH < 4.0

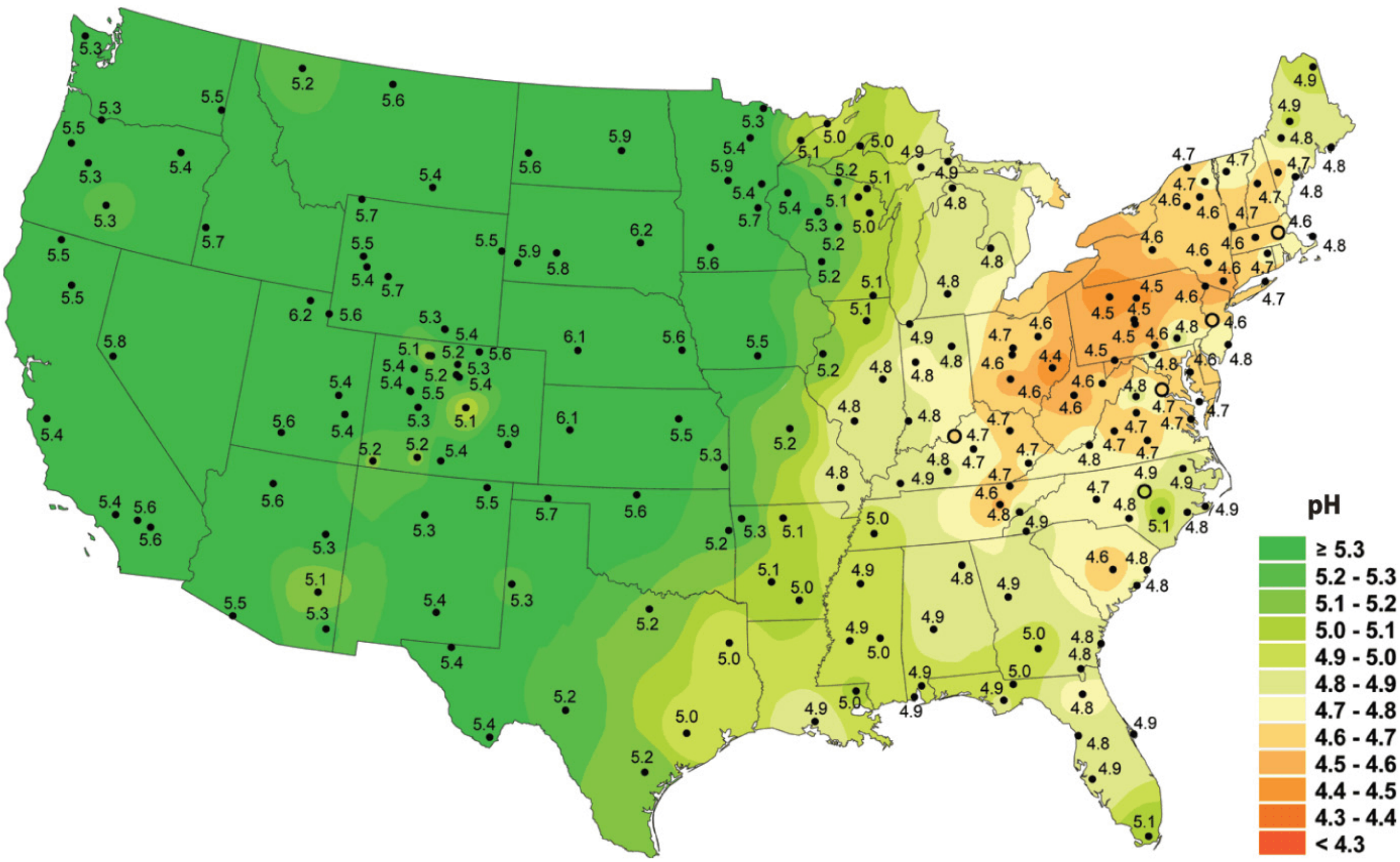
About 500 lakes in northeast & Canada are now devoid of life

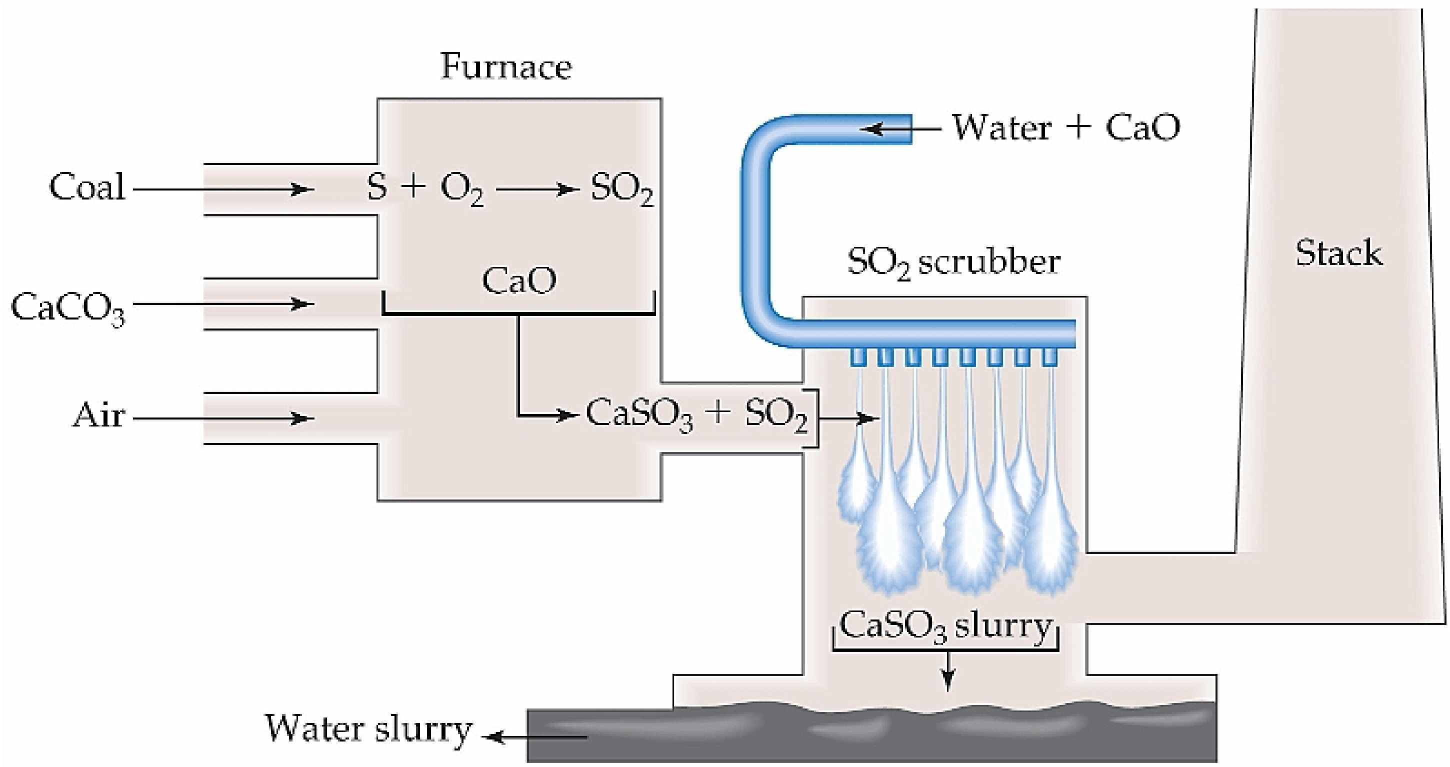
Corrodes metals & building materials

$CaCO_3$ (limestone)

- more soluble in acidic soln.

Clean Air Act (~ 1980) - reduced SO_2 emissions by > 40% by requiring use of scrubbers on power plants


pH
≥ 5.3
5.2 - 5.3
5.1 - 5.2
5.0 - 5.1
4.9 - 5.0
4.8 - 4.9
4.7 - 4.8
4.6 - 4.7
4.5 - 4.6
4.4 - 4.5
4.3 - 4.4
< 4.3


Furnace
Water + CaO
Coal
S + O2 → SO2
CaCO3
CaO
SO2 scrubber
Stack
Air
CaSO3 + SO2
CaSO3 slurry
Water slurry

C) Nitrogen Oxides & Photochem Smog

Majority of NO_x (x = 1 or 2) emissions (~ 50%) comes from transportation & some other from electric power plants

1) Nitric Oxide, NO

$$N_2\,(g) + O_2\,(g) \rightleftharpoons 2\,NO\,(g)$$

ΔH = 180.8 kJ (endothermic)

$K_p \approx 10^{-15}$ at 300 K

$K_p \approx 0.05$ at 2400 K

(temp. auto cylinder)

More favorable (more NO) at high temp.

2) Nitrogen Dioxide, NO_2

$$2\ NO\ (g) + O_2\ (g) \rightleftharpoons 2\ NO_2\ (g)$$

$$\Delta H = -180.8\ \text{kJ (exothermic)}$$

$K_p \approx 10^{12}$ at 300 K

$K_p \approx 10^{-5}$ at 2400 K

3) Photochemical Smog

Photodissociation of NO_2 initiates rxns associated with smog

$$NO_2\,(g) + h\nu \rightarrow NO\,(g) + O\,(g)$$

$$O\,(g) + O_2\,(g) + M\,(g) \rightarrow O_3\,(g) + M^*\,(g)$$

NO : slightly toxic but also
an impt. physiological
cmpd. (vasodilator)

NO_2 : yellow-brown, poisonous,
choking odor

when put in H_2O leads to HNO_3 &
contributes to acid rain

O_3 : reactive, toxic at grd. level

D) Greenhouse Gases & Climate Chg.

Atmosphere is essential in maintaining a reasonably uniform & moderate temp. on Earth's surface

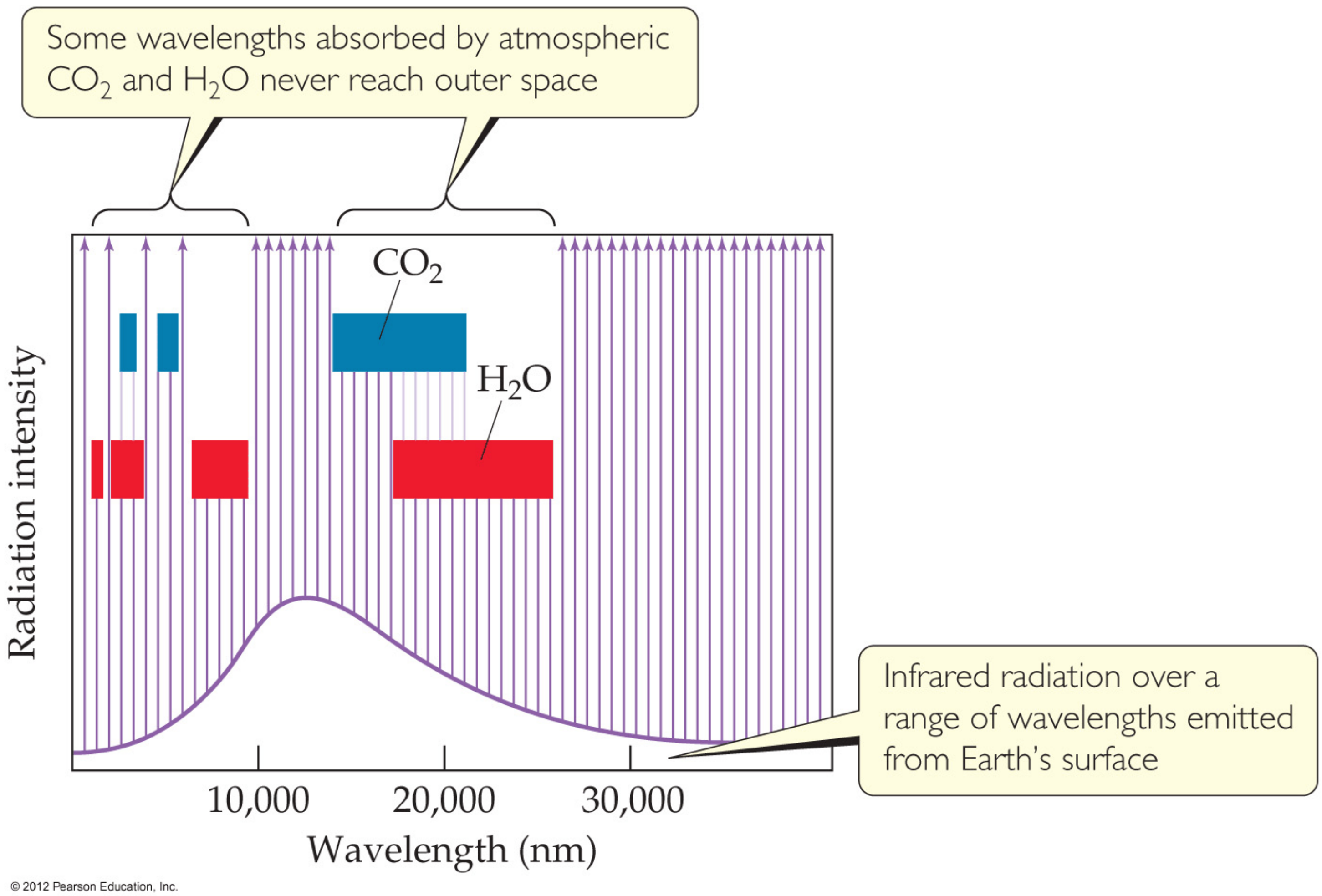
H_2O and CO_2 absorb IR radiation leaving surface and radiate part of it back to the surface as heat.

Greenhouse Effect

H_2O & CO_2 main greenhouse gases

1) H_2O

largest contributor to GH effect. Without it Earth would cool off greatly at night.


Some wavelengths absorbed by atmospheric CO_2 and H_2O never reach outer space
CO_2
H_2O
Radiation intensity
Infrared radiation over a range of wavelengths emitted from Earth's surface
10,000
20,000
30,000
Wavelength (nm)
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2) CO_2

plays secondary but very impt. role in affecting surface temp.

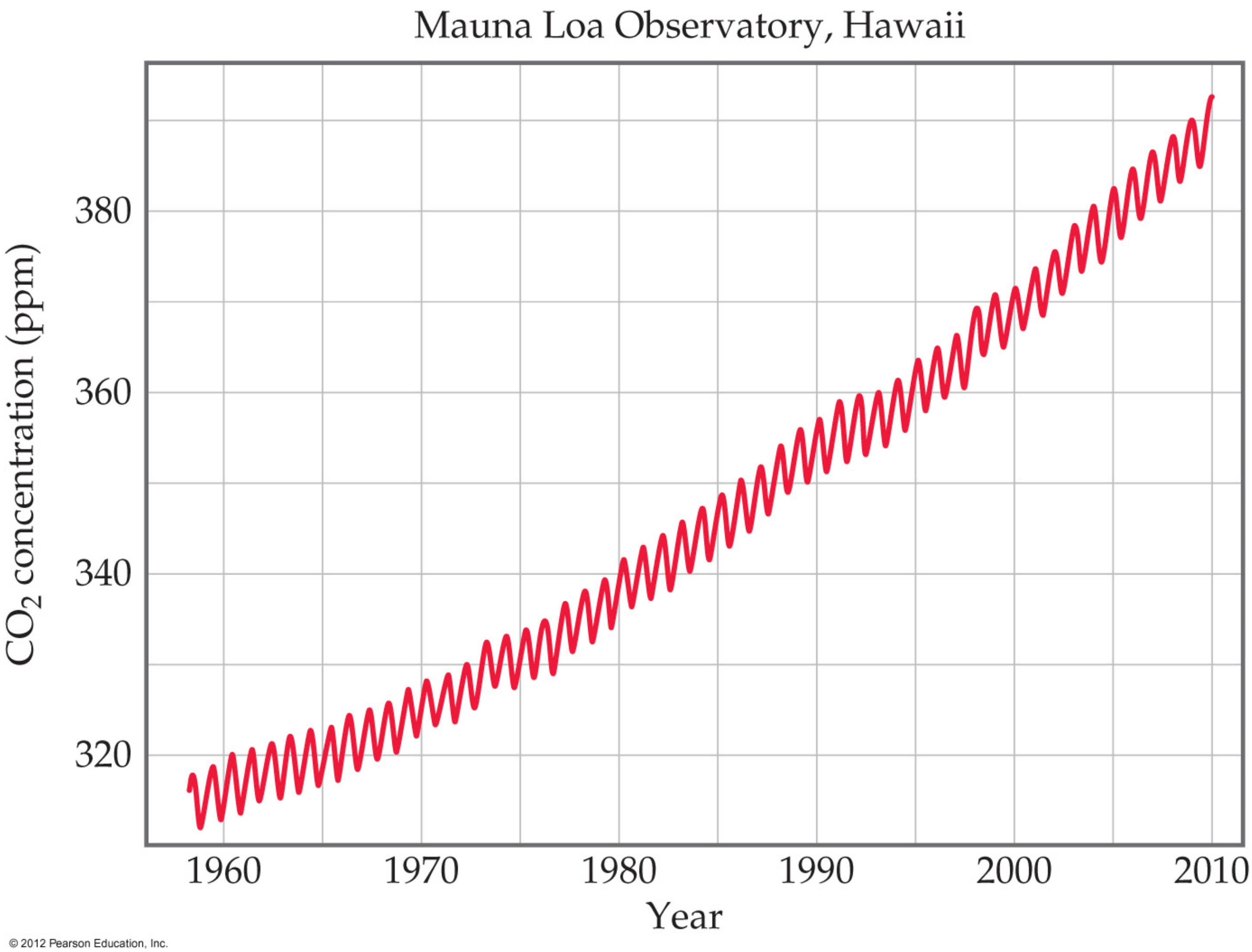
Combustion of fossil fuels responsible for majority of extra CO_2

get ~ 3 g of CO_2 per g of gasoline (mostly C_8H_{18})

~ 2.2×10^{16} g (24×10^{9} tons) of CO_2 annually

CO_2 levels remained fairly constant for about 10,000 yr until about 300 yr ago (Industrial Revolution)

- steady inc. since (by ~30%)



In last 120 yrs avg. temp. inc. somewhere between 0.4 & 0.8 °C (0.8 - 1.4 °F)

3) Climate Change

Rise in CO_2 seems to parallel a rise in global air temp.

Are these changes a natural occurrence or caused by human activity?

97% of Climatologists agree human activity plays a major role in the level of GH gases and rise in temp.

Temp. inc. affect wind and ocean currents in ways that will cool some areas and warm others

Some areas (Alaska, Arctic, Northern Eurasia) have warmed by up to 6 °C (10 °F) while other areas (N. Atlantic & Central N. Pacific) have cooled somewhat

- some due to natural phenomena but not all

a) Fixes?

Capture CO_2

- store it undergrd.
- use it for other purposes

Will only account for a small fraction of emissions

4) Other Greenhouse Gases

a) CH_4 (methane)

1 CH_4 has ~ 25 times greenhouse effect of 1 CO_2

Inc. from pre-industrial values of about 0.3 - 0.7 ppm to ~ 1.8 ppm

Biological processes, landfills, ruminant animals, natural gas extraction & transport.

Inc. by ~ 1%/yr due to humans

Causes production of other GH gases in atmosphere

- climate effects are about half those of CO_2

b) CFCs and HFCs

CFCs : chloroflurocarbons

HFCs : hydroflurocarbons

Used as refrigerants

HFCs replaced CFCs to help protect ozone

Unintended consequences

III) Earth's Water

A) Oceans & Seas

Salty water

fairly constant composition

- mostly NaCl

Vol. of 1.35×10^9 km^3 (1.35×10^{21} L)

- 97.2% of all H_2O

  - remaining H_2O

    2.1% in ice caps and glaciers

    0.6% fresh water

Transport of heat, salts & other chemicals throughout ocean influenced by changes in physical prop. of seawater

Affects ocean currents & climate

Only 3 commercially impt. substances

NaCl, Br, Mg

CO_2 absorption by ocean plays impt. role in global climate

pH : 8.0 – 8.3

pH dec. due to inc. in CO_2 in air

- forms H_2CO_3

B) Freshwater & Groundwater

< 500 ppm of dissolved salts & solids

US has ~ 1.7×10^{15} L (660×10^{12} gal) estimated reserve of freshwater

~ 9×10^{11} L used every day

Personal consumption: ~ 300 L/day

- way above subsistence level

Groundwater

~ 20% freshwater in aquifers

- can be very pure
- sometimes contaminated naturally (As found around world)

IV) Human Activities & Water

KEEP IT CLEAN !!!

A) Contamination

1) Heavy Metals

Pb^{2+}, Hg^{2+}, Cd^{2+}, Sr^{2+}, As, Th

- take the place of essential minerals
  Zn, Cu, Mg, Ca

- deactivate enzymes

2) Fertilizers

Nitrogen and Phosphorus

Excessive algae & plant growth

3) Organics

Dioxanes, PCBs, solvents (benzene, dichloromethane - CH_2Cl_2)

- accumulate in environment & living organisms

4) Pharmaceuticals

Hormones (birth control), Narcotics, Antipsychotics, etc.

In water supply. Effects aquatic life.

5) Trihalomethanes (THMs)

$CHCl_3$, $CHBr_3$, $CHCl_2Br$, $CHClBr_2$

carcinogens, endocrine disruptors

V) Green Chemistry

A) Supercritical solvents

Reusable, more environ. friendly

Replace volatile organic solvents
(some are carcinogenic)

supercritical CO_2 :

dry cleaning, decaffeinating coffee, producing polymers

supercritical H_2O :

polyethylene terephthalate (PET) and other polyester fibers.

B) Recycling

Many things are recyclable

Cuts down on waste in landfills

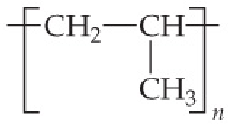
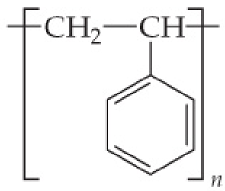
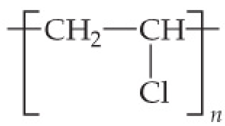
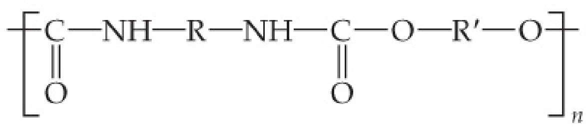
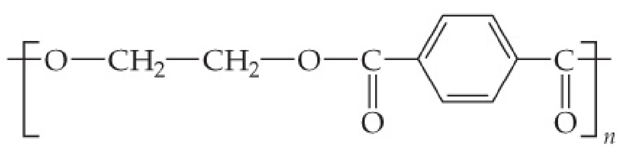
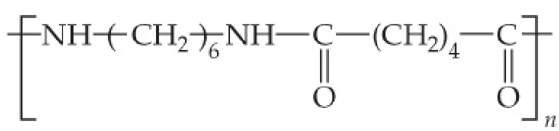
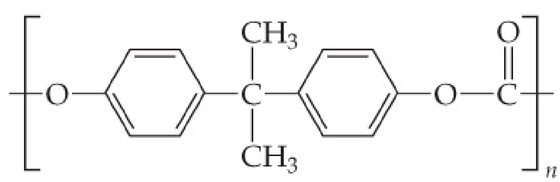
Many plastics (polymers) recyclable

- #1 and #2 almost everywhere
- others can be recycled but not in many locations

TABLE 12.6 • Categories Used for Recycling Polymeric Materials in the United States

Number	Abbreviation	Polymer
1	PET or PETE	Polyethylene terephthalate
2	HDPE	High-density polyethylene
3	V or PVC	Polyvinyl chloride (PVC)
4	LDPE	Low-density polyethylene
5	PP	Polypropylene
6	PS	Polystyrene

TABLE 12.5 • Polymers of Commercial Importance

Polymer	Structure	Uses
Addition Polymers		
Polyethylene	$-\!\!(\!CH_2-CH_2\!)_n\!-$	Films, packaging, bottles
Polypropylene		Kitchenware, fibers, appliances
Polystyrene		Packaging, disposable food containers, insulation
Polyvinyl chloride (PVC)		Pipe fittings, clear film for meat packaging
Condensation Polymers		
Polyurethane	 R, R′ = $-CH_2-CH_2-$ (for example)	"Foam" furniture stuffing, spray-on insulation, automotive parts, footwear, water-protective coatings
Polyethylene terephthalate (a polyester)		Tire cord, magnetic tape, apparel, soft-drink bottles
Nylon 6,6		Home furnishings, apparel, carpet, fishing line, toothbrush bristles
Polycarbonate		Shatterproof eyeglass lenses, CDs, DVDs, bulletproof windows, greenhouses