APES CHAPTER 15 NOTES (MRS. BAUCK):
AIR POLLUTION AND STRATOSPHERIC OZONE DEPLETION

[NOTE: The abbreviations NO_x and SO_x are often used, but they usually refer to NO_2 and SO_2.]

MODULE 46: Major Air Pollutants and Their Sources

I. Composition of Earth's atmospheric gases
(*ppm = parts per million = mg/L for air and water = mg/kg for soil)*

from Thad Godish's Air Quality:

ATMOSPHERIC CONSTITUENTS: CONSTANT CONCENTRATIONS

CONSTITUENT	FORMULA	CONCENTRATION (ppm)
Nitrogen	N_2	780,840.00
Oxygen	O_2	209,460.00
Argon	*Ar*	9340.00
Neon	*Ne*	18.18
Helium	*He*	5.24
Krypton	*Kr*	1.14
Hydrogen	H_2	0.50
Xenon	*Xe*	0.09

ATMOSPHERIC CONSTITUENTS: VARIABLE CONCENTRATIONS

CONSTITUENT	FORMULA	CONCENTRATION (ppm)
Water vapor	H_2O	0.1 – 30,000.00
Carbon dioxide	CO_2	350.00
Methane	CH_4	1.67
Nitrous oxide	N_2O	0.30
Carbon monoxide	*CO*	0.19
Ozone	O_3	0.04
Ammonia	NH_3	0.004
Nitrogen dioxide	NO_2	0.001
Sulfur dioxide	SO_2	0.001
Nitric oxide	*NO*	0.0005
Hydrogen sulfide	H_2S	0.00005

II. Air Pollution – Natural vs. Anthropogenic

From weather.com:

"*The average adult breathes up to 3,000 gallons of air every day*. Children breathe even more air per pound of body weight and are more susceptible to air pollution. The elderly are also more sensitive to air pollution because they often have heart or lung disease…

The AQI (Air Quality Index) is an index for forecasting daily air quality. It tells you how clean or polluted your air is, and what associated health concerns you should be aware of. T he AQI focuses on health effects that can happen within a few hours or days after breathing polluted air.

The EPA uses the AQI for **six major air pollutants regulated by the Clean Air Act: ground-level ozone, particulate matter (particle pollution), carbon monoxide, lead, sulfur**

dioxide and nitrogen dioxide. For each of these pollutants, EPA has established *national ambient air quality standards* to protect against harmful health effects."

A. *Natural Air Pollution*

1) *types*

volcanic eruptions	*ozone from electrical storms*
forest fires	*stratospheric intrusion*
decomposition of plants and animals	*photochemical reactions*
soil erosion	*ocean spray*
pollen and mold spores	
VOCs: volatile organic compounds from vegetation (such as isoprene)	

2) Why are these not a threat?
   a) levels of contaminants are usually very low
   b) usually long distance between the source and dense human populations
   c) episodic and short-lived

B. *Human-made pollution = anthropogenic*

1) sources: transportation vehicles, electricity generation, fires, road dust…
2) *smog*—severe ambient pollution conditions
3) **haze**
   a) *moderate reduction in visibility*
   b) summer time conditions in Midwest, NE and SE U.S.
   c) mainly caused by particulate matter (PM) / sulfates
4) *nontraditional air pollutants*
   a) *noise*
   b) *heat*
   c) *ionizing radiation*
   d) *em (electromagnetic) fields*

**** p. 521 table ****

5) *traditional air pollutants: gases, aerosols, and particulate matter*
   a) **suspended particulate matter (PM)/particle pollution**
   b) **VOCs – volatile organic compounds**
   c) **CO – carbon monoxide**
   d) **NO_x – nitrogen oxides**
   e) **SO_x – sulfur oxides**
   f) **Pb, Hg and other heavy metals**
   g) **O_3 and other photochemical oxidants *(secondary)***
   h) **air toxics / Rn (radon)**
   i) **PAN – peroxyacteyl nitrates *(secondary)***

C. Information from the American Lung Association

1) Air quality by state:
   http://www.lung.org/our-initiatives/healthy-air/sota/
2) Most polluted cities:

http://www.lung.org/our-initiatives/healthy-air/sota/city-rankings/most-polluted-cities.html

III. Major Air Pollutants and Sources

A. Pollutants and Atmospheric Cleansing

1) **air pollution**—gases, aerosols, microorganisms and particulates with harmful effects

2) atmospheric cleansing – natural processes

a) *dispersion / dilution in the atmosphere*

b) *breakdown of compounds in the soil by microorganisms*

c) *hydroxyl radical (OH*)*, the "detergent of the troposphere"

- the neutral form of the hydroxide ion (OH^-)
- *oxidizes many pollutants, often the first step toward removal*
- primary removal mechanism for CO: $OH^* + CO \rightarrow H^* + CO_2$
- Volatile Organic Compounds (VOCs) reactions:

$OH^* + RH \rightarrow H_2O + R^*$ (alkyl radical formation) $\quad R^* + O_2 \rightarrow RO_2^*$ (*peroxy radical* formation)

- NO_x reactions:

$HO_2^* + NO \rightarrow NO_2 + OH^*$

$OH^* + NO_2 \rightarrow HNO_3$ (*nitric acid* formation)

B. The Appearance of Smog ("smog" = smoke + fog)

1) **industrial smog (sulfurous smog, London smog, gray smog, reducing smog)**

a) London—*coal combustion* causes emission of *particulate matter and water vapor, SO_x, NO_x*

b) produces eye irritation and poor visibility

2) **photochemical smog (LA smog, brown smog, oxidizing smog, urban smog)**

a) *sources for formation*

- *light energy (uv)*
- *hydrocarbons/VOCs (from fossil fuel combustion)*
- *NO_x (from fossil fuel combustion)*

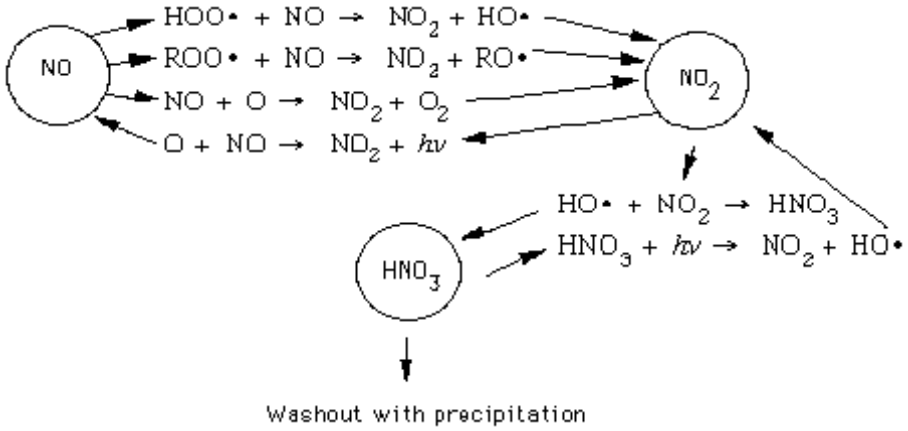
b) often contains ozone (O_3)

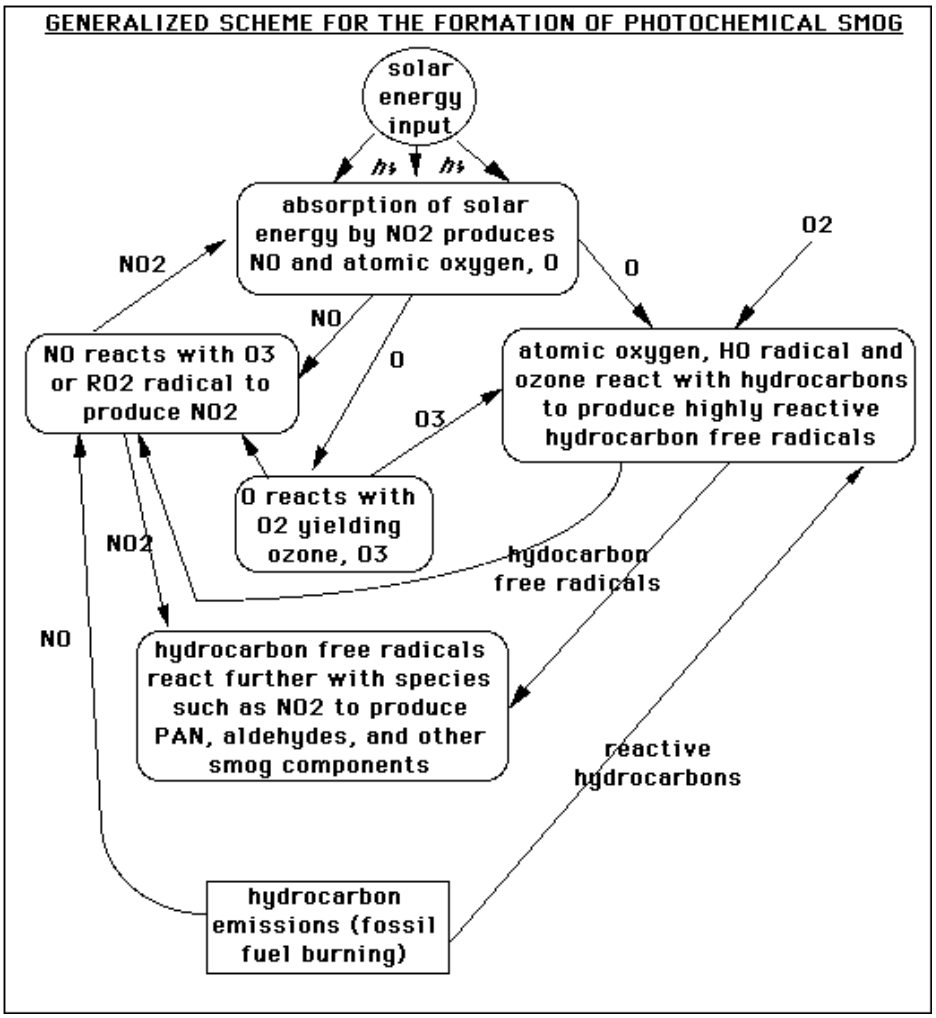
c) large reduction in visibility

d) NO_2 makes smog a brown color

e) Los Angeles basin—photochemical smog

Two diagrams from http://www.shodor.org/master/environmental/air/photochem/smogapplication.html





3) impact of smog
    1) aggravates asthma, emphysema, and other respiratory issues
    2) air-pollution disaster = when lethal effects are observed

IV. Major Air Pollutants and Their Sources (from weather.com and the EPA)

A. **EPA criteria pollutants** https://www.epa.gov/criteria-air-pollutants ***

"The Clean Air Act requires EPA to set *National Ambient Air Quality Standards (NAAQS)* for six common air pollutants. These commonly found air pollutants (also known as 'criteria pollutants') are found all over the United States. They are **particle pollution (often referred to as particulate matter), photochemical oxidants and ground-level ozone, carbon monoxide, sulfur oxides, nitrogen oxides, and lead.** These pollutants can harm your health and the environment, and cause property damage. EPA calls these pollutants 'criteria' air pollutants because it sets NAAQS for them based on the human health-based and/or environmentally-based criteria (characterizations of the scientific information)."

B. **primary pollutants *****
   1) **particulate matter ($PM_{2.5}$, PM_{10}), VOCs, CO, NO_x, SO_x, Pb**
   2) *they are direct products from combustion or other actions*

C. **secondary pollutants ***—***formed from reaction of primary pollutants*
   - *ozone O_3, PANs, sulfuric acid H_2SO_4, nitric acid HNO_3*

D. **emissions—***amounts of a substance given off*

V. **Suspended Particulate Matter (PM) / particle pollution**

A. general info.
   1) *particles found in air: dust, dirt, soot, smoke, and liquid droplets*
   2) **$PM_{2.5}$** *(less than 2.5 μm in diameter): fine particles*
   3) **PM_{10}** *(between 2.5 and 10 μm in diameter): coarse dust*
   4) carried over long distances by wind; settle on ground or water
   5) solid and *liquid* suspension in air = *aerosol*
      - types: fume aerosols, duct aerosols, mists, smoke

B. sources of fine particles
   1) all types of *combustion* (motor vehicles, power plants, wood, etc.)
   2) some industrial processes

C. sources of coarse particles
   1) *crushing or grinding* operations
   2) dust from paved or unpaved roads

D. *health effects*
   1) *can be inhaled into, and accumulate in, the respiratory system*
   2) *coughing and painful breathing; shortness of breath*
   3) can aggravate asthma and chronic bronchitis
   4) adverse health effects from chronic, intermediate, or acute exposure
   5) *premature death or hospital admissions*: very young, elderly, people with chronic obstructive pulmonary disease/congestive heart disease

E. *environmental effects*
   1) *acidifying streams and lakes*
   2) *changing nutrient balance in coastal waters and large river basins*
   3) *depleting soil nutrients*
   4) *damaging sensitive forests and farm crops*
   5) *affecting the diversity of ecosystems*
   6) soot stains and damages stone and other materials, including culturally important objects such as monuments and statues

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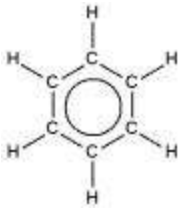
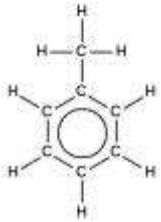
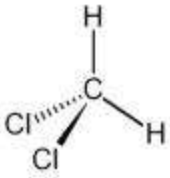
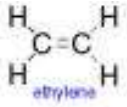
VI. **VOCs – volatile organic compounds**
   1) general info.
      1) *volatile*—easily escaping into the air
      2) chemicals such as benzene, toluene, methylene chloride, formaldehyde, ethylene


benzene


toluene


methylene chloride


formaldehyde


ethylene

B. sources
   1) *combustion of fuel* (gasoline, oil, wood coal, natural gas, etc.); cars…
   2) *solvents, paints, glues*, etc.

C. health effects
   1) *many are classified as hazardous air pollutants (HAZMATs)*
   2) *many are carcinogenic*

D. environmental effects
   1) contribute to *ozone formation*: **$VOC + NO_x + Sunlight = O_3$**
   2) cause damage to plants

VII. **CO – carbon monoxide**

A. general info.: colorless, odorless gas

(One coordinate bond and two normal covalent bonds between C and O. C is the electron acceptor and oxygen is the electron donor.)

B. outdoor sources
   1) *incomplete combustion of fuel*: $C_xH_y + O_2 \rightarrow CO + H_2O$
   2) *motor vehicle exhaust*: ~56% of U.S. CO emissions
   3) *non-road vehicles and boats*: ~22%
   4) *industrial*: metal processing, chemical manufacturing
      a) residential *wood burning*
      b) forest fires
      c) seen in colder months' temperature inversions
   5) *indoor sources*
      a) *woodstoves, gas stoves*
      b) *cigarette smoke*
      c) *unvented gas / kerosene space heaters*
   6) *health effects*
      a) *at high levels, it is poisonous*
      b) *at very high levels, it is lethal*
      c) *reduces oxygen delivery to the body's organs*
      d) affects people with heart disease
      e) vision problems, reduced ability to work or learn, reduced manual dexterity
   7) environmental effects: contributes to the formation of ground-level ozone

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VIII. **NO_x – nitrogen oxides**

A. general info.
   1) *NO_x family— highly reactive gases*
   2) *nitrogen dioxide (NO_2)—brown gas with a stinging odor*

B. sources
    1) *combustion of fuel at high temperatures*
    2) *motor vehicle exhaust*
    3) stationary sources: *electric utilities*, industrial boilers

C. *health effects*
    1) *coughing, wheezing, and shortness of breath*
    2) *aggravates asthma and existing respiratory problems*
    3) long-term exposure:
        - may increase susceptibility to respiratory infection
        - may cause permanent structural changes in the lungs

D. *environmental effects*
    1) *major role in the reactions forming ground-level ozone*
       VOC + NO_x + Sunlight = O_3
    2) *component of smog*
    3) *strong oxidizing agent; reacts to form nitric acid (HNO_3)* and toxic organic nitrates
    4) *eutrophication of bodies of water*

IX. **SO_x – sulfur oxides**

A. general info
    1) *SO_2 sulfur dioxide*
    2) *$(SO_4)^{2-}$ sulfate ion*

B. sources
    1) *combustion of sulfur-containing fuel* (coal, oil)
        - over 65% from coal-burning power plants
    2) *gasoline extraction from oil*
    3) *metal extraction from ore*
    4) petroleum refineries, cement manufacturing, and metal processing facilities, locomotives, large ships, some diesel equipment

C. health effects
    1) contributes to *respiratory illness*, particularly in children and the elderly
    2) aggravates asthma
    3) bronchoconstriction: wheezing, chest tightness, shortness of breath
    4) *aggravates existing heart and lung diseases*
    5) chronic exposure: can cause respiratory illness, alter the lung's defense mechanisms, and aggravate existing cardiovascular disease

D. environmental effects
    1) *dissolves easily in water: SO_2 contributes to the formation of acid precipitation (important!)*
    2) *visibility impairment (haze) by sulfate particles*
    3) aesthetic damage: accelerates decay of building materials and paints
    4) *plant and water damage by acid rain*
        a) acid rain damages forests and crops
        b) changes the makeup of soil
        c) makes bodies of water acidic and unsuitable for fish
        d) continued exposure changes ecosystem balance

X. **Pb and other heavy metals**

A. general info.:

Aluminum, Al	Antimony, Sb	*Arsenic, As*	Beryllium, Be
Cadmium, Cd	*Chromium, Cr*	Cobalt, Co	*Copper, Cu*
Iron, Fe	**Lead, Pb**	Manganese, Mn	**Mercury, Hg**
Molybdenum, Mo	Nickel, Ni	Selenium, Se	Silver, Ag
Tin, Sn	Vanadium, V	*Zinc, Zn*	

B. sources

1) leaded gasoline (being phased out)
2) *paint, inks, dyes*
3) smelters (metal refineries)
4) manufacture of *lead storage batteries*
5) *pesticides*
6) *industrial use*

C. health effects (Pb)

1) *brain and other nervous system damage*
2) may cause birth defects
3) may cause cancer
4) digestive problems

D. health effects (Hg)

1) *brain and other nervous system damage*
2) may cause birth defects

E. environmental effects: *harm wildlife*

XI. **O_3** and other **photochemical oxidants**

A. general info

1) *"good ozone" = stratospheric ozone*
2) *"bad ozone" = tropospheric (ground-level) ozone*

B. sources

1) *chemicals* from cars, power plants, industrial boilers, refineries, chemical plants, etc. …*reacting with sunlight*
2) O_3 pollution is *a concern during the summer months* with optimal conditions to form ground-level O_3(abundant sunlight, hot temperatures)
3) the length of the *ozone season* varies from one area of the U.S. to another; states in the S-SW U.S. may have an ozone season lasting the entire year

C. *health effects*

1) *irritation and inflammation of lung airways*
2) *wheezing, coughing*
3) *painful deep breathing, breathing difficulties during exercise or outdoor activities*
4) *aggravated asthma, reduced lung capacity*
5) *increased susceptibility to respiratory illnesses*

Repeated exposure to ozone pollution for several months may cause permanent lung damage.
Anyone who spends time outdoors, especially in the summer, is at risk.
Ozone damage can occur without any noticeable signs.
Ozone continues to cause lung damage even when the symptoms have disappeared.

D. environmental effects
    1) damages crops and other vegetation
    2) major component of photochemical smog
        a) interferes with the ability of plants to produce and store food, making them more susceptible to disease, insects, other pollutants, and harsh weather
        b) damages plant leaves
        c) reduces crop and forest yields
        d) increases plant vulnerability to disease, pests, and harsh weather

XII. **Hazardous air pollutants (HAPs)** or **air toxics**

A. general info from the EPA
    1) *EPA lists 187 current toxic air pollutants*
    www.epa.gov/ttn/atw/188polls.html
    https://www.epa.gov/national-air-toxics-assessment/2011-national-air-toxics-assessment
    2) "Sources are to use *Maximum Available Control Technology (MACT)* to reduce pollutant releases; this is a very high level of pollution control."

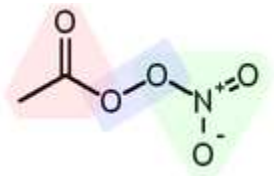
B. sources
    1) *breathing contaminated air*
    2) *eating contaminated food products*
    3) *drinking water contaminated by toxic air pollutants*
    4) *ingesting contaminated soil (especially with children)*
    5) *skin contact with contaminated soil, dust, or water*

C. health effects
    1) *increased risk of cancer*
    2) *damage to the immune system*
    3) *neurological, reproductive (e.g., reduced fertility), developmental, respiratory problems*

D. environmental effects: *biomagnification*

XIII. **PAN – peroxyacetyl nitrates**

the most common PAN



A. general info
B. sources: photochemical reactions (VOC + NO_x)
C. health effects
    1) *low concentrations: eye/lung irritation*
    2) *increased risk of skin cancer*
D. environmental effects: *vegetation damage*

XIV. Humidity as a contributor to air quality

Possible Effects of Indoor Humidity TOO DRY (< 30%)
▪ Damage to wood floors, furniture, musical instruments ▪ Static electricity; electronic equipment damage ▪ Respiratory, throat, and skin irritations ▪ Increased dust

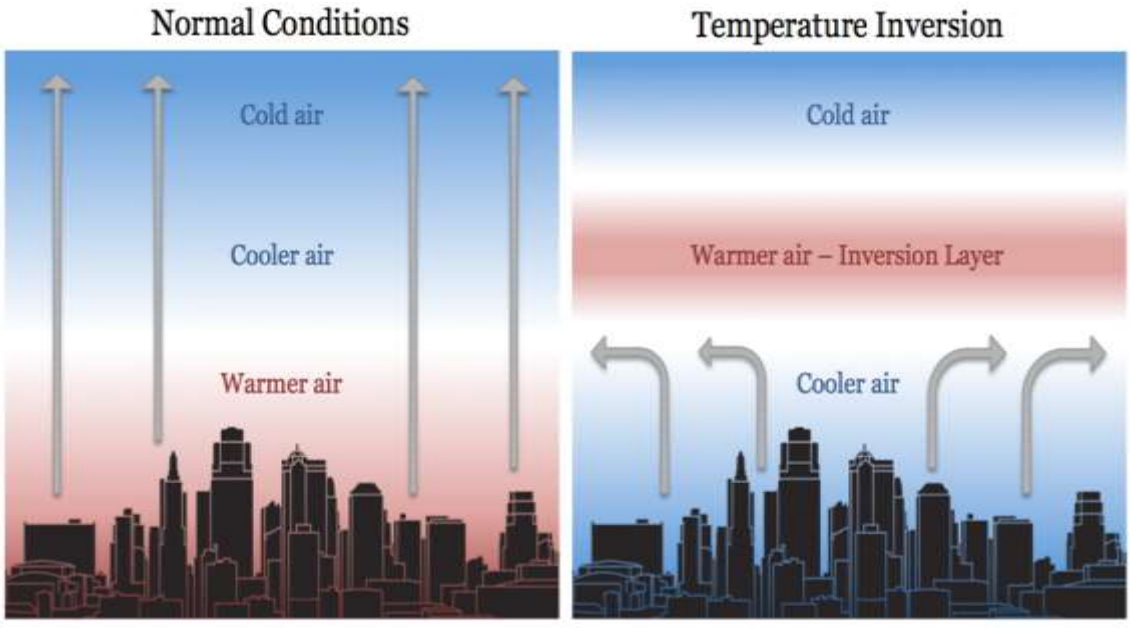
TOO WET (> 50%)
▪ Termites, cockroaches, and other insects ▪ Condensation and stains on walls, ceilings, windows ▪ Flaking paint and peeling wallpaper ▪ Mold, mildew, dust mite growth; allergic reactions

MODULE 47: Photochemical Smog and Acid Rain

I. Photochemical Smog
- A. refer back to Module 46, section III
- B. general ozone formation rxns. – low VOC, more sunlight
  1) $NO_2 \rightarrow NO + O^*$
  2) $O^* + O_2 \rightarrow O_3$
- C. general ozone destruction rxns. – less sunlight, evening

$$O_3 + NO \rightarrow O_2 + NO_2$$

II. **Thermal/temperature inversions**—*cooler air layered below warmer air*
- A. traps smog close to the ground
- B. relatively short-lived (morning sun dissipates it)
- C. **inversion layer** – warm air layer
- D. can trap PM, CO, other substances



Source: NC State

III. Acid Deposition *** Review **Acid Deposition** from Ch. 14, module 42 ***
- A. Acid – base characteristics
  1) **acids**
     a) *compounds producing hydrogen ions (H^+) when dissolved in water*

b) acidic solutions: $[H^+] > [OH^-]$
c) acid formulas usually begin with H (or end with COOH)
d) examples

hydrochloric – HCl	*sulfuric – H_2SO_4*
nitric – HNO_3	*acetic – CH_3COOH or $HC_2H_3O_2$*
phosphoric – H_3PO_4	*carbonic – H_2CO_3*

2) **bases**
a) *produce hydroxide ions (OH^-) when dissolved in water*
b) basic (alkaline) solutions: $[OH^-] > [H^+]$
c) base formulas typically end in OH
d) examples

sodium hydroxide – NaOH	*calcium hydroxide – $Ca(OH)_2$*
potassium hydroxide – KOH	*ammonium hydroxide – NH_4OH*

B. Water
1) ion product constant for water = K_w $\quad K_w = [H^+]\,[OH^-] = 10^{-14}$ M
2) self-ionization of water

$H_2O \rightarrow H^+ + OH^-$
water → hydrogen ion + hydroxide ion

$\underline{2}\ H_2O \rightarrow H_3O^+ + OH^-$
water → hydronium ion + hydroxide ion

3) *pure water is neutral: $[H^+] = [OH^-]$*
$[H^+] = 10^{-7}$ M and $[OH^-] = 10^{-7}$ M

From Ch. 14…

C. What is acid deposition?
1) **acid precipitation**—precipitation with a pH of 5.6 or less
2) **acid deposition**
a) *wet deposition*: acidic rain, fog, and snow
b) *dry deposition*: acidic gases and particles
3) Normal rain is slightly acidic because CO_2 dissolves into it, so it has a pH of about 5.6. $\quad \mathbf{CO_2\,(g) + H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq)}$
4) The most acidic rain falling in the U.S. has a pH of about 4.3.

D. Chemical causes: **NONMETAL OXIDE + WATER → ACID**
1) *sulfur dioxide (SO_2)* → *forms* **H_2SO_4 (sulfuric acid)**

$\mathbf{2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)}$ oxidation to form sulfur trioxide

$\mathbf{SO_3(g) + H_2O(l) \rightarrow H_2SO_4\,(aq)}$ formation of sulfuric acid

$SO_2\,(g) + H_2O\,(l) \rightleftharpoons H_2SO_3\,(aq)$ formation of sulfurous acid

2) *nitrogen oxides (NO_x)* → *forms* **HNO_3 (nitric acid)**

$\mathbf{2NO_2\,(g) + H_2O\,(l) \rightarrow HNO_2\,(aq) + HNO_3\,(aq)}$ formation of nitrous and nitric acids

3) *carbon dioxide (CO_2)* → *forms* **H_2CO_3 (carbonic acid)**
$\mathbf{CO_2\,(g) + H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq)}$

- In the U.S., ~ 2/3 of all SO_2 and ~ 1/4 of all NO_x comes from electric power generation that relies on burning fossil fuel

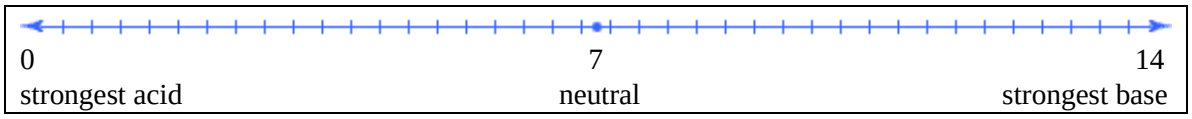
E. How it is measured

1) **pH** = *the negative logarithm of the hydrogen ion concentration*

pH = -log [H^+]

2) pH values

a) *acid pH < 7*
b) *base pH > 7*
c) *neutral pH = 7*



Example problems (NOTE: APES focuses on pH only.)

Example 1) If [H+] of a solution = 1.0 x 10^{-8} M…

a) Find pH. b) Find pOH. c) Find [OH^-]. d) Acid, base, or neutral?

a) [H^+] = 1.0 x 10^{-8} M so pH = 8
b) pH + pOH = 14 8 + pOH = 6 pOH = 6
c) [H^+] [OH^-] = 10^{-14} M [10^{-8}] [OH^-] = 10^{-14} M [OH^-] = 10^{-6} M
d) base (pH = 8)

Example 2) If [H^+] of a solution = 1.0 x 10^{-1} M…

a) Find pH. b) Acid, base, or neutral?

a) [H^+] = 1.0 x 10^{-1} M so pH = 1
b) acid (pH = 1)

F. Effects of acid deposition https://www.epa.gov/acidrain/effects-acid-rain

1) *lowering pH of bodies of water—affects aquatic ecosystems*
   a) most lakes and streams: pH 6-8
   b) affects sensitive bodies of water which are located in watersheds whose soils have a limited ability to neutralize acidic compounds (called **buffering capacity***)*
   c) water itself and its surrounding soil cannot buffer the acid rain enough to neutralize it
   d) acid rain also releases Al^{3+} and other metal ions from soils into surface waters, which is highly toxic to many species of aquatic organisms
2) *lowering soil pH of terrestrial ecosystems*
   a) trees do not grow as quickly at a healthy pace
   b) leaves and needles turn brown and fall off
   c) individual trees or entire areas of the forest may die off
   d) soil degradation
   e) negative synergistic effects with pollution, insects, disease, drought, or very cold weather
3) *environmental effects on abiotic factors*
   a) effects on *visibility reduction from SO_2 and NO_x*
      - sulfate $(SO_4)^{2-}$ particles account for a majority of the visibility reduction in the eastern part of the U.S.

- in the western U.S., nitrates $(NO_3)^-$ and carbon also play a role

b) effects on materials
- *corrosion* of metals such as bronze
- deterioration of paint and stone (such as marble and limestone)
- reduce value to society of buildings, bridges, cultural objects
- dry deposition can dirty buildings and other structures, leading to increased maintenance costs

G. Monitoring through EPA-sponsored networks
1) The National Atmospheric Deposition Program measures wet deposition.
2) The Clean Air Status and Trends Network (CASTNET) measures dry deposition.
3) they check acid rain's pH and the chemicals that cause acid rain

MODULE 48: Pollution Control Measures

I. Bringing Air Pollution Under Control
A. Impacts of Air Pollutants
1) ambient SO_2 and sulfate levels are down in the eastern U.S.
2) wet sulfate deposition has decreased in the NE and SE U.S.
3) signs of recovery in acidified lakes and streams are evident in the Adirondacks, the northern Appalachian Plateau, and the upper Midwest: lower concentrations of sulfates and nitrates, and improvements in acid neutralizing capacity.

B. **Clean Air Act (CAA) of 1970** (amended 1977 and 1990, minor revisions later)
http://www.epa.gov/air/caa/peg/
1) *1990 Clean Air Act amendments (CAAA)*

Title I – Air Pollution, Prevention and Control
Title II – Emission Standards for Moving Sources
Title III – General
Title IV – Acid Deposition Control
Title V – Permits
Title VI – Stratospheric Ozone Protection

https://www.fema.gov/clean-air-act-caa-1990-amended

"The Clean Air Act amendments of 1990 requires federal agencies to assess the impact that projects will have on air quality and to take actions to prevent air quality degradation."

2) **command and control** approach—industry is commanded by law to achieve reduced levels of specific pollutants, using control equipment (contrast with "emission allowances.")
3) goals
a) *set* **ambient standards—***levels which will protect human and environmental health*
- *primary pollutants: particulates, SO_2, CO, NO_x*
- *secondary pollutant: O_3*

b) *set control methods and time tables*

- lowering the electric power industry's annual emissions of sulfur dioxide (SO_2)
- lowering the electric power industry's annual emissions of nitrogen oxides (NO_X)

4) CAA established *two types of national air quality standards*
   a) **primary standards**
      - based on the *highest tolerable level* (+/- a safety margin)
      - set limits to protect public health, including the health of sensitive populations such as asthmatics, children, the elderly
   b) **secondary standards**
      - set limits to protect public welfare, including protection against decreased visibility, damage to animals, vegetation, buildings

C. *National Ambient Air Quality Standards (NAAQS)*

1) **Criteria pollutants**:

particle pollution/particulate matter (PM_{10} and $PM_{2.5}$)	**SO_2**	**CO**
NO_x	**O_3**	**Pb**

NAAQS from the EPA https://www.epa.gov/criteria-air-pollutants/naaqs-table

Pollutant [links to historical tables of NAAQS reviews]		**Primary/ Secondary**	**Averaging Time**	**Level**	**Form**
Carbon Monoxide (CO)		primary	8 hours	9 ppm	Not to be exceeded more than once per year
			1 hour	35 ppm	
Lead (Pb)		primary and secondary	Rolling 3 month average	0.15 µg/m^3	Not to be exceeded
Nitrogen Dioxide (NO_2)		primary	1 hour	100 ppb	98th percentile of 1-hour daily maximum concentrations, averaged over 3 years
		primary and secondary	1 year	53 ppb	Annual Mean
Ozone (O_3)		primary and secondary	8 hours	0.070 ppm	Annual fourth-highest daily maximum 8-hour concentration, averaged over 3 years
Particle Pollution (PM)	$PM_{2.5}$	primary	1 year	12.0 µg/m^3	annual mean, averaged over 3 years
		secondary	1 year	15.0 µg/m^3	annual mean, averaged over 3 years
		primary and secondary	24 hours	35 µg/m^3	98th percentile, averaged over 3 years
	PM_{10}	primary and secondary	24 hours	150 µg/m^3	Not to be exceeded more than once per year on average over 3 years
Sulfur Dioxide (SO_2)		primary	1 hour	75 ppb	99th percentile of 1-hour daily maximum concentrations, averaged over 3 years
		secondary	3 hours	0.5 ppm	Not to be exceeded more than once per year

D. *National Emission Standards for Hazardous Air Pollutants (NESHAPs)*

1) *Toxic air pollutants* https://www.epa.gov/criteria-air-pollutants

2) "Sources are to use *Maximum Available Control Technology (MACT)* to reduce pollutant releases; this is a very high level of pollution control."

3) Common Hazardous Air Pollutants (priority HAPs underlined)……..
https://www3.epa.gov/ttn/atw/orig189.html

acrolein	C_3H_4O	formaldehyde	H_2CO
arsenic	As	**hydrogen chloride**	HCl (g)
asbestos	(mineral fibers: amphiboles, serpentines)	hydrogen fluoride	HF (g)
benzene	C_6H_6	**lead**	Pb
beryllium	Be	manganese	Mn
cadmium	Cd	**mercury**	Hg
chromium	Cr	nickel	Ni
coke oven emissions	(coal; C)	radionuclides	
dioxins *(chlorinated dibenzo-p-dioxins (CDDs), chlorinated dibenzofurans (CDFs), certain polychlorinated biphenyls* ***(PCBs)***		vinyl chloride	CH_2=CHCl

II. Control Strategies

A. *command and control* (contrast with "emission allowances")

1) *point sources—specific large industrial sites*

2) *area sources—local small contributing site, such as a dry cleaner*

B. *reducing particulates (PM)*

1) CAA 1970 measures

a) banned open burning of refuse (garbage)

b) mandated industrial stack emissions reduced to almost zero

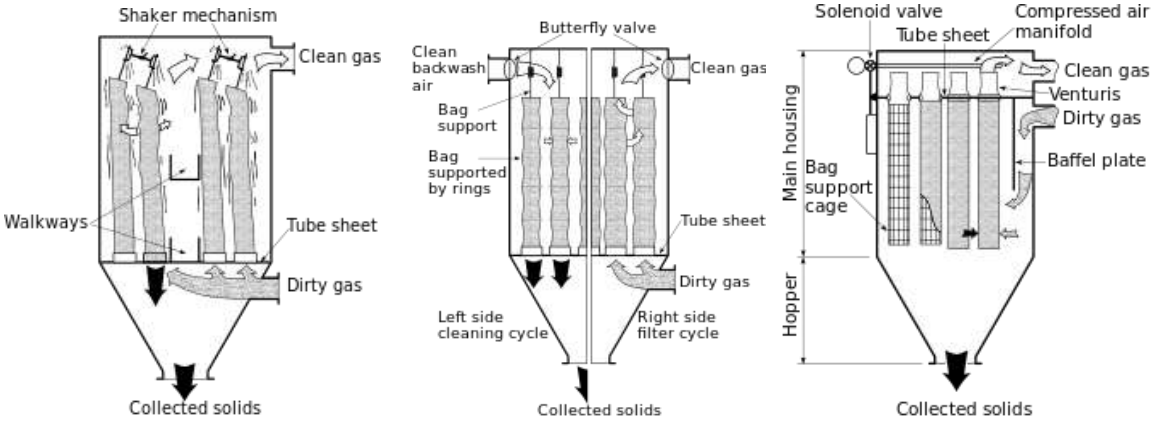
c) attainment plans

- report submitted to the EPA outlining when and how the PM emissions will be reduced
- *RACT – reasonably available control technology*

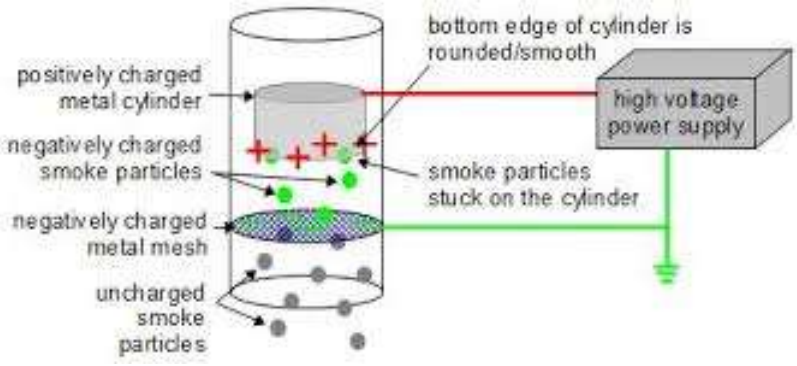
d) added PM 2.5 as a new category

2) gravitational settling in the smokestack

3) fabric/baghouse filters - mechanical shaker, reverse air, pulse jet



4) electrostatic precipitators



Source: rimstar.org

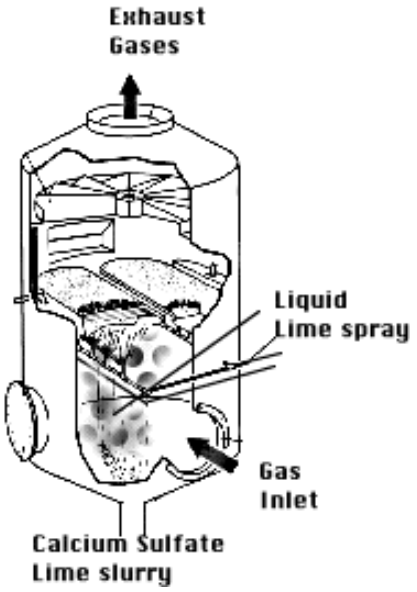
5) scrubbers

a) definition rom https://www3.epa.gov/ttn/

"Scrubbers are air-pollution-control devices that remove harmful gases and particulates from the smokestacks of incinerators, chemical manufacturing facilities, and electric power plants before they enter the atmosphere."

b) can be wet or dry, regenerative or nonregenerative

c) most common – *wet nonregenerative-- captures SO_2 from coal/oil-burning power plants*



Source: Ophardt

$$SO_2 + CaCO_3 + \tfrac{1}{2}O_2 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + CO_2$$

- limestone and water slurry is sprayed into the flue gases
- gypsum (calcium sulfate dihydrate) is formed—can be deposited in landfills or recycled as wallboard, fertilizer, concrete

"Scrubbers remove 80-95 % of the SO_x… They are costly to retrofit to existing power plants… Scrubbers are like 'liquid' filters for the gases resulting from combustion. (EPA)

d) particulate removal in scrubbers

"*Particulates can be removed using venturi and centrifugal or condensation scrubbers.* Flue gas enters through the top of the cone-shaped venturi scrubber and water, injected horizontally, forms droplets that absorb dust and other particles. The resulting slurry discharges from the bottom of the unit or can be separated from the clean gas by centrifugation or spinning at high speed." (EPA)

C. smog reduction

http://www.epa.gov/airtrends/2005/ozonenbp/summaryregions.pdf

1) old mindset: reduce VOCs to reduce tropospheric O_3 produced
2) new mindset: interactions between VOCs, NO_x, and O/O_2 makes things more complex
3) In 1997, stricter O_3 standards were challenged in court, but the EPA won.

The EPA determined that the one-hour ozone standard of 0.12 ppm in effect since the late 1970s did not adequately protect the public from adverse health effects. Health effects occur at

levels lower than the one-hour standard and exposure times longer than one hour are of concern. In July 1997, the agency replaced the one-hour standard with an eight-hour standard of 0.08 ppm. Above this level is considered an exceedance.

4) NO_x regulations
   a) *Ozone Transport Rule: CAAA established the Ozone Transport Commission (OTC)* to coordinate the development of control plans for ground-level ozone in the Northeast and Mid-Atlantic Regions of the U.S.
   b) *CAAA Standards:* Two sets of standards have been defined for light-duty vehicles in the Clean Air Act Amendments of 1990

III. Limiting pollutants from motor vehicles
   A. **CAFE** (corporate average fuel economy) **standards** set by NHSTA (National Highway Traffic Safety Administration)

"*NHTSA's CAFE program requires manufacturers of passenger cars and light trucks, produced for sale in the U.S., to meet CAFE standards, expressed in miles per gallon (mpg). The purpose of the CAFE program is to reduce the nation's energy consumption by increasing the fuel economy of cars and light trucks.* Fuel economy standards improve our nation's energy security, address climate change and save consumers money at the pump… Manufacturers' compliance obligations are based on the vehicles that are produced for sale in the U.S. in a model year within each of the three fleets: domestic passenger cars (DP), import passenger cars (IP) and light trucks (LT).

Once a manufacturer's CAFE standard is calculated for each of its fleets, NHTSA compares each of the fleet's actual mpg performance against the applicable standard. If a manufacturer's actual average mpg level for a given fleet exceeds the applicable standard, then the manufacturer earns 'credits.' … On the other hand, if a manufacturer's actual average mpg level for a given fleet does not meet the applicable standard, then the manufacturer has a 'shortfall' for that fleet. Shortfalls can be satisfied by using… compliance flexibilities" such as

Carry forward - credits earned in a particular model year can be carried forward and applied for up to five model years after the year in which the credits were earned.

Carry back – credits earned in a particular model year can be carried backward and applied for up to three model years before the year in which the credits were earned.

Civil penalty – manufacturers can pay a civil penalty = $5.50 per credit shortfall

Trade – manufacturers can acquire credits from other manufacturers / credit holders.

Transfer – manufacturers can transfer credits from one of their fleets (DP, IP, or LT) to one of their other fleets

   B. *catalytic converter ("cat con")* introduced in 1975
      1) summary of reactions
         a) *uses a Pt (platinum) catalyst*
         b) *VOCs are oxidized into CO_2 and H_2O*
         c) *CO changed into CO_2*
         d) *NO_x changed into N_2*
      2) three-way cat con
         a) **reduction catalyst** (with platinum or rhodium Pt/Rh catalyst)

General: $2NO_x \rightarrow N_2 + XO_2$

Specific: $2NO_2 \rightarrow N_2 + 2O_2$

Specific: $2NO \rightarrow N_2 + O_2$

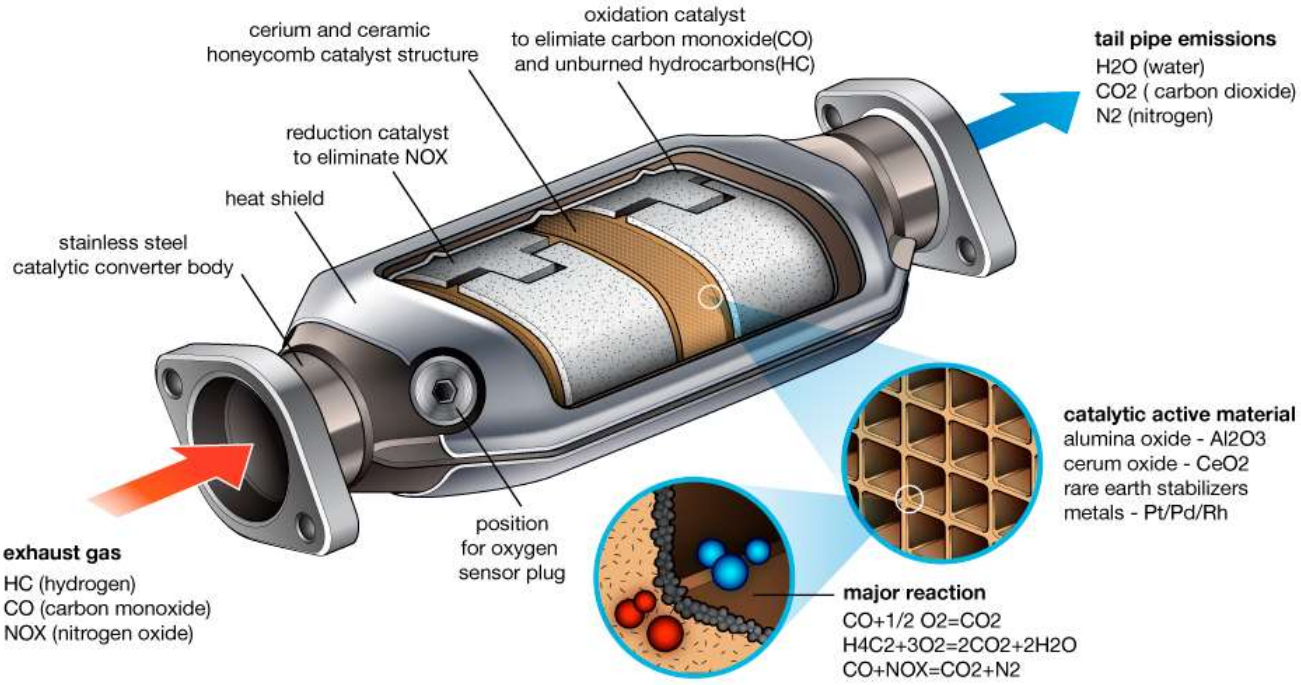
b) **oxidation catalyst** (with platinum/palladium Pt/Pd catalysts)

$2CO + O_2 \rightarrow 2CO_2$

c) **control system/exhaust monitoring**

- uses oxygen sensors to send info to the fuel injection system
- adjustments made to the air-to-fuel ratio
- **General: $C_xH_y + O_2 \rightarrow CO_2 + H_2O$**
- General, alkane combustion:
  $C_xH_{(2x+2)} + [(3x+1)/2]O_2 \rightarrow XCO_2 + (X+1)H_2O$
- Specific, combustion of octane:
  $2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$

CAT CON (Source: cars.com)



IV. Coping with Acid Deposition

A. *Title IV of the Clean Air Act Amendments (CAAA) of 1990*

1) goals and purposes

The purpose of Title IV is to reduce the adverse effects of acid deposition through reductions in annual emissions of SO_2 (10,000,000 tons from 1980 emission levels) *and*, in combination with other provisions of this Act, of *NO_x emissions* (approximately 2,000,000 tons from1980 emission levels), *in the 48 contiguous States and the District of Columbia.*

It is the intent to effectuate such reductions by *requiring compliance by affected sources with prescribed emission limitations by specified deadlines*, which limitations may be met through alternative methods of compliance provided by an emission allocation and transfer system.

It is also the purpose of this Title to *encourage energy conservation, use of renewable and clean alternative technologies, and pollution prevention as a long-range strategy,* for reducing air pollution and other adverse impacts of energy production and use.

2) uses *emission allowances*, not command and control
(1 allowance = 1 ton SO_2)

B. positive outcomes
a) utilities switching to *low-S coal*
- Low sulfur coal (0-1% sulfur) is surface mined in the Western states of Wyoming and Montana
- High sulfur coal (2-4% sulfur) is currently mined in the Midwestern states of Illinois, Indiana, Ohio, West Virginia, and Kentucky

b) utilities are *trading emission allowances*

V. Innovation in Pollution Control – possible solutions
A. Controlling gasoline spills
B. Restrictions on evaporation of dry-cleaning fluid (VOCs)
C. Reduction of use of wood-burning stoves and fireplaces
D. Encouraging carpooling; tolls for one passenger in a car
E. Expansion of public transportation to discourage individual car use
F. Restriction on when cars can be driven
G. Increase tolls (road-use fees)
H. *Sulfur emission allowances* which can be traded among businesses
(1 allowance = 1 ton SO_2)

MODULE 49: Stratospheric Ozone Depletion

I. Depletion of the Ozone Layer
A. radiation and Importance of the shield
1) ultraviolet light
a) UVA—long-wave, not absorbed by ozone layer; soft UV
b) UVB—medium–wave; mostly absorbed by ozone layer; intermediate UV
c) UVC—short-wave; completely absorbed by ozone layer; hard UV
d) ~1% of UVB reaches Earth
2) **ozone shield, ozone layer**—*stratospheric ozone (O_3)*

B. formation and breakdown of the shield
1) chemical reactions

FORMATION OF OZONE: $O_2 + UVB \rightarrow 2O^*$ ***(O* = singlet oxygen)***
$O^* + O_2 \rightarrow O_3$

DESTRUCTION OF OZONE: $O^* + O_3 \rightarrow 2O_2$
$O_3 + UVB \rightarrow O^* + O_2$

2) halogens in the atmosphere – CFCs
from http://www.ratical.org/ratville/ozoneDepletion.html

"By the time they were banned internationally during the 1980s, CFCs had been used in roughly 90 million car and truck air conditioners, 100 million refrigerators, 30 million freezers,

and 45 million air conditioners in homes and other buildings. *Because CFCs remain in the stratosphere for up to 100 years, they will deplete ozone long after industrial production of the chemicals ceases*."

Chemical reactions involving chlorine

$CFCl_3 + UV \rightarrow Cl^* + CFCl_2$

CHLORINE CYCLE: a) $\mathbf{Cl^* + O_3 \rightarrow ClO^* + O_2}$

b) $O^* + ClO^* \rightarrow 2Cl^* + O_2$

$\mathbf{Cl^* + CH_4 \rightarrow HCl + CH_3^*}$

One Cl atom could destroy 100,000 ozone molecules before being removed in the above rxn.

$ClO + NO_2 \rightarrow ClONO_2$

$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3$

$ClOOCl + energy \rightarrow Cl^* + ClO_2$

$ClO_2 \rightarrow Cl^* + O_2$

3) reactions involving NO_x

NO_x REACTIONS

$NO + O_3 \rightarrow NO_2 + O_2$

$NO_2 + O^* \rightarrow NO + O_2$

$O^* + N_2O \rightarrow 2NO$

$HO_2^* + NO \rightarrow OH^* + NO_2$

(HO_2^*, the hydroperoxy radical, is an odd oxygen species produced in photochemical rxns.)

$\mathbf{NO_2 + OH^* \rightarrow HNO_3}$

4) reactions involving bromine

$\mathbf{Br^* + O_3 \rightarrow BrO^* + O_2}$

$BrO^* + O^* \rightarrow Br^* + O_2$

5) *The Ozone "Hole"*
   a) actually a thinning, not a hole
   b) first confirmed in 1985-1988
   c) *significant O_3 depletion was observed over the South Pole in the austral (S. Hemispheric) spring*
   d) **chlorine reservoirs** cause depletion of O_3 : high concentrations of Cl* and ClO

$\mathbf{HCl + 2O_3 + NO_2 \rightarrow HNO_3\ (s) + 2O_2 + ClO}$ **(deposition)**

6) Controversy over ozone depletion
   a) first wave of ozone depletion
      - *testing nuclear weapons in the atmosphere*
      - *SST (supersonic transport) planes*

The NASA High-Speed Research (HSR) Program was phased out in fiscal year 1999. Concorde planes are now popular museum attractions.

   b) second wave of ozone depletion
      - *use of CFCs as refrigerants and propellants*
        (Rowland-Molina Theory linked CFCs to O_3 depletion)
   c) skeptics say this has always been going on but our equipment has not been effective enough to detect it

II. Dealing with Ozone Depletion

A. international agreements

1) **Montreal Protocol** *(AKA "The Montreal Protocol on Substances That Deplete the Ozone Layer")*

a) *international treaty designed to protect stratospheric ozone layer*

b) originally signed in 1987 and begun in 1989

c) amended multiple times since then

https://www.epa.gov/ozone-layer-protection/international-actions-montreal-protocol-substances-deplete-ozone-layer

From the Protocol:
… "Recognizing that world-wide emissions of certain substances can significantly deplete and otherwise modify the ozone layer in a manner that is likely to result in adverse effects on human health and the environment ... Determined to protect the ozone layer by taking precautionary measures to control equitably total global emissions of substances that deplete it, with the ultimate objective of their elimination on the basis of developments in scientific knowledge ... Acknowledging that special provision is required to meet the needs of developing countries..."

2) *The Vienna Convention for the Protection of the Ozone Layer* (1985), which outlines responsibilities for protecting human health and the environment against the adverse effects of ozone depletion, established the framework for the Montreal Protocol

B. action in the U.S.

1) **Clean Air Act (CAA) of 1970**

2) **Clean Air Act Amendments of 1990 (CAAA)** (minor changes since then)

a) regulation servicing refrigeration and AC units

b) ozone-depleting substance (CFC = chlorofluorocarbon) restrictions

- Class I substances:
  - Group I: CFC-11, CFC-12, CFC-113, CFC-114, CFC-115
  - Group II: halon-1211, halon-1301, halon-2402
  - Group III: CFC-13, CFC-111, CFC-112, CFC-211, CFC-212, CFC-213, CFC-214, CFC-215, CFC-216, CFC-217
  - Group IV: carbon tetrachloride
  - Group V: methyl chloroform
- Class II Substances:

HCFC-21, HCFC-22, HCFC-31, HCFC-121, HCFC-122, HCFC-123, HCFC-124, HCFC-131, HCFC-132, HCFC-133, HCFC-141, HCFC-142, HCFC-221, HCFC-222, HCFC-223, HCFC-224, HCFC-225, HCFC-226, HCFC-231, HCFC-232, HCFC-233, HCFC-234, HCFC-235, HCFC-241, HCFC-242, HCFC-243, HCFC-244, HCFC-251, HCFC-252, HCFC-253, HCFC-261, HCFC-262

"PHASE-OUT OF PRODUCTION AND CONSUMPTION OF CLASS II SUBSTANCES.
(a) Restriction of Use of Class II Substances. Effective January 1, 2015, it shall be unlawful for any person to introduce into interstate commerce or use any class II substance unless such substance
(1) has been used, recovered, and recycled;
(2) is used and entirely consumed (except for trace quantities) in the production of other chemicals; or
(3) is used as a refrigerant in appliances manufactured prior to January 1, 2020."

C. alternatives: **HFCs—hydrofluorocarbons**

Earth Systems Research Laboratory Global Monitoring Division:
"*Hydrofluorocarbons (HFCs) are compounds containing carbon, hydrogen, and fluorine. Certain chemicals within this class of compounds are viewed by industry and the scientific community as acceptable alternatives to chlorofluorocarbons and hydrochlorofluorocarbons on a long-term basis. Because the HFCs contain no chlorine they do not directly affect stratospheric ozone.*"

https://www.epa.gov/ozone-layer-protection/recent-international-developments-under-montreal-protocol

"On October 15, 2016, with the United States' leadership, 197 countries adopted an amendment to phase down HFCs under the Montreal Protocol… countries committed to cut the production and consumption of HFCs by more than 80% over the next 30 years."

MODULE 50: Indoor Air Pollution

I. Indoor Air Pollution
   A. Developing Countries – burning wood, biomass, or coal in a confined space
   B. Developed Countries
      1) closed buildings, stale air
      2) petrochemical components of buildings
      3) poor air quality due to improperly maintained air conditioning systems

II. Indoor vs. Outdoor Air Pollutants
   A. *carbon monoxide (CO)*
      1) CO is colorless and odorless
      2) CO can build up inside due to malfunctioning space heaters
      3) CO detectors can be installed inside
      4) high concentrations of CO are fatal … On average, exposures at 100 ppm or greater is dangerous to human health.

   B. *asbestos*
      1) a group of six natural silicate minerals with long, fibrous crystals https://www.asbestos.com/asbestos/types/
      2) the crystals have micro "fibrils" that can be released with abrasion; asbestos is not dangerous if not in the airborne PM state
      3) heat resistant, good insulator; can be pulled into a fluffy state
      4) can be found in ceiling tiles, pipe insulation, acoustical plaster
      5) can cause lung cancer and asbestosis
      6) **AHERA – Asbestos Emergency Hazard Response Act of 1986**
         a) implemented under the Toxic Substance Control Act in 1986
         b) deals specifically with school buildings

   https://www.asbestosnetwork.com/blog/2015/09/what-is-the-asbestos-hazard-emergency-response-act-ahera.shtml

C. *radon (Rn-222)*

1) radioactive; occurs naturally from U decay
2) can be in granitic rock, soil, and groundwater
3) Rn decays into Po-210, which is also radioactive
4) can be inhaled
5) can cause lung cancer

https://www.lung.org/our-initiatives/healthy-air/indoor/indoor-air-pollutants/radon.html

D. *VOCs* at home – most common https://freshome.com/10-most-common-vocs/

1) acetone (CH_3COCH_3)
   a) found in nail polish remover, furniture polish, wallpaper
   b) acetone-free alternatives are available
2) benzene (C_6H_6)
   a) found in paint, glue, carpeting, and emissions from gasoline combustion
   b) alternative paints and glues are available
3) butanal (butyraldehyde, $CH_3CH_2CH_2CHO$)
   a) found in BBQ emissions, burning candles, outdoor stoves, cigarettes
   b) avoid secondhand smoke; beeswax, soy, and/or cotton-wick candles are safer
4) carbon disulfide (CS_2)
   a) found in chlorinated tap water
   b) use a filter
5) dichlorobenzene ($C_6H_4)Cl_2$
   a) found in mothballs and some deodorizers
   b) use cedar chips, air-tight containers, lavender
6) ethanol (CH_3CH_2OH)
   a) found in glass cleaners, some detergents
   b) open windows; aerate the area
7) formaldehyde (CH_2O)
   a) found in floor lacquers, some molded plastics
   b) alternatives are available; avoid plastic in general; use BPA-free plastics
8) terpenes (VOCs found in essential oils of plants, especially conifers and citrus trees; based on a cyclic molecule $C_{10}H_{16}$).
   a) found as a fragrance in soaps, detergents, etc.
   b) alternatives are available
9) toluene ($C_6H_5)CH_3$
   a) found in some paint
   b) alternatives are available; open windows; aerate the area; paint outside if possible
10) xylene (dimethylbenzene, ($C_6H_4)(CH_3)_2$)
   a) found in traffic emissions; found in some paints and printing inks
   b) keep car windows closed in heavy traffic; alternative paint and inks are available

E. **sick building syndrome**– *a buildup of pollutants in an airtight space*

1) symptoms and causes

"Actually, the National Institute for Occupational Safety and Health (www.cdc.gov/niosh) prefers the term 'Indoor Air Quality.' *If 20% of the work force has symptoms— including watering eyes; hoarseness; headaches; dry, itchy skin; dizziness; nausea; heart palpitations; miscarriages; shortness of breath; nosebleeds; chronic fatigue; mental fogginess; tremors; swelling of legs or ankles; and cancer -- the building may be labeled a 'sick building.' The telling factor is if the symptoms ease when workers are at home or on vacation."* (WebMD)

2) EPA-identified reasons
   a) ventilation issues
   b) chemical contamination from indoor sources
   c) chemical; contamination from outdoor sources
   d) biological contamination (pollen, mold, etc.)