

Chemistry Olympiad - Kolack

Electrochemistry, nuclear chemistry,
environmental chemistry and other topics



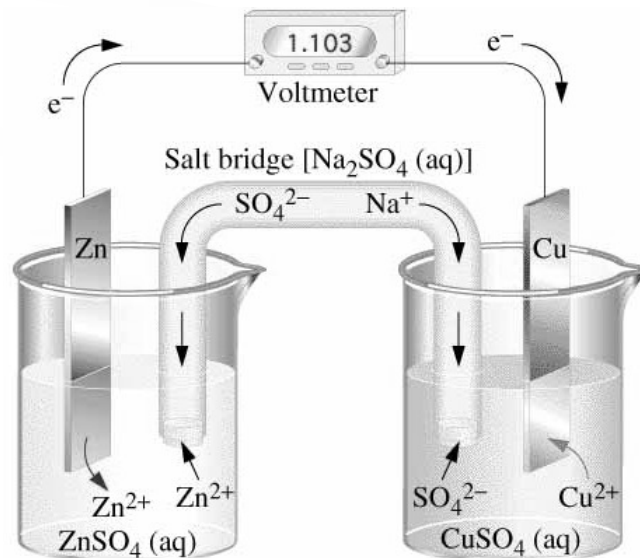
Electrochemistry

Electrochem summary

- Reduction occurs at the cathode of a galvanic (aka voltaic) cell (so it's positive)
- Oxidation occurs at the anode (negative, since it's the source of electrons)
- Since $\Delta G = -nFE_{\text{cell}}$ you need a positive E_{cell} to be spontaneous (negative ΔG)
- More positive reduction potential means ions in solution will displace metal (s)
 - Ag^+ displaces Cu, but Zn^{2+} does not
 - Ag^+ 0.800, Cu^{2+} 0.535, Zn^{2+} -0.763

Redox revisited

- An oxidation reaction (where something loses e^-) and a reduction reaction (where something gains e^-) can be coupled to do (electrical) work
- $\text{Zn(s)}|\text{Zn}^{2+}(\text{aq})||\text{Cu}^{2+}(\text{aq})|\text{Cu(s)}$



Jargon

- HALF-CELL consists of a metal electrode immersed in a solution of its ions
- Two half cells are joined by a SALT BRIDGE since electrons cannot carry charge through a solution, only ions can
- ELECTRIC POTENTIAL is the energy per unit of charge that flows in V (J/C)
- CELL POTENTIAL or CELL VOLTAGE (E_{cell}) is the difference in potential between two points in a circuit

Electrode potentials

| Standard Potential (V) | Reduction Half-Reaction |
|------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 2.87 | $\text{F}_2(\text{g}) + 2\text{e}^- \longrightarrow 2\text{F}^-(\text{aq})$ |
| 1.51 | $\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \longrightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$ |
| 1.36 | $\text{Cl}_2(\text{g}) + 2\text{e}^- \longrightarrow 2\text{Cl}^-(\text{aq})$ |
| 1.33 | $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \longrightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$ |
| 1.23 | $\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \longrightarrow 2\text{H}_2\text{O}(\text{l})$ |
| 1.06 | $\text{Br}_2(\text{l}) + 2\text{e}^- \longrightarrow 2\text{Br}^-(\text{aq})$ |
| 0.96 | $\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3\text{e}^- \longrightarrow \text{NO}(\text{g}) + \text{H}_2\text{O}(\text{l})$ |
| 0.80 | $\text{Ag}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Ag}(\text{s})$ |
| 0.77 | $\text{Fe}^{3+}(\text{aq}) + \text{e}^- \longrightarrow \text{Fe}^{2+}(\text{aq})$ |
| 0.68 | $\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{H}_2\text{O}_2(\text{aq})$ |
| 0.59 | $\text{MnO}_4^-(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) + 3\text{e}^- \longrightarrow \text{MnO}_2(\text{s}) + 4\text{OH}^-(\text{aq})$ |
| 0.54 | $\text{I}_2(\text{s}) + 2\text{e}^- \longrightarrow 2\text{I}^-(\text{aq})$ |
| 0.40 | $\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \longrightarrow 4\text{OH}^-(\text{aq})$ |
| 0.34 | $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Cu}(\text{s})$ |
| 0 | $2\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{H}_2(\text{g})$ |
| -0.28 | $\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Ni}(\text{s})$ |
| -0.44 | $\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Fe}(\text{s})$ |
| -0.76 | $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Zn}(\text{s})$ |
| -0.83 | $2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \longrightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$ |
| -1.66 | $\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \longrightarrow \text{Al}(\text{s})$ |
| -2.71 | $\text{Na}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Na}(\text{s})$ |
| -3.05 | $\text{Li}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Li}(\text{s})$ |

Electrochem summary (cont'd)

- $E_{\text{cell}} = E_{\text{cat}} - E_{\text{an}}$ **reduction potentials for both!**
- $E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}}$ **reduction potentials for both!**
- Standard notation is:
anode|halfcell||cathode|halfcell
– Zn(s)|Zn²⁺(aq)||Cu²⁺(aq)|Cu(s)
- $E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$ **reduction potentials for both!**
- $2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$ (1atm, Pt electrode) $E^\circ=0\text{V}$
standard hydrogen electrode (SHE) reference

Electrolytic cell

- Reversing the direction of the electron flow turns a galvanic/voltaic cell into an electrolytic cell
- Reduction still occurs at the cathode, and oxidation at the anode, BUT
- In a electrolytic cell, the cathode is negative, and the anode (attracts anions) is positive

Faraday

- In physics and chemistry, the Faraday constant (named after Michael Faraday) is the magnitude of electric charge per mole of electrons.
- $F = N_A e$ where
 - $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$
 - $e = 1.602 \times 10^{-19} \text{ C}$
- Most uses of the Faraday constant (F) have been replaced by the standard SI unit, the coulomb.
- The Faraday is still widely used in calculations in electrochemistry.
- It has the currently accepted value $F = 96,485.3399 \text{ C/mol}$ (or 96,500 C/mol on the SAT II)

end of section

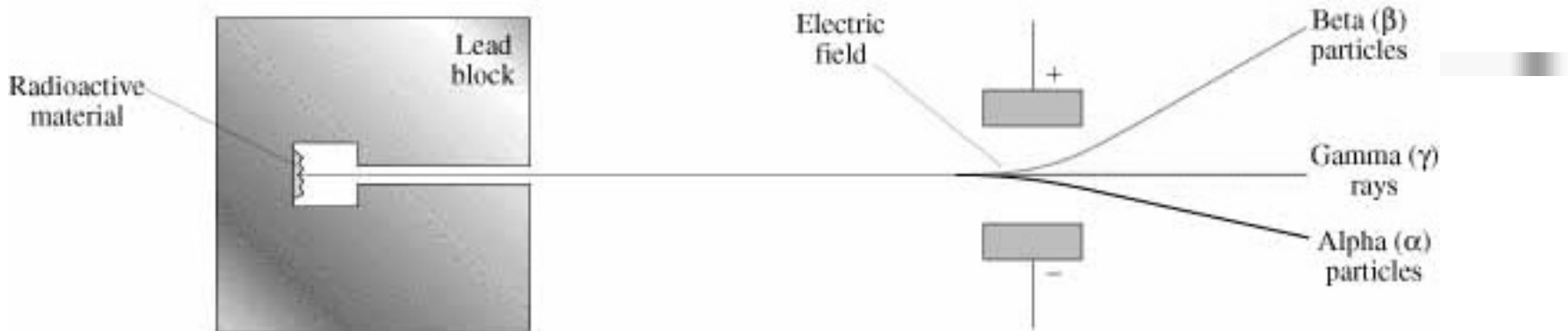
Nuclear chemistry

- RADIOACTIVITY is the spontaneous decay of the nuclei of certain atoms, accompanied by the emission of subatomic particles and/or high frequency EM radiation
- Protons and neutrons are NUCLEONS
- A nucleus with a specific number of protons/neutrons is a NUCLIDE
 - Isotopes of an element have varying nuclides

Types of radioactive decay

- Alpha emission (α), ${}^4\text{He}$ nucleus
 - Remaining nucleus atomic number -2
 - (mass number -4)
- Beta emission (β^-), electron
 - Remaining nucleus atomic number $+1$
 - (mass number unchanged)
- Gamma emission (γ), EM radiation
 - No change to remaining nucleus
- Positron emission (β^+), positron
 - Remaining nucleus atomic number -1
 - From conversion of proton to neutron
 - (mass number unchanged)
- Electron capture (EC), X ray
 - Remaining nucleus atomic number -1

Decay particles



- α stopped by sheet of paper
- β^- stopped by 2-3 mm of Al foil
- γ stopped by a few feet of lead
- Detected with a Geiger counter

Balancing radioactive reactions

- Balance superscripts and subscripts

Decay rate

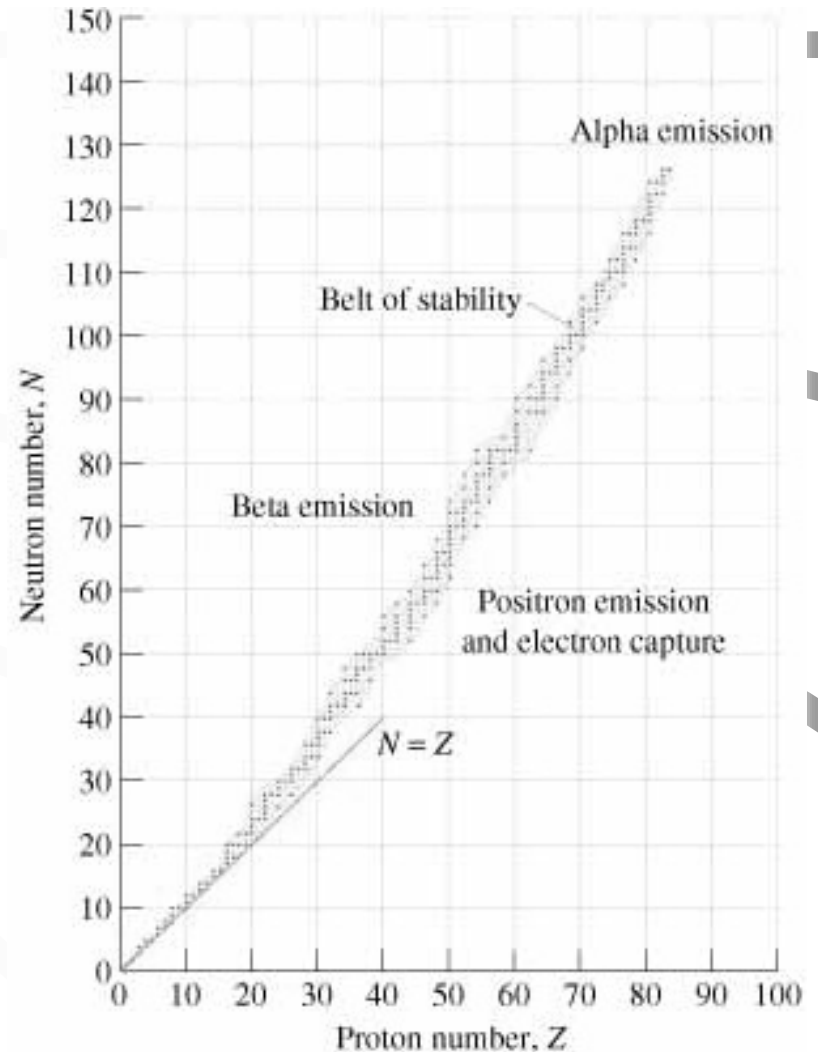
- Remember that radioactive decay is first order, rate = $k[A]$
- Half life is the amount of time for half to decay = $.693/\lambda$, where λ is the decay constant (rate constant)
- Half lives vary, making them useful in some instances and not others
 - ^{14}C 5730 years
 - ^{238}U 4.51×10^9 years
 - ^{59}Fe 44.496 days

Alchemy

- The first synthetic nuclide was generated by Rutherford in 1919
- ^{17}O is not radioactive- it's one of oxygen's naturally-occurring nuclides

Why are elements radioactive?

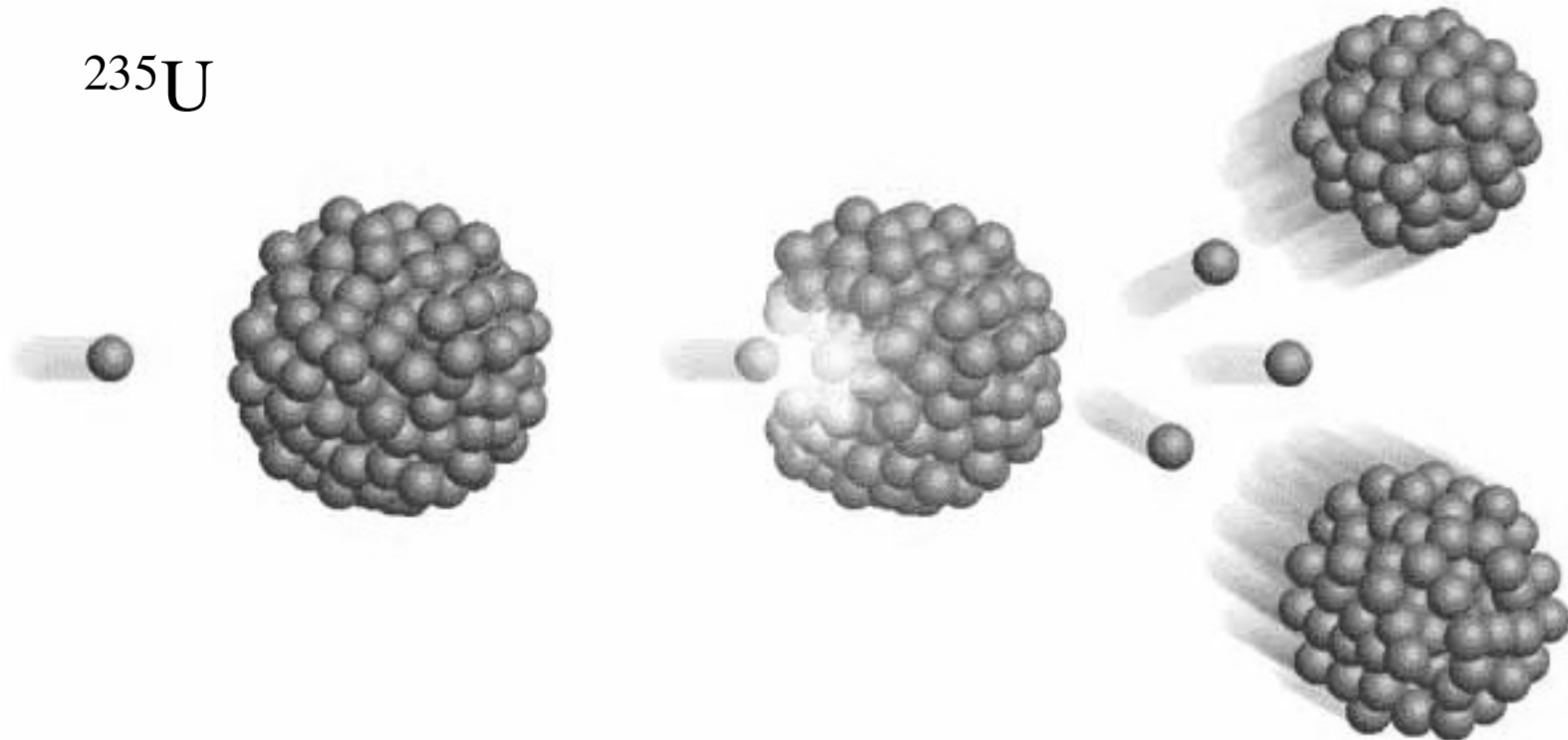
- Band of stability
- Trivia:
 - 160 have even p, even n
 - 50 have even p, odd n
 - 50 have odd p, even n
 - 4 have odd p, odd n



Energetics

- Using Einstein's equation, can calculate the energy released in a nuclear reaction, but not necessary for AP

^{235}U





Environmental chemistry

Qualitative analysis

- Identity not amount (*quantitative analysis*)
- A series of solubility tests can identify an unknown

Air and water- composition and pollution

- Smog and ozone
- Global warming
- Algae blooms
- Acid rain and limestone

Further topics

- Nitrogen cycle
- Carbon cycle

Poisons

- Carcinogens
- Corrosives
- Heavy metals
- Nerve gas
- Oxygen transport blockers

Atmospheric composition, structure, and natural cycles

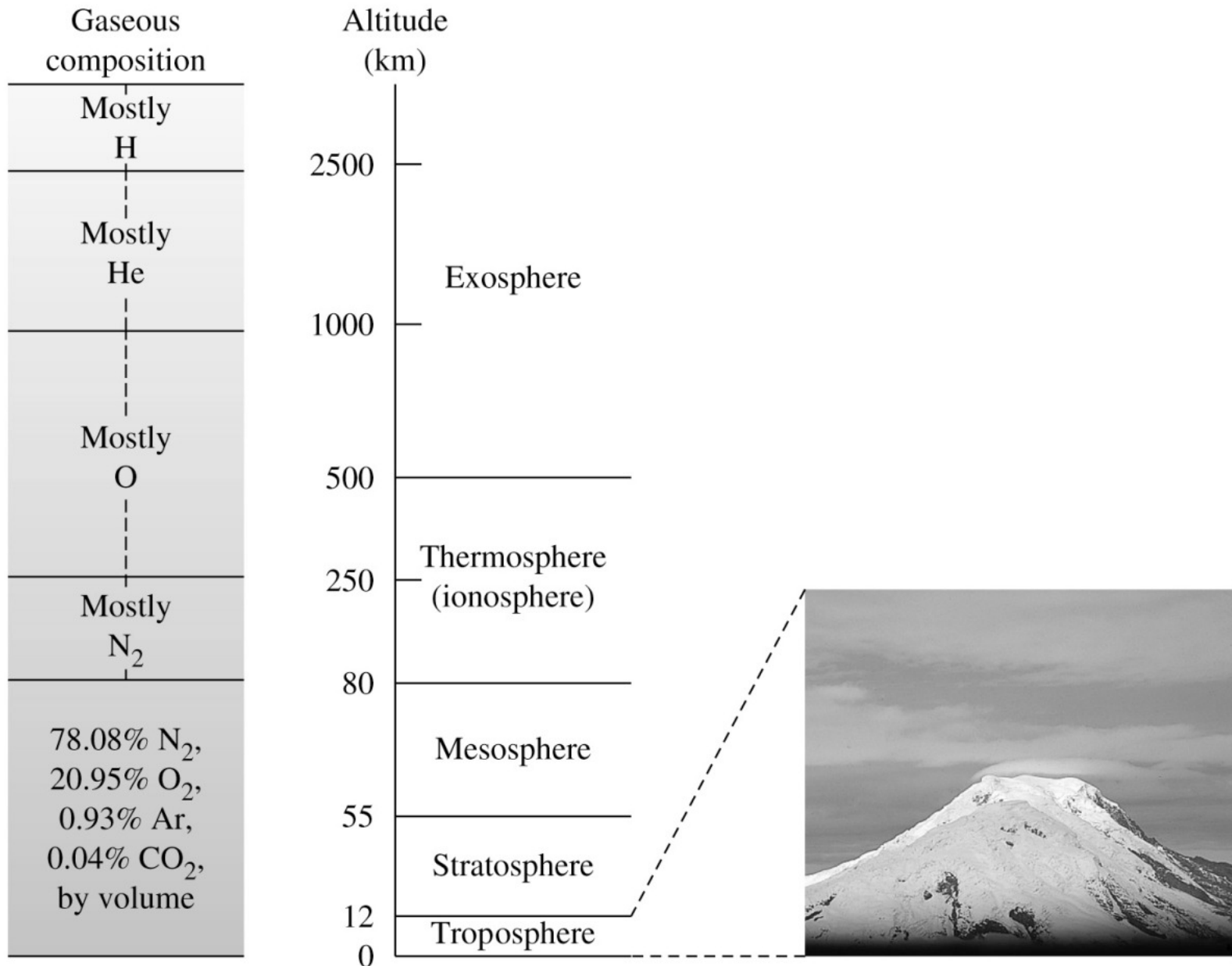
- Oxygen gas is essential to the basic processes of respiration and metabolism; however, the other components of the atmosphere are necessary as well.
- The oxygen in air is diluted with nitrogen, lessening the tendency for oxidation of everything in contact with air.
- Carbon dioxide and water vapor are but minor components in air, but are primary raw materials of the plant kingdom.
- Even ozone, a gas present only in trace quantities, plays vital roles in shielding Earth's surface from harmful ultraviolet radiation and in maintaining a proper energy balance in the atmosphere.

Table 25.1 Composition of Dry Air (near sea level)

| Component | Mole Percent^a |
|----------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Nitrogen (N ₂) | 78.084 |
| Oxygen (O ₂) | 20.946 |
| Argon (Ar) | 0.934 |
| Carbon dioxide (CO ₂) | 0.0368 |
| Neon (Ne) | 0.001818 |
| Helium (He) | 0.000524 |
| Methane (CH ₄) | 0.0002 |
| Krypton (Kr) | 0.000114 |
| Hydrogen (H ₂) | 0.00005 |
| Dinitrogen monoxide (N ₂ O) | 0.00005 |
| Xenon (Xe) | 0.000009 |
| | Plus traces of: ozone (O ₃); sulfur dioxide (SO ₂); nitrogen dioxide (NO ₂); ammonia (NH ₃); carbon monoxide (CO); iodine (I ₂) |

^a The compositions of gaseous mixtures are often expressed in percent by volume. Volume percent and mole percent compositions have the same numeric values.

Layers of the atmosphere



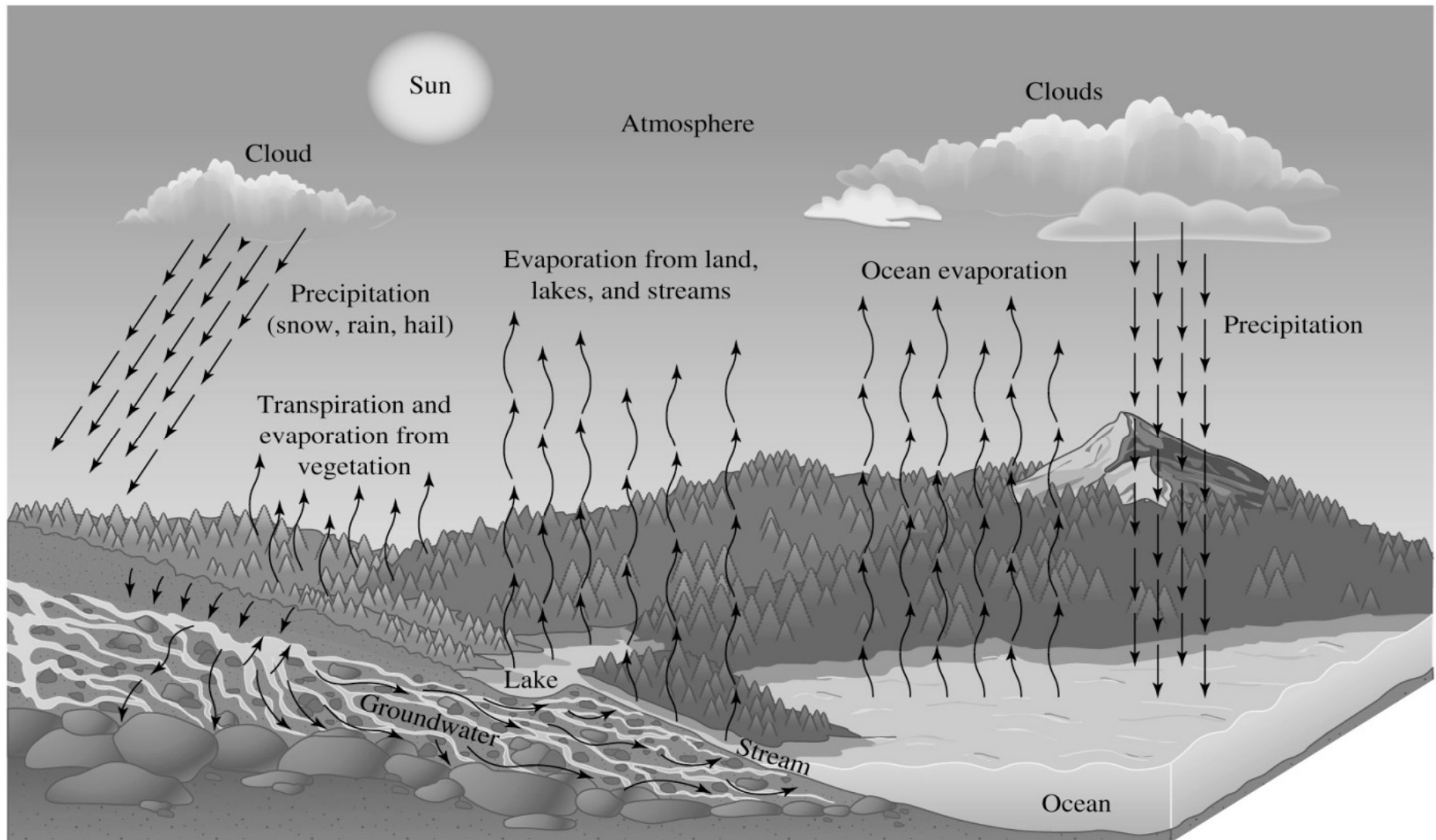
Water vapor in the atmosphere

- Humidity is a general term describing the water vapor content of air.
- Relative humidity of air is a measure of water vapor content as a percentage of the maximum possible.

$$\text{Relative humidity} = \frac{\text{partial pressure of water vapor}}{\text{vapor pressure of water}} = x \times 100$$

- The highest temperature at which water vapor can condense from an air sample is known as the dew point.
- The condensation of water vapor on a solid followed by solution formation is called deliquescence.

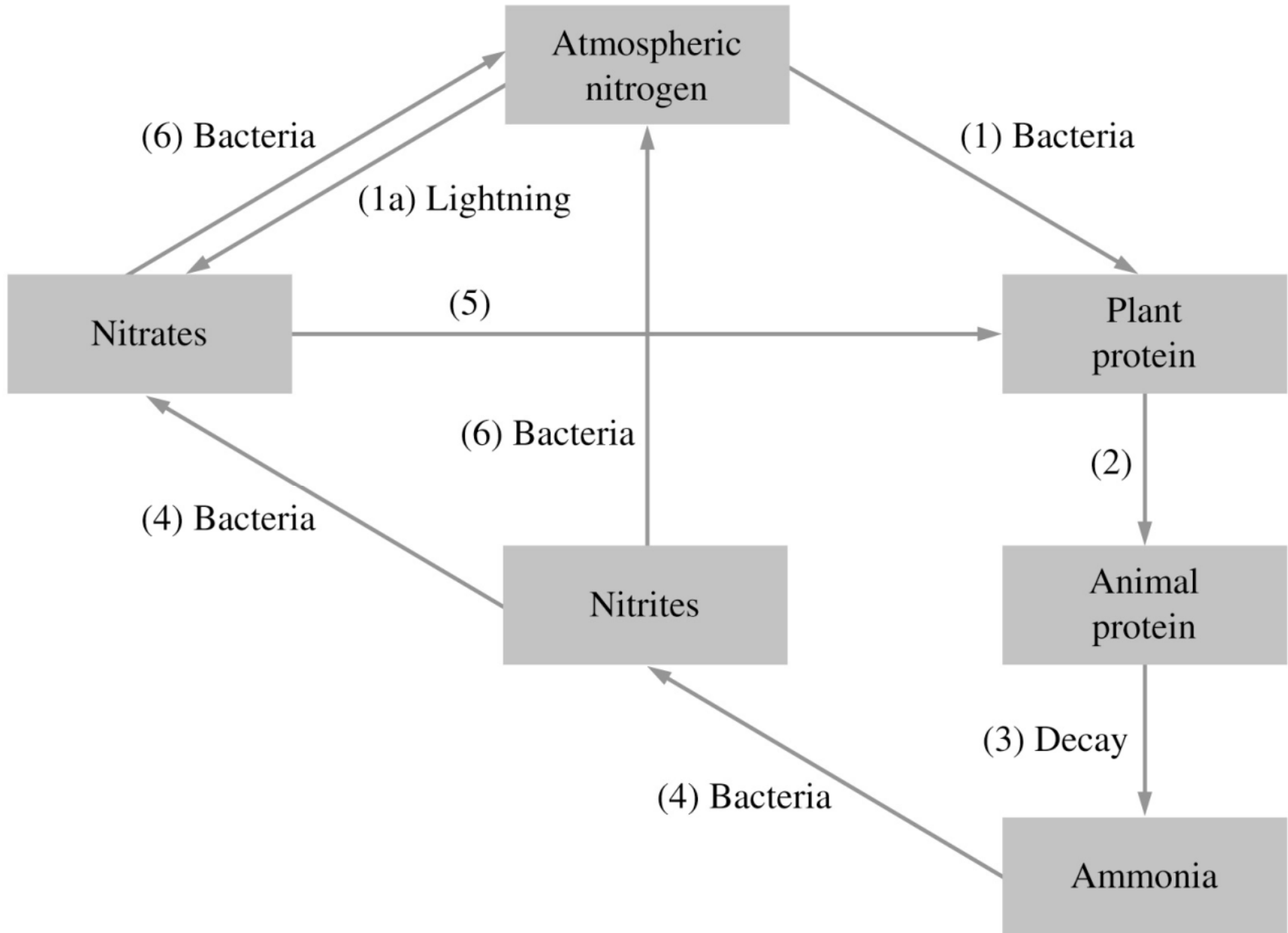
The hydrologic (water) cycle



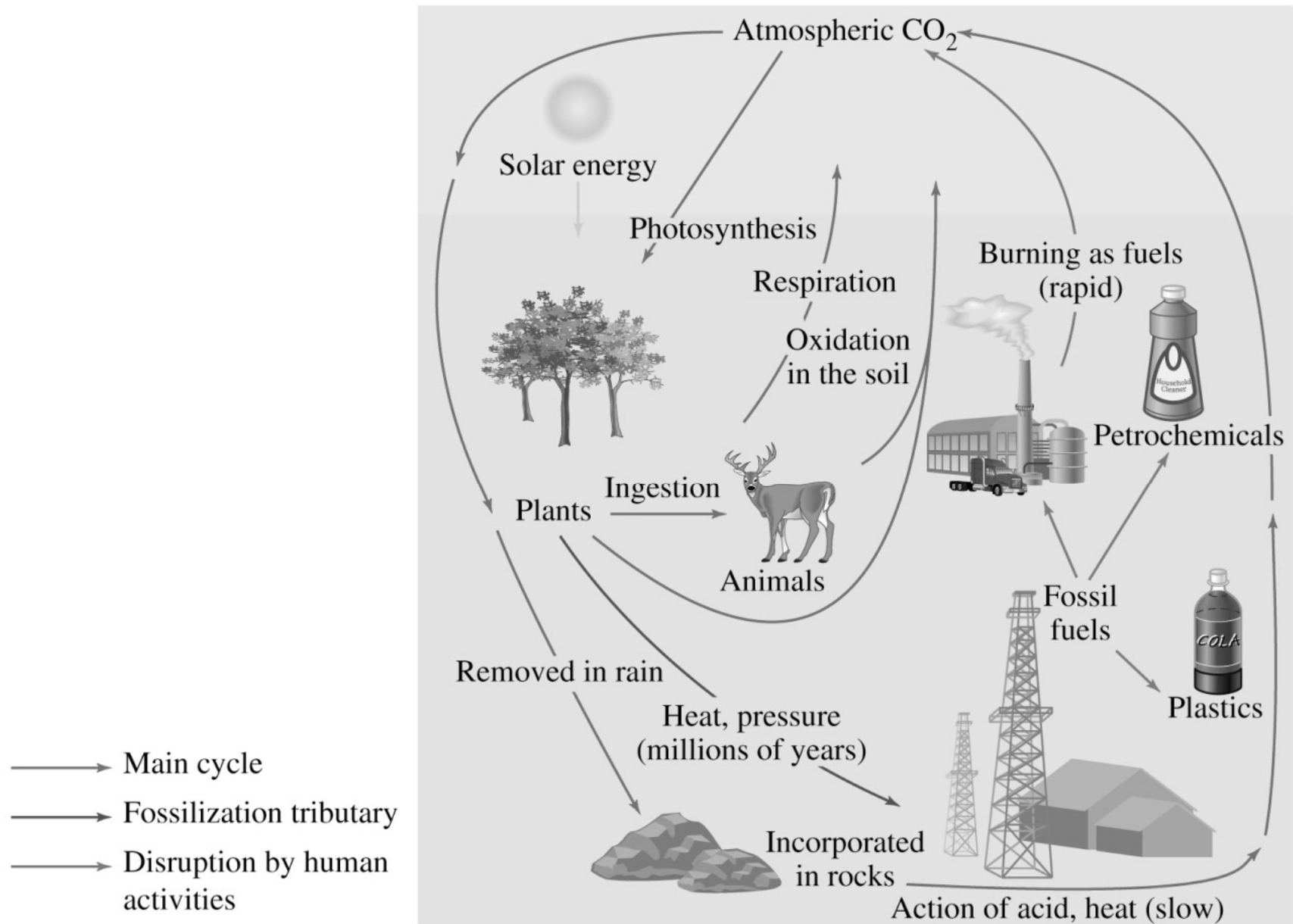
Nitrogen fixation: the nitrogen cycle

- Nitrogen gas cannot be used directly by higher plants or animals.
- The conversion of atmospheric nitrogen into nitrogen compounds is called nitrogen fixation.
- Certain bacteria that live in root nodules of specific plants are able to fix atmospheric nitrogen by converting it to ammonia.
- These nitrogen-fixing bacteria are concentrated in the roots of leguminous plants, such as clover, soybeans, and peas.
- The decay of plant and animal life returns nitrogen to the environment as nitrates and ammonia.

The nitrogen cycle



The carbon cycle



Air pollution

- An air pollutant is a substance found in air in greater abundance than normally occurs naturally, and having one or more harmful effects on human health or the environment.
- Carbon monoxide (CO) and carbon dioxide (CO₂) are formed in varying quantities when fossil fuels are burned.
- Carbon monoxide replaces O₂ molecules normally bonded to Fe²⁺ ions in hemoglobin in blood.
- The symptoms of carbon monoxide poisoning are those of oxygen deprivation.

Photochemical smog

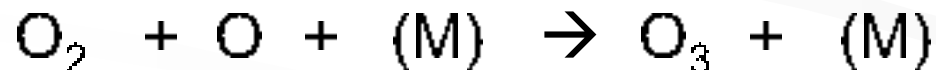
- When sunlight falls on air containing a mix of nitrogen oxides, hydrocarbons, and other substances, it produces a mix of pollutants called *photochemical smog*.
- Automobile exhaust is a crucial contributor to the production of photochemical smog.
- Most measures to reduce the levels of photochemical smog focus on automobiles, but potential sources of smog precursors range from power plants to lawn mowers to charcoal lighter fluid.
- Automobiles are now equipped with *catalytic converters* which convert nitrogen oxides and CO to N₂ and CO₂.

Industrial smog

- ***Industrial smog*** occurs mainly in cool, damp weather and is usually characterized by high levels of sulfur oxides (SO_x) and of particulate matter (dust, smoke, aerosols, etc.)
- ***Particulate matter*** consists of solid and liquid particles of greater than molecular size.
- When inhaled deeply into the lungs, these pollutants break down the cells of the tiny air sacs, called *alveoli*, where oxygen and carbon dioxide exchange normally occurs.
- *Soot* (unburned carbon) and *fly ash* (fine particulate residue from combustion) can be removed from smokestack gases in several ways including scrubbing and chemical reactions.

The ozone layer

- The ***ozone layer*** is a band of the stratosphere about 20 km thick, centered at an altitude of about 25 to 30 km.
- Ozone absorbs harmful ultraviolet (UV) radiation, and the ozone layer thus protects life on Earth.
- Ozone is produced in the upper atmosphere in a sequence of two reactions:



- Of all the human activities that affect the ozone layer, release of chlorofluorocarbons (CFCs) is thought to be the most significant.
- Stratospheric ozone = “good”
- Tropospheric ozone = “bad”

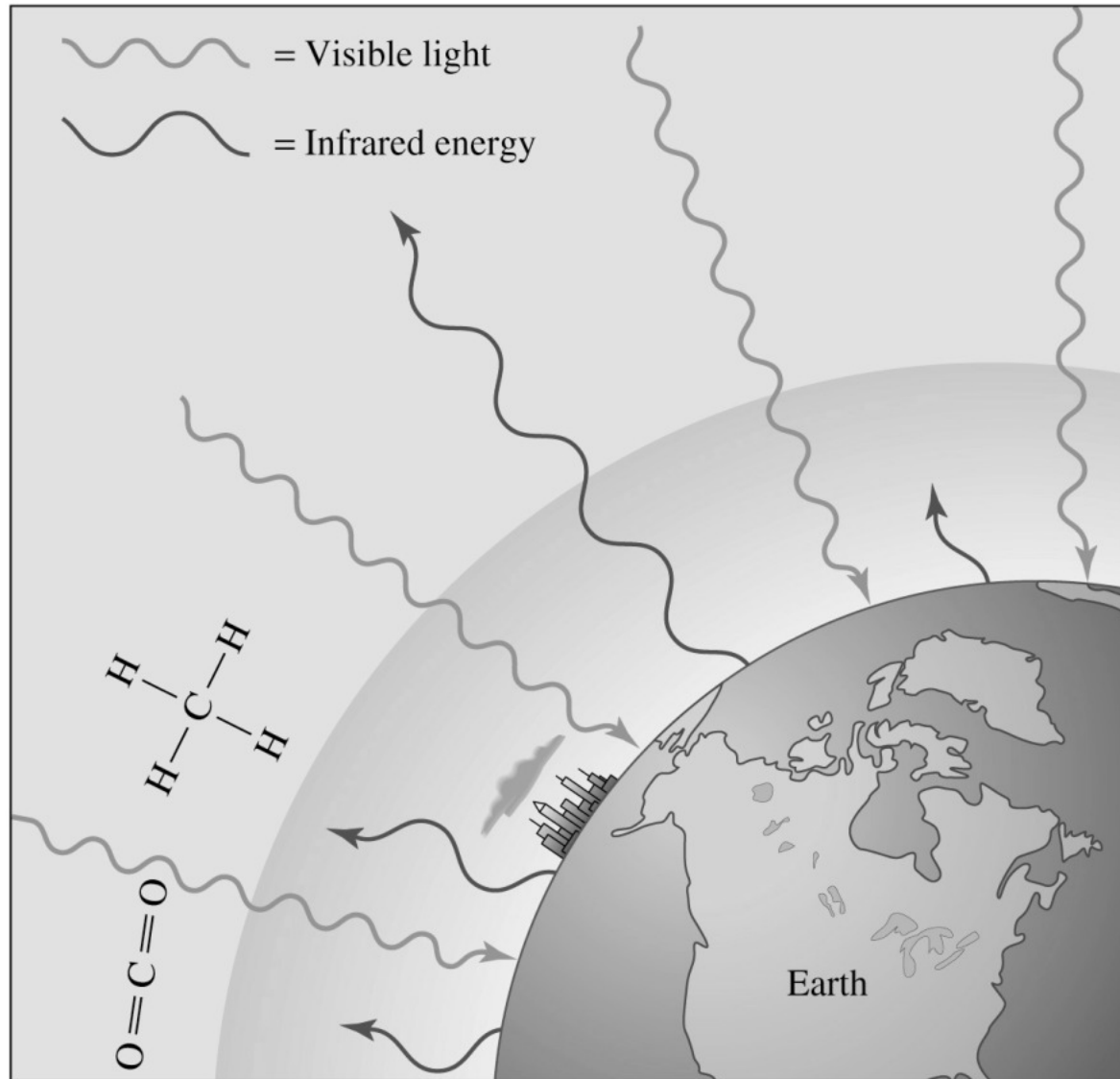
Ozone depletion

- One CFC molecule (resulting in stratospheric chlorine) can catalyze the destruction of up to 30,000 ozone molecules
- Though not the “hot” topic it once was, due to the phase out of CFC’s by *most* countries (!), ozone depletion may not be as critical today, and the hole may be repairing itself
- Current data seems to indicate that compliance with the Montreal Protocol will result in ozone layer recovery by 2050
- <http://www.epa.gov/ozone/index.html>
- Mario Molina, joint winner of the 1995 Nobel Prize for Chemistry for his work on ozone depletion, is Professor of Atmospheric Chemistry at MIT

Global warming: CO₂ and the greenhouse effect

- Small increases in the concentration of CO₂ could have a profound effect on the environment by producing a significant increase in the average global temperature, an effect called ***global warming***.
- The ***greenhouse effect*** occurs when radiant energy is retained by the atmosphere and warms it.
- ~~Most~~ ALL atmospheric scientists think that global warming is already under way and anthropogenic.
- MOST “news” organizations disagree.
- The main strategy for countering possible global warming is to curtail the use of fossil fuels.
- Other greenhouse gases include methane

The greenhouse effect



Copyright © 2005 Pearson Prentice Hall, Inc.

Earth's natural waters

- Water commonly occurs as a liquid, the only prevalent naturally occurring liquid on Earth's surface.
- Ice is less dense than liquid water.
- Water has a higher density than most other familiar liquids; hydrocarbons and other organic compounds that are insoluble in water and less dense than water float on its surface.
- Water has a high specific heat and a high heat of vaporization.
- Although three-fourths of Earth's surface is covered with water, nearly 98% is salty seawater, unfit for drinking and unsuitable for most industrial purposes.

Water pollution

- Early people did little to pollute the water and the air, if only because their numbers were few.
- Contamination of water supplies by microorganisms from human wastes was a severe problem throughout the world until about 100 years ago.
- The threat of biological contamination has not been totally eliminated from the developed nations.
- Hepatitis A, a viral disease spread through drinking water and contaminated food, at times threatens to reach epidemic proportions, even in developed nations.

Table 25.3 Average Daily Per-Person Use of Water in the United States

| Use | Amount (L) |
|---------------------------------------------|-------------|
| Direct use | |
| Drinking and cooking | 7 |
| Flushing toilets | 80 |
| Supplying swimming pools and watering lawns | 85 |
| Dish washing | 14 |
| Bathing | 70 |
| Laundry | 35 |
| Miscellaneous | 90 |
| Total direct use | 400 |
| Indirect use | |
| Industrial | 3800 |
| Irrigation (agriculture) | 2150 |
| Municipal water (nonindustrial) | 550 |
| Total indirect use | 6500 |
| Total overall use | 6900 |

Every drop helps, but does direct use water conservation really add up?

3800
2150
550

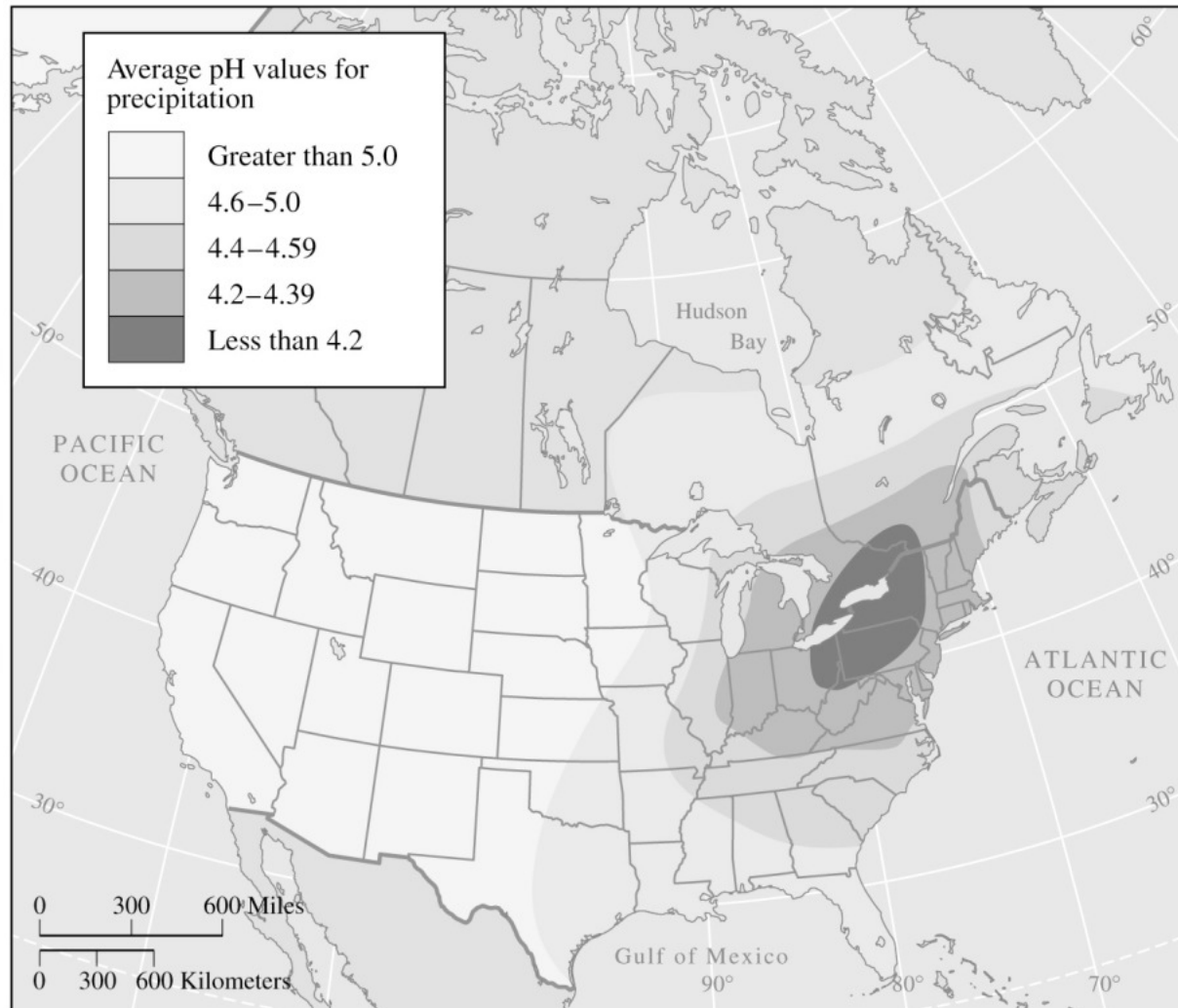
Chemical contamination of water

- In the past, factories often were built on the banks of streams, and wastes were dumped into the water to be carried away.
- Toxic chemicals have been found in both surface water and groundwater.
- Industries in the U.S. have eliminated a considerable proportion of the water pollution they once produced.
- Many of the food industry wastes are usually treated by regular sewage treatment plants.
- “No phosphates” on detergents prevents algae blooms

Acid rain

- Acid rain is rainfall that is more acidic than it would be if it contained just dissolved atmospheric CO₂.
- Acid rain corrodes metals, limestone, and marble, and even ruins the finishes on our automobiles.
- Acid water is detrimental to life in lakes and streams.
- Acid rain has been linked to declining crop and forest yields.
- Acids are no threat to lakes and streams in areas where the rock is limestone, which can neutralize excess acid.
- Acidic waters can be neutralized by adding lime or pulverized limestone, but the process is costly and the results last only a few years.

Acid rain in North America

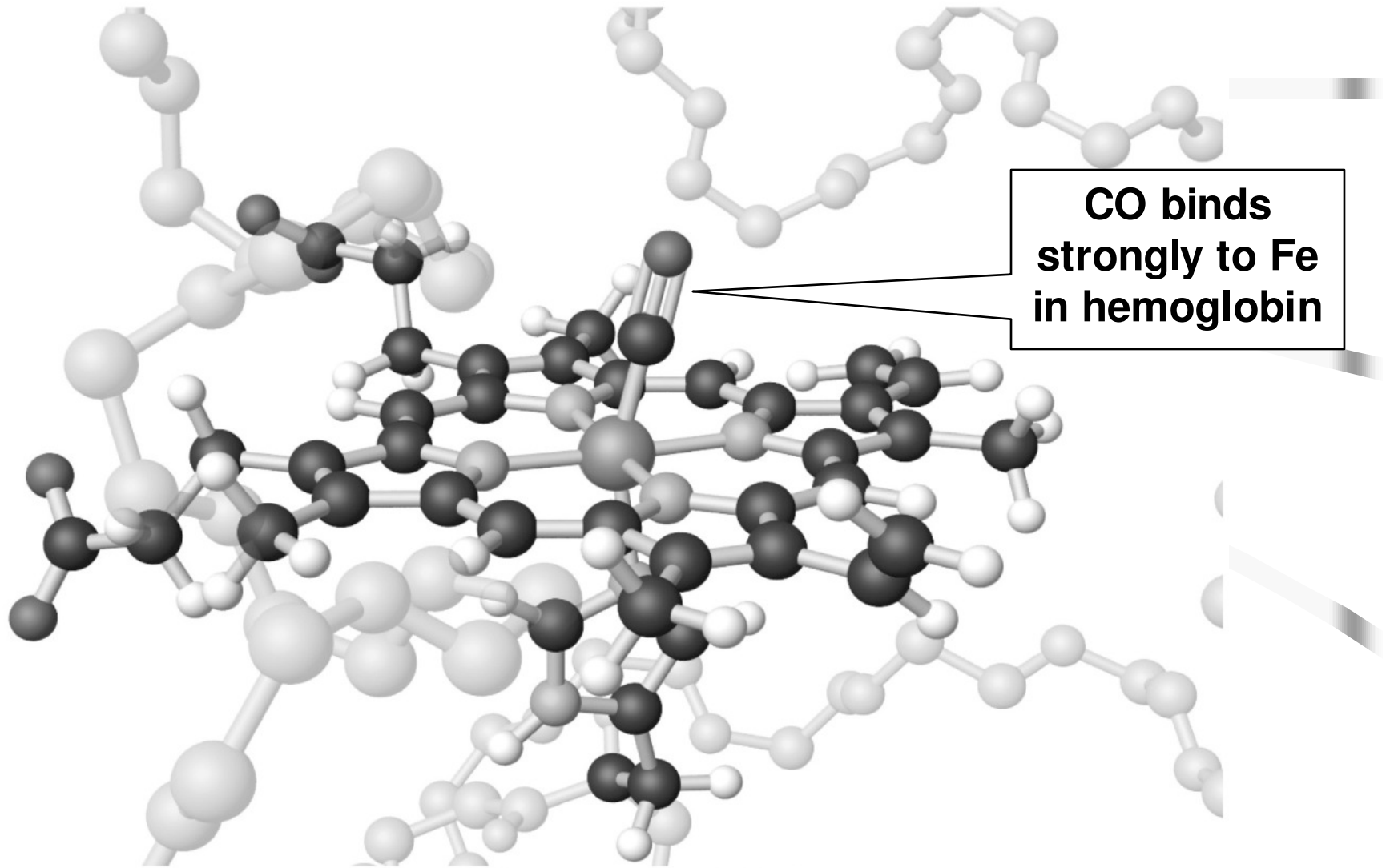


Copyright © 2005 Pearson Prentice Hall, Inc.

Poisons

- A substance may be harmless—or even a necessary nutrient—in one amount, and injurious, or even deadly, in another. Many household chemicals are poisonous.
- Strong acids and bases and strong oxidizing agents can be highly corrosive to human tissue.
- Carbon monoxide and cyanide ion block oxygen transport and use in the human body.
- Many heavy metals are poisons by deactivating enzymes.
- Some poisons interfere with nerve cell communications and are called *nerve poisons*.

Molecular view of CO poisoning



Carcinogens and anticarcinogens

- *Tumors*, abnormal growths of new tissue, may be either benign (harmless) or malignant (cancerous).
- A ***carcinogen*** is a material that causes cancer.
- Some of the more notorious carcinogens are polycyclic aromatic hydrocarbons and the aromatic amines.
- Few of the known carcinogens are synthetic chemicals.
- Some substances in food act as ***anticarcinogens***, substances which help to prevent cancer.
- The vitamins that are antioxidants (C, E, and β -carotene) seem to exhibit the strongest anticancer properties.

Table 25.6 Industrial Products and Hazardous Waste By-products

| Product | Associated Waste |
|----------------|------------------------------------------------------------------------------------------------------------------------------|
| Plastics | Organic chlorine compounds |
| Pesticides | Organic chlorine compounds, organophosphate compounds |
| Medicines | Organic solvents and residues, heavy metals (for example, mercury and zinc) |
| Paints | Heavy metals, pigments, solvents, organic residues |
| Oil, gasoline | Oil, phenols and other organic compounds, heavy metals, ammonium salts, acids, caustics |
| Metals | Heavy metals, fluorides, cyanides, acidic and alkaline cleaners, solvents, pigments, abrasives, plating salts, oils, phenols |
| Leather | Heavy metals, organic solvents |
| Textiles | Heavy metals, dyes, organic chlorine compounds, solvents |

Trivia

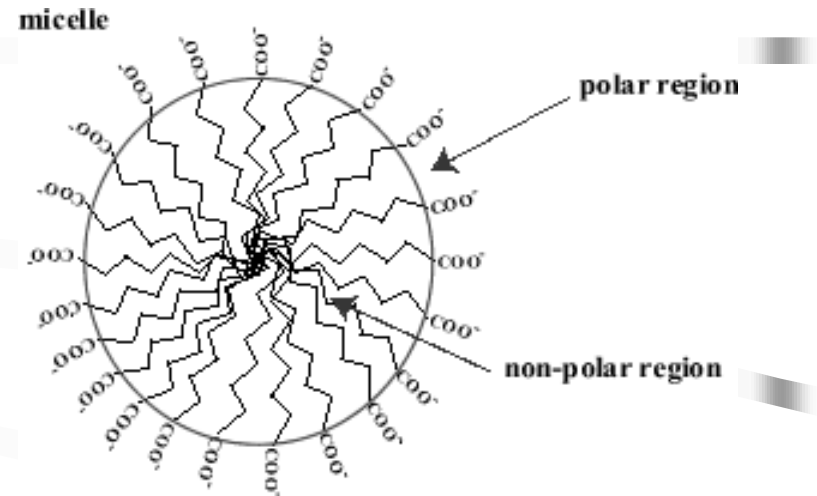
- NH_3 is ammonia gas (NH_4OH when in water)
- CH_3COOH is acetic acid (vinegar)
- NaCl is table salt
- KCl is “no salt” salt alternative
- CaCO_3 is limestone
- O_2 is oxygen (context!)
- NaHCO_3 sodium bicarbonate (hydrogen carbonate, bicarbonate of soda) is baking soda (baking powder is different)
- H_2CO_3 carbonic acid is unstable and decomposes to CO_2 and H_2O
- $\text{Mg}(\text{OH})_2$ is milk of magnesia (antacid)

More trivia

- Group 1- alkali metals
- Group 2- alkaline earth metals
- Group 6- chalcogens
- Group 7- halogens
- Group 8- noble/inert gases
- Fluoride in toothpaste converts hydroxyapatite in teeth ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) into fluoroapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$) which is less prone to decay (why?)
- Water “softening” is the exchanging of “hard” ions (which precipitate out soap residues) like Ca^{2+} and Mg^{2+} with “soft” ions like Na^+ and K^+ using an ion exchange resin

Even more trivia

- How soap works
 - like dissolves like
 - fatty end
 - hydrophobic
 - conj. base end
 - hydrophilic



- Only liquids on the periodic table are bromine and mercury
- Mercury forms dangerous organics
 - “Mad Hatter’s Disease” was likely Hg poisoning since it was used to cure fur for felt hats
 - used in dental amalgams (alloys- solid/solid solution)

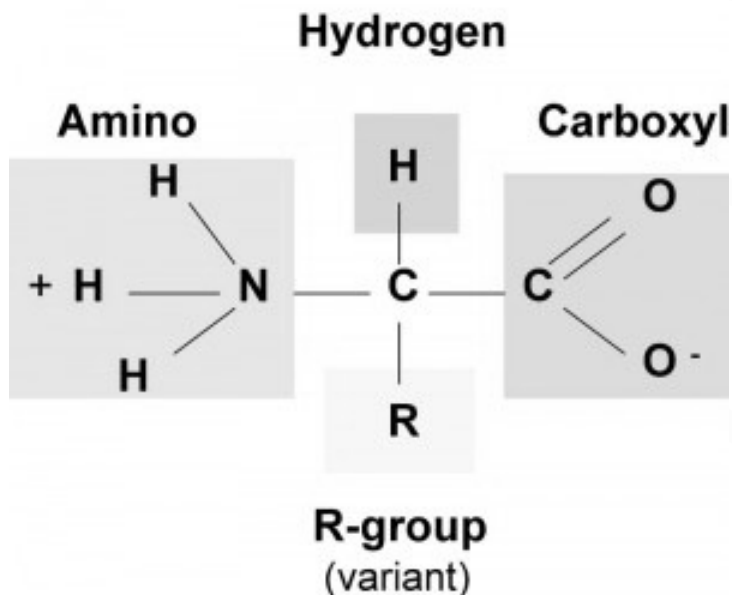
...and more trivia

- Saturated fat- no C=C double bonds
 - generally solids below 120°F
 - why, and why is that a problem
- Monounsaturated fat- only one C=C double bond
- Polyunsaturated fat- more than one C=C double bond
- Carbohydrates are of the form $C_x(H_2O)_y$
- Monosaccharides are single sugars
- Disaccharides are composed of two monosaccharides
- Polysaccharides (starch, glycogen, cellulose) are more than 10

...and even more trivia

- Proteins are polymers of amino acids
- 2 AA form a dipeptide
- Multiple AA form a polypeptide (protein)
- Enzymes are protein catalysts

Amino Acid Structure



Amino acids have the general form $\text{NH}_2 - \text{CHR} - \text{COOH}$, where R can be any one of about 20 different groups. They link together into proteins through amide (peptide) bonds as shown here:

