

Professor K

Lab and other topics

Review

- Solubility was introduced earlier with the formation of precipitates
- LeChatelier's Principle tells us that formation of a solid from aqueous reactants drives a reaction in the forward direction
- Using what we learned about equilibrium constants, we can discuss how soluble something is

Example

- $\text{BaSO}_4(s) \rightleftharpoons \text{Ba}^{2+}(aq) + \text{SO}_4^{2-}(aq)$
- The equilibrium constant (or *solubility product constant* here),
 $K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = 1.1 \times 10^{-10}$ at 25°C
since solids don't appear in the expression
-not very soluble, which is why it can be taken prior to being X-rayed
- K_{sp} s are influenced by a complex set of factors
- Given K_{sp} , you can calculate an ion concentration and *vice versa*

Table 16.1 Some Solubility Product Constants at 25 °C

Solute	Solubility Equilibrium	K_{sp}
Aluminum hydroxide	$\text{Al(OH)}_3(\text{s}) \rightleftharpoons \text{Al}^{3+}(\text{aq}) + 3 \text{OH}^{-}(\text{aq})$	1.3×10^{-33}
Barium carbonate	$\text{BaCO}_3(\text{s}) \rightleftharpoons \text{Ba}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$	5.1×10^{-9}
Barium sulfate	$\text{BaSO}_4(\text{s}) \rightleftharpoons \text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$	1.1×10^{-10}
Calcium carbonate	$\text{CaCO}_3(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$	2.8×10^{-9}
Calcium fluoride	$\text{CaF}_2(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + 2 \text{F}^{-}(\text{aq})$	5.3×10^{-9}
Calcium sulfate	$\text{CaSO}_4(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$	9.1×10^{-6}
Calcium oxalate	$\text{CaC}_2\text{O}_4(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{C}_2\text{O}_4^{2-}(\text{aq})$	2.7×10^{-9}
Chromium(III) hydroxide	$\text{Cr(OH)}_3(\text{s}) \rightleftharpoons \text{Cr}^{3+}(\text{aq}) + 3 \text{OH}^{-}(\text{aq})$	6.3×10^{-31}
Copper(II) sulfide	$\text{CuS}(\text{s}) \rightleftharpoons \text{Cu}^{2+}(\text{aq}) + \text{S}^{2-}(\text{aq})$	8.7×10^{-36}
Iron(III) hydroxide	$\text{Fe(OH)}_3(\text{s}) \rightleftharpoons \text{Fe}^{3+}(\text{aq}) + 3 \text{OH}^{-}(\text{aq})$	4×10^{-38}
Lead(II) chloride	$\text{PbCl}_2(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2 \text{Cl}^{-}(\text{aq})$	1.6×10^{-5}
Lead(II) chromate	$\text{PbCrO}_4(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + \text{CrO}_4^{2-}(\text{aq})$	2.8×10^{-13}
Lead(II) iodide	$\text{PbI}_2(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2 \text{I}^{-}(\text{aq})$	7.1×10^{-9}
Magnesium carbonate	$\text{MgCO}_3(\text{s}) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$	3.5×10^{-8}
Magnesium fluoride	$\text{MgF}_2(\text{s}) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + 2 \text{F}^{-}(\text{aq})$	3.7×10^{-8}
Magnesium hydroxide	$\text{Mg(OH)}_2(\text{s}) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + 2 \text{OH}^{-}(\text{aq})$	1.8×10^{-11}
Magnesium phosphate	$\text{Mg}_3(\text{PO}_4)_2(\text{s}) \rightleftharpoons 3 \text{Mg}^{2+}(\text{aq}) + 2 \text{PO}_4^{3-}(\text{aq})$	1×10^{-25}
Mercury(I) chloride	$\text{Hg}_2\text{Cl}_2(\text{s}) \rightleftharpoons \text{Hg}_2^{2+}(\text{aq}) + 2 \text{Cl}^{-}(\text{aq})$	1.3×10^{-18}
Mercury(II) sulfide	$\text{HgS}(\text{s}) \rightleftharpoons \text{Hg}^{2+}(\text{aq}) + \text{S}^{2-}(\text{aq})$	2×10^{-53}
Silver bromide	$\text{AgBr}(\text{s}) \rightleftharpoons \text{Ag}^{+}(\text{aq}) + \text{Br}^{-}(\text{aq})$	5.0×10^{-13}
Silver chloride	$\text{AgCl}(\text{s}) \rightleftharpoons \text{Ag}^{+}(\text{aq}) + \text{Cl}^{-}(\text{aq})$	1.8×10^{-10}
Silver iodide	$\text{AgI}(\text{s}) \rightleftharpoons \text{Ag}^{+}(\text{aq}) + \text{I}^{-}(\text{aq})$	8.5×10^{-17}
Strontium carbonate	$\text{SrCO}_3(\text{s}) \rightleftharpoons \text{Sr}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$	1.1×10^{-10}
Strontium sulfate	$\text{SrSO}_4(\text{s}) \rightleftharpoons \text{Sr}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$	3.2×10^{-7}
Zinc sulfide	$\text{ZnS}(\text{s}) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + \text{S}^{2-}(\text{aq})$	1.6×10^{-24}

K_{sp} and molar solubility

- K_{sp} is an equilibrium constant
- **Molar solubility** is the number of moles of compound that will dissolve per liter of solution.
- Molar solubility is **related** to the value of K_{sp} , but molar solubility and K_{sp} are **not** the same thing.
- In fact, “smaller K_{sp} ” doesn’t always mean “lower molar solubility.”
- Solubility depends on both K_{sp} and the form of the equilibrium constant expression.

Example

At 20 °C, a saturated aqueous solution of silver carbonate contains 32 mg of Ag_2CO_3 per liter of solution. Calculate K_{sp} for Ag_2CO_3 at 20 °C. The balanced equation is



Example

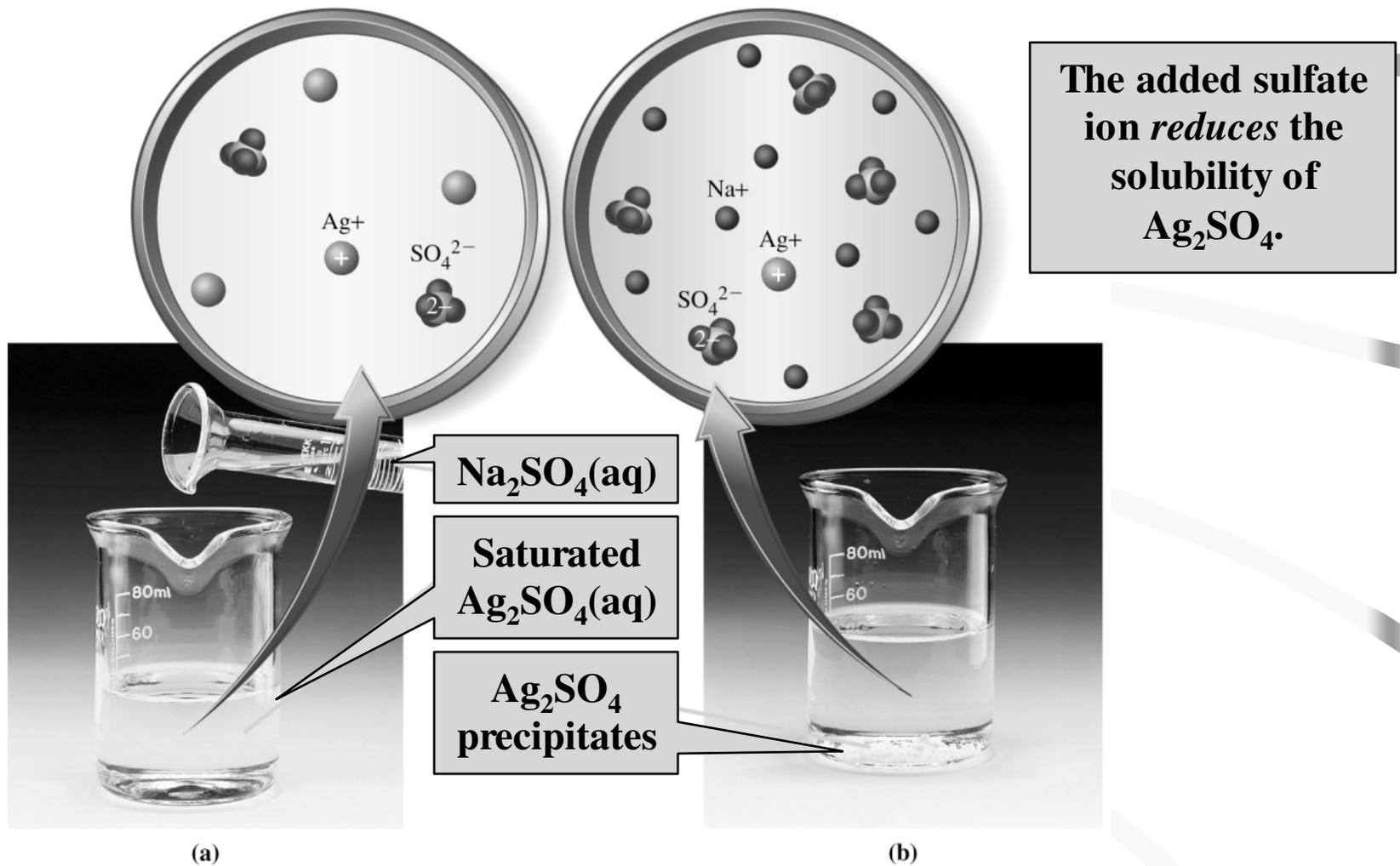
From the K_{sp} value for silver sulfate, calculate its molar solubility at 25 °C.



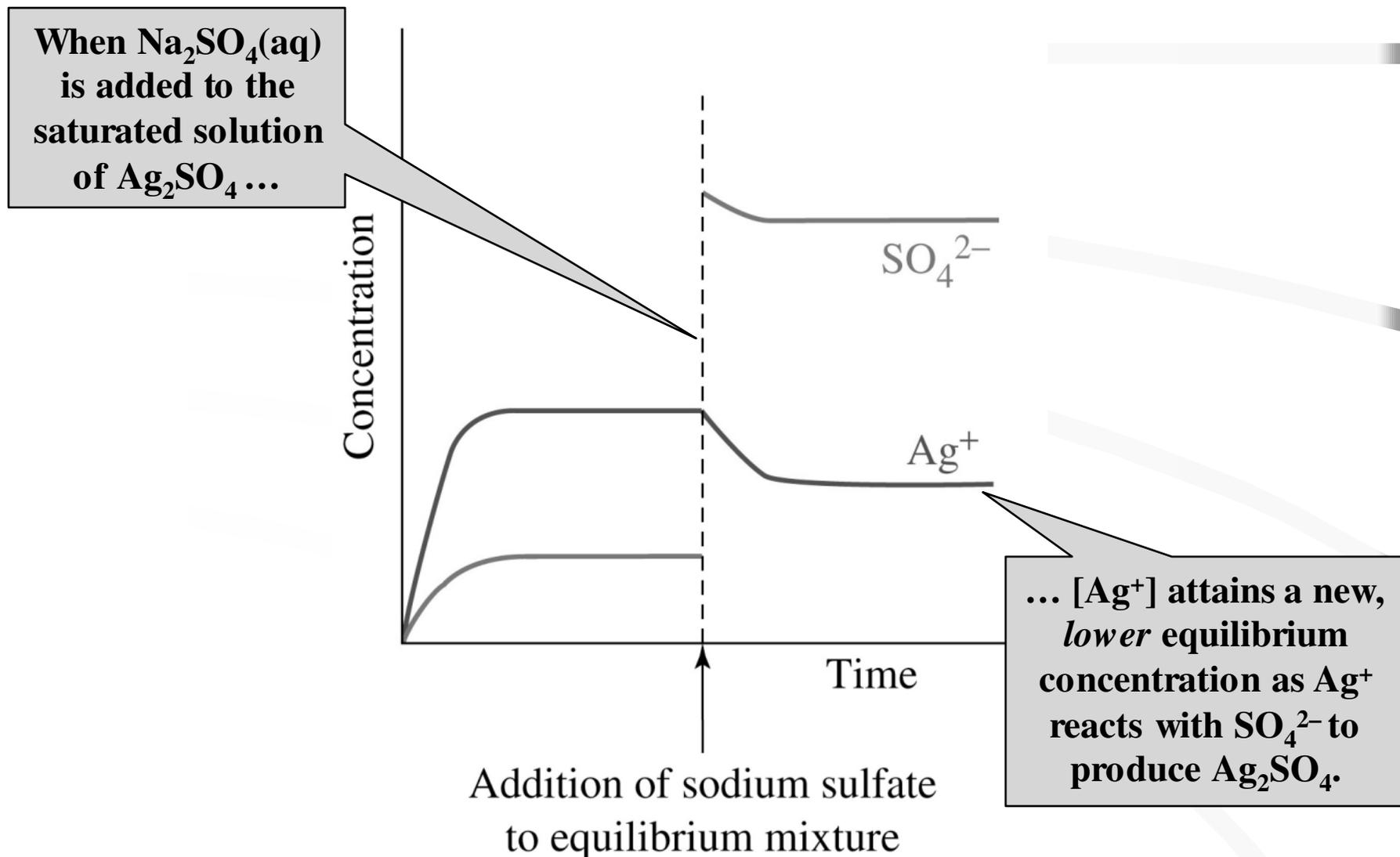
Common ion effect revisited

- LeChatelier's Principle re-revisited
 - The common ion effect affects solubility equilibria as it does other aqueous equilibria.
 - The solubility of a slightly soluble ionic compound is lowered when a second solute that furnishes a common ion is added to the solution.

Common ion effect illustrated



Common ion effect illustrated (cont'd)



Solubility and activities

- Ions that are not common to the precipitate can also affect solubility.
 - CaF_2 is more soluble in 0.010 M Na_2SO_4 than it is in water.
- Increased solubility occurs because of interionic attractions.
- Each Ca^{2+} and F^- is surrounded by ions of opposite charge, which impede the reaction of Ca^{2+} with F^- .
- The effective concentrations, or activities, of Ca^{2+} and F^- are lower than their actual concentrations.
- Again, activities will not be explored in detail

Q versus K (again)

- Reaction (or Ion Product) quotient, Q_{ip}
- Comparing Q_{ip} to K_{sp} tells whether precipitation will occur
- For $Q_{ip} > K_{sp}$, precipitation of the supersaturated solution should occur
- For $Q_{ip} < K_{sp}$, precipitation of the unsaturated solution cannot occur
- For $Q_{ip} = K_{sp}$, the solution is saturated
- In applying the precipitation criteria, the effect of dilution when solutions are mixed must be considered.

Example

If 1.00 mg of Na_2CrO_4 is added to 225 mL of 0.00015 M AgNO_3 , will a precipitate form?



$$K_{\text{sp}} = 1.1 \times 10^{-12}$$

To determine whether precipitation is complete

- A slightly soluble solid does not precipitate totally from solution ...
- ... but we generally consider precipitation to be “complete” if about 99.9% of the target ion is precipitated (0.1% or less left in solution).
- Three conditions generally favor completeness of precipitation:
 1. A very small value of K_{sp} .
 2. A high initial concentration of the target ion.
 3. A concentration of common ion that greatly exceeds that of the target ion.

Example

To a solution with $[\text{Ca}^{2+}] = 0.0050 \text{ M}$, we add sufficient solid ammonium oxalate, $(\text{NH}_4)_2\text{C}_2\text{O}_4(\text{s})$, to make the initial $[\text{C}_2\text{O}_4^{2-}] = 0.0051 \text{ M}$. Will precipitation of Ca^{2+} as $\text{CaC}_2\text{O}_4(\text{s})$ be complete?

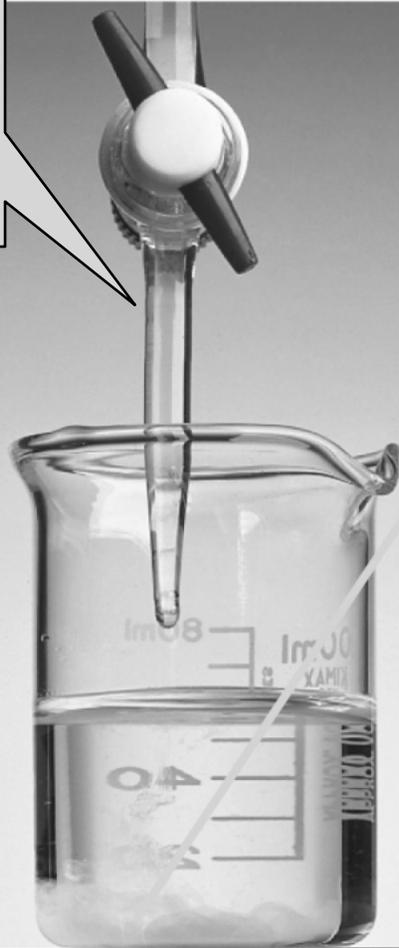


Selective precipitation

AgNO_3 added to
a mixture
containing Cl^-
and I^-

AgI (yellow)
precipitates first.

All AgI
precipitates
before any
 AgCl (white)
precipitates.



(a)

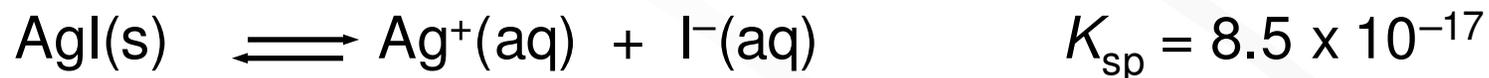


(b)

Example

An aqueous solution that is 2.00 M in AgNO_3 is slowly added from a buret to an aqueous solution that is 0.0100 M in Cl^- and also 0.0100 M in I^- .

- Which ion, Cl^- or I^- , is the first to precipitate from solution?
- When the second ion begins to precipitate, what is the remaining concentration of the first ion?
- Is separation of the two ions by selective precipitation feasible?



pH effect

- If the anion of a precipitate is that of a weak acid, the precipitate will dissolve somewhat when the pH is lowered:



Added H^+ reacts with, and *removes*, acetate; LeChâtelier's principle says more acetate forms.

- If, however, the anion of the precipitate is that of a strong acid, lowering the pH will have no effect on the precipitate.



H^+ does not consume Cl^- ; acid does not affect the equilibrium.

Example

What is the molar solubility of $\text{Mg}(\text{OH})_2(\text{s})$ in a buffer solution having $[\text{OH}^-] = 1.0 \times 10^{-5} \text{ M}$, that is, $\text{pH} = 9.00$?



Complex ions

- Why is toothpaste fluoridated?
- We will not focus on this topic deeply.

Equilibria involving complex ions

Table 16.2 Solubility of Silver Chloride in NaCl(aq)

[Cl ⁻], M	Predicted Solubility (mol AgCl/L) × 10 ⁵	Measured Solubility (mol AgCl/L) × 10 ⁵
0.000	1.3	1.3
0.0039	0.0046	0.072
0.036	0.00050	0.19
0.35	0.000051	1.7
1.4	0.000013	18
2.9	0.0000063	1000

Decreasing solubility (for Predicted Solubility)

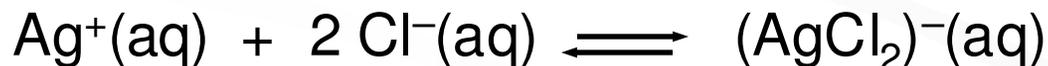
Decreasing solubility (for Measured Solubility, from 0.0039 M to 0.35 M)

Increasing solubility (for Measured Solubility, from 0.35 M to 2.9 M)

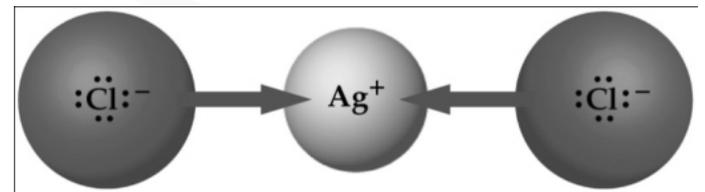
Silver chloride becomes *more* soluble, not *less* soluble, in high concentrations of chloride ion.

Complex ion formation

- KEY POINT– A **complex ion** consists of a central metal atom or ion, with other groups called **ligands** bonded to it.
- The metal ion acts as a Lewis acid (accepts electron pairs).
- Ligands act as Lewis bases (donate electron pairs).
- The equilibrium involving a complex ion, the metal ion, and the ligands may be described through a **formation constant, K_f** :



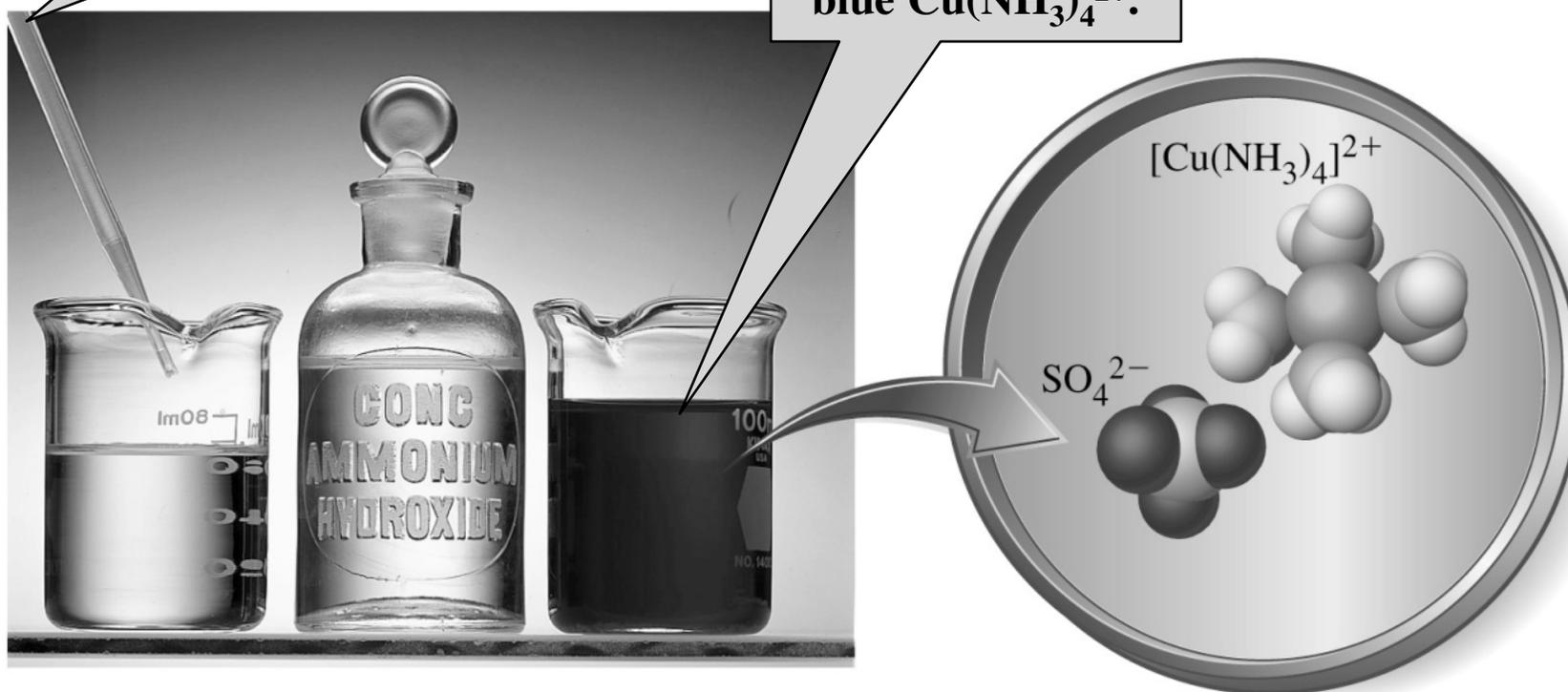
$$K_f = \frac{[\text{AgCl}_2^-]}{[\text{Ag}^+][\text{Cl}^-]^2} = 1.2 \times 10^8$$



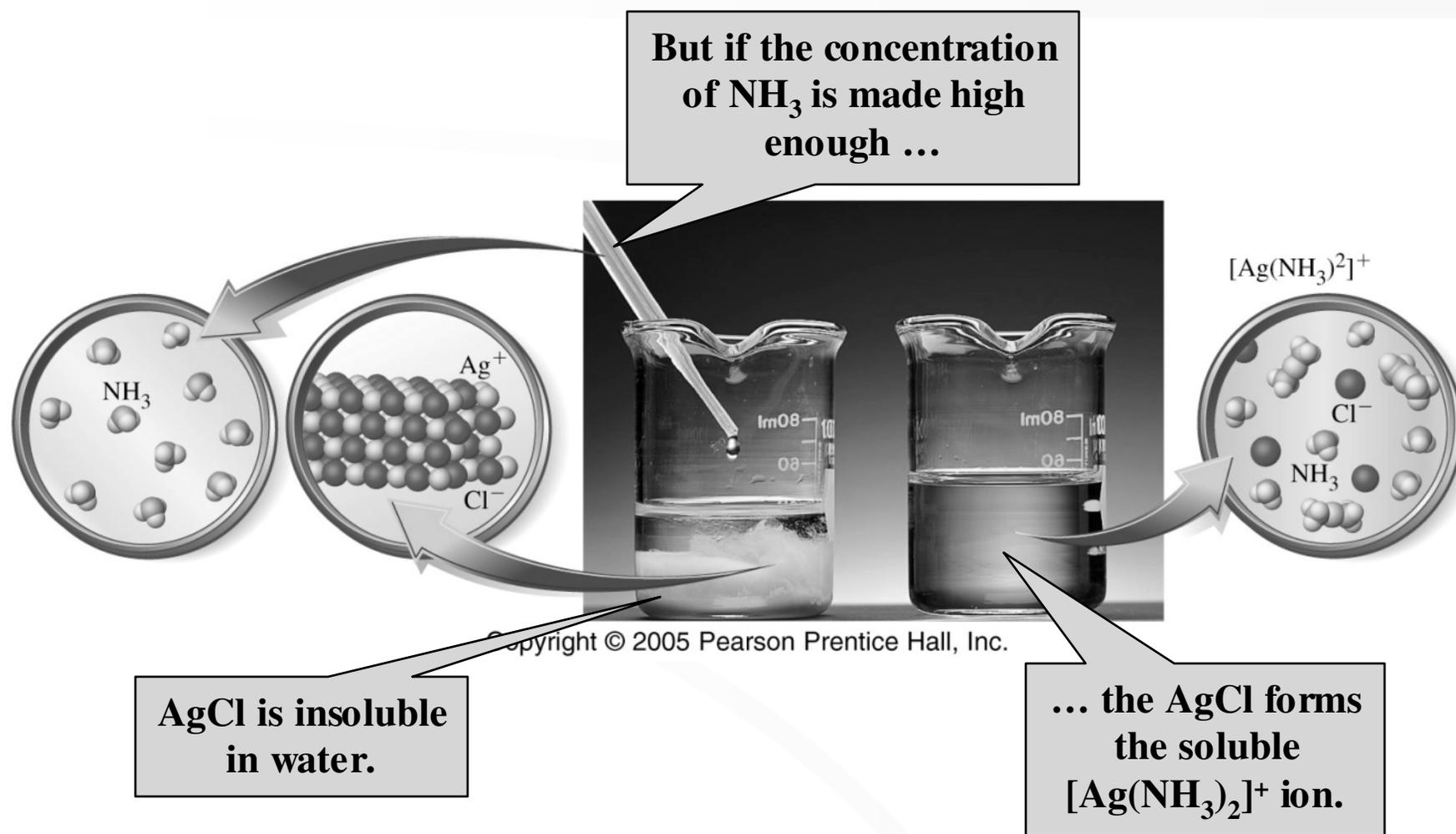
Complex ion formation (cont'd)

Concentrated NH_3
added to a solution of
pale-blue Cu^{2+} ...

... forms deep-
blue $\text{Cu}(\text{NH}_3)_4^{2+}$.

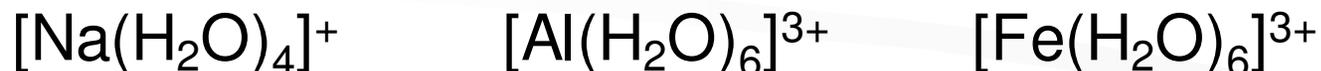
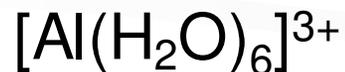


Complex ion formation and solubility



Complex ions in acid–base reactions

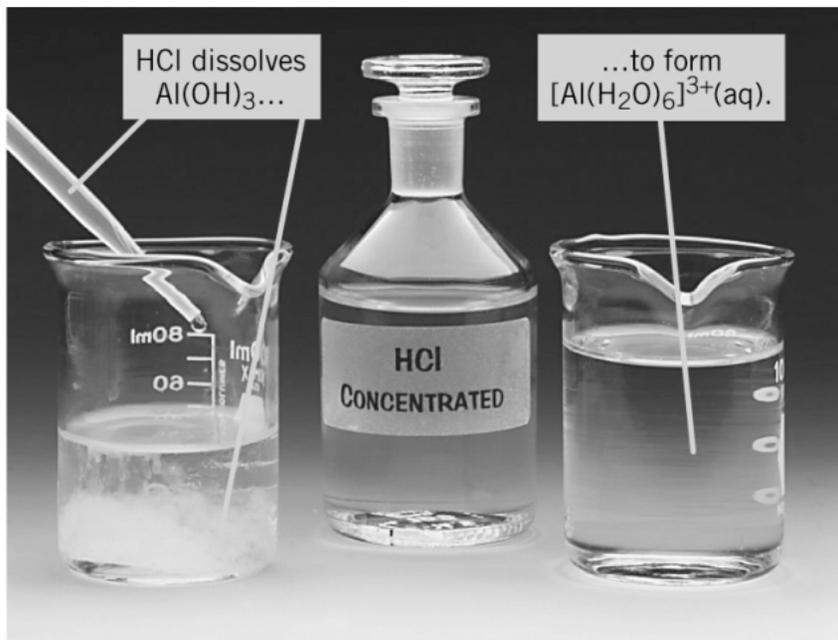
- Water molecules are commonly found as ligands in complex ions (H₂O is a Lewis base).



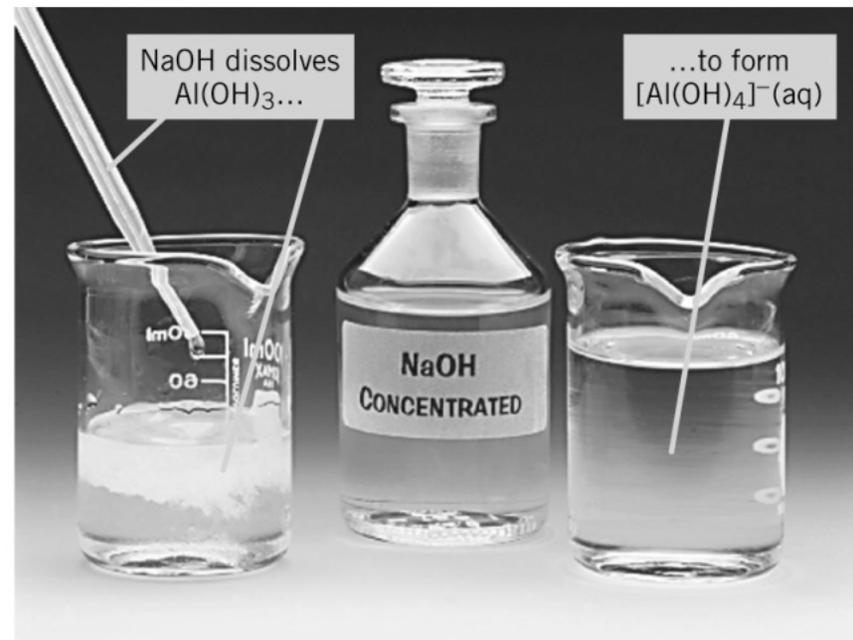
- The electron-withdrawing power of a ***small, highly charged*** metal ion can weaken an O—H bond in one of the ligand water molecules.
- The weakened O—H bond can then give up its proton to another water molecule in the solution.
- The complex ion acts as an ***acid***.

Amphoteric compounds

- Certain metal hydroxides, insoluble in water, are ***amphoteric***; they will react with both strong acids and strong bases.
- $\text{Al}(\text{OH})_3$, $\text{Zn}(\text{OH})_2$, and $\text{Cr}(\text{OH})_3$ are amphoteric.



(a)



(b)

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

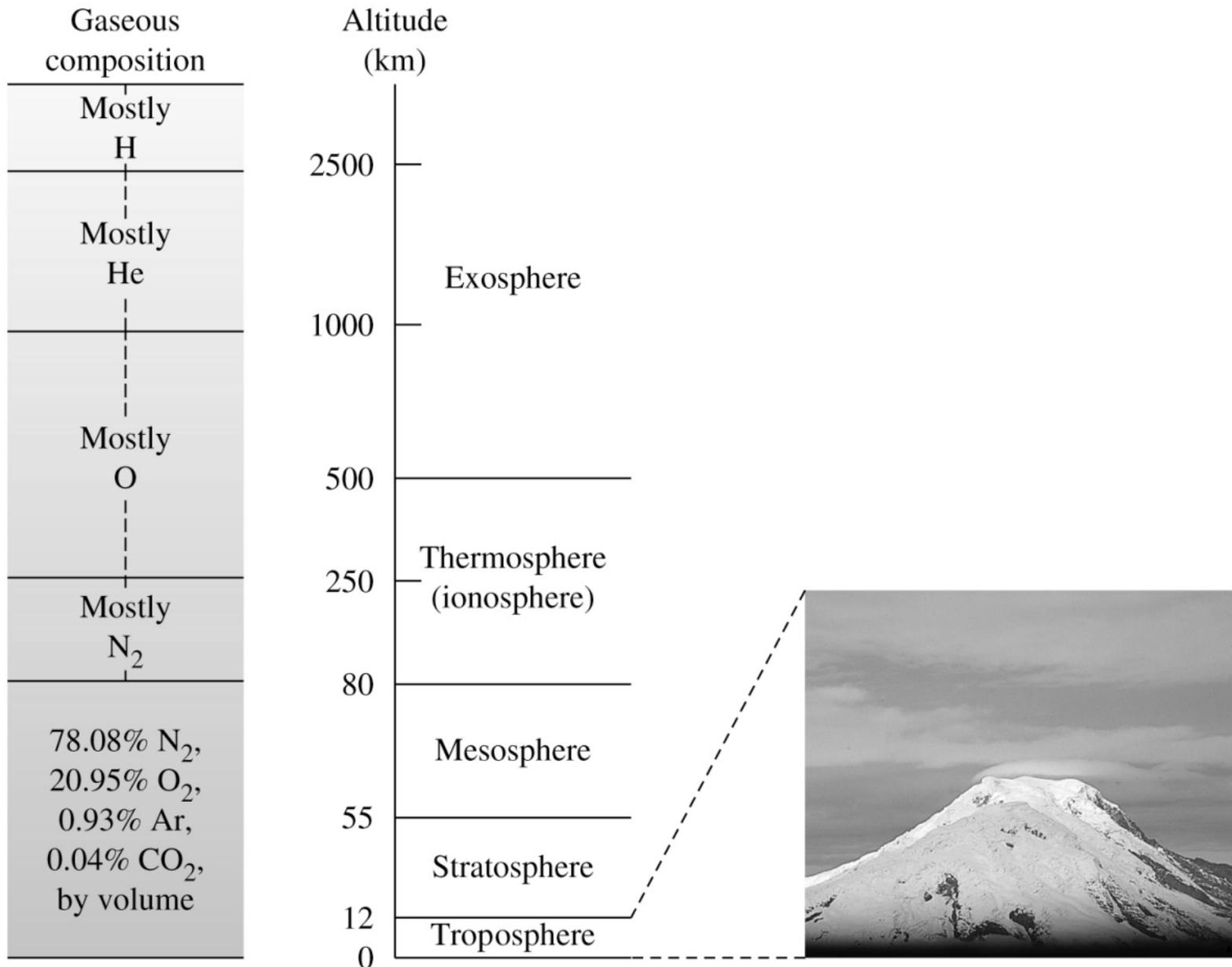
- Oxygen gas is essential to the basic processes of respiration and metabolism; however, the other components of the atmosphere are necessary as well.
- The oxygen in air is diluted with nitrogen, lessening the tendency for oxidation of everything in contact with air.
- Carbon dioxide and water vapor 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



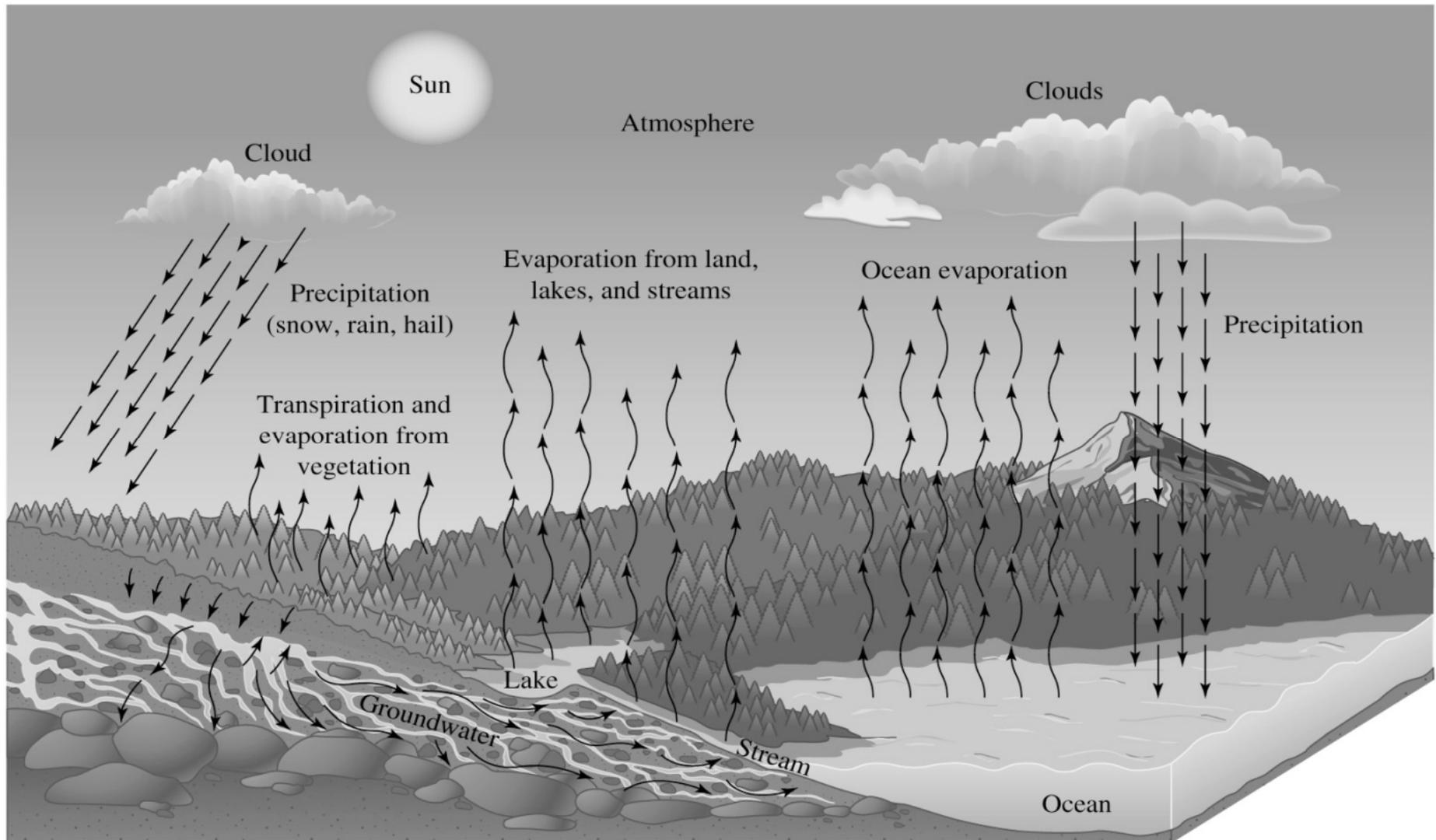
Water vapor in the atmosphere

- 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.

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

- 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.

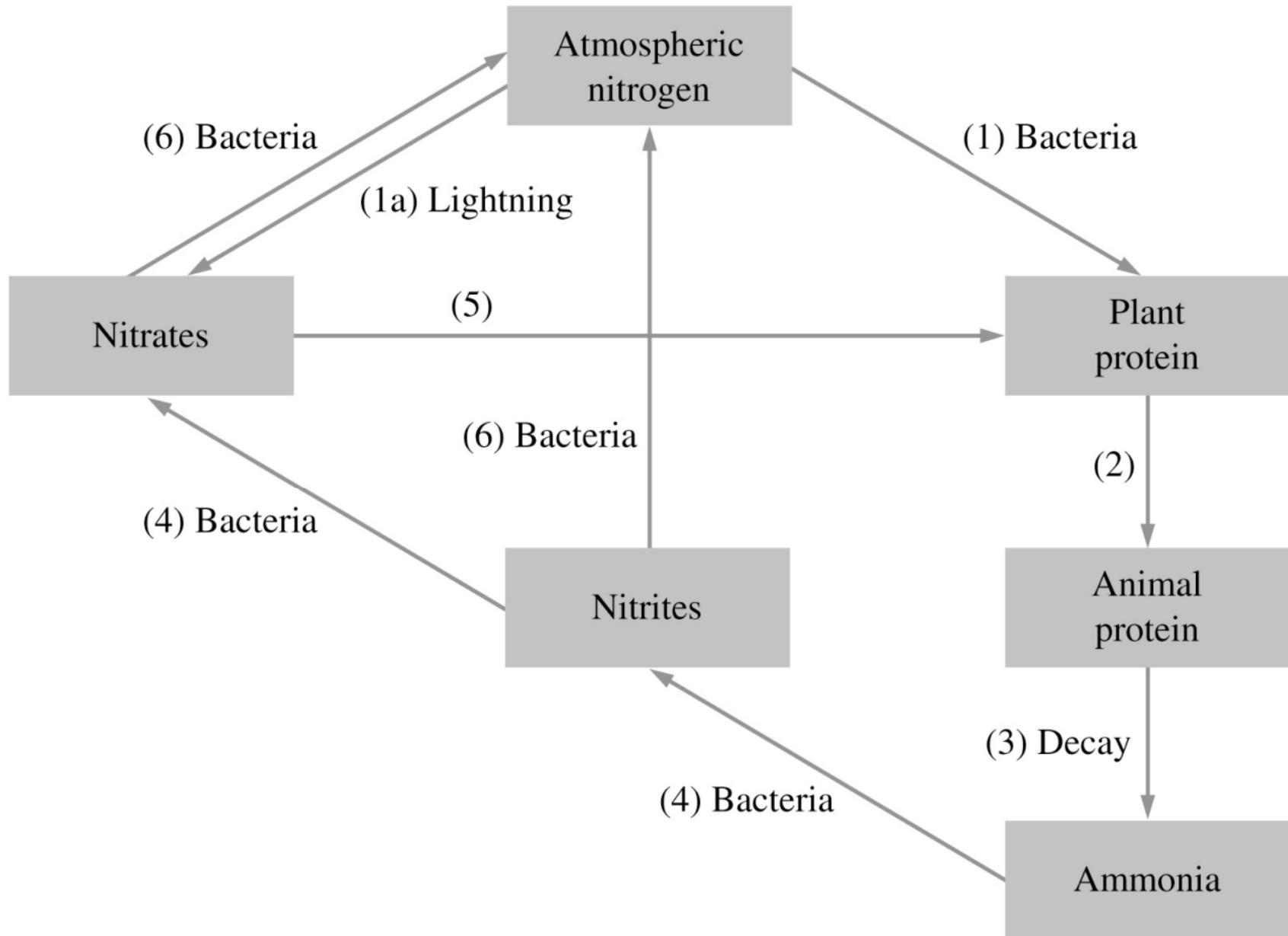
The hydrologic (water) cycle



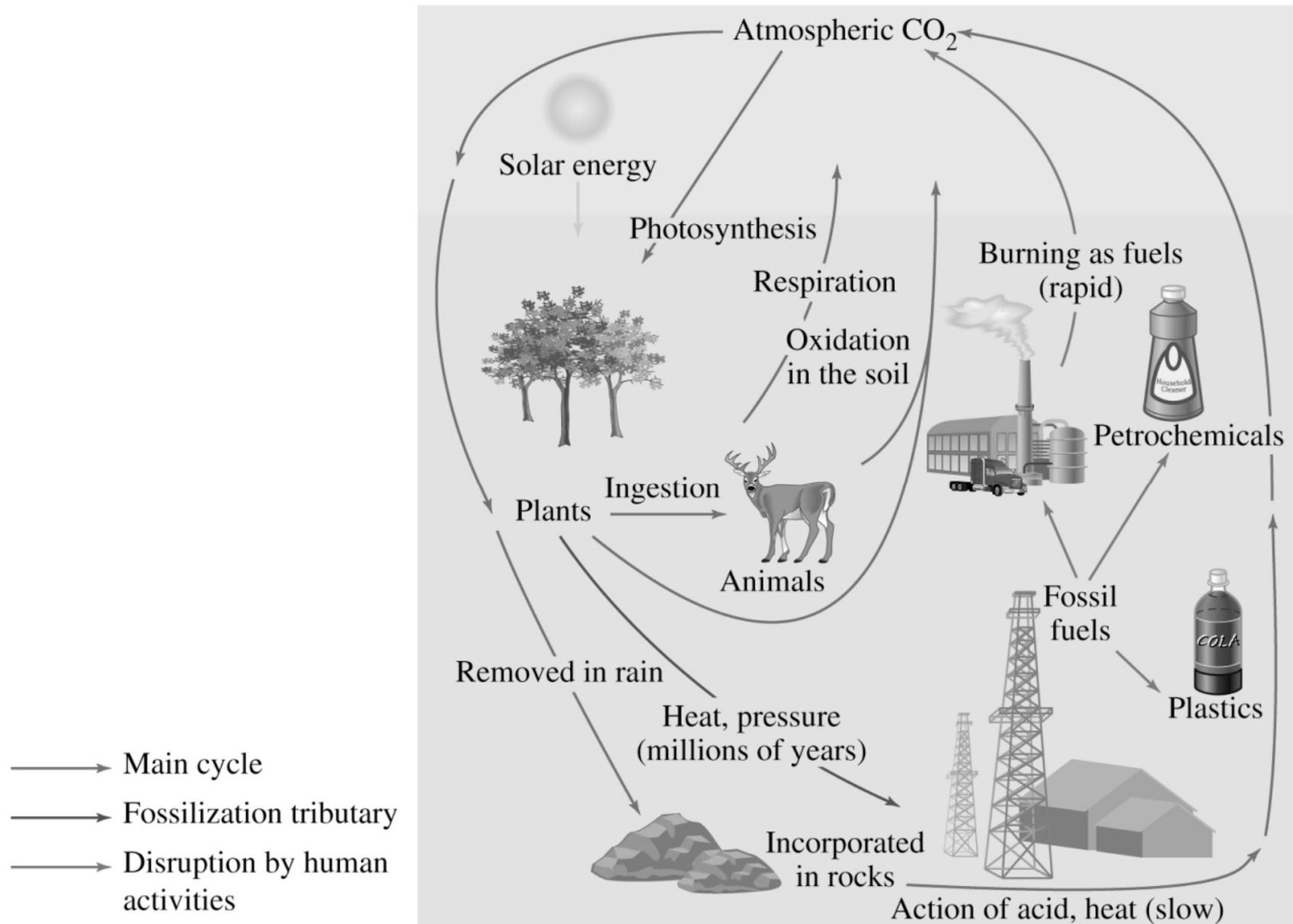
Nitrogen fixation: the nitrogen cycle

- 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”

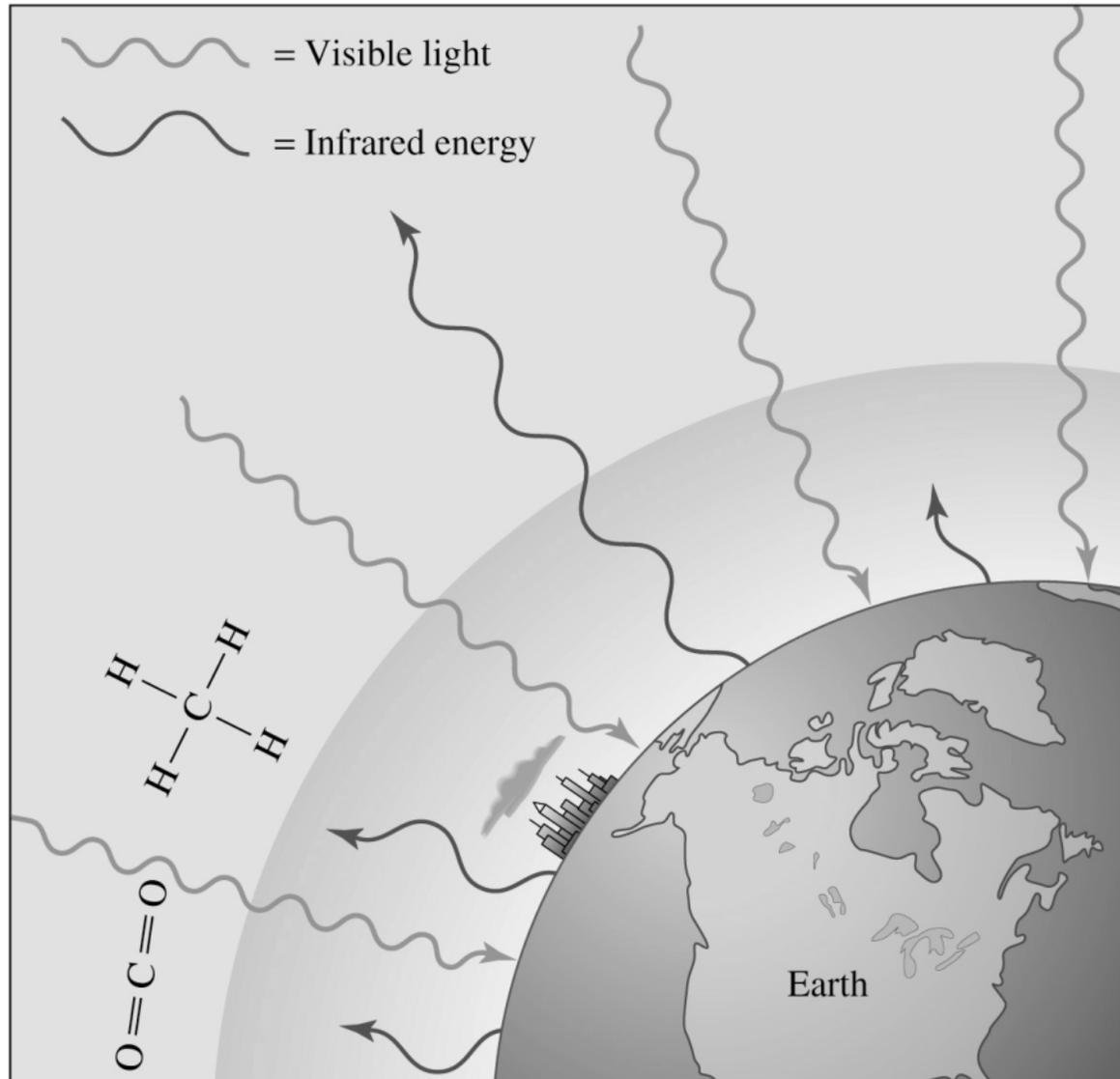
Ozone depletion

- 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.
- 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



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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

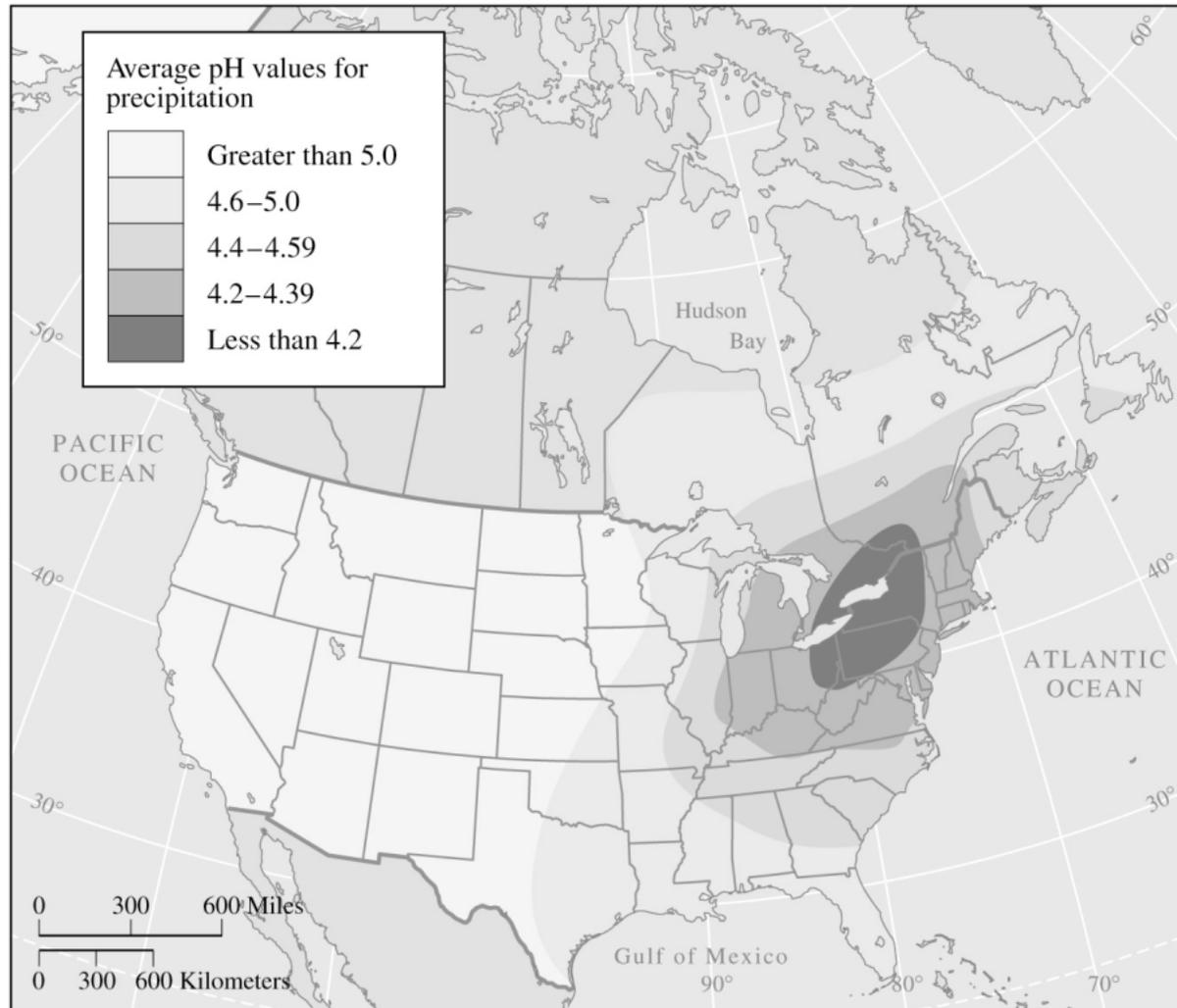
Chemical contamination of water

- 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

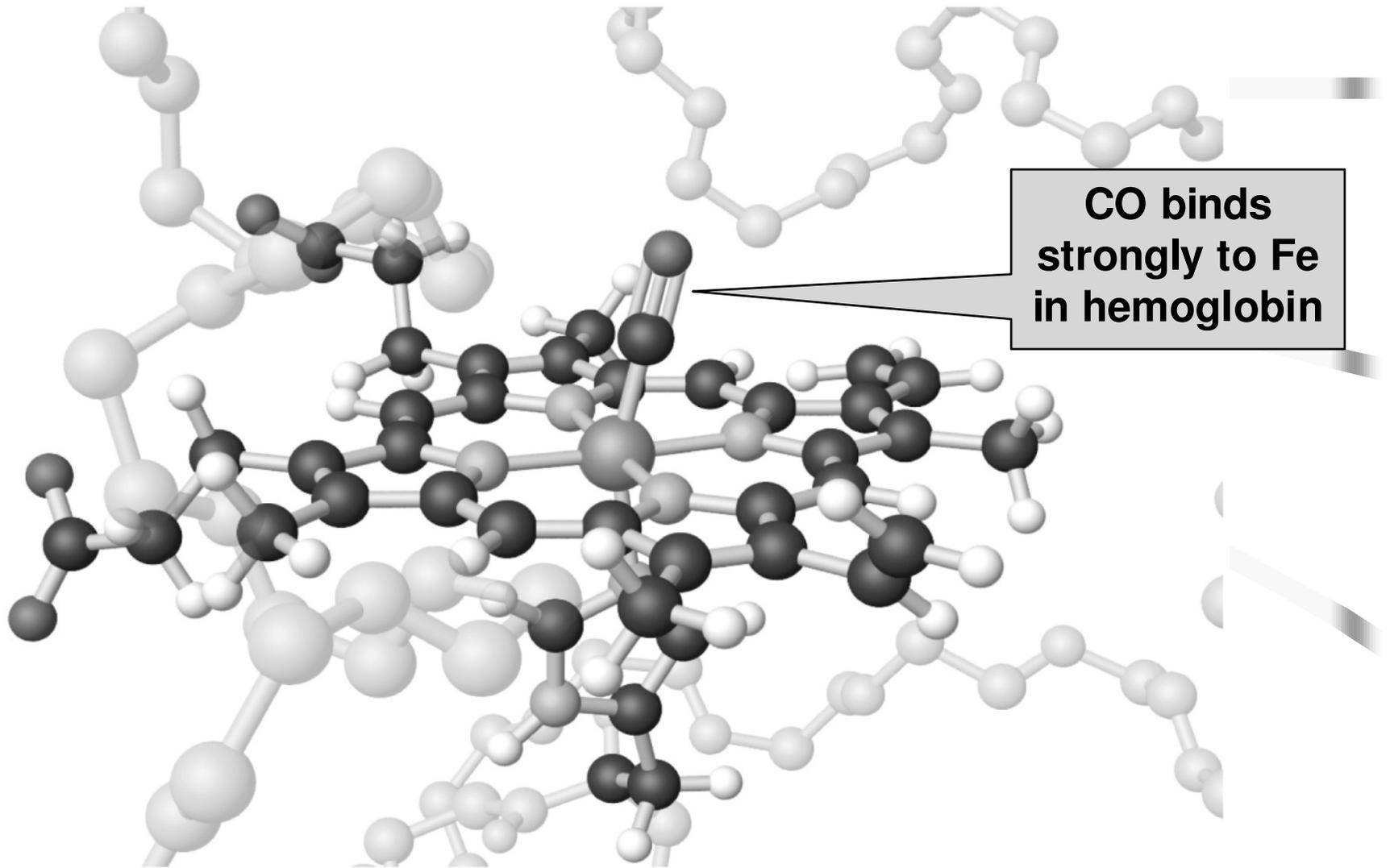


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Poisons

- 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



**CO binds
strongly to Fe
in hemoglobin**

Carcinogens and anticarcinogens

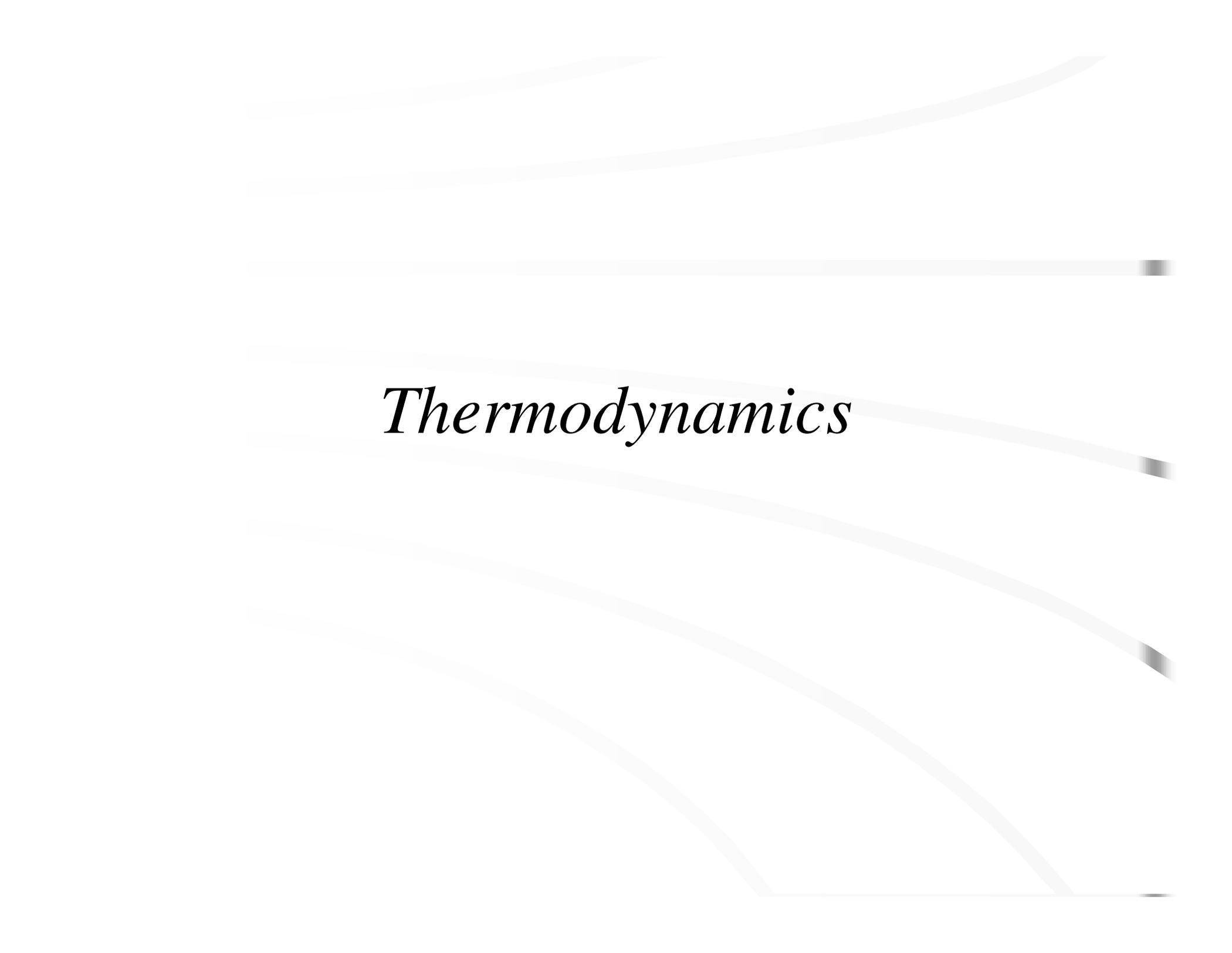
- *Tumors*, abnormal growths of new tissue, may be either benign (harmless) or malignant (cancerous).
- A ***carcinogen*** is a material that causes cancer.
- Some of the more notorious carcinogens are polycyclic aromatic hydrocarbons and the aromatic amines.
- Few of the known carcinogens are synthetic 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.

Hazardous materials (HazMat)

- Ignitable materials are substances that catch fire easily.
- Corrosive materials are substances that corrode storage containers and equipment.
- Reactive materials are substances that react or decompose readily, possibly producing hazardous byproducts.
- Toxic chemicals are substances that are injurious when inhaled or ingested.
- Many hazardous materials can be rendered less harmful by chemical treatment.
- Biodegradation of wastes may be the way of the future. Some microorganisms can degrade hydrocarbons in gasoline; others can degrade chlorinated hydrocarbons.

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

The background features several light gray, wavy, horizontal lines that create a sense of motion or depth. A thin, dark gray horizontal bar is positioned near the top of the page. The word "Thermodynamics" is centered in a black, italicized serif font.

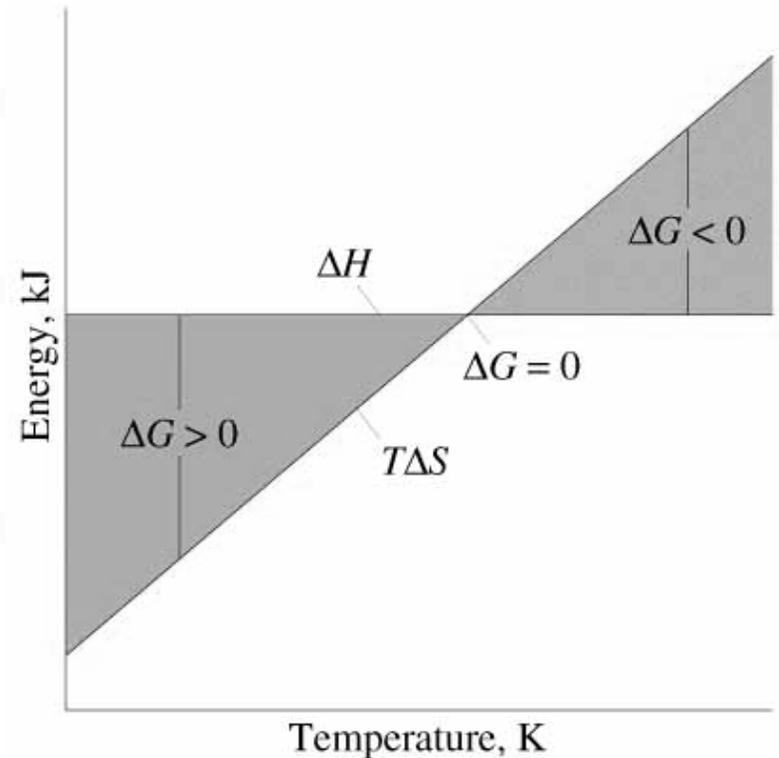
Thermodynamics

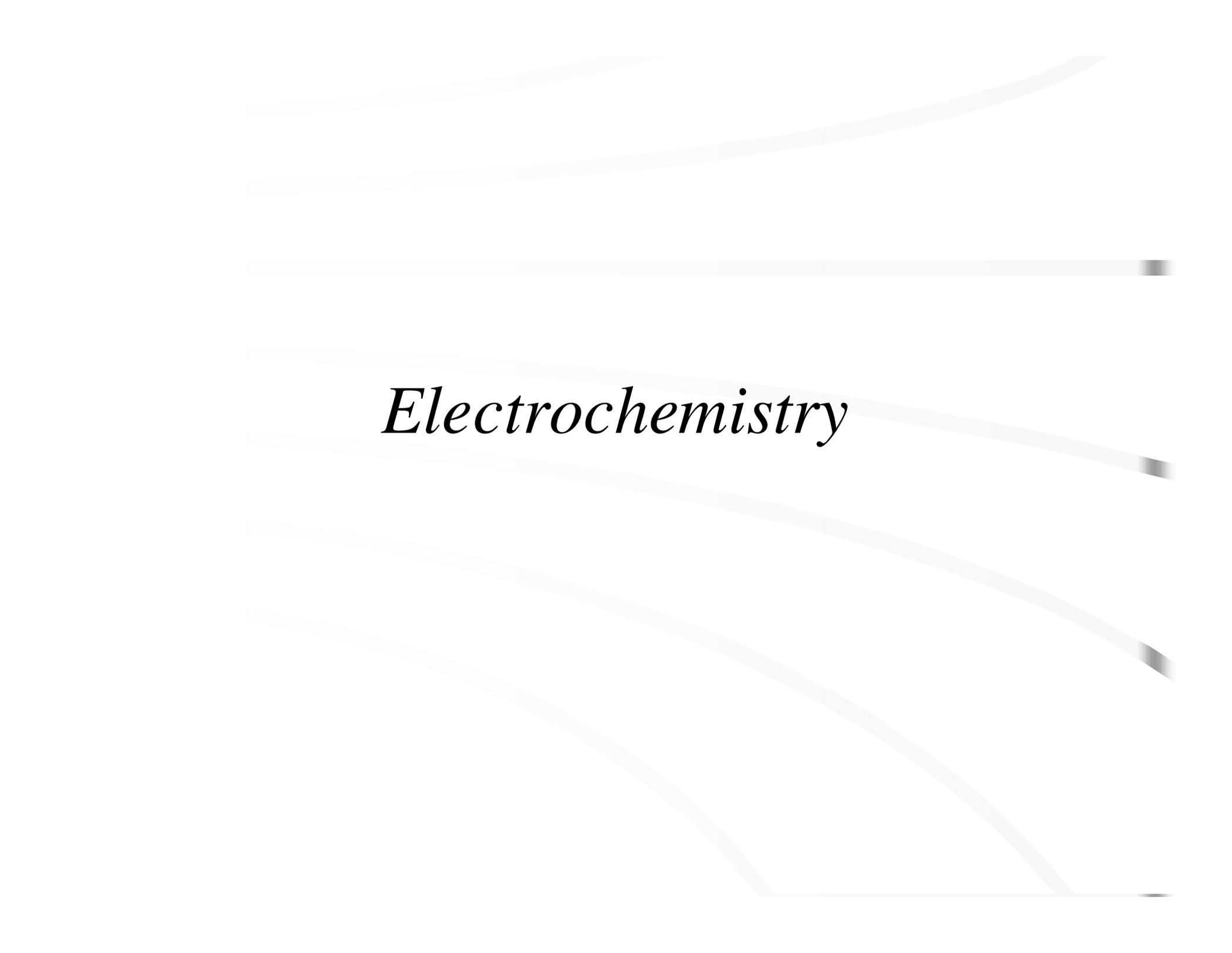
Jargon

- SPONTANEITY- whether or not a process can occur unassisted
 - If forward reaction is spontaneous, then reverse reaction is not and vice versa
- ENTROPY- measure of randomness
 - $\Delta S_{\text{univ}} > 0$
- ENTHALPY- heat of reaction
- FREE ENERGY- relates enthalpy and entropy to spontaneity
 - $\Delta G = \Delta H - T\Delta S$

Free energy

- $\Delta G < 0$ spontaneous
- $\Delta G > 0$ nonspontaneous
- $\Delta G = 0$ equilibrium
- ΔH neg, ΔS pos, ΔG neg, spont
- ΔH pos, ΔS neg, ΔG pos, nonspont
- ΔH pos, ΔS pos, spont at high T
- ΔH neg, ΔS neg, spont at low T





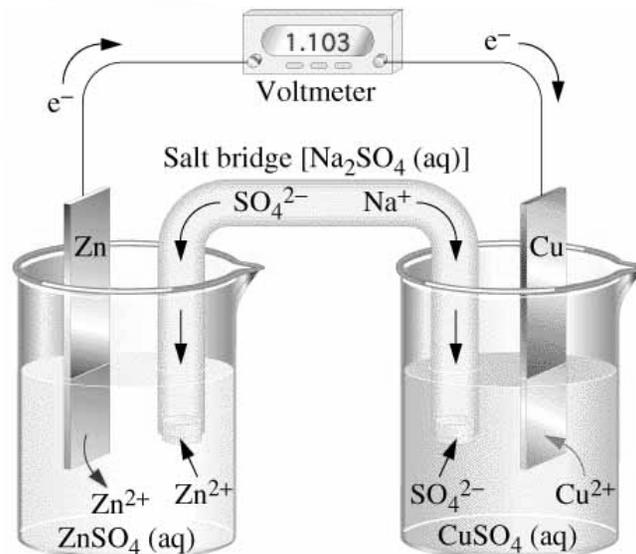
Electrochemistry

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

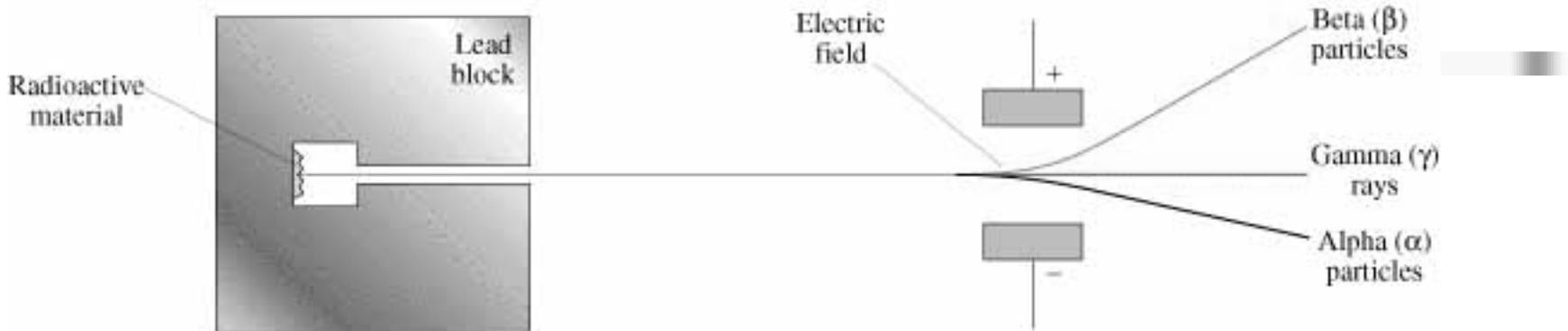
Nuclear chemistry

- 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

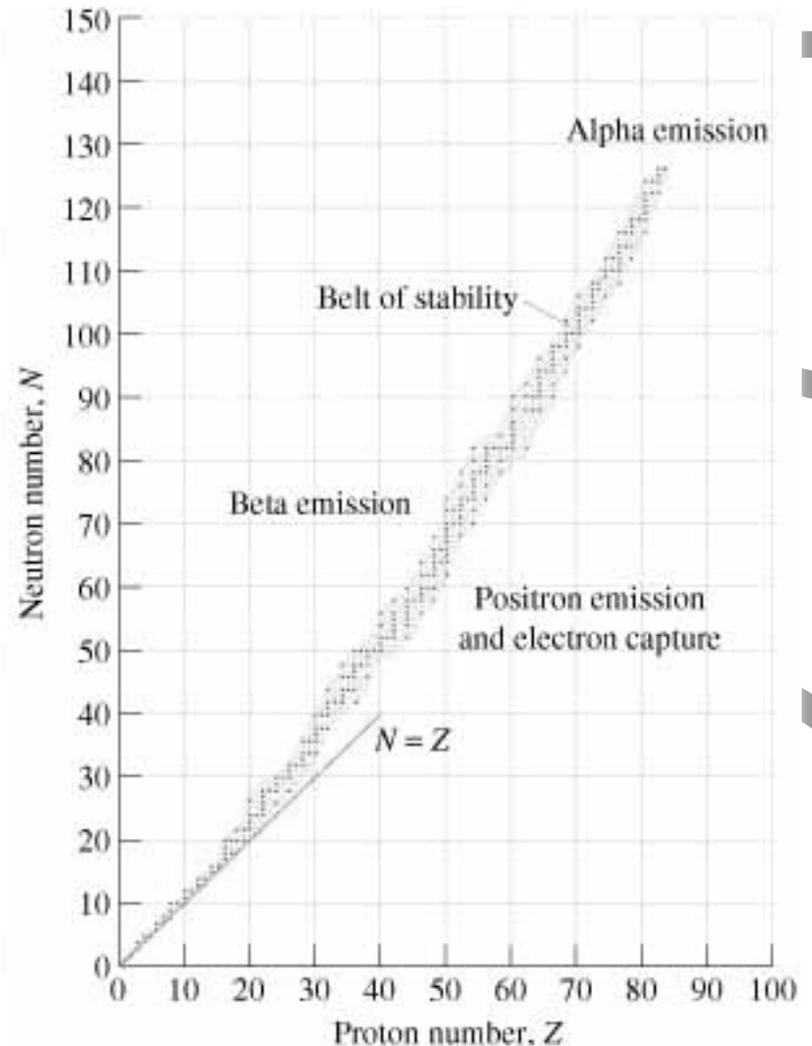
- Remember that radioactive decay is first order, rate = $k[A]$
- Half life is the amount of time for half to decay = $.693/\lambda$, where λ is the decay constant (rate constant)
- Half lives vary, making them useful in some instances and not others
 - ^{14}C 5730 years
 - ^{238}U 4.51×10^9 years
 -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

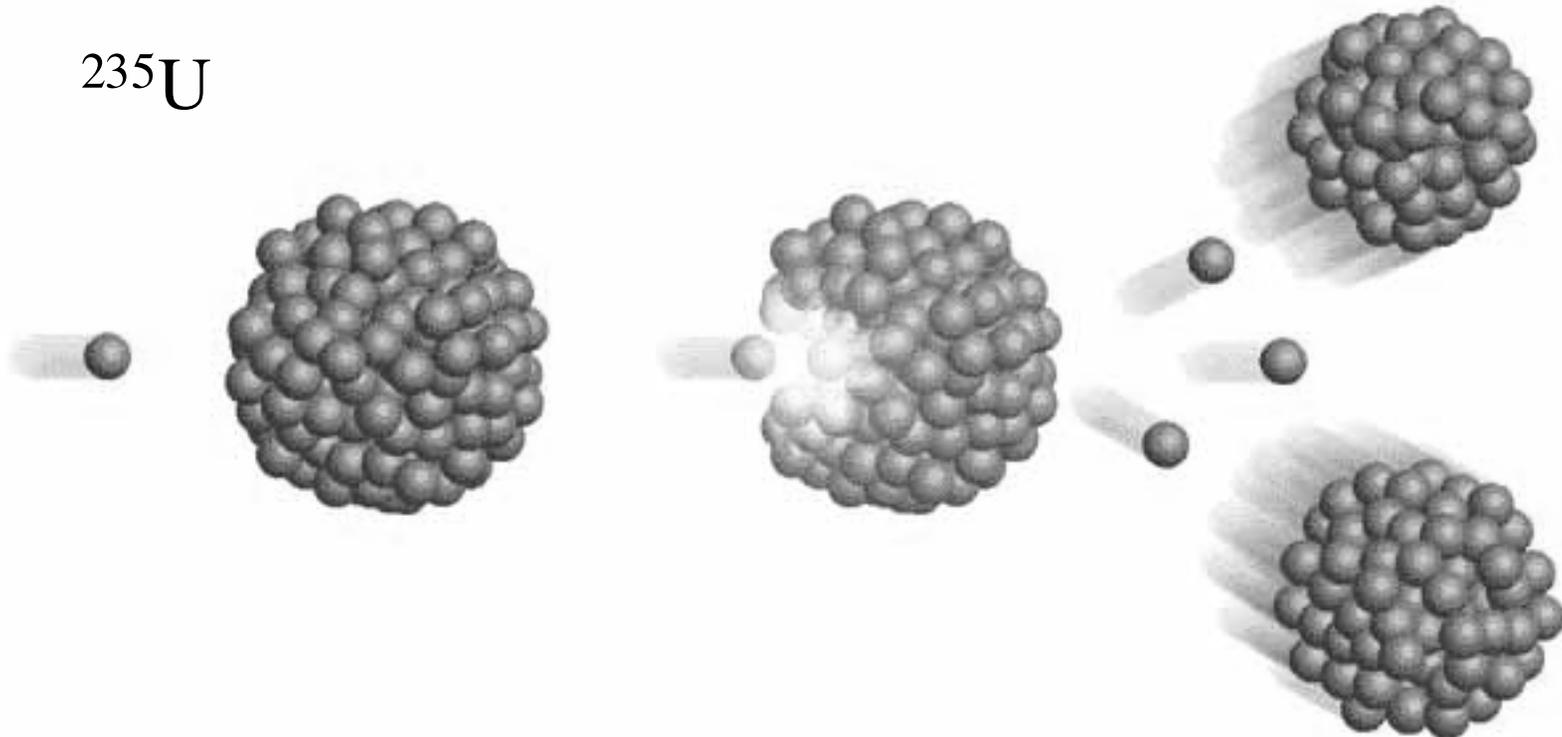
- Band of stability
- Trivia:
 - 160 have even p, even n
 - 50 have even p, odd n
 - 50 have odd p, even n
 - 4 have odd p, odd n



Energetics

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

^{235}U

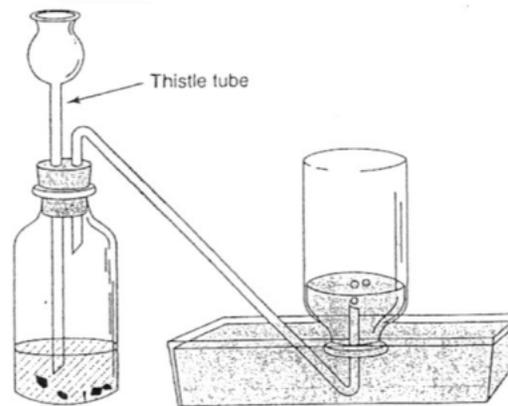
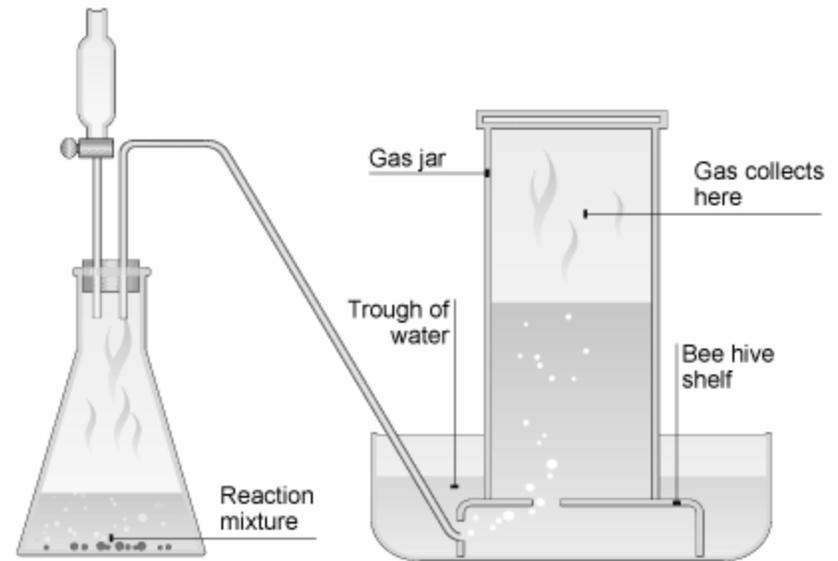


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Lab

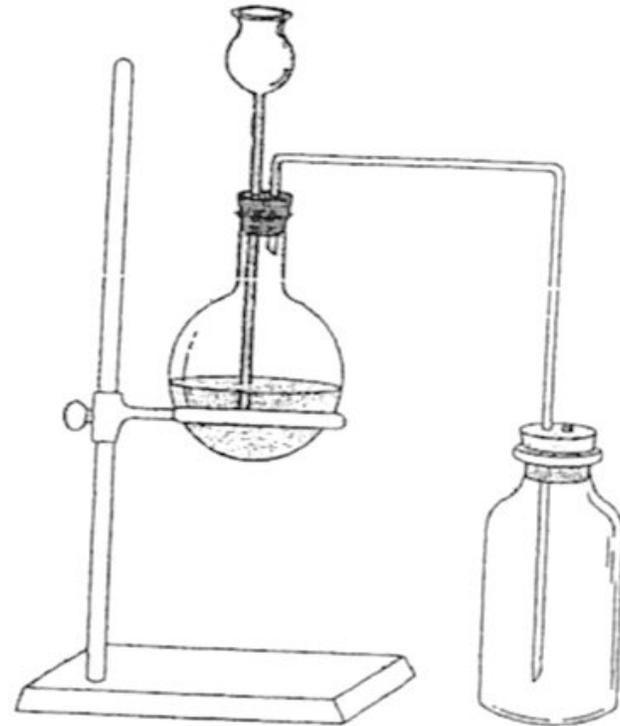
Collection over water

- Must know P_{atm}
- Must equalize pressure
- Must have thistle tube submerged
- Gas cannot be water soluble
 - CO_2 is OK
 - O_2 is OK
 - no ammonia



Heavier than air

- Must be hole for air to escape out
- Thistle tube submerged
- CO₂ usually
- Obviously, not He
- Not H₂ or CH₄



Flame color

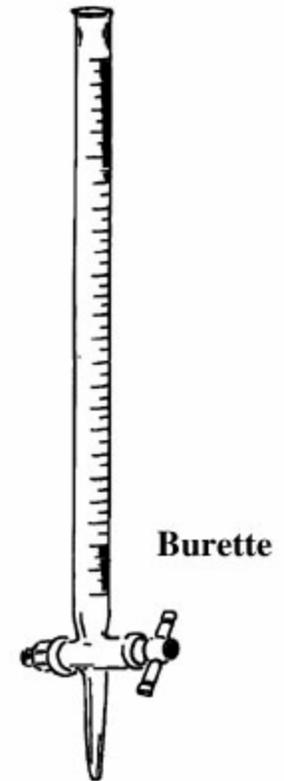
- Li^+ , Sr^{2+} , Ca^{2+} Red
- Na^+ Yellow
- K^+ Purple (pink)
- Ba^{2+} Light green
- Cu^{2+} Blue-green
- Fe^{3+} Gold

Solution color

- Cu^{2+} Blue
- Fe^{3+} Yellow-orange (rusty)
- Ni^{2+} Green
- MnO_4^- Purple
- CrO_4^{2-} Yellow
- $\text{Cr}_2\text{O}_7^{2-}$ Orange

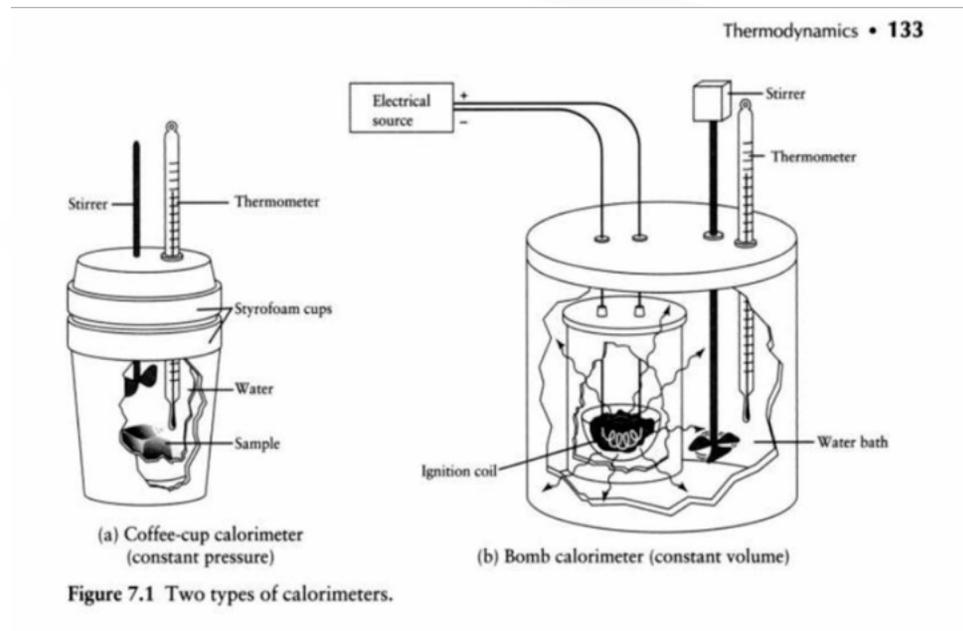
Don't forget about titrations

- Use a buret
- Blue litmus turns red in acid, and red litmus turns blue in base
- Phenolphthalein is clear in acid, pink in base



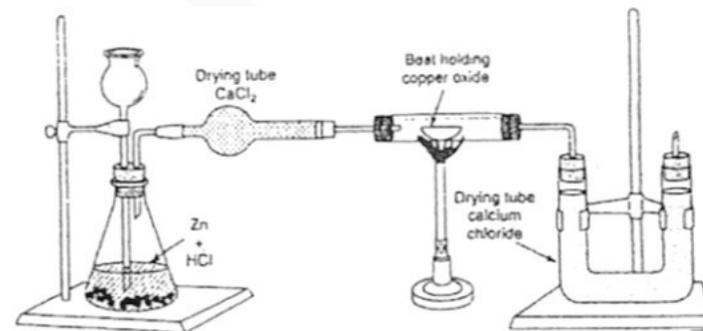
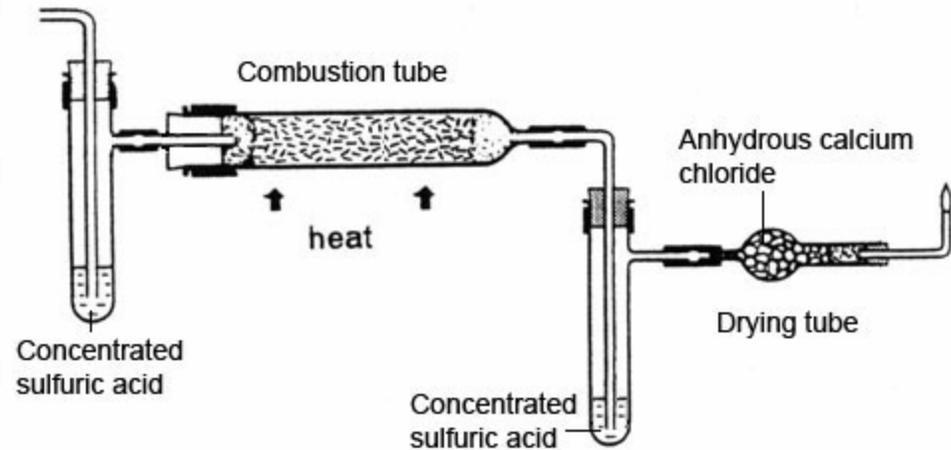
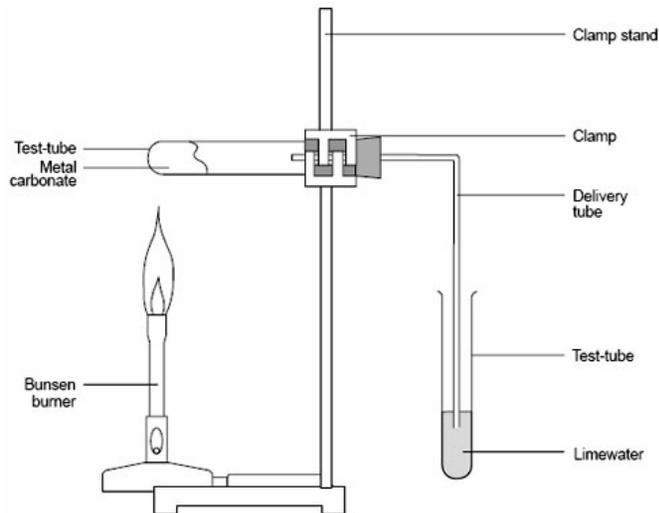
Calorimetry

- Measure heat transfer, using a coffee cup in class
- Assumes all heat from reaction is transferred to water in cup



Decomposition

- May find the amount of water or some other element in a compound



Free stuff

- <http://www.Professorkshow.com>
- <http://www.sparknotes.com/testprep/books/sat2/chemistry/chapter11section5.rhtml>