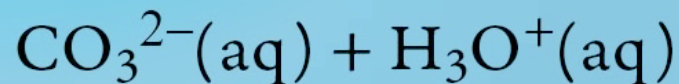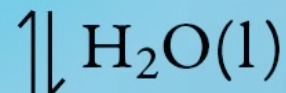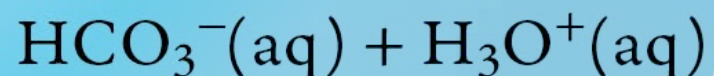# Requested Review Topics for the Final Exam
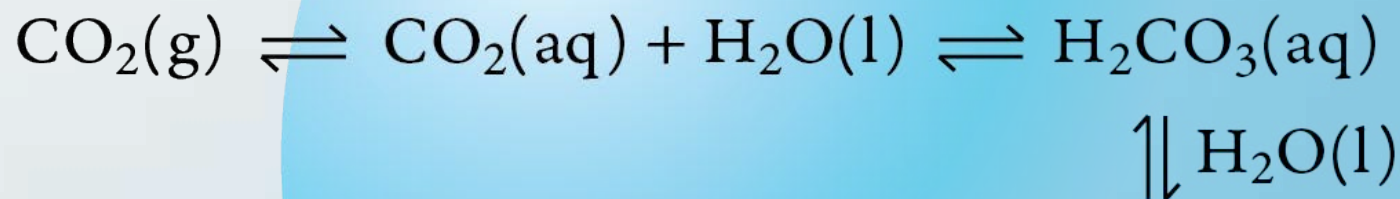
IPOL 8512

Raindrop Equilibria

$$2H_2O(l) \rightleftharpoons OH^-(aq) + H_3O^+(l)$$

$$CO_2(g) \rightleftharpoons CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

$$\Updownarrow H_2O(l)$$

$$HCO_3^-(aq) + H_3O^+(aq)$$

$$\Updownarrow H_2O(l)$$

$$CO_3^{2-}(aq) + H_3O^+(aq)$$

Carbonate Equilibria

- Water molecules dissociate.

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

$$\text{or } H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$
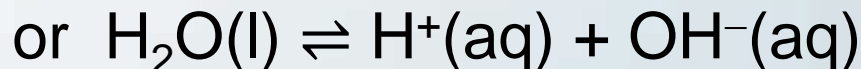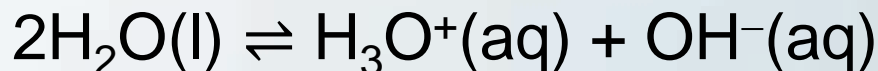
- When CO_2 and H_2O are in contact, some of the CO_2 dissolves and forms H_2CO_3
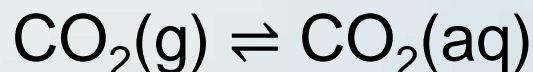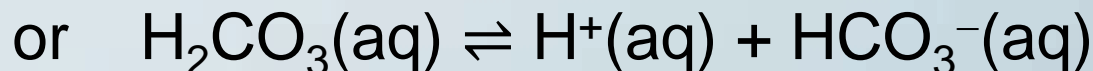
$$CO_2(g) \rightleftharpoons CO_2(aq)$$

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

- H_2CO_3 is a weak acid, so it to forms H_3O^+ and HCO_3^-.

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$$

$$\text{or } H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$
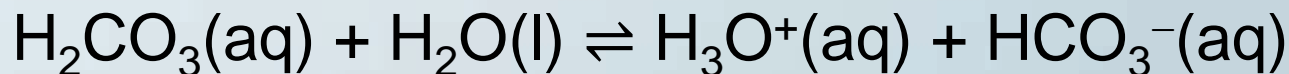
- HCO_3^- in turn ionizes into H_3O^+ and CO_3^{2-}

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$$

$$\text{or } HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$$
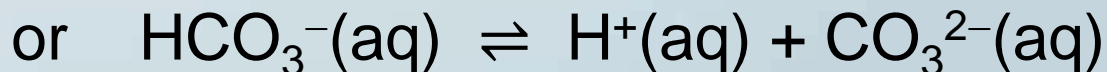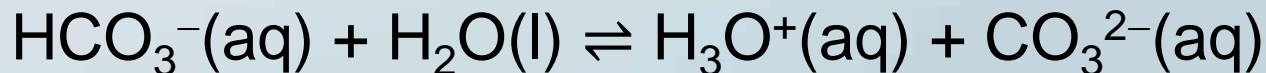
Carbonate Equilibria

- If other sources of these species are present in the solution - for example, dissolved $CaCO_3$ from limestone or sea shells - then these must also be taken into account in finding the concentrations.

$$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$$
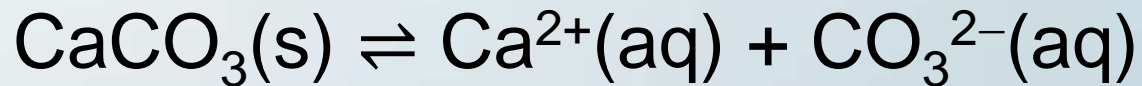
Dynamic Equilibrium for Gas Dissolved in Liquid

The solubility limit is reached when the rate of solution equals the rate of escape.

For every gas particle that escapes from the liquid, another gas particle collides with the surface and goes into solution.
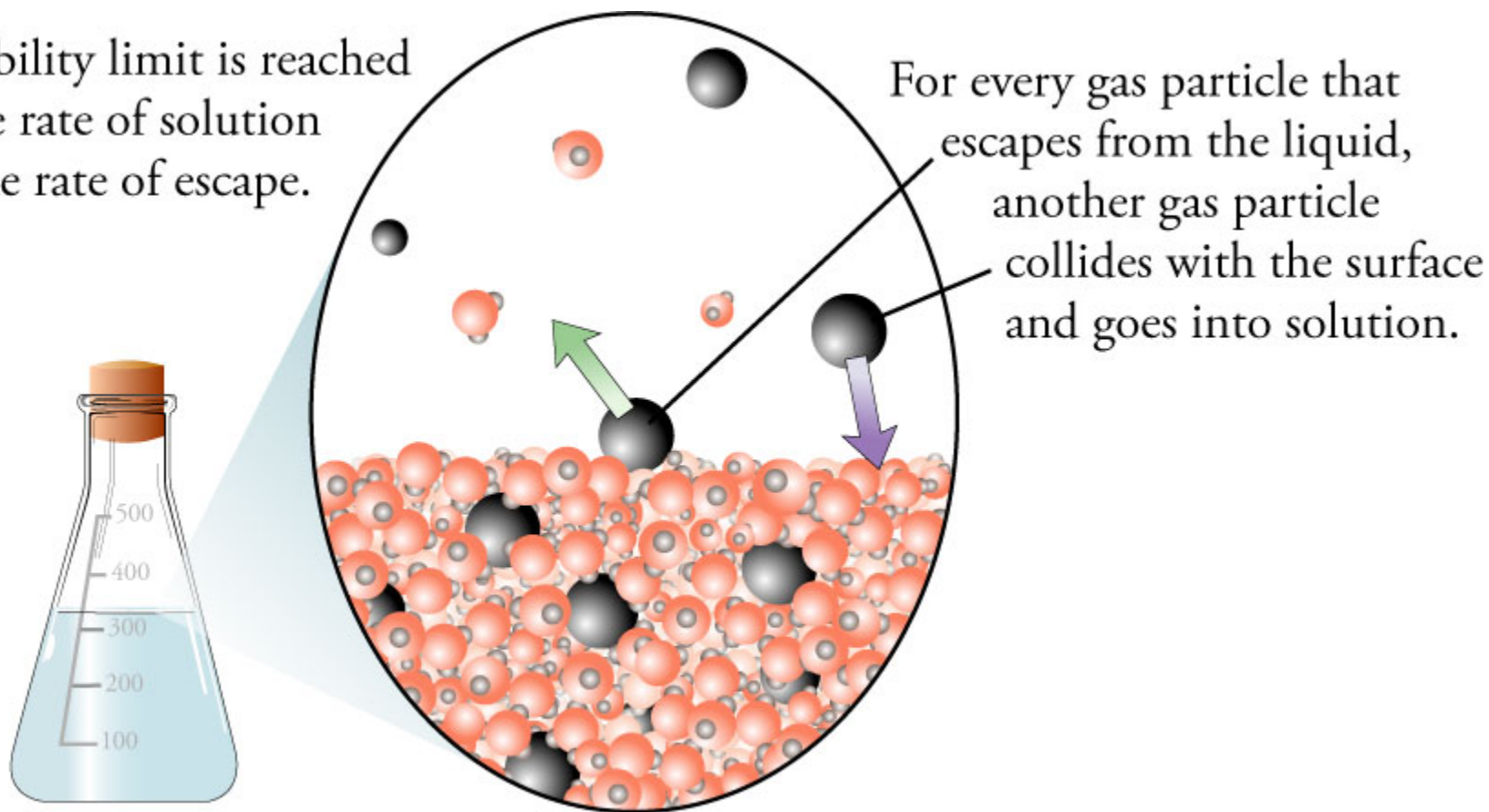
Gas Solubility

Add a gas above a liquid in a closed container

↓

Initially, the rate of solution is greater than the rate of escape → Net shift of particles into solution

↓

Increased rate of escape... ← Increased concentration of dissolved gas

↓

...Until the rate of escape equals rate of solution ⟶ Constant changes between dissolved and undissolved gas, but no net change in amount of either

Dynamic equilibrium (solubility limit)

The solubility limit is reached when the rate of solution equals the rate of escape.

For every gas particle that escapes from the liquid, another gas particle collides with the surface and goes into solution.
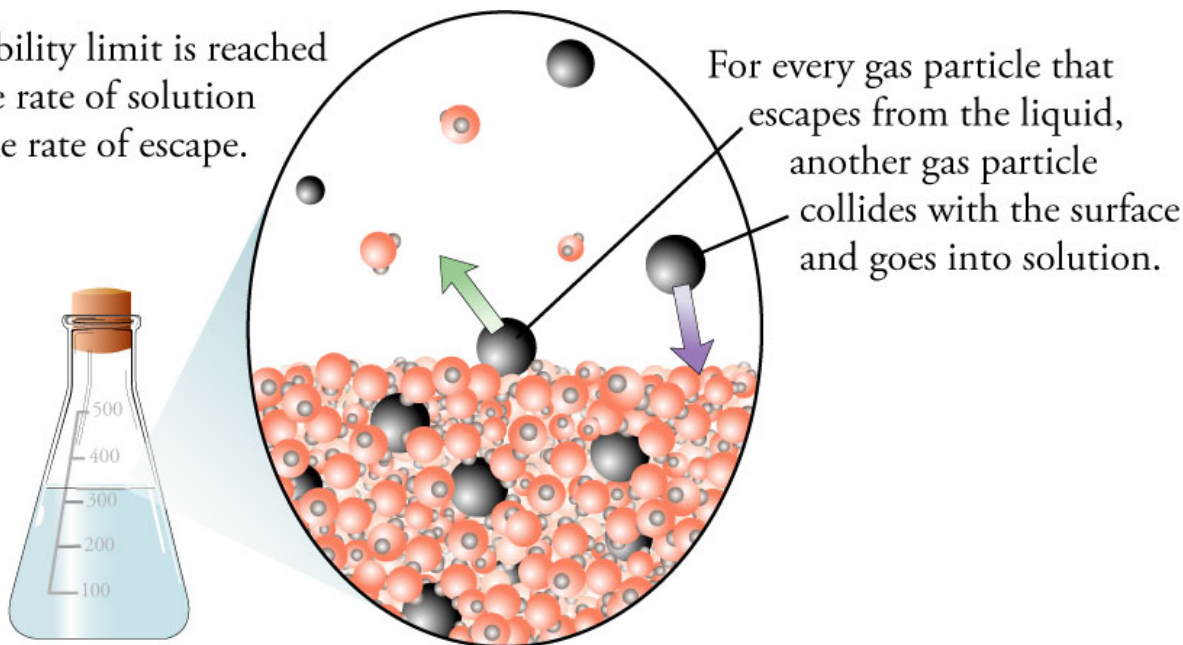
Partial Pressure and Gas Solubility

Increased partial pressure of a gas over a liquid in a system initially at dynamic equilibrium (Rate of solution = Rate of escape)

↓

Increased rate of collision between gas particles and liquid ⟶ Increased rate of solution

↓

Net movement of gas particles into solution ← Rate of solution greater than rate of escape

↓

Increased concentration of solute in solution ⟶ Increased rate of escape until it equals the higher rate of solution

Greater solubility

The solubility limit is reached when the rate of solution equals the rate of escape.

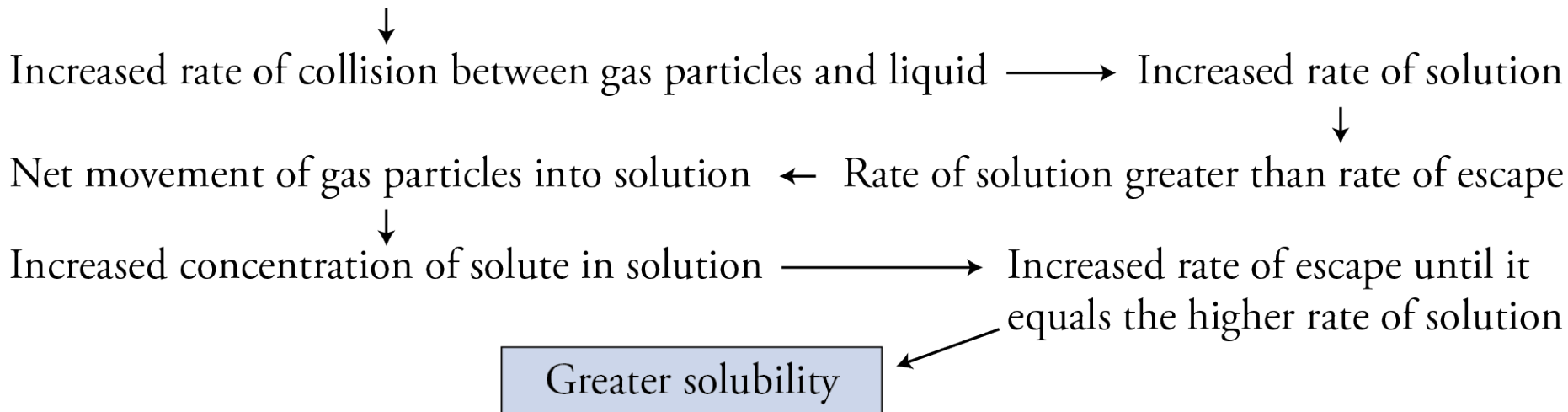For every gas particle that escapes from the liquid, another gas particle collides with the surface and goes into solution.
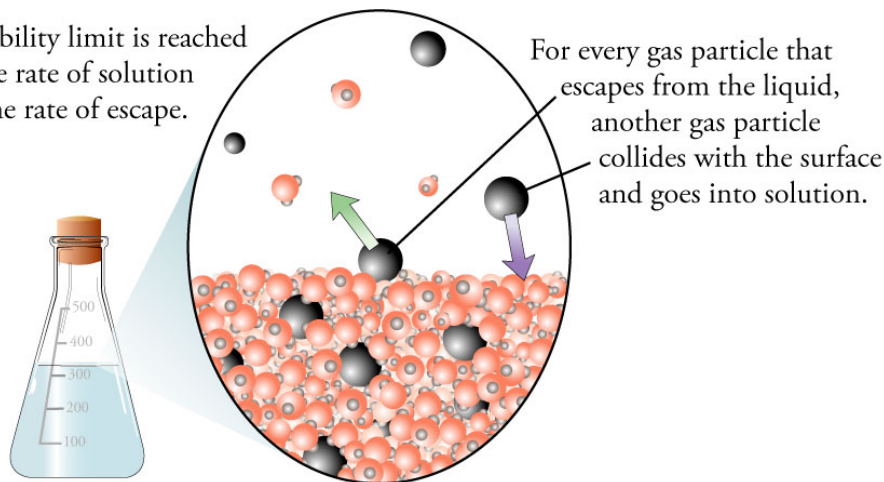
Henry's Law

- **Henry's law** states that *at a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid.*

- Henry's law can be put into mathematical terms (at constant temperature) as

$$c = p \, k_H$$

  c is the concentration of the solute in mol/L

  p is the partial pressure of the solute in the gas above the solution

  k_H is Henry's constant, which is different for each gas/solvent combination.

- For carbon dioxide and water, k_H is 0.03400 mol/L·atm

- As of June, 2012, the CO_2 concentration in the atmosphere was 395 ppm. We can use this and Henry's Law to calculate the concentration of CO_2 in water.

CO$_2$ Concentration in Water

$$\frac{P_{CO_2}}{P_{atm}} = \frac{n_{CO_2}}{n_{atm}} = \frac{395 \text{ mol}}{10^6 \text{ mol}} = 3.95 \times 10^{-4}$$

$$P_{CO_2} = 3.95 \times 10^{-4} P_{atm} = 3.95 \times 10^{-4} (1 \text{ atm}) = 3.95 \times 10^{-4} \text{ atm}$$

$$c = p\, k_H = 3.95 \times 10^{-4} \text{ atm} \left(0.03400 \text{ mol/L·atm}\right)$$
$$= 1.34 \times 10^{-5} \text{ mol/L}$$

CO$_2$ Solution

- When carbon dioxide dissolves in water, it exists in a chemical equilibrium with carbonic acid:

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

- The hydration equilibrium constant, K_h, at 25 °C is

$$[H_2CO_3]/[CO_2] = 1.70 \times 10^{-3}$$

- This shows that the majority of the carbon dioxide is not converted into carbonic acid. Most of it remains as CO$_2$ molecules.

- H$_2$CO$_3$* can be used to represent the CO$_2$ and the H$_2$CO$_3$ together.

$$H_2CO_3^* \rightleftharpoons HCO_3^- + H^+ \quad K_{a1(app)} = 4.6 \times 10^{-7} \text{ at 25 °C}$$

$$K_{a1(app)} = \frac{[H^+][HCO_3^-]}{[H_2CO_3^*]} = 4.6 \times 10^{-7}$$

H$_2$CO$_3$ Equilibrium

- Because H$_2$CO$_3$ is a diprotic acid, there is a second ionization that forms carbonate ion CO$_3^{2-}$:

    $$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$$

    $$K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 4.69 \times 10^{-11}$$

    at 25 °C

Summary of Equations

$$[H^+][OH^-] = 1.0 \times 10^{-14}$$

$$P_{CO_2} = \frac{n_{CO_2}}{n_{atm}} \, P_{atm}$$

$$[CO_2] = P_{CO_2} \, (0.03400 \text{ mol/L·atm}) = [H_2CO_3\text{*}]$$

$$K_{a1(app)} = \frac{[H^+][HCO_3^-]}{[H_2CO_3\text{*}]} = 4.6 \times 10^{-7}$$

$$K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 4.69 \times 10^{-11}$$

$$[H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]$$

pH Natural Water

$[H^+][OH^-] = 1.0 \times 10^{-14}$ $\qquad$ $[OH^-] = \dfrac{1.0 \times 10^{-14}}{[H^+]}$

$[CO_2] = P_{CO_2}(0.03400 \text{ mol/L·atm}) = 1.34 \times 10^{-5} \text{ mol/L} = [H_2CO_3*]$

$\dfrac{[H^+][HCO_3^-]}{[H_2CO_3*]} = \dfrac{[H^+][HCO_3^-]}{1.34 \times 10^{-5}} = 4.6 \times 10^{-7}$ $\qquad$ $[HCO_3^-] = \dfrac{4.6 \times 10^{-7}(1.34 \times 10^{-5})}{[H^+]} = \dfrac{6.2 \times 10^{-12}}{[H^+]}$

$\dfrac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 4.69 \times 10^{-11}$

$[CO_3^{2-}] = \dfrac{4.69 \times 10^{-11}[HCO_3^-]}{[H^+]} = \dfrac{4.69 \times 10^{-11}(6.2 \times 10^{-12})}{[H^+]\qquad[H^+]} = \dfrac{2.9 \times 10^{-22}}{[H^+]^2}$

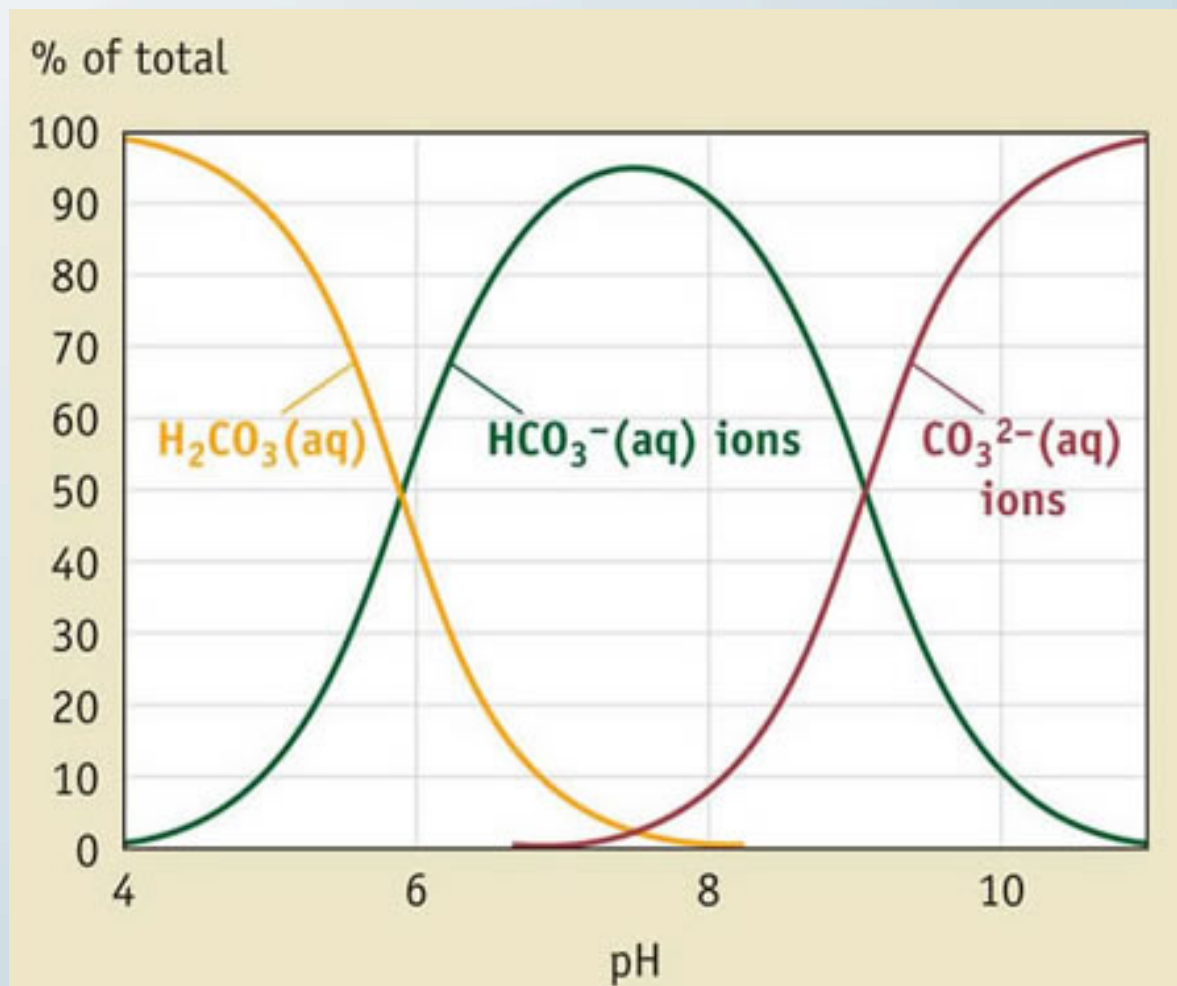$[H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}]$

$[H^+] = \dfrac{1.0 \times 10^{-14}}{[H^+]} + \dfrac{6.2 \times 10^{-12}}{[H^+]} + 2\times\dfrac{2.9 \times 10^{-22}}{[H^+]^2} \approx \dfrac{6.2 \times 10^{-12}}{[H^+]} = [H^+]$

$[H^+]^2 = 6.2 \times 10^{-12}$ $\qquad$ $[H^+] = 2.5 \times 10^{-6}$ $\qquad$ $pH = -\log(2.5 \times 10^{-6}) = \mathbf{5.60}$

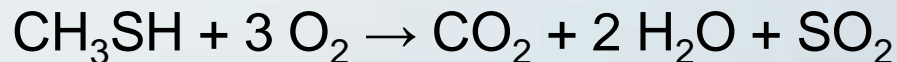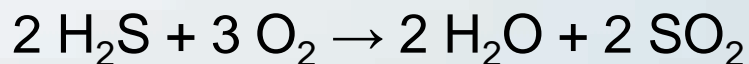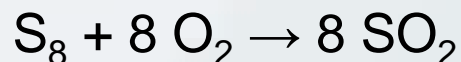# Carbonate Equilibria and pH

The following graph shows the variation in $[H_2CO_3]$, $[HCO_3^-]$, and $[CO_3^{2-}]$ with changes in pH.
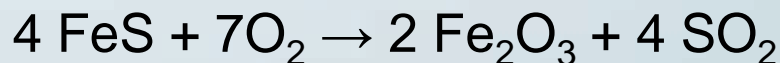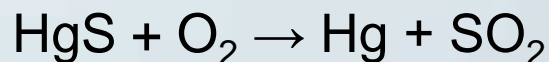
32 - Formation of Sulfur Dioxide in Combustion

- Sulfur dioxide is the product of the burning of sulfur or of burning materials that contain sulfur:

  $S_8 + 8 O_2 \rightarrow 8 SO_2$

  $2 H_2S + 3 O_2 \rightarrow 2 H_2O + 2 SO_2$

  $CH_3SH + 3 O_2 \rightarrow CO_2 + 2 H_2O + SO_2$

- The roasting of sulfide ores also releases SO_2:

  $4 FeS_2 + 11 O_2 \rightarrow 2 Fe_2O_3 + 8 SO_2$

  $2 ZnS + 3 O_2 \rightarrow 2 ZnO + 2 SO_2$

  $HgS + O_2 \rightarrow Hg + SO_2$

  $4 FeS + 7 O_2 \rightarrow 2 Fe_2O_3 + 4 SO_2$
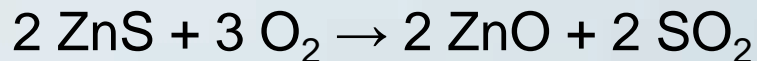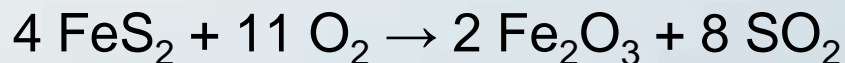
- Volcanic eruptions, which involve a combination of these reactions, produces the largest amount of sulfur dioxide. They can release millions of metric tons of SO_2.

Anthropogenic

- 60-100 Mt(S)/y emitted into atmosphere worldwide

- US emissions: 32 Mt/y(1973)

$\rightarrow$ 9.5 (2006) Mt/y SO_2

    – Coal-burning in power plants
    – Oil-burning (vehicles)
    – Industrial (smelting, etc.); responsible for intense local damage

- Biomass burning: 1-6 Mt(S)/y worldwide

Natural

- volcanoes (6-20 Mt(S)/y as SO_2)

39 - Acid Neutralization

- Reaction with natural bases

$$CaCO_3 + 2H^+ \rightleftharpoons Ca^{2+} + CO_2 + H_2O$$

$$Al(OH)_3 + 3H^+ \rightleftharpoons Al^{3+} + 3H_2O$$
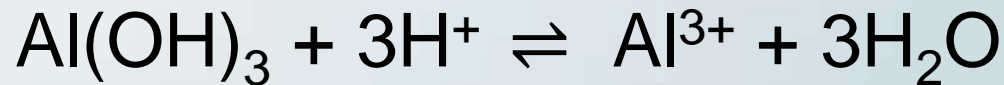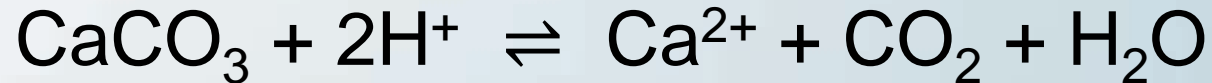
- Nutrient leaching:

$$K\text{-[soil]} + H^+ \rightleftharpoons H\text{-[soil]} + K^+$$
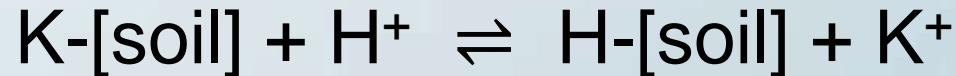
39 - Carbonate Reactions

- Weathering reactions with carbonate minerals (calcite, dolomite, various limestones, etc.):

$$CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^-$$

$$CaSiO_3 + 2CO_2 + H_2O$$
$$\rightleftharpoons Ca^{2+} + SiO_2 + 2HCO_3^-$$
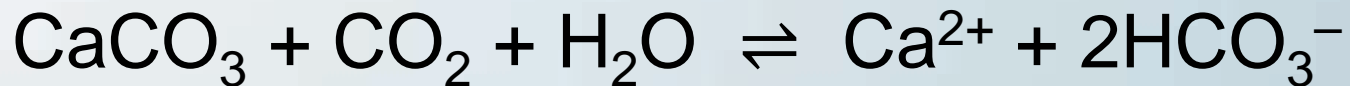
- When acid is added to water, equilibria shift and bicarbonate neutralizes some of the acid:

$$HCO_3^- + H^+ \rightleftharpoons H_2O + CO_2$$
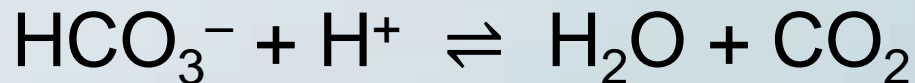
Alkalinity

- Alkalinity is a measure of the "buffering" or "acid-neutralizing capacity" (ANC) of a solution:

$$ANC = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$$

- Water saturated with $CaCO_3$:
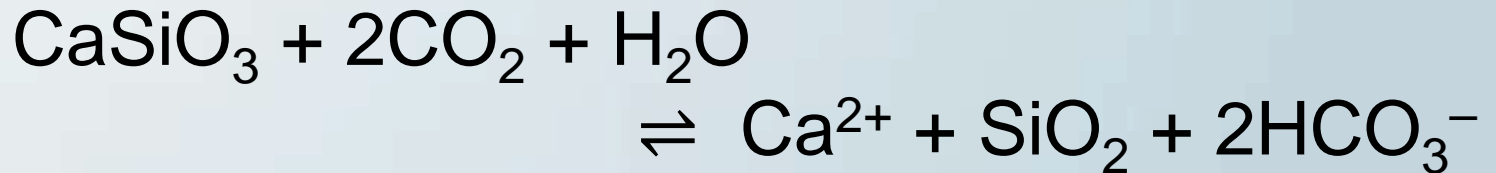
$$ANC = 970 \times 10^{-6} \text{ Eq/L} = 970 \text{ } \mu\text{eq/L}$$

  - For bases, an equivalent (Eq) is the amount of a substance which will react with one mole of hydronium ions (H_3O^+).
  - 1 mol CO_3^{2-} = 2 Eq CO_3^{2-}

- ANC depends on watershed soil characteristics.

Alkalinity

- Surface water with ANC $\approx$200 µeq/L is normal; healthy lakes have ANC > 100 µeq/L; water with ANC < 50 µeq/L is highly sensitive to acidification.

- Acidified waters have ANC < 0 µeq/L.

- As acidity [H^+] is added to a lake, ANC is consumed. Because of the buffering, the pH decreases slowly at first, but as the basic components of the buffer react with the acid, the water loses its buffering ability, and the pH drops more rapidly.

Buffer Solutions

- A **buffer** is an aqueous solution a weak acid (H_2CO_3) and its conjugate base (HCO_3^-) or a weak base (CO_3^{2-}) and its conjugate acid (HCO_3^-).

  - Conjugate base = acid less one H^+

  - Conjugate base = base plus one H^+

  $H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$
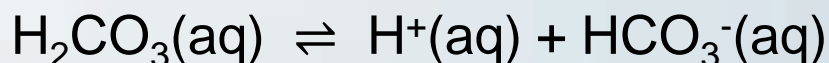
  $$K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$

  $$[H^+] = K_{a1}\frac{[H_2CO_3]}{[HCO_3^-]}$$

  $$[H^+] = K_a\frac{[\text{weak acid}]}{[\text{conjugate base}]}$$

- As long as there are significant concentrations of the weak acid (H_2CO_3) and the conjugate base (HCO_3^-), changing one or the other does not change the ratio of acid to base much so the $[H^+]$ and pH stay relatively constant.

Simplistic Calculation to Illustrate Buffering

- pH pristine natural water is about 5.6.
- Calculate the pH of a solution where enough strong acid is added to water to yield a 0.1 M H^+ solution.

$$pH = -\log(10^{-1}) = 1$$

- Calculate the pH of a solution of 1 M H_2CO_3 and 1 M HCO_3^-.

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 4.5 \times 10^{-7}$$

$$[H^+] = 4.5 \times 10^{-7} \, \frac{[H_2CO_3]}{[HCO_3^-]} = 4.5 \times 10^{-7} \, \frac{1 \text{ M } H_2CO_3}{1 \text{ M } HCO_3^-}$$

$$[H^+] = -\log 4.5 \times 10^{-7} = \textbf{6.35}$$

Simplistic Calculation to Illustrate Buffering

- Calculate the pH of a solution of 1 M H_2CO_3 and 1 M HCO_3^- when enough strong acid is added to the solution to make the solution 0.1 M strong acid.

    $HCO_3^-(aq) + H^+(aq) \rightarrow H_2CO_3(aq)$

    $[HCO_3^-] = 1\ M - 0.1\ M = 0.9\ M\ HCO_3^-$

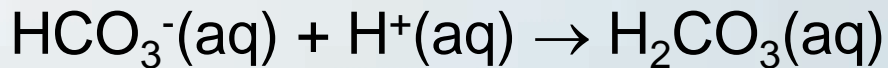 $[H_2CO_3] = 1\ M + 0.1\ M = 1.1\ M\ H_2CO_3$

    $$K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 4.5 \times 10^{-7}$$

    $$[H^+] = 4.5 \times 10^{-7}\ \frac{[H_2CO_3]}{[HCO_3^-]} = 4.5 \times 10^{-7}\ \frac{1.1\ M\ H_2CO_3}{0.9\ M\ HCO_3^-}$$

    $[H^+] = -\log 5.5 \times 10^{-7} = $ **6.26**

pH vs. ANC

Slow change in pH
due to buffering

Buffering ability lost
and pH drops rapidly
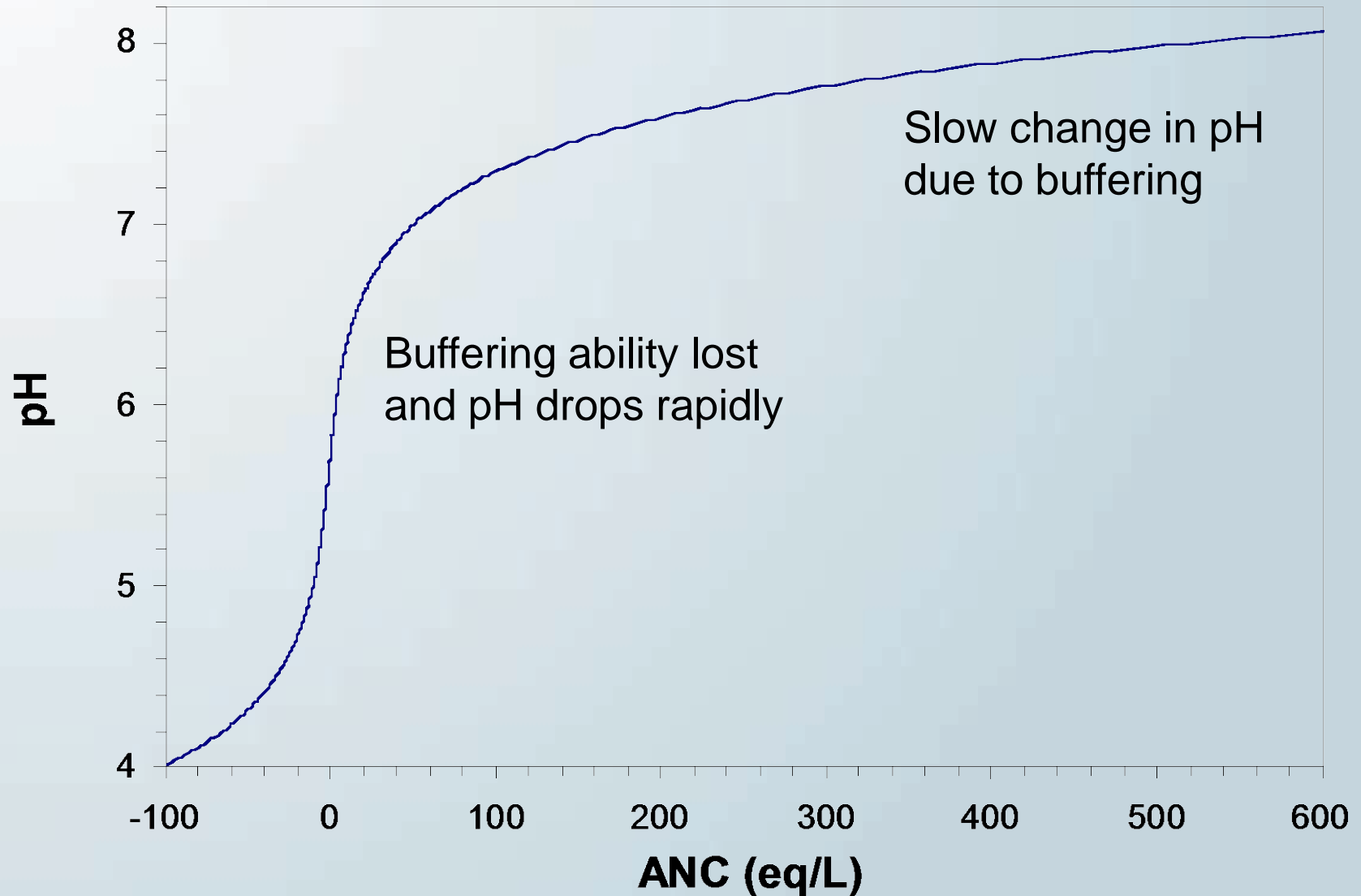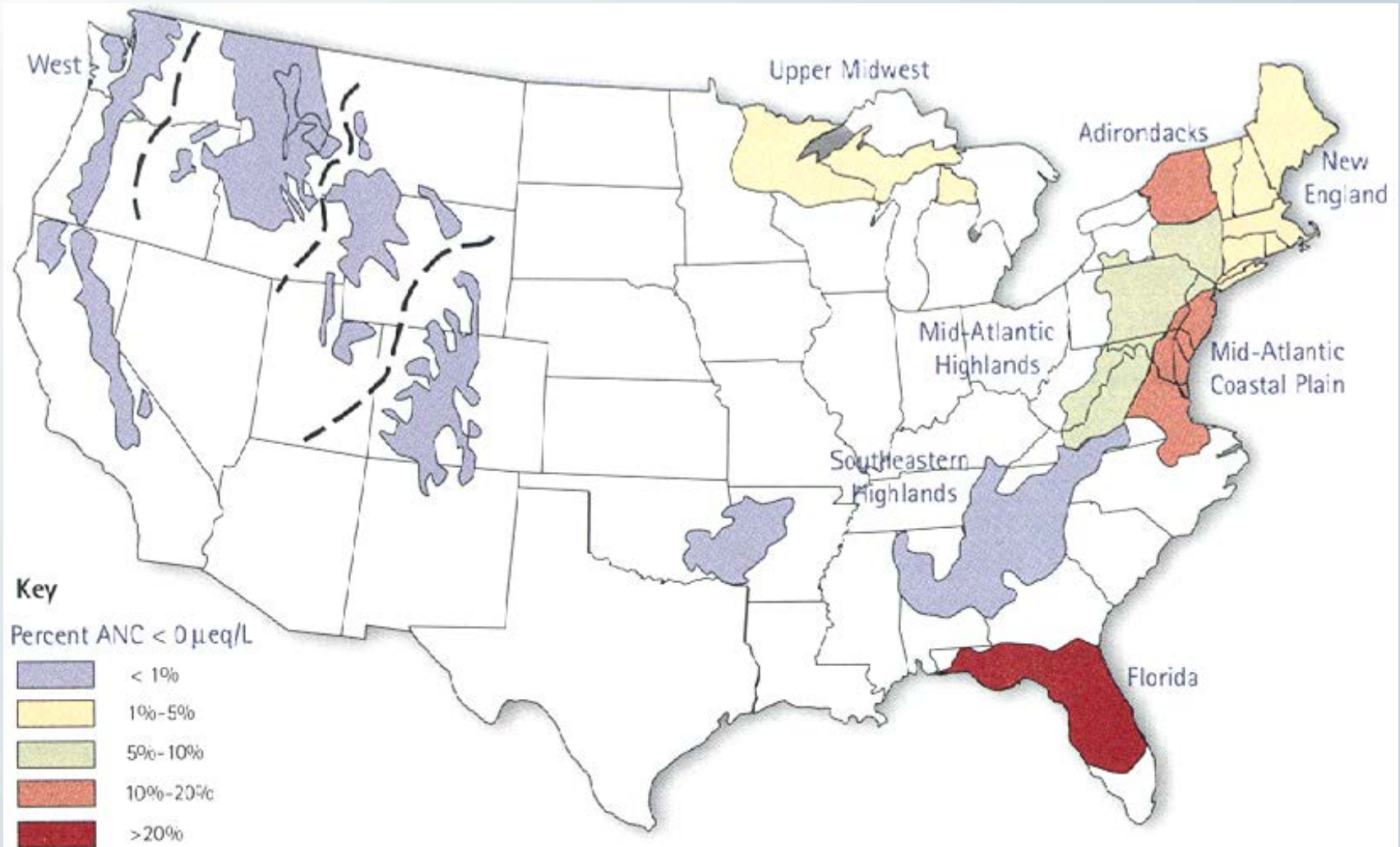
Sensitive Areas

Source: NAPAP. 1991. 1990 Integrated Assessment Report.

Sensitive Areas

Legend:
- **Potential problem areas because of sensitive soils** (green)
- **Potential problem areas because of air pollution: emissions leading to acid deposition** (orange)
- **Current problem areas (including lakes and rivers)** (red)
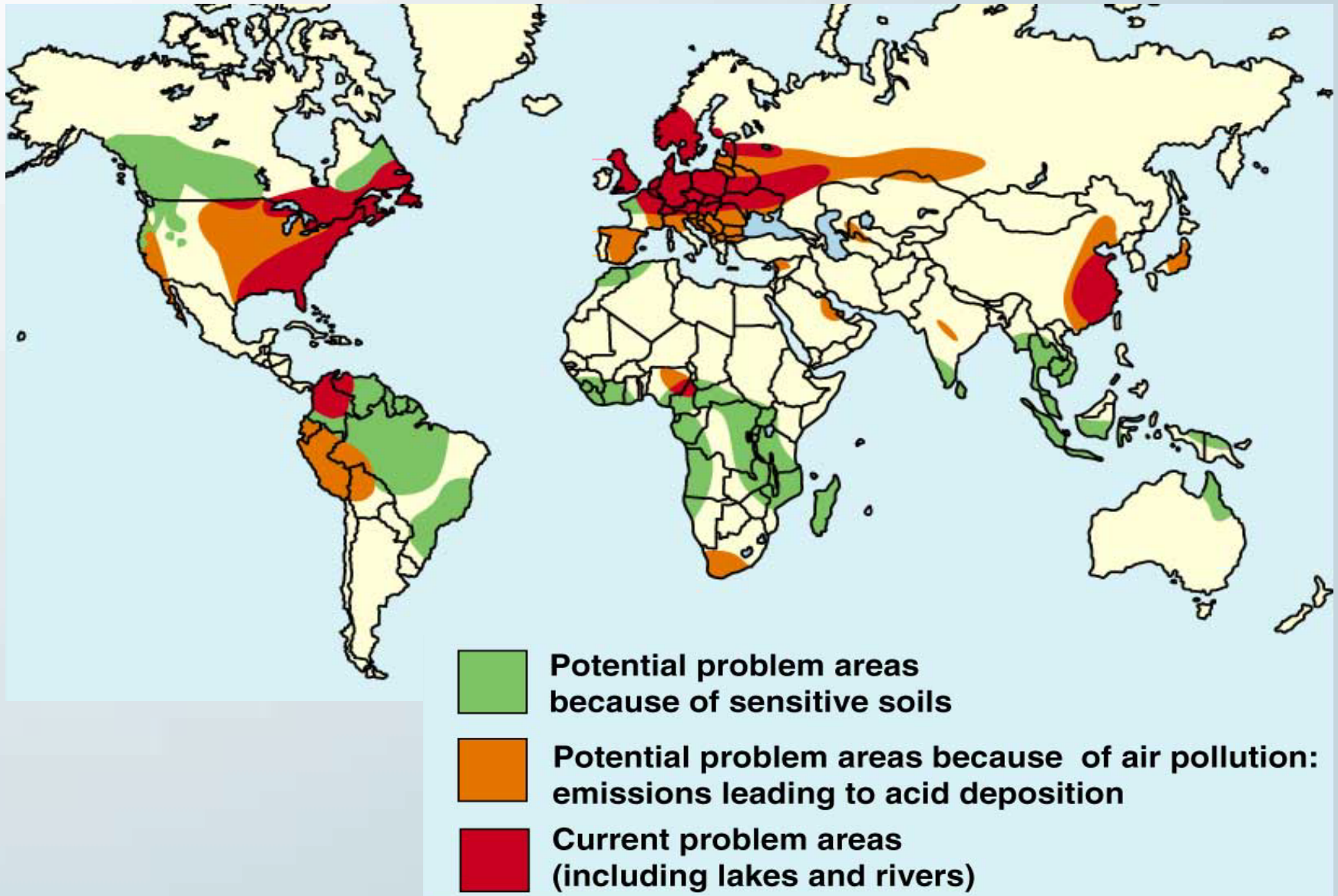
Nuclides

- ***Nuclide*** = a particular type of nucleus, characterized by a specific atomic number and nucleon number

- ***Nucleon number*** or *mass number* = the number of ***nucleons*** (protons and neutrons) in the nucleus of a nuclide.

- Nuclide symbol

Mass number (nucleon number)

$$^A_Z X$$

Atomic number   Element symbol

Gamma Emission

$$^{137}_{55}\text{Cs} \longrightarrow {}^{137}_{56}\text{Ba}^* + {}^{0}_{-1}\text{e} \longrightarrow {}^{137}_{56}\text{Ba} + \gamma\text{-photon}$$

Excited state

Beta emission

e^-

γ
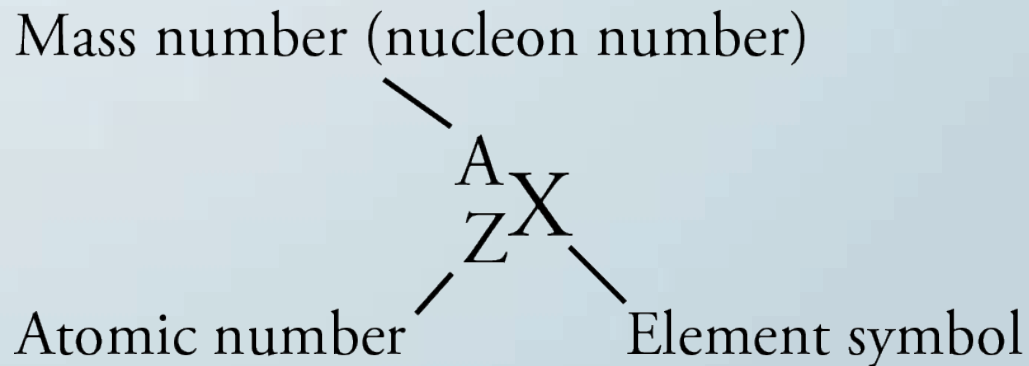
Gamma photon
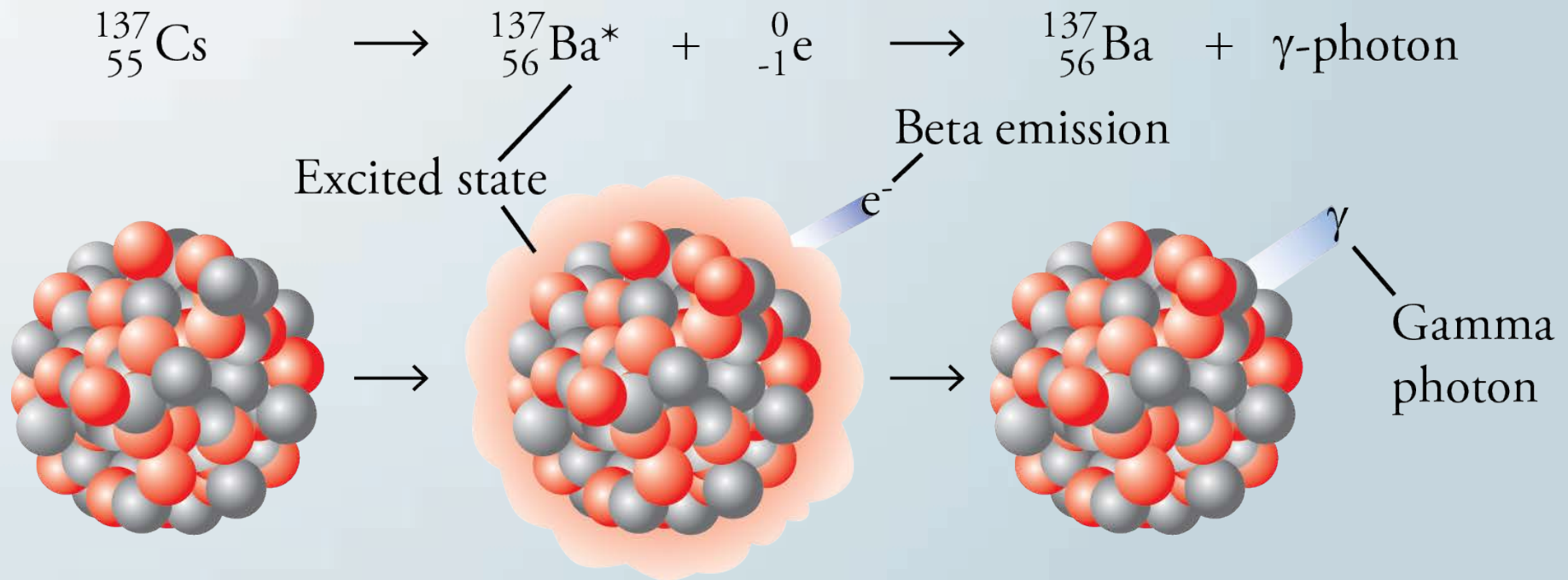
Half-life = the time it takes for one-half of a sample to disappear.

Percentage of radioactive nuclei remaining (y-axis)

50% remaining after one half-life

25% remaining after two half-lives

12.5% remaining after three half-lives

6.25% remaining after four half-lives

3.125% remaining after five half-lives

Half-lives (x-axis)
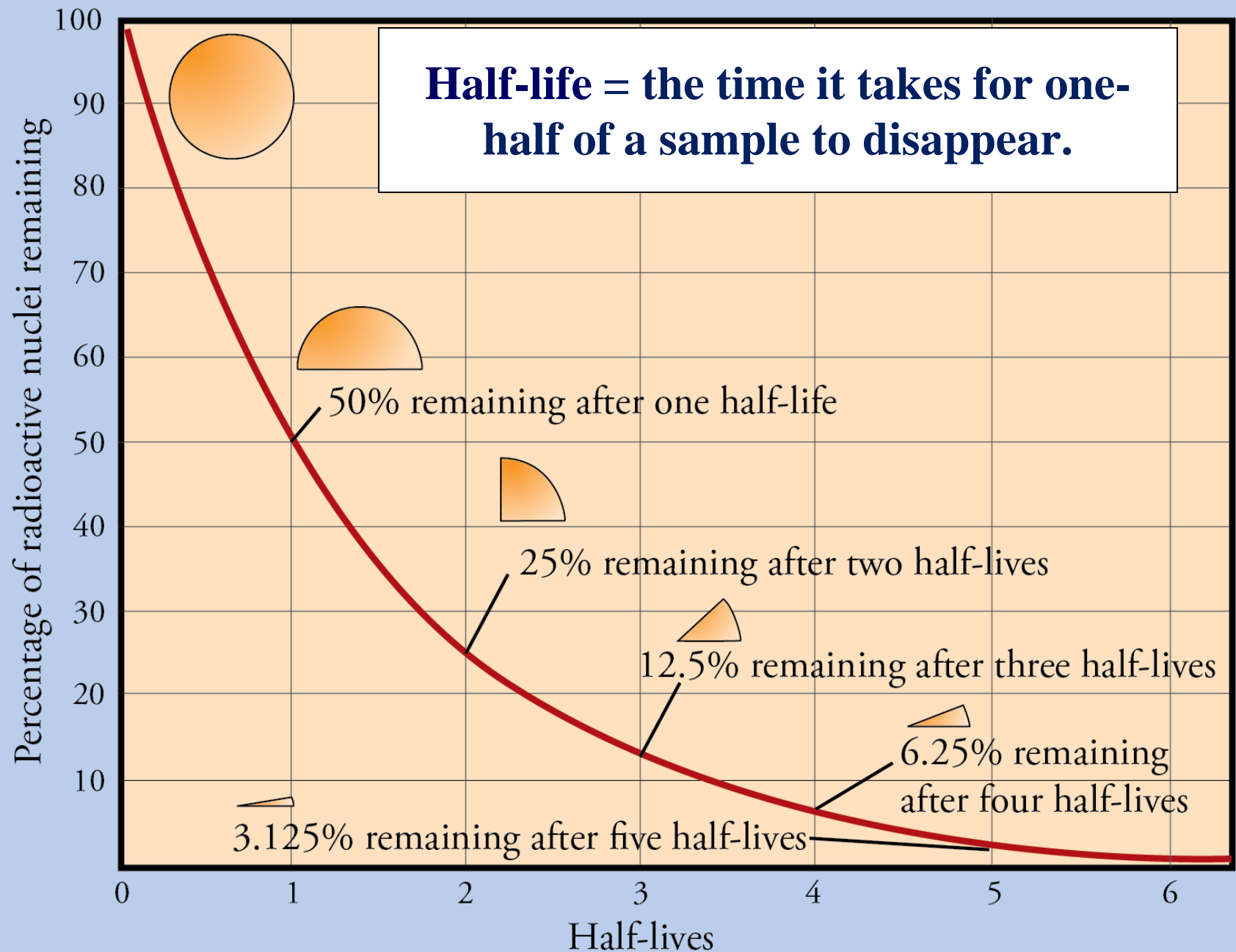
Exponential Decline Example

- Iodine-131 has a half-life of 8.0197 days. If we start with 37 GBq (or 1 curie) of I-131, how much is left after 14 days?

    – The **becquerel** (symbol **Bq**) (pronounced: 'be-kə-rel) is the SI-derived unit of radioactivity. One Bq is defined as the activity of a quantity of radioactive material in which one nucleus decays per second. The Bq unit is therefore equivalent to an inverse second, s^{-1}.

    – The curie is a common non-SI unit. It is now defined as 37 GBq.

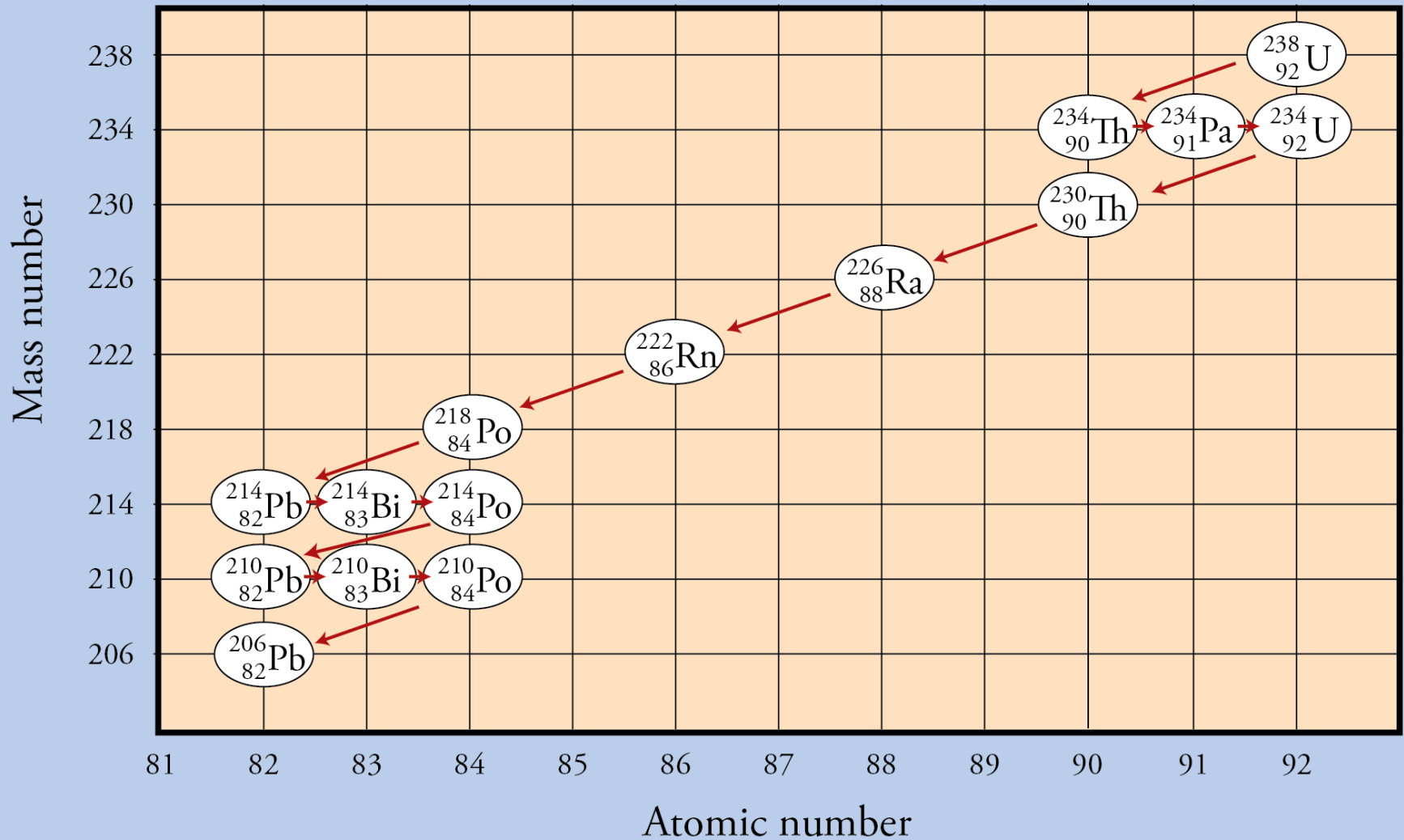**Iodine-131 has a half-life of 8.0197 days. If we start with 37 GBq (or 1 curie) of I-131, how much is left after 14 days?**

$$t_{1/2} = \frac{0.693}{k} \qquad k = \frac{0.693}{t_{1/2}} = \frac{0.693}{8.0197 \text{ day}} = 0.0864 \text{ day}^{-1}$$

$$S(t) = S_o \, e^{-kt} = 37 \text{ GBq} \, e^{-0.0864 \, 1/\text{day}(14 \text{ day})} = \textbf{11 GBq}$$

Radioactive Decay Series

Ionizing Radiation

- All of the forms of radioactive emissions can lead to the formation of ions.

Interaction of ionizing radiation with matter

The energy lost to deceleration of beta particles is emitted in the form of X-rays called "bremsstrahlung," which translates to "braking radiation".

charged particles interact strongly and ionize directly

A neutron can knock a proton out of a nucleus, and the proton can cause ionizations.

neutral particles interact less, ionize indirectly and penetrate farther

Neutron capture can lead to beta decay.

Relative Biological Effectiveness

- The ratio of biological effectiveness of one type of ionizing radiation relative to another, given the same amount of absorbed energy.

Type	RBE (QF = quality factor)
x-rays	1
γ-rays	1
β-particles	1-3
α-particles	5-20
neutrons	5-20

http://en.wikipedia.org/wiki/Relative_Biological_Effectiveness

Radiation Dose

- **Physical dose** = energy absorbed per kg of tissue:

  - 1 rad = 100 erg/g = 0.01 Gy

  - 1 Gray (Gy) = 1 J/kg = 100 rad

- **Biological dose** = physical dose × biological effectiveness:

  - QF = Quality Factor
    = RBE = relative biological effectiveness

  - 1 rem = 1 rad × (QF = 1)

  - ? rem = # rad × QF

  - 1 Sievert (Sv) = 1 Gy × (QF = 1) = 100 rem

  - ? Sv = # Gy × QF

Example: Risk of Cancer

- Because of the uranium content of the granite in the U.S. Capitol Building, radiation levels inside the building are ≈0.85 mSv/yr, which is close to the regulatory limit.

- According to the ICRP model, someone who spent 20 years inside the capitol building would have an extra one in a thousand chance of getting cancer, over and above any other existing risk.

$$? \% = 20 \, y \left(\frac{0.85 \text{ mSv}}{1 \, y} \right) \left(\frac{1 \text{ Sv}}{10^3 \text{ mSv}} \right) \left(\frac{5.5 \%}{1 \text{ Sv}} \right) \approx \mathbf{0.1\%}$$

- An average American would have a one in ten chance of getting cancer during this same 20 year period, even without any exposure to artificial radiation.

Nuclear Energy

- *Binding energy* = the amount of energy released when a nucleus is formed.

- Binding energy per nucleon generally increases from small atoms to atoms with a mass number around 56. Thus fusing small atoms to form medium-sized atoms (*nuclear fusion*) releases energy.

- Binding energy per nucleon generally decreases from atoms with a mass number around 56 to larger atoms. Thus splitting large atoms to form medium-sized atoms (*nuclear fission*) also releases energy.
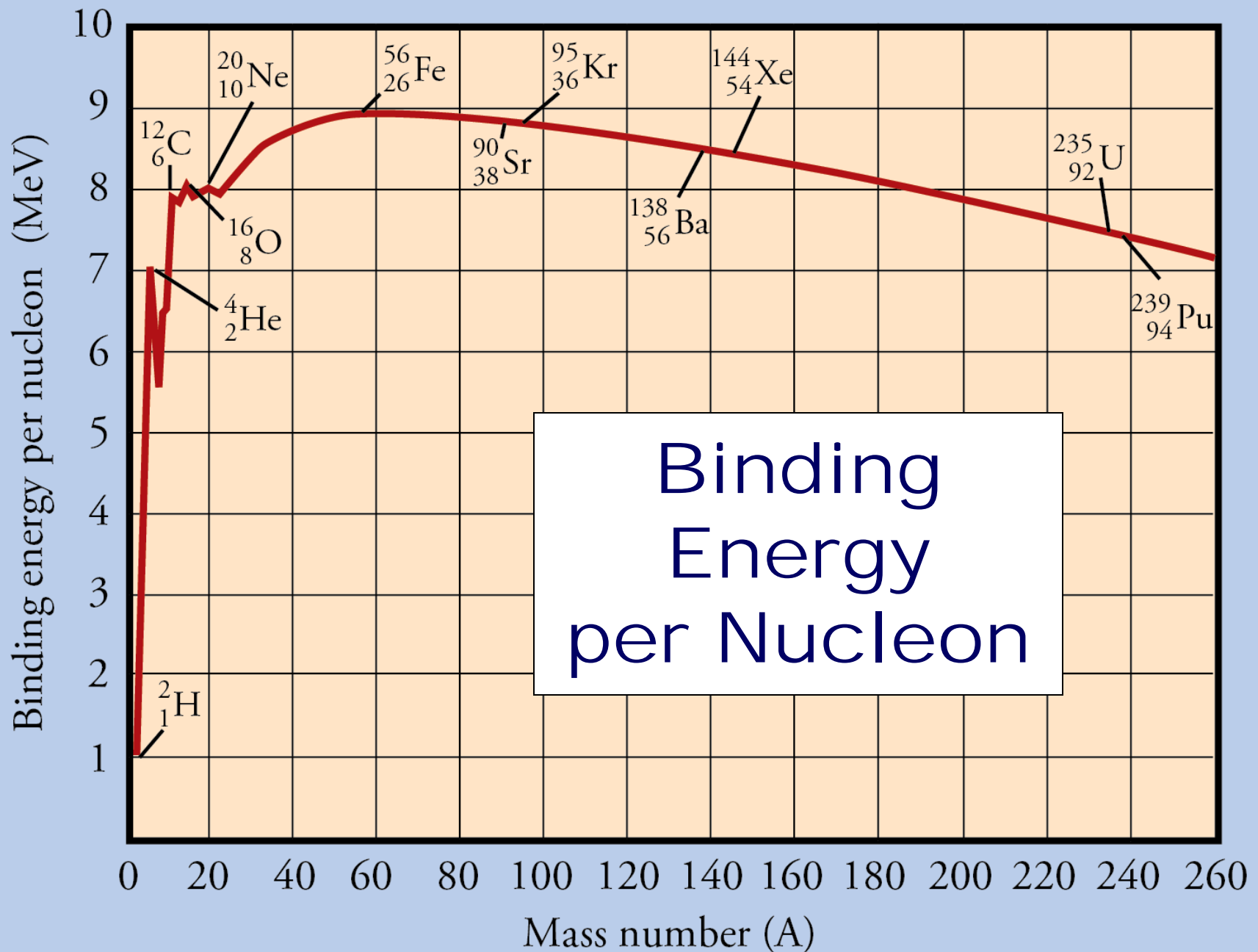
Nuclear Power Plant
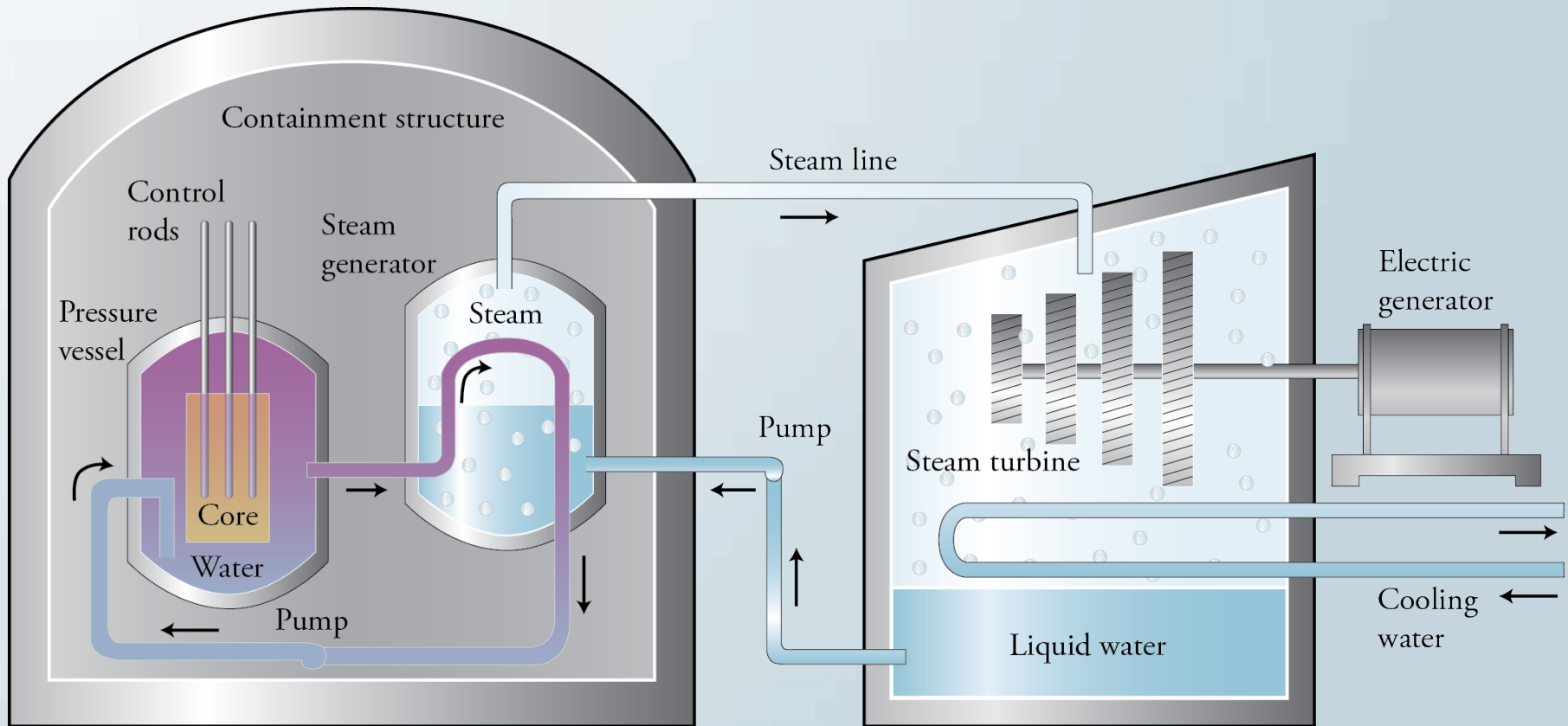
Prompt Critical

- **Critical** = if each fission event causes, on average, exactly one other. This causes a self-sustaining fission chain reaction.

- **Supercriticality** = if each fission event causes, on average, more than one other.

- **Prompt critical** = if for each nuclear fission event, one or more of the immediate or prompt neutrons released causes an additional fission event. This causes a rapid, exponential increase in the number of fission events. Prompt criticality is a special case of supercriticality.

$^{1}_{0}n$

$^{235}_{92}U$

$^{236}_{92}U$

$^{138}_{56}Ba$

$3\,^{1}_{0}n$

$^{95}_{36}Kr$

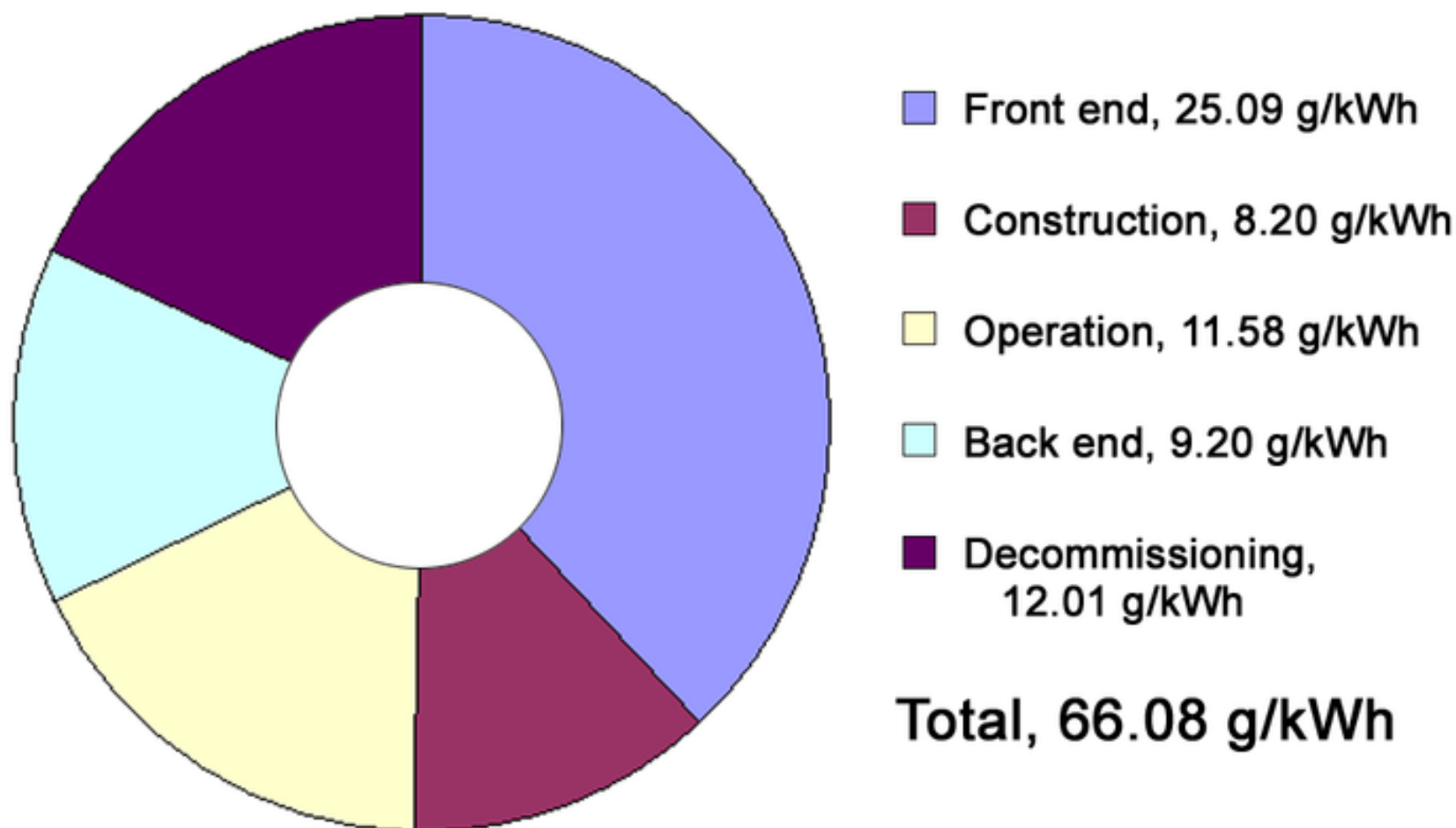+ Energy
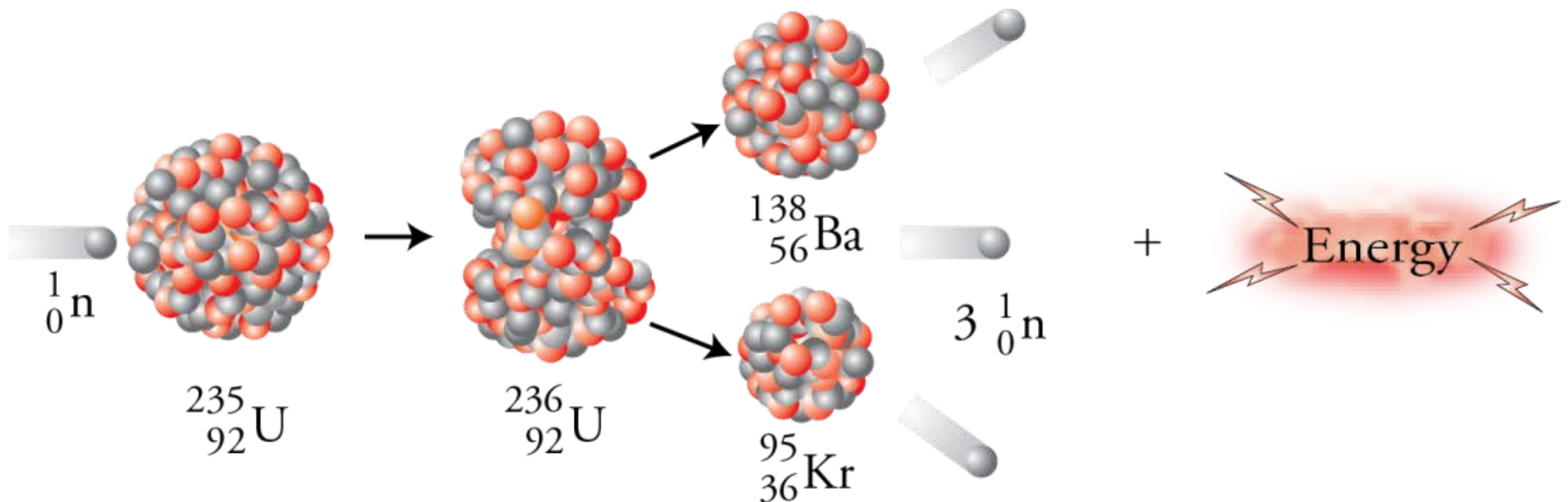
Delayed Neutrons

- A small fraction of the fission products that undergo beta decay are excited enough to be able to decay by emitting a neutron.

- The neutron emission happens orders of magnitude later compared to the emission of the prompt neutrons, which are released in the fission reaction.

- The ability of delayed neutrons to cause a new fission reaction is important in the design and safe operation of nuclear power plants.

Delayed Neutrons

- If a nuclear reactor happened to be prompt critical, the number of neutrons would increase exponentially, and very quickly the reactor would become uncontrollable.

- Because of the delayed neutrons, it is possible to leave the reactor in a subcritical state as far as only prompt neutrons are concerned.

- If the fission reaction begins to increase too rapidly, neutron production overall still grows exponentially, but on a time scale that is governed by the delayed neutron production, which is slow enough to be controlled.

Carbon emissions from nuclear power
Sovacool life cycle study survey, 2008

- Front end, 25.09 g/kWh
- Construction, 8.20 g/kWh
- Operation, 11.58 g/kWh
- Back end, 9.20 g/kWh
- Decommissioning, 12.01 g/kWh

Total, 66.08 g/kWh

Mean value of carbon dioxide emissions from qualified life cycle studies among 103 surveyed. Includes results of 1997 Vattenfall study.
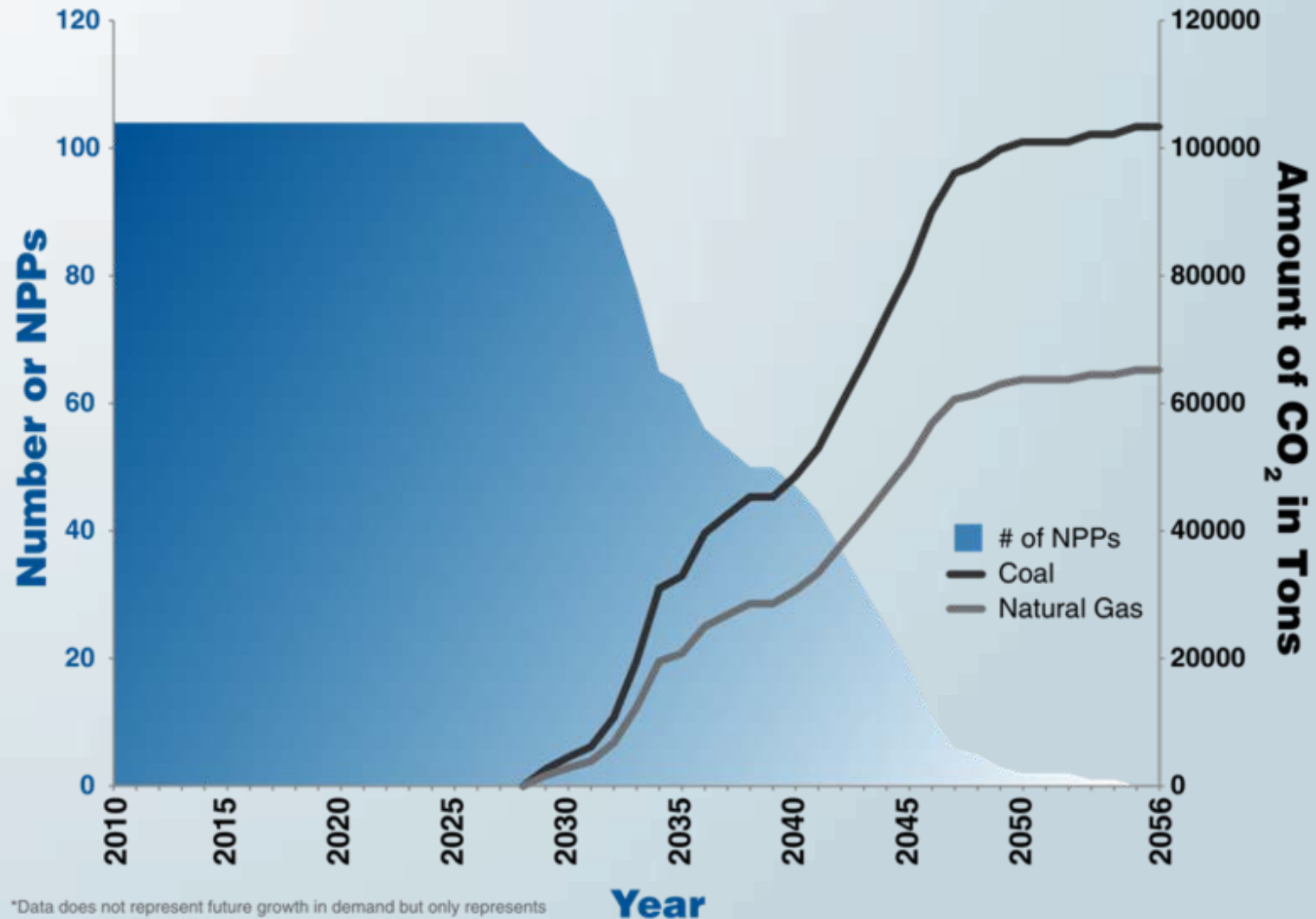
Lifecycle Greenhouse Gas Emission Estimates for Electricity Generators

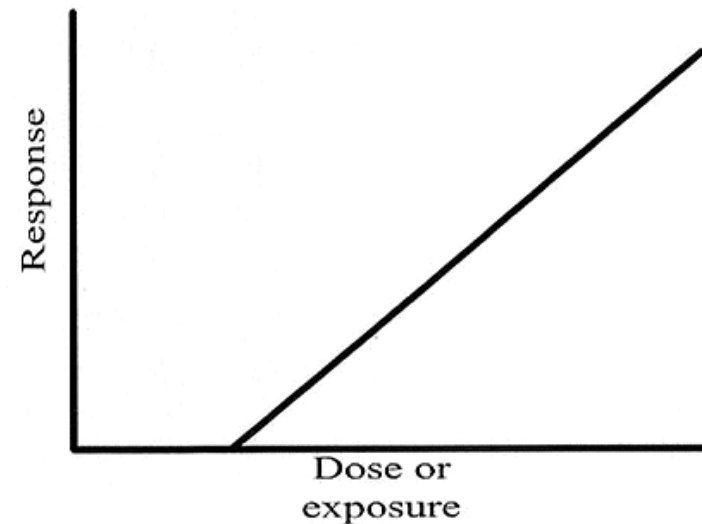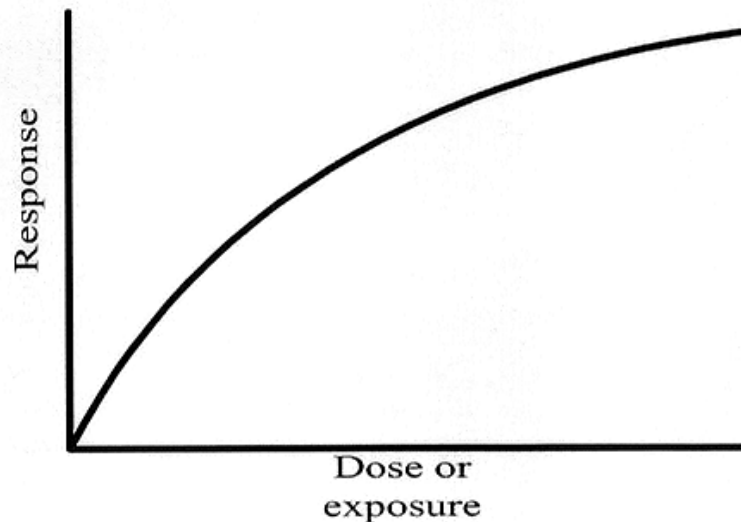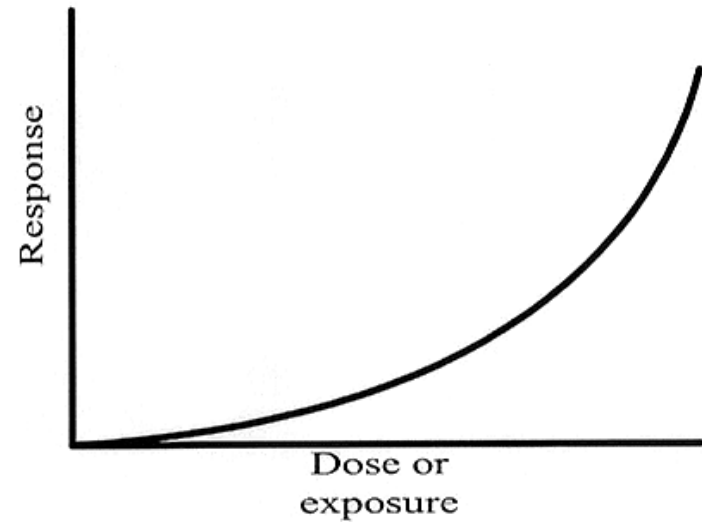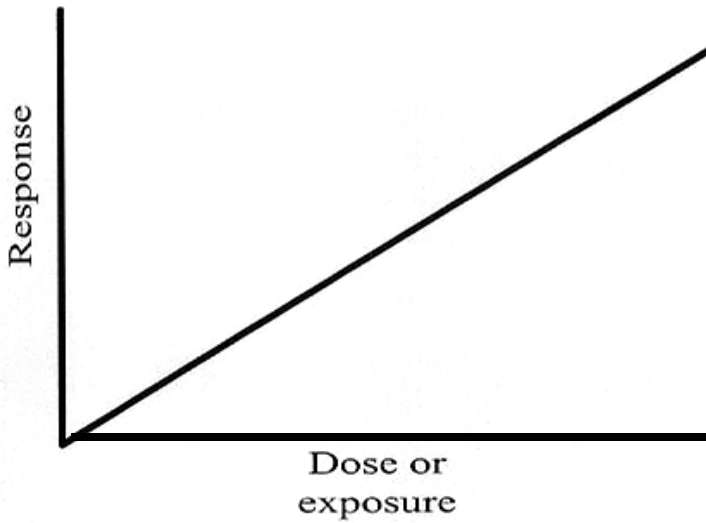| Technology	Description	Estimate (g CO2/kWh$_e$)
Wind	2.5 MW offshore	9
Hydroelectric	3.1 MW reservoir	10
Wind	1.5 MW onshore	10
Biogas	Anaerobic digestion	11
Hydroelectric	300 kW run-of-river	13
Solar thermal	80 MW parabolic trough	13
Biomass	various	14-35
Solar PV	Polycrystaline silicon	32
Geothermal	80 MW hot dry rock	38
Nuclear	various reactor types	66
Natural gas	various combined cycle turbines	443
Fuel Cell	hydrogen from gas reforming	664
Diesel	various generator and turbine types	778
Heavy oil	various generator and turbine types	778
Coal	various generator types with scrubbing	960
Coal	various generator types without scrubbing	1050

http://en.wikipedia.org/wiki/Comparisons_of_life-cycle_greenhouse-gas_emissions

Retiring Nuclear Power Plants

Impact of NPP Retirement on Carbon Emissions

*Data does not represent future growth in demand but only represents the increase in CO2 emissions to replace what nuclear produces today.

# Different Shapes of Dose-Response Curve

Describing Toxic Risk: Carcinogens

Slope factor = the slope of the line expressing how much cancer risk increases per milligram of the substance ingested/inhaled per kilogram of body weight per day

Unit risk = the cancer risk resulting from a continuous exposure to a "unit" concentration of a carcinogen (e.g. continuous exposure to 1 mg/L or $1\mu g/m^3$)

Acceptable concentration = concentration of a carcinogen in water or air that results in an "acceptable" risk (often 10^{-6}) for a continuous (usually lifetime) exposure to that concentration
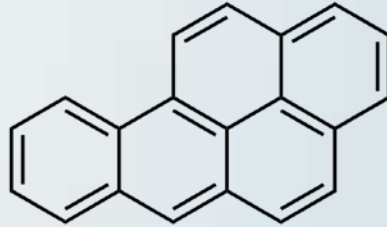
Example: Benzo(a)pyrene (BAP)
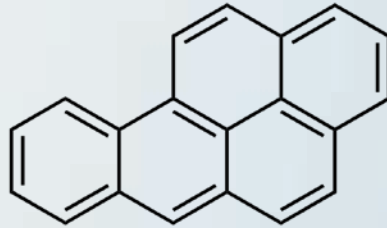
- BAP oral slope factor

$$11.5 \text{ cancer/mg/kg·day} = \frac{11.5 \text{ cancer}}{1 \text{ mg/kg·day}} = \frac{11.5 \text{ cancer·kg·day}}{1 \text{ mg}}$$

- Convert to unit risk: divide by mass of subject (e.g. 70 kg) and multiply by daily consumption (e.g. 2 liters of H_2O per day):

$$\frac{? \text{ cancer}}{\text{mg/L}} = \frac{? \text{ L·cancer}}{\text{mg}} = \frac{11.5 \text{ cancer·\cancel{kg}·\cancel{day}}}{1 \text{ mg}} \left(\frac{2 \text{ L}}{1 \text{ \cancel{day}}} \right) \left(\frac{1}{70 \text{ \cancel{kg}}} \right) = 0.3 \text{ cancer/mg/L}$$

Example: Benzo(a)pyrene (BAP)

- To find the BAP concentration that gives a 1 in a million cancer risk, divide 10^{-6} by the unit risk:

$$\frac{?\ ng/L}{\text{million cancers}} = \frac{?\ ng}{\text{million cancers·L}}$$

$$= \frac{mg}{0.3\ cancer\text{·}L}\left(\frac{1\ cancer}{10^6\ cancers}\right)\left(\frac{1\ g}{10^3\ mg}\right)\left(\frac{10^9\ ng}{1\ g}\right)$$

$$= 3\ ng/L$$

Rate of Solar Energy Striking Earth

Solar energy flux (S_0 or Ω, called the solar "constant") is 1368 W/m^2 at *top* of atmosphere in plane perpendicular to incoming beam

$A_{sphere} = 4\pi r^2$

$A_{circle} = \pi r^2$
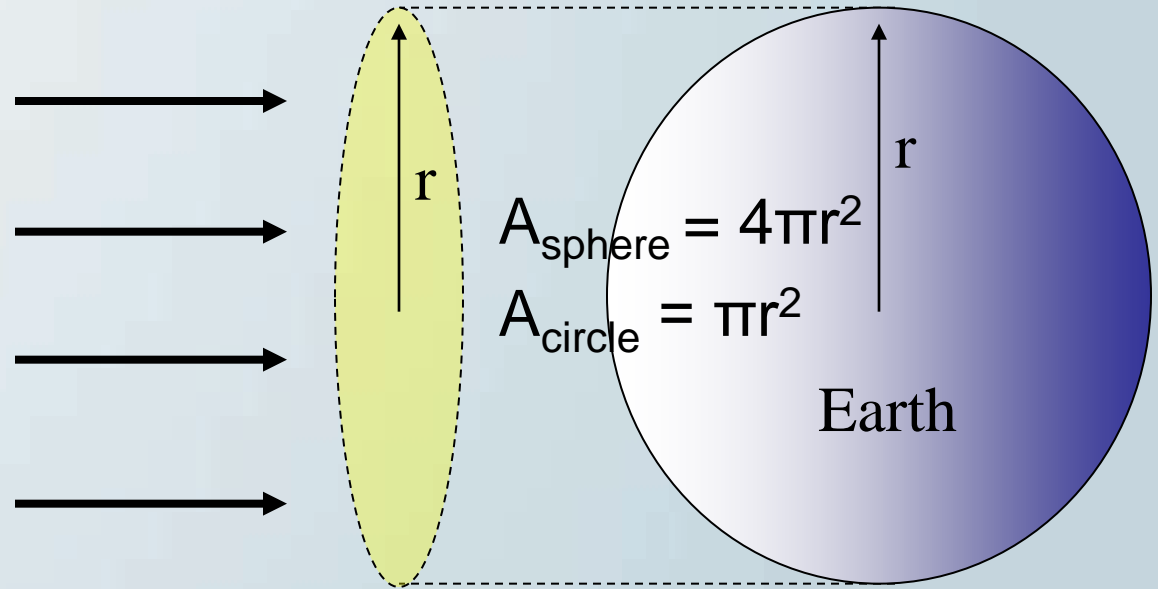
Earth

Energy striking the Earth = $\Omega\pi r^2$

Energy spread out over the surface of the Earth
= energy striking Earth/surface area of the Earth
= $\Omega\pi r^2 / 4\pi r^2 = \Omega/4 = 1368/4$ W/m^2 = 342 W/m^2

Goal

- The goal is to develop a model that explains the average temperature of the Earth, 288 K or 15 °C.

- Three attempts

  - Earth as a blackbody with no greenhouse gases

  - Earth with two layers of greenhouse gases where the atmosphere is totally transparent to incoming sunlight and with the only mechanism for energy loss being infrared radiation loss with no IR radiation escaping the atmosphere unabsorbed. (A layer is the portion of atmosphere within which each IR photon would be absorbed and emitted once.)

  - Earth with two layers of greenhouse gases with corrections for incoming sunlight absorbed, some IR through the atmosphere unabsorbed, some heat transferred to the atmosphere as latent heat, and some energy transferred to the atmosphere via convection.

Assuming that the Earth is a blackbody with no greenhouse gases gives a temperature that is too low (255 K = -18 °C)
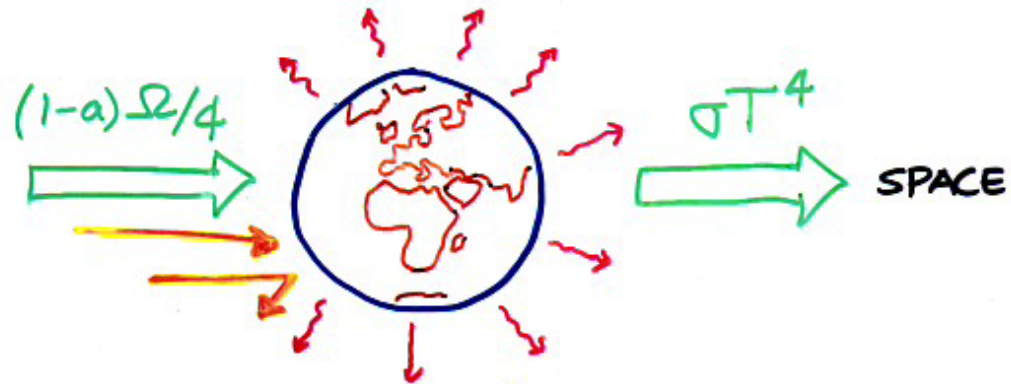
.

The Earth's Energy Balance

Solar Flux $\Omega \approx 1360$ W/m²

avg. over surface $\rightarrow \Omega/4 \approx 340$ W/m²

Albedo (reflectivity) $a \approx 0.3$ (avg.)

Blackbody Radiation: $P(W/m²) = \sigma T^4$

$\sigma = 5.67 \times 10^{-8}$ W/m².K⁴

$(1-a)\Omega/4 \qquad \sigma T^4 \qquad$ SPACE

$(1-a)\Omega/4 = \sigma T^4$ (energy conservation)

$$T^4 = \frac{(1-a)\Omega}{4\sigma} = \frac{0.7 \times 340 \text{ W/m}^2}{5.67 \times 10^{-8} \text{ W/m}^2 \cdot K^4}$$
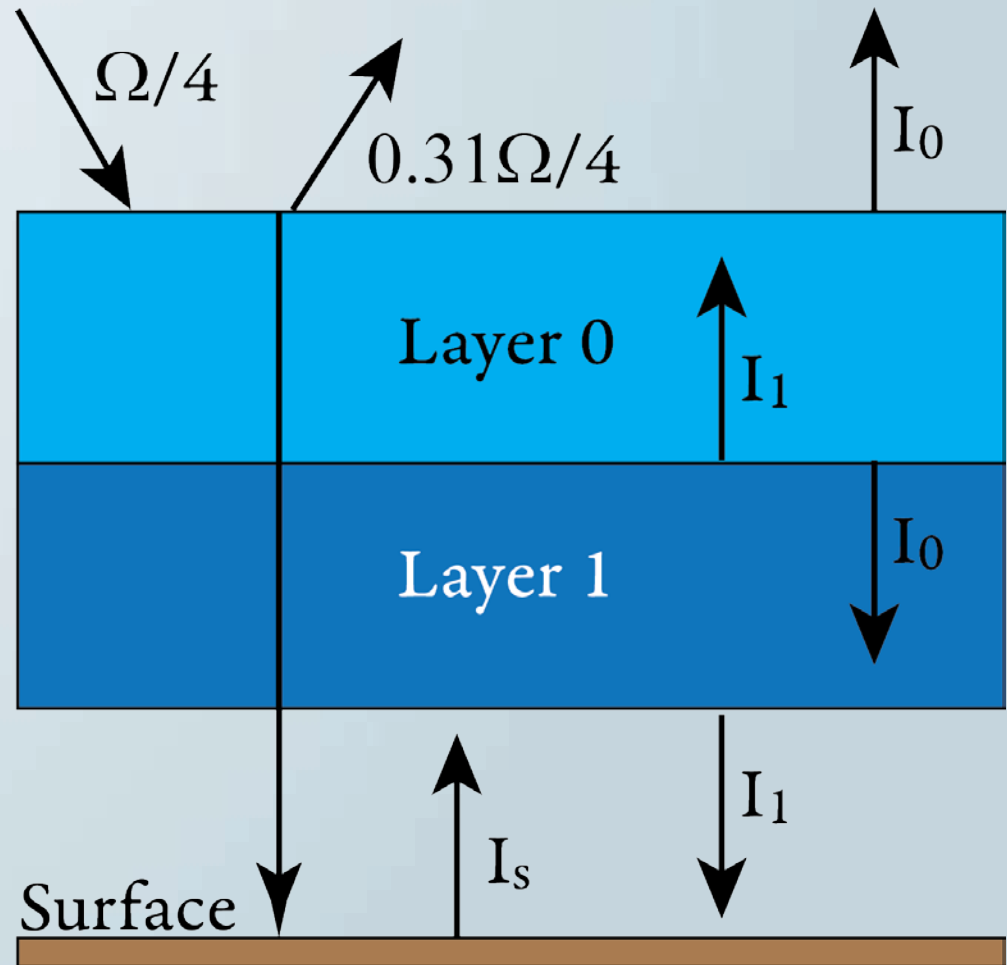
$\rightarrow T = 255$ K

Two Layers of Greenhouse Gases

- Each layer is thick enough so that each IR photon that enters the layer is absorbed and emitted once.

- Surface and each layer act as black bodies (perfect absorbers and emitters)

$$I = \sigma T^4$$

- No incoming shortwave radiation is absorbed

- No outgoing IR escaping unabsorbed

Two Layers of Greenhouse Gases

Assumes only energy out and only energy exchange between layers was infrared (I)

Flux in total = Flux out total

$$0.69\Omega/4 = I_0 = \sigma T_0^4$$

$$I_1 = 2I_0 = 2\sigma T_0^4$$
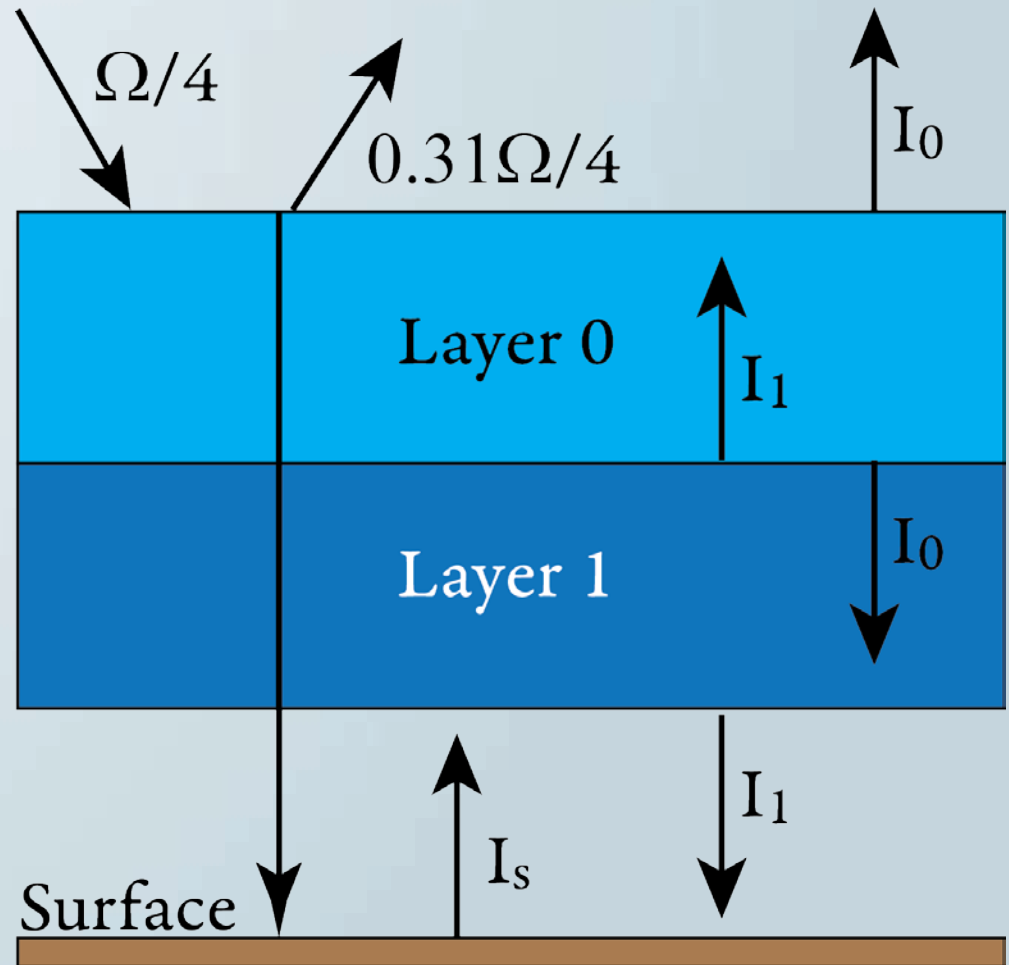
$$I_S = \sigma T_s^4 = 0.69\Omega/4 + I_1$$

$$\sigma T_s^4 = \sigma T_0^4 + 2\sigma T_0^4$$

$$T_s^4 = T_0^4 + 2T_0^4$$

$$T_s^4 = (1+2)T_0^4$$

$$T_s = 3^{1/4}T_0 = 3^{1/4}(255\text{ K})$$
$$= 336\text{ K} = 63\ {}^\circ\text{C (too high)}$$

Adjustments

- Some incoming sunlight absorbed (Energy flux = F_{abs})
- Some IR radiation escapes unabsorbed (Energy flux = F_{esc})
- Some energy escapes from the surface by
  - Energy flux due to convection (F_C)
  - Energy flux due to latent heat (F_L)

$$I_s = (I_{incoming} + I_1) - (1.7F_{abs} + 2F_{esc} + F_C + 1.5F_L)$$

$$\sigma T_s^4 = [(0.69\Omega/4 + 2(0.69\Omega/4)] - [1.7(86 \text{ W/m}^2) + 2(20 \text{ W/m}^2) + (17 \text{ W/m}^2) + 1.5(80 \text{ W/m}^2)]$$

$$T_s = 289 \text{ K } (16 \text{ °C})$$

Simple earth's temperature balance

The emission temperature is defined as

$$T_e = \left[\frac{(1-\alpha_p)S}{4\sigma}\right]^{\frac{1}{4}}, \tag{1}$$

where α_p is the planetary albedo, S the solar flux, and σ the Stefan-Boltzmann constant.

***Important equation☺

Exam questions

1. At present the emission temperature of the Earth is 255 K, and its albedo is 30%. How would the emission temperature change if:

   (a) the albedo were reduced to 10% (and all else were held fixed);

   (b) the infrared absorptivity of the atmosphere — ϵ in Fig.2.8 — were doubled, but albedo remains fixed at 30%.

2. Suppose that the Earth is, after all, flat. Specifically, consider it to be a thin circular disk (of radius 6370 km), orbiting the Sun at the same distance as the Earth; the planetary albedo is 30%. The vector normal to one face of this disk always points directly towards the Sun, and the disk is made of perfectly conducting material, so both faces of the disk are at the same temperature. Calculate the emission temperature of this disk, and compare with Eq.(2.4) for a spherical Earth.

Answer Question 1.

The emission temperature is defined as

$$T_e = \left[\frac{(1 - \alpha_p)S}{4\sigma} \right]^{\frac{1}{4}}, \tag{1}$$

where α_p is the planetary albedo, S the solar flux, and σ the Stefan-Boltzmann constant.

(a) If albedo were reduced from $\alpha_p = 30\%$ to $\alpha'_p = 10\%$, the emission temperature would change from T_e (at present) to T'_e, where

$$\frac{T'_e}{T_e} = \left[\frac{1 - \alpha'_p}{1 - \alpha_p} \right]^{\frac{1}{4}} = \left[\frac{0.9}{0.7} \right]^{\frac{1}{4}} = 1.0648,$$

so the new emission temperature would be $255 \times 1.0648 = 271.5$K.

(b) Emission temperature—the temperature at which the Earth emits to space—would not change at all if atmospheric IR opacity were doubled but albedo remained fixed. Emission temperature—unlike surface temperature—depends only on how much of the solar energy flux is absorbed by the Earth and, by (1), depends only on α_p, S, and σ.

Answer question 2:
More practice

Incoming solar flux $S_0 = 1367 \mathrm{Wm}^{-2}$; planetary albedo $\alpha_p = 0.3$. Area of disk intercepting solar flux $= \pi a^2$. So,

$$\text{Net solar input} = S_0 \pi a^2 (1 - \alpha_p).$$

Disk has temperature on both faces, so area emitting thermal radiation is $2\pi a^2$. Disk emits σT_e^4 per unit area, so

$$\text{Net thermal emission} = 2\pi a^2 \sigma T_e^4.$$

Balancing input and emission,

$$(1 - \alpha_p) S_0 \pi a^2 = 2\pi a^2 \sigma T_e^4,$$

i.e.,

$$T_e = \left[\frac{(1 - \alpha_p) S_0}{2\sigma} \right]^{\frac{1}{4}} = 303.1 \mathrm{K}.$$

The expression for T_e is a factor $2^{\frac{1}{4}}$ larger than we found for a spherical Earth—the disk has the same cross-section as the sphere (and so intercepts the same amount of solar radiation) but one-half of the surface area, so must increase T_e^4 by a factor of 2 to compensate.