Environmental Chemistry-4

-Organic and Nuclear Chemistry

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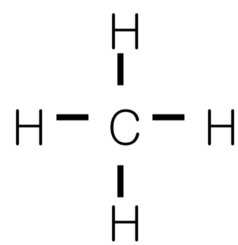
Organic Chemistry

✓ **Carbon: Versatile atom capable of 4 covalent bonds**

- 4 single bonds:



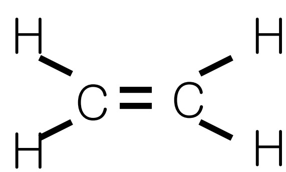
Methane

- 2 double bonds:

$O=C=O$

Carbon Dioxide

- 1 double + 2 single:



Ethene

- 1 triple + 1 single:

$H-C \equiv C-H$

Acetylene

Organic Chemistry

- Why 4 bonds?
- To achieve a stable configuration with **<u>8</u>** outmost electrons
  - 4 e^- in outer shell
  - Needs 4 more e^-s

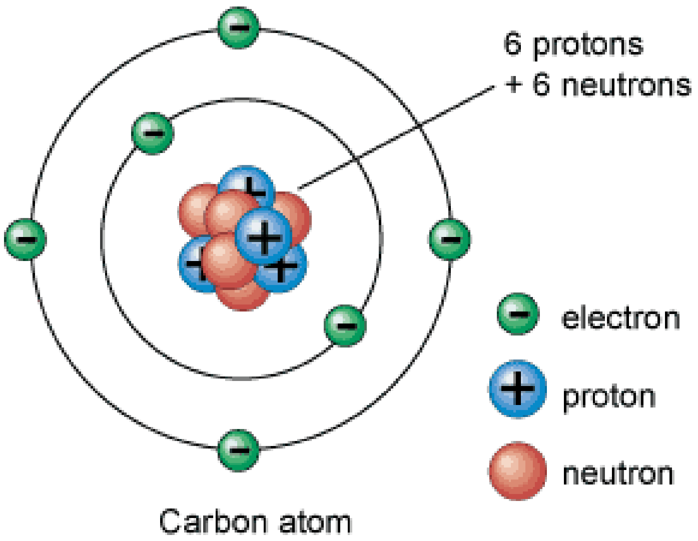
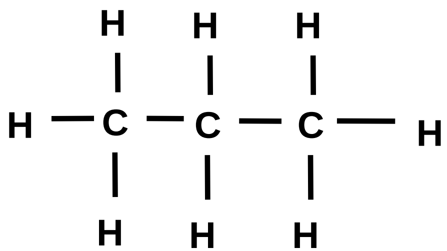


Image courtesy of http://newenergyandfuel.com

Organic Chemistry

- Organic compounds – generally carbon-containing compounds
- Hydrocarbons – compounds containing H and C only



propane

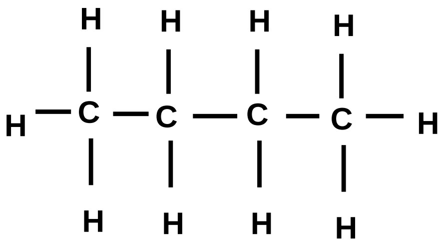
- Naming convention uses Greek prefixes:
  - Methane CH_4
  - Ethane C_2H_6
  - Propane C_3H_8
  - Butane C_4H_{10}
  - Octane C_8H_{18}

Organic Chemistry

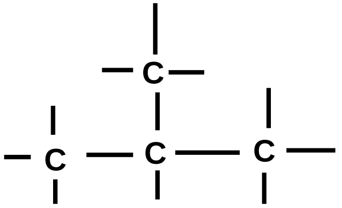
- Alkane – hydrocarbon where each carbon has four single bonds, saturated hydrocarbons
- In general, alkane formula:

  C_nH_{2n+2}

- Isomers
  - Same molecular formula but different structure
  - Structural differences result in very different chemical, physical & toxic properties
  - Butane and higher alkanes have isomers.



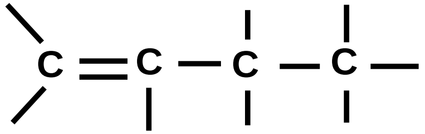
n-butane



iso-butane

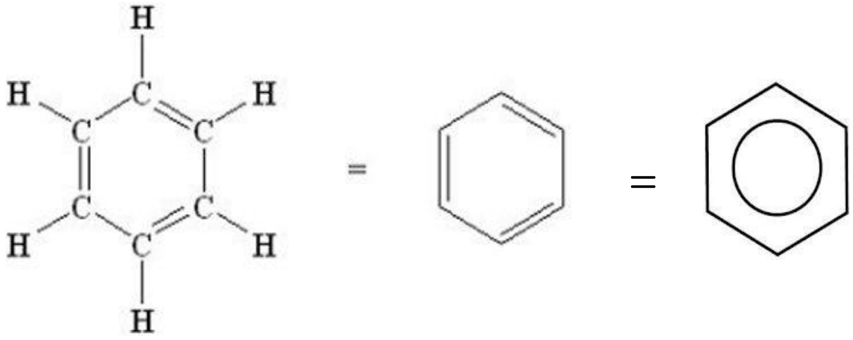
Organic Chemistry

- **Alkenes**
  - There is a double bond between carbons
  - Same name as alkanes, but with -ene



butene

- **Aromatics**
  - Another large group of hydrocarbons with benzene rings



Organics of Environmental Concern

√ **A wide spectrum of organics are of environmental concern!**

- TCE (trichloroethylene)
  - Widely used solvent
  - Carcinogenic
- DDT (dichlorodiphenyltrichloroethane)
  - Onerous insecticide
- PCBs (polychlorinated biphenyls)
  - Previously used in transformers as dielectric and coolant fluids (207 congeners)
- BTEX (benzene, toluene, ethylene, xylenes)
  - Common groundwater contaminants

And so many more….

Fate and Transport of Organics

- Organic compounds go through physical, chemical, biological transformations and transports in natural environment and environmental engineering processes.
  - Partitioning (gas/liquid/solid)
  - Chemical transformation

- Transformations
  - Hydrolysis
  - Redox reactions
  - Photolysis
  - Biodegradation

Hydrolysis

Source: Environmental Organic Chemistry

- Nucleophiles: nucleus-liking species

  attracted by the electron-deficient atoms in molecules

- Electrophiles: electron-liking species

  attracted by the electron-rich atoms in molecules

- Hydrolysis (of organic compounds):

  a type of nucleophilic substitution or elimination

Table 13.1 Examples of Important Environmenal Nucleophiles

increasing nucleophilicity for reaction at a saturated carbon (↓)

ClO_4^-
H_2O
NO_3^-
F^-
SO_4^{2-}, CH_3COO^-
Cl^-
HCO_3^- ,HPO_3^{2-}
NO_2^-
PhO^{-a}, Br^-, OH^-
I^-, CN^-
HS^-,R_2NH^b
$S_2O_3^{2-}$,SO_3^{2-},PhS^-

[a] Ph = C_6H_5 (phenyl)
[b] R = CH_3, C_2H_5

Hydrolysis

Source: Environmental Organic Chemistry

Table 13.2 Examples of Environmentally Relevant Chemical Reactions Involving Nucleophiles and/or Bases

Reactants		Products
Nucleophilic Substitutions at Saturated Carbon Atoms		
$CH_3Br + H_2O$ Methyl bromide	⟶	$CH_3OH + H^+ + Br^-$ Methanol
$CH_3Cl + HS^-$ Methyl chloride	⟶	$CH_3SH + Cl^-$ Methane thiol (Methyl mercaptan)
$CH_3O{-}P(=O)(OCH_3)_2 + H_2O$ Trimethylphosphate	⟶	$CH_3OH + {}^-O{-}P(=O)(OCH_3)_2 + H^+$ Methanol, Dimethylphosphate
β-Elimination		
$Cl_2HC{-}CHCl_2 + HO^-$ 1,1,2,2-Tetrachloroethane	⟶	$Cl_2C{=}CHCl + Cl^- + H_2O$ Trichloroethene

Ester Hydrolysis

Reactants		Products
$H_3C{-}C(=O){-}OCH_2CH_3 + H_2O$ Ethyl acetate (Acetic acid ethylester)	⟶	$H_3C{-}C(=O){-}O^- + HO{-}CH_2CH_3 + H^+$ Acetate, Ethanol

Parathion ⟶ O,O-Diethyl-thiophosphoric acid + 4-Nitrophenol

Carbamate Hydrolysis

Carbofuran ⟶ Methylamine + 2,3-Dihydro-3,3-dimethyl-7-benzo-furanol

Redox Reactions

Source: Environmental Organic Chemistry

- Definition of reduction & oxidation reactions (i.e., redox reactions)
  - Oxidation: loss of e^- or H, gain of O, increase of oxidation number
  - Reduction: gain of e^- or H, loss of O, decrease of oxidation number

e.g., $C + H_2 \rightarrow CH_4$

$C + O_2 \rightarrow CO_2$

$Fe^0 \rightarrow Fe^{2+} + 2e^-$

Redox Relationship between O_2 and H_2O

Reduction

O_2

H_2O

Oxidation

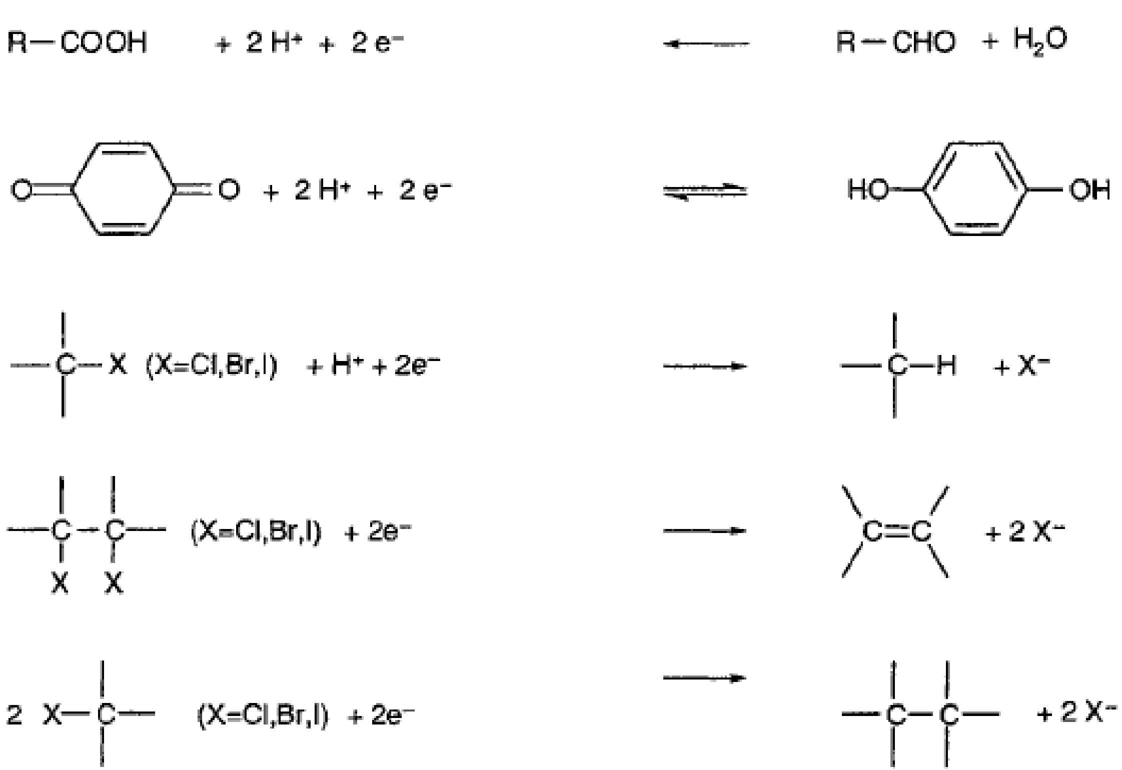
Redox Reactions

Source: Environmental Organic Chemistry

Table 14.1 Examples of Some Simple Redox Reactions That May Occur Chemically in the Environment [a]

Oxidized Species	Reduction ⇌ Oxidation	Reduced Species

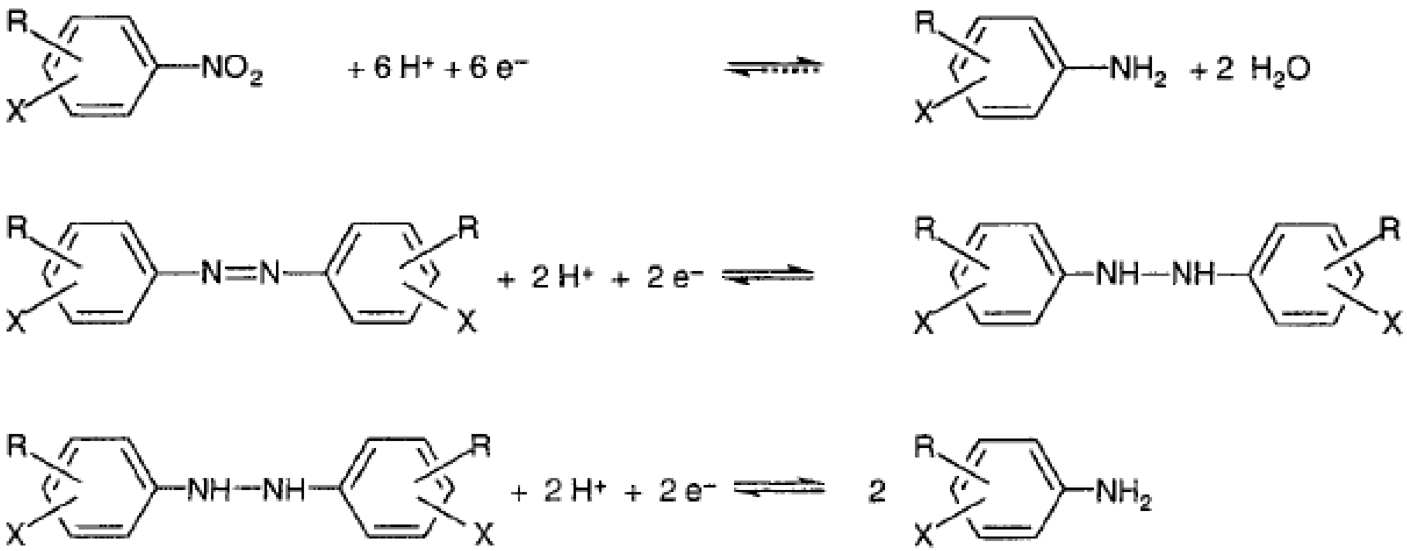
Change in Oxidation State of Carbon Atom(s)



Redox Reactions

Source: Environmental Organic Chemistry

Change in Oxidation State of Nitrogen Atom(s) [b]



Change in Oxidation State of Sulfur Atom(s) [c]

$$R-S-S-R + 2\,H^+ + 2\,e^- \rightleftharpoons 2\ R-SH$$

$$R-S(=O)-R' + 2\,H^+ + 2\,e^- \rightleftharpoons R-S-R' + H_2O$$

Photolysis

Source: Environmental Organic Chemistry

- Direct photolysis vs. Indirect photolysis
- Primary photo-processes

$$A + h\nu \rightarrow A^* \quad \text{(photo-excitation)}$$

$$A^* \rightarrow A + \text{heat} \quad \text{(thermal decay)}$$

$$A^* \rightarrow A + h\nu' \quad \text{(fluorescence)}$$

$$A^* \rightarrow A + h\nu'' \quad \text{(phosphorescence)}$$

$$A^* \rightarrow B \quad \text{(photolysis)}$$

- Quantum yield

$$A + h\nu \rightarrow B$$

$$\phi_A = \frac{\text{Molecules (mole) of A decomposed per unit volume per unit time}}{\text{Quanta of light (Einstein) absorbed by A per unit volume per unit time}}$$

Photolysis

Source: Environmental Organic Chemistry

- Reactive oxygen species (ROS) produced by sunlight-induced photochemical reactions

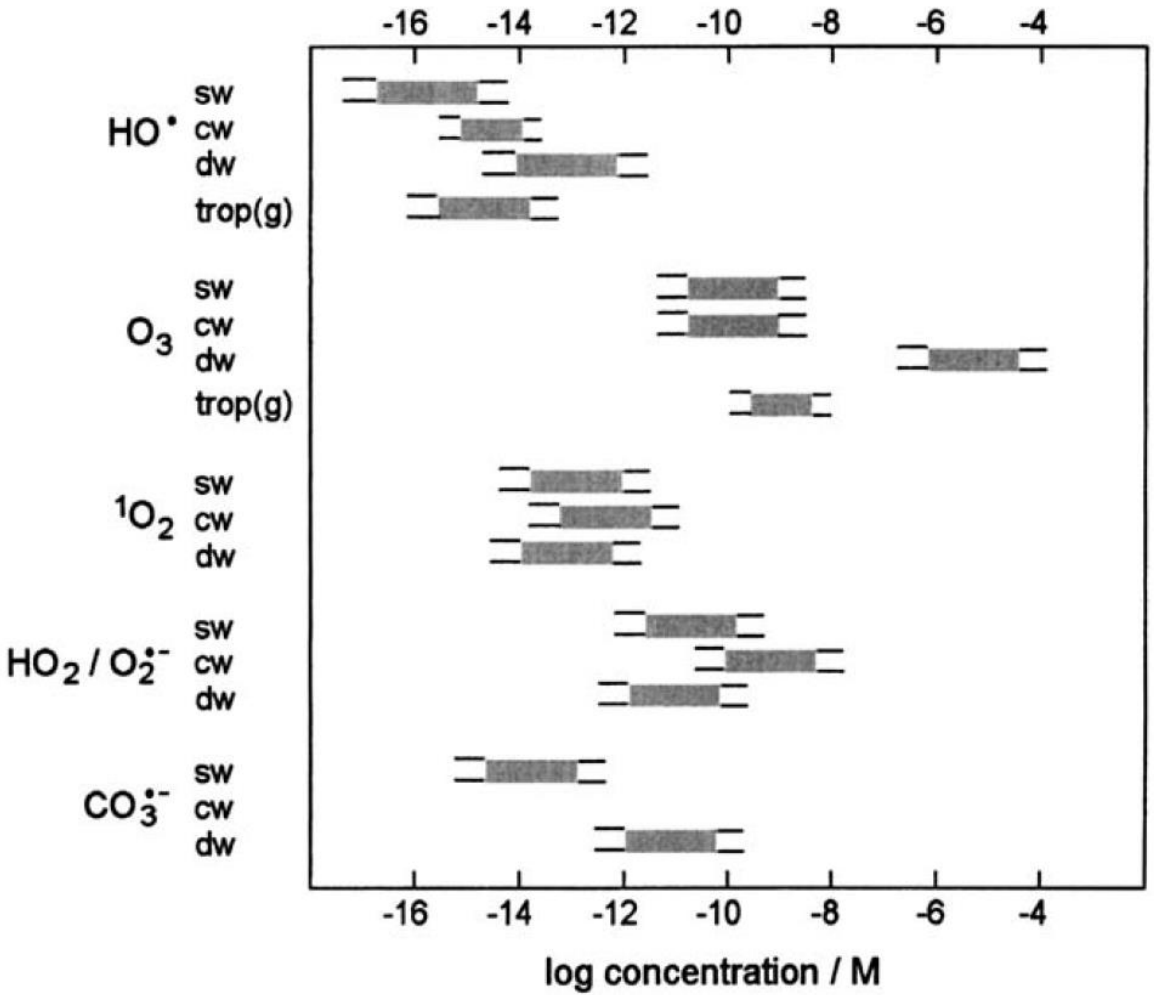
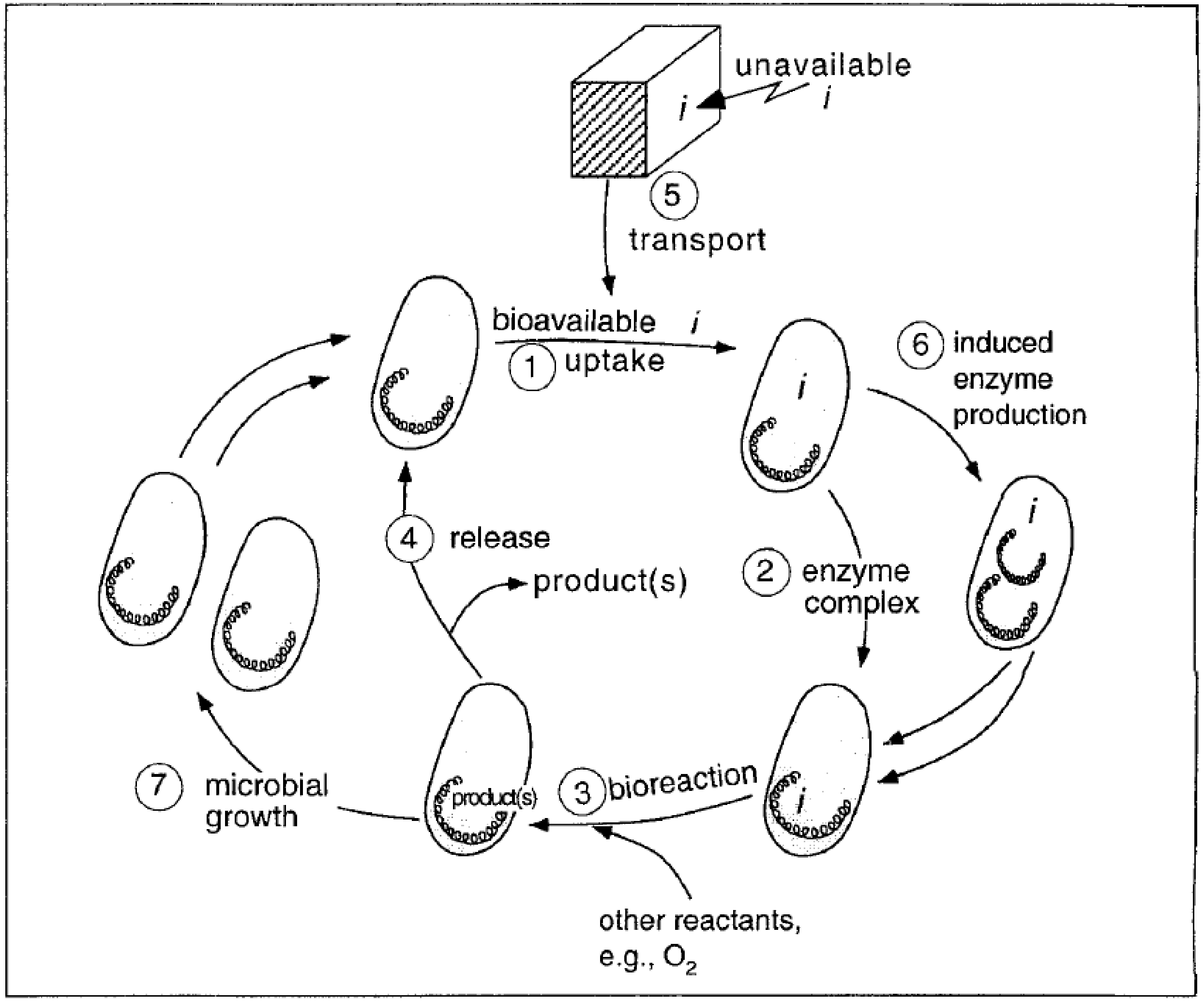


Figure 16.1 Ranges of steady-state concentrations of reactive oxygen species in sunlit surface waters (sw), sunlit cloud waters (cw), drinking-water treatment (dw), and the troposphere (trop(g)). Data from Sulzberger et al. (1997) and Atkinson et al. (1999).

Biodegradation

Source: Environmental Organic Chemistry

Figure 17.1 Sequence of events in the overall process of biotransformations: (1) bacterial cell containing enzymes takes up organic chemical, *i*, (2) *i* binds to suitable enzyme, (3) enzyme:*i* complex reacts, producing the transformation product(s) of *i*, and (4) the product(s) is(are) released from the enzyme. Several additional processes may influence the overall rate such as: (5) transport of *i* from forms that are unavailable (e.g., sorbed) to the microorganisms, (6) production of new or additional enzyme capacity [e.g., due to turning on genes (induction), due to removing materials which prevent enzyme operation (activation), or due to acquisition of new genetic capabilities via mutation or plasmid transfer], and (7) growth of the total microbial population carrying out the biotransformation of *i*.



Nuclear Chemistry

- Some atomic nuclei are unstable or radioactive
  - Spontaneously change form and emit radiation

- Example: $^{235}_{92}U$ $^{238}_{92}U$

  Uranium-235 **Uranium-238**

- Radioactivity can be damaging to organisms
- Also can be a useful tracer

Radiation

√ **Types of radiation emitted by radioactive decay:**

- Alpha
  - Massive particles (helium atoms: 2 protons + 2 neutrons)
  - Skin protects us, but can be breathed into lungs
- Beta
  - Electrons
  - Can penetrate skin a few cm
  - Shield with a cm of aluminum
- Gamma
  - No mass; very damaging short wavelength radiation
  - Causes ionization, makes biological molecules unstable
  - Need a few cm of Pb for protection

Radiation

√ **Radioactive environmental problems:**

- Radon – inhalation (a particle) when gas leaks into house
- Plutonium – waste product of nuclear reactors
- Uranium and decay products (Cs, I)
- Radioactive heavy metals excavated in mines

Radiation Units

- There are several units of radiation.

- Curie (Ci)
  - Used to measure emission at source
  - 1 Ci = disintegration of 3.7×10^{10} atoms/s (Ra)

    (the disintegration rate for 1 g of Radium)

- Becquerel (Bq)
  - Same purpose, 1 Ci = 3.7×10^{10} Bq

    (Bq = 1 radioactive disintegration per second)

Radiation Units (continued)

- Roentgen (R), measures source strength
  - Gives ionizations produced in a given amount of air by X or γ rays
  - 1 R = 2.58×10^{-4} C/kg
- Rad (radiation absorbed dose), measures exposure
  - Used for exposure
  - Note, 1 Gray (Gy) = 100 rads = 1 J/kg
- Rem (roentgen equivalent man), measures effect
  - Accounts for differences in effect of radiation type
  - e.g. 10 rads of β has same rem of 1 rad of α
  - Note, 1 Sievert (Sv) = 100 rem
  - 1 Banana Equivalent Dose (BED) = 0.1 mSv (from Potassium 40)

Radiation and Decay

- Radiation and ionization are dangerous to organisms:
  - Somatic effects: cancer, sterility, cataracts
  - Genetic effects: mutation of chromosomes

- Half-Life ($t_{1/2}$)
  - Important parameter in nuclear chemistry
  - Related to decay rate.
  - 1 half-life, half of atoms decays into other elements

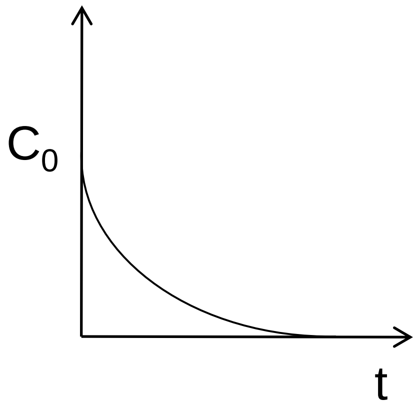
- $t_{1/2}$ ranges from 3.8 days (Rn) to 24,390 years (Pu)

Radiation and Decay (continued)

- **The decay (dC/dt) follows first-order kinetics.**

$$\frac{dC}{dt} = -kC$$

  - Integrating, $$C = C_o e^{-kt}$$



  - Rearranging, $$t = \frac{\ln\left[{}^{Co}/_{C}\right]}{k}$$

  - By definition, $$t_{1/2} = \frac{\ln[2]}{k} \text{ and } k = \frac{0.693}{t_{1/2}}$$