Nuclear Chemistry

- Up to now, we have been concerned mainly with the electrons in the elements because of their role in bonding and electrochemistry
  - the nucleus has just been a positively charged thing that attracts electrons
- The nucleus may also undergo changes
- Radioactivity results when the nucleus changes
- Radioactivity is the emission of particles or light by the nucleus

Nuclear Chemistry

- We use a special notation to describe nuclear particles:

$$^{\text{mass \#}}_{\text{atomic \#}}X$$

X is elemental symbol

The mass number=total number of protons and neutrons in the nucleus

The atomic number=the total charge of particle: for nuclei, atomic number is number of protons

Nuclear Chemistry

- Examples:

  $^{12}_{6}C$: Carbon with 6 neutrons

  $^{13}_{6}C$: Carbon with 7 neutrons

  $^{235}_{92}U$: Uranium with 143 neutrons

  $^{238}_{92}U$: Uranium with 146 neutrons
- Neutrons act as glue to hold the nucleus together
  - for the smaller elements, the ratio of neutron to proton is ~1:1
  - as size increase, the ratio of neutron to proton increases to ~ 1.5:1

Types of Radioactivity

- There are three main types of radioactive emissions

1. Alpha particles—alpha particles are simply the nucleus of helium, *i.e.*, 2 protons and 2 neutrons

   The symbol for an alpha particle is $^{4}_{2}\alpha$
2. Beta particles—beta particles are simply electrons

   The symbol for beta particles is $^{0}_{-1}\beta$
3. Gamma rays—gamma radiation consists of high energy photons

   The symbol for gamma radiation is $^{0}_{0}\gamma$

Nuclear Reactions

- We can express nuclear reactions as chemical equations just as we do other types of reactions
- Requirements:
  - Mass number and atomic number on each side of the equation must balance
  - Total charge must balance
- Differences:
  - The types of elements on each side need not be the same—nuclear reactions may change the identity of the nucleus, thus changing the elemental symbol

Nuclear Reactions

- Examples:

$${}^{238}_{92}U \longrightarrow {}^{234}_{90}Th + {}^{4}_{2}\alpha \qquad \text{alpha decay}$$

$${}^{234}_{90}Th \longrightarrow {}^{234}_{91}Pa + {}^{0}_{-1}\beta \qquad \text{beta decay}$$

$${}^{234}_{91}Pa \longrightarrow {}^{234}_{92}U + {}^{0}_{-1}\beta \qquad \text{beta decay}$$

$${}^{230}_{90}Th \longrightarrow {}^{226}_{88}Ra + {}^{4}_{2}\alpha \qquad \text{alpha decay}$$

$${}^{226}_{88}Ra \longrightarrow {}^{222}_{86}Rn + {}^{4}_{2}\alpha \qquad \text{alpha decay}$$

Nuclear Reactions

- Examples:

$$^{239}_{93}Np \longrightarrow ? + ^{0}_{-1}\beta \qquad ^{239}_{94}Pu$$

$$^{232}_{89}Ac \longrightarrow ^{228}_{87}Pa + ? \qquad ^{4}_{2}\alpha$$

$$? \longrightarrow ^{234}_{92}U + ^{0}_{0}\gamma \qquad ^{234}_{92}U$$

Nuclear Reactions

- Other types of nuclear reactions:
  - Positron emission—a positron has the same mass as an electron, but has a charge of +1

    Symbol is $^{0}_{+1}e$

    $$^{207}_{84}Po \longrightarrow ^{207}_{83}Bi + ^{0}_{+1}e$$

  - Electron capture—the nucleus captures an electron, it combines with a proton, and forms a neutron

    $$^{7}_{4}Be + ^{0}_{-1}e \longrightarrow ^{7}_{3}Li$$

Nuclear Stability

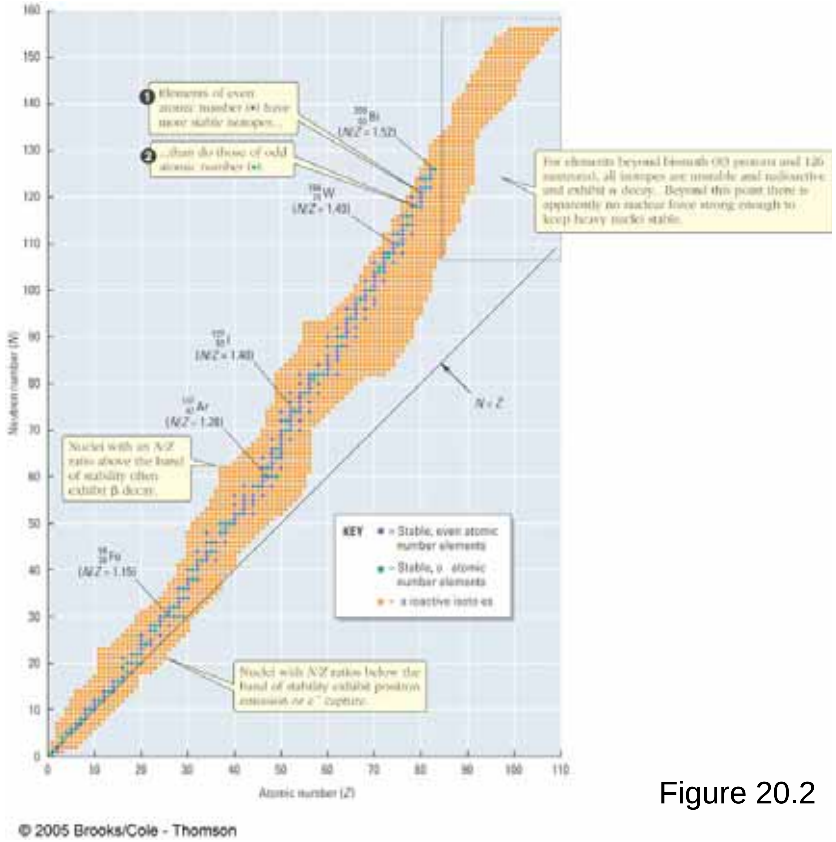

Figure 20.2

Energy of Nuclear Reactions

- Suppose a neutron decomposes into an electron and a proton:

$$ {}^{1}_{0}n \longrightarrow {}^{1}_{1}H + {}^{0}_{-1}e $$

m(neutron) = $1.67492716 \times 10^{-27}$ kg

m(proton) = $1.67262171 \times 10^{-27}$ kg

m(electron) = $9.10938188 \times 10^{-31}$ kg

$\Delta m = (1.67262171 \times 10^{-27}\ \text{kg} + 9.10938188 \times 10^{-31}\ \text{kg})$

$\quad - 1.67492716 \times 10^{-27}$ kg

$\quad = -1.39451 \times 10^{-30}$ kg

The mass of the products is less than the mass of the reactants—where did the “lost” mass go?

Energy of Nuclear Reactions

- Einstein showed, in his theory of special relativity, that mass and energy are simply different manifestations of the same fundamental quantity
- Mass and energy are related by the famous:

  $E = mc^2$

  where c = speed of light
- This relationship says that we can convert matter to energy and energy to matter

Energy of Nuclear Reactions

- For the neutron decomposition problem:

  $\Delta m = -1.39451 \times 10^{-30}$ kg

  $E = (-1.39451 \times 10^{-30} \text{ kg})(2.9979 \times 10^{8} \text{ m/s})^2$

  $= -1.2533 \times 10^{-13}$ J
- For one mole of neutrons undergoing decomposition:

  $E = -7.547 \times 10^{7}$ kJ/mol

  This much energy is released in the decomposition process—it corresponds to the “binding energy” of the nucleus

Energy of Nuclear Reactions

- For a nuclear power plant, the reaction is:

$$^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{141}_{56}Ba + {}^{92}_{36}Kr + 3\,{}^{1}_{0}n$$

<u>masses</u>

$^{235}_{92}U$ = 235.0439 g/mol

$^{141}_{56}Ba$ = 140.9144 g/mol

$^{92}_{36}Kr$ = 91.9258 g/mol

$^{1}_{0}n$ = 1.008665 g/mol

Δm = -.1864 g/mol

$E = -1.68 \times 10^{10}$ kJ/mol

Energy of Nuclear Reactions

- Comparison of reaction enthalpies:

Propane combustion: ΔH^o_{rxn} = -2044 kJ/mol

TNT explosion: ΔH^o_{rxn} = -3296 kJ/mol

$^{235}_{92}U$ fission: $\Delta H^o_{rxn} = -1.68 \times 10^{10}$ kJ/mol

Energy of Nuclear Reactions

- There are two different types of nuclear reactions used:
- Fission reactions
  - In nuclear fission, a heavy nucleus splits into lighter fragments

    $^{235}_{92}U + ^{1}_{0}n \rightarrow ^{142}_{54}Xe + ^{92}_{38}Sr + 2\ ^{1}_{0}n$
  - This reaction is initiated by bombardment of $^{235}_{92}U$ by a neutron
  - Bombardment reactions are those in which the target nucleus is hit by another particle to start a nuclear reaction

Energy of Nuclear Reactions

- There are two different types of nuclear reactions used:
- Fusion reactions
  - In nuclear fusion, two lighter nuclei are brought together to form a heavier nucleus

    $^{2}_{1}H + ^{2}_{1}H \rightarrow ^{3}_{2}He + ^{1}_{0}n$

    $^{3}_{2}He + ^{1}_{1}p \rightarrow ^{4}_{2}He + ^{0}_{+1}e$
  - Fusion reactions require tremendous temperatures in order for the nuclei to collide with sufficient energy to overcome the electrostatic repulsion of the nuclei
  - The sun is fusion reactor

Rate of Radioactive Decay

- The radioactive decay of a nucleus is a 1st order kinetic process
- The rate of decay depends on:
  1. the initial amount of material present
  2. the decay rate constant
- The expression for 1st order kinetics is:

$$[X(t)] = [X]_o \exp\{-kt\}$$

$[X]_o$ = initial concentration of X

k = rate constant

t = time

Rate of Radioactive Decay

- The half-life of a reaction, $t_{½}$:
  - time required for the concentration of X to be reduced by half

    $[X(t_{½})] = ½[X]_o$

$$[X(t_{1/2})] = 1/2[X]_o = [X]_o \exp\{-kt_{1/2}\}$$

Substitution into rate expression

$$\frac{1/2[X]_o}{[X]_o} = \frac{1}{2} = \exp\{-kt_{1/2}\}$$

Re-arrangement and cancel $[X]_o$

Rate of Radioactive Decay

$\ln\left(\frac{1}{2}\right) = \ln\left(\exp\{-kt_{1/2}\}\right)$ Take natural log of both sides

$-\ln 2 = -kt_{1/2}$ Simplify resulting expression using ln(1/2) = -ln(2)

$t_{1/2} = \frac{\ln 2}{k}$ Re-arrange, solving for half-life

The half-life depends only on the rate constant, not the initial concentration of the radioactive species

Half-lives are constant

Rate of Radioactive Decay

- The half-life of a radioactive species can be used to determine the age of a sample:

  ^{14}C has a half-life of 5.73×10^3 yr

  All living systems acquire ^{14}C from uptake of $^{14}CO_2$

  As long as the system is living, the rate of uptake remains constant, and the ratio of ^{14}C:^{12}C is constant

  When the system dies, ^{14}C is no longer incorporated in to its biomass, and the concentration of ^{14}C begins to decrease

Rate of Radioactive Decay

Suppose the ratio of ^{14}C:^{12}C is measured to be 25% of the original ratio, how old is the sample?

In one half-life, the ratio will be reduced by a factor of 2, *i.e.*, reduced by 50%

In one more half-life, the ratio will be reduced by another factor of 2 resulting in a total reduction of 75%, or 25% of the ^{14}C remains

The age of the sample is two half-lives or 11,460 years old

Rate of Radioactive Decay

<u>Example:</u> The ratio of ^{40}K to ^{40}Ar in a rock found by a fossil is 1.0085 times greater than the same ratio found in modern potassium samples. How old is the rock?

The reaction is: $^{40}_{19}K \rightarrow {}^{40}_{18}Ar + {}^{0}_{+1}e$

The half-life for this reaction is 1.13×10^{10} years

<u>Step 1:</u> determine rate constant

$k = .693/t_{1/2} = (.693)/(1.13 \times 10^{10} \text{ years})$

$= 6.13 \times 10^{-11} \text{ yrs}^{-1}$

Rate of Radioactive Decay

Step 2: set up kinetic expression

$$\frac{[^{40}Ar]}{[^{40}Ar]_o} = 1.0085 = \exp\{-(6.13 \times 10^{-11}\ yrs^{-1})\ t\}$$

Step 3: solve for t

$$t = \frac{\ln(1.0085)}{-6.13 \times 10^{-11}\ yrs^{-1}} = -1.38 \times 10^{8}\ yrs$$

The rock is 138 million years old