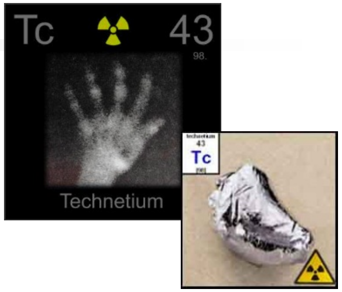
CHEMISTRY 1000



Topic #1: Atomic Structure and Nuclear Chemistry

Fall 2020

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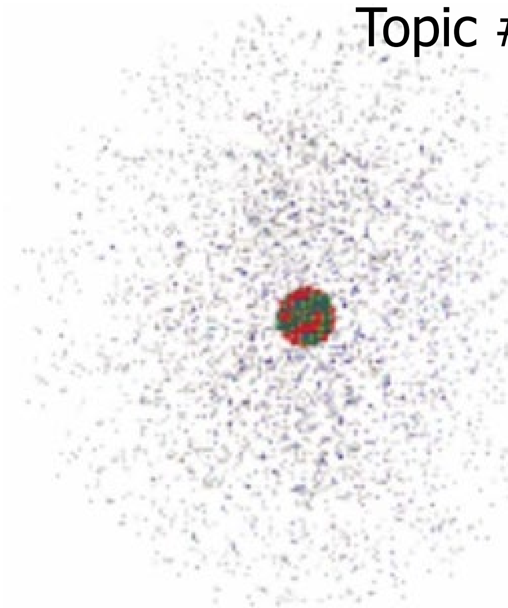
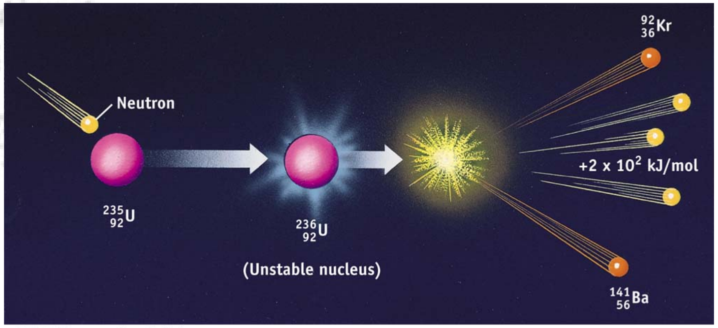
See Exercise 2.7





Measuring Radioactivity

- Earlier, we saw that radiation can be measured in terms of how much energy it carries:
    - Absorbed dose, measured in grays (1 Gy = 1 J/kg)
    - Equivalent dose, measured in sieverts (1 Sv = 1 J/kg)

- Neither of these reports the quantity of radiation, though (i.e. the number of particles carrying the energy). The same amount of energy could be carried by:
    - A single particle
    - Two particles (on average, each carrying half the energy)
    - Ten particles (on average, each carrying one tenth of the energy)
    - Thousands of particles
    - Millions of particles
    - Billions of particles
    - etc.

Measuring Radioactivity

- The quantity of radiation emitted by a radioactive sample over a given time period is determined by the sample's **activity** (A).* The unit used for activity is the becquerel (Bq):

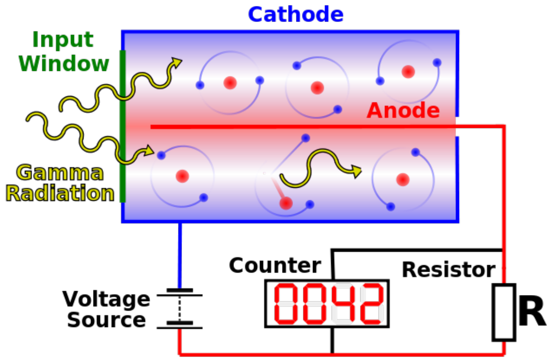
- Activity is the number of atoms decaying over a given time period:

  This is usually the same as the number of particles emitted:
  - Alpha decay produces one alpha particle per atom decaying
  - Beta decay produces one beta particle per atom decaying
  - Positron emission produces one positron per atom decaying
  - etc.

* This A (activity) should not be confused with the other A (mass number). You should be able to determine which A is relevant from context.

Measuring Radioactivity

- Not every atom in a radioactive sample decays at the same time, so we can't just calculate the number of atoms to find the activity. Instead, we measure activity experimentally:
  - A Geiger counter contains a tube of gas. Every time a particle of radiation (α, β or γ) strikes an atom of gas and ionizes it, the gas can carry a current for a very short period of time. By attaching a speaker, a click can be heard for each ionization.



  - A scintillation counter operates via a similar principle. Instead of a gas, it contains a material that fluoresces when ionized (some crystals (e.g. CsI), some plastics, some organic liquids, etc.). These flashes of fluorescence are counted.

Image from http://commons.wikimedia.org/wiki/File:Geiger_Mueller_Counter_with_Circuit-en.svg

Kinetics of Radioactive Decay

- While activity (A) is not equal to the number (N) of radioactive atoms in a sample, it is directly proportional to the number of radioactive atoms in a sample:

  What must the units be for the **decay constant** (k) relating these two terms?

- Any time the rate of a reaction is directly proportional to the amount of a single reactant, the reaction is classified as a **first order** reaction – where the order of reaction refers to the exponent applied to the amount of reactant in the rate law (rate of decay = activity = $k \times N^1$).

Kinetics of Radioactive Decay

- Both A and N change with time, so it is not practical to measure both in order to calculate k.

- How would you expect the activity of a radioactive sample to change over time? *Assume that the product is not radioactive.*

- How would your answer to the previous question differ for samples with different values for k? (i.e. larger k vs. smaller k)

Kinetics of Radioactive Decay

- A more useful approach to calculating k is to take advantage of this difference. Calculus can be used to generate the following formula describing how the number of radioactive atoms decreases with time:

  $$\boxed{N_2 = N_1 e^{-k\Delta t}}$$

  where N_2 = number of radioactive atoms after time has passed, N_1 = original number of radioactive atoms, k = decay constant and Δt = time elapsed *(sometimes written as $t_2 - t_1$)*

- Activity is directly proportional to the number of radioactive atoms (and is much easier to measure) so we can also say that:

  $$\boxed{A_2 = A_1 e^{-k\Delta t}}$$

  where A_2 = activity after time has passed, A_1 = original activity, k = decay constant and Δt = time elapsed *(sometimes written as $t_2 - t_1$)*

Kinetics of Radioactive Decay

- This equation can be rearranged to isolate k:

- More typically, the equation is shown as:

$$\boxed{ln(A_2) = ln(A_1) - k\Delta t}$$

since this resembles the standard equation for a line (x axis is time; y axis is ln(activity); slope is -k).

Or:

$$\boxed{ln\left(\frac{A_2}{A_1}\right) = -k\Delta t}$$

* These equations all have counterparts in which N is compared instead of A. After all, $A = kN$ therefore $A \propto N$!

Kinetics of Radioactive Decay

- As long as we know the activity for a sample at two different points in time, we can calculate the decay constant.

  e.g. If a sample of ^{35}S has an activity of 2.568 × 10^5 Bq at noon on January 1st and an activity of 2.279 × 10^5 Bq at noon on January 16th of the same year, what is the decay constant for ^{35}S?

Kinetics of Radioactive Decay

- If a sample has a decay constant of 2 s^{-1} and an initial activity of 400 Bq, how long will it take for the activity to reach 200 Bq?
- How long will it take for the same sample to drop from 200 Bq to 100 Bq?
- …100 Bq to 50 Bq?
- …50 Bq to 25 Bq?

Kinetics of Radioactive Decay

- Possibly because they are more intuitive than rate constants, **half-lives** are often reported for radioactive materials. A material's half-life ($t_{½}$) is literally the time it takes for half of it to decay.

- A material's half-life can be calculated from its decay constant, and its decay constant can be calculated from its half-life. The formula for doing so can be readily derived:

$$\boxed{ln\left(\frac{N_2}{N_1}\right) = -k\Delta t}$$

- Go back and calculate the half-life for ^{35}S *(p. 9 of these notes)*

Kinetics of Radioactive Decay

- A material's half-life tells us how long the sample will remain radioactive:
  - Some fission products have half-lives in the millions of years. Nuclear waste containing these isotopes requires long-term storage!
  - If a radioactive isotope is to be used for medical imaging, it must have a long enough half-life that significant amounts will remain throughout the whole imaging process – but a short enough half-life that the patient is not continually exposed to radiation for long after the test. Technetium-99m (a **m**etastable form of ^{99}Tc), used for this purpose, has a half-life of six hours.
  - Radioactive dating is possible for a variety of different timeframes, depending on the isotope chosen. e.g. Carbon dating (^{14}C; $t_{½}$=5730 years) is useful for many archaeological samples. Geological samples that are millions or billions of years old, on the other hand, are analyzed using techniques involving isotopes such as ^{235}U ($t_{½}$=704 million years), ^{238}U ($t_{½}$=4.5 billion years), ^{40}K ($t_{½}$=1.25 billion years) or ^{87}Rb ($t_{½}$=49 billion years).

Carbon Dating

- At the moment an organism dies, it has the same $^{12}C : ^{13}C : ^{14}C$ ratio as the atmosphere. From that moment on, the ^{14}C decays slowly while the ^{12}C and ^{13}C levels remain constant. Scientists can therefore use the fraction of total carbon that is ^{14}C to estimate the age of an item. At natural abundance today, ^{14}C is responsible for 0.255 Bq of radioactivity per gram total carbon.

- ^{14}C undergoes beta decay. Write a balanced equation for this reaction.

Carbon Dating

- A wooden tool has an activity of 0.195 Bq per gram total carbon. How old is the wood?

Carbon Dating

- Question 20.81 from Olmsted, Williams & Burk:
  - The amount of radioactive carbon in any once-living sample eventually drops too low for accurate dating. This detection limit is about 0.03 g^{-1} min^{-1}, whereas fresh samples exhibit a count rate of 15.3 g^{-1} min^{-1}. What is the upper limit for age determinations using carbon dating?