Chemistry 1000 Lecture 4: Kinetics of radioactive decay

Marc R. Roussel

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Measuring radioactivity

- We can detect the radiation produced by a sample and therefore count the number of decay events.

  Example: one beta particle is produced in each beta decay, so if we count the number of beta particles emitted, we have a direct measurement of the number of decays that occurred in a given time span.

- Radioactivity (A) is measured in becquerel (Bq).

  $1\,\text{Bq} = 1\,\text{decay/s}$

  $A = \frac{\text{decays}}{\text{time}} = -\frac{\Delta N}{\Delta t}$

  ΔN = change in the number of radioactive atoms in time Δt

- Older unit: curie (Ci)

  $1\,\text{Ci} = 3.7 \times 10^{10}\,\text{Bq}$

Geiger counter: Ionizing radiation (alpha, beta, gamma) ionizes a gas in a tube, making it conductive. This allows the gas to carry a current for a very short period of time. When connected to a speaker, a Geiger counter produces a click for every radioactive event.

Scintillation counter: Some materials (some crystalline materials like CsI, some plastics, some organic liquids, . . .) fluoresce briefly when ionized. The flashes of fluorescence can be counted.

Rate law

- A is a rate, i.e. an amount of change over time.
- Side note: We should really write A as a derivative: $A = -\frac{dN}{dt}$.
- A rate law is a relationship between a rate of change and the number or concentrations of chemical species in the system.
- Radioactive decay obeys a first-order rate law, meaning that the rate (A) is directly proportional to the number of reactant (radionuclide) atoms/molecules at any given time:

$$A = kN$$

  k is called a rate constant or specific activity.
  Units of A: of k:

How do we get the rate constant?

First idea: We could just write $k = A/N$ or plot A vs N.

Problem: Both A and N depend on time, and we need simultaneous values of these variables. We can measure A fairly easily, but to get N we need mass spectrometry. We can get both "simultaneously" only for very slow decay processes.

Better approach: Use calculus!

Derivation (for those of you with a bit of calculus):

$$-A = \frac{dN}{dt} = -kN$$

$$\therefore \frac{dN}{N} = -k\,dt$$

$$\therefore \int_{N_0}^{N} \frac{dN}{N} = -k \int_0^t dt$$

$$\therefore \ln N \big|_{N_0}^{N} = -k\,t\big|_0^t$$

$$\therefore \ln N - \ln N_0 = -k(t - 0)$$

$$\therefore \ln\left(\frac{N}{N_0}\right) = -kt$$

$$\therefore \frac{N}{N_0} = e^{-kt}$$

$$\therefore N = N_0 e^{-kt}$$

Result:

$$N = N_0 e^{-kt} \tag{1}$$

where N_0 is the initial number of radioactive atoms, and e is Napier's number.
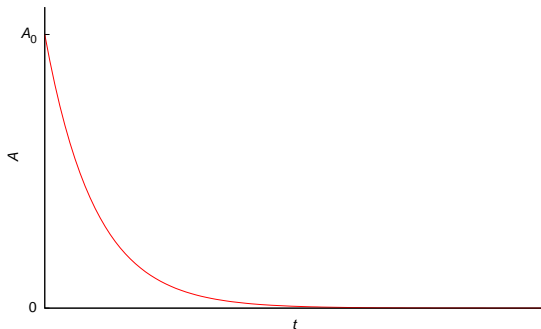
On your calculator, the function e^x might be labeled as either e^x or exp.

Note 1: Equation (1) shows that N decays exponentially.

Note 2: Since $A \propto N$, $A = A_0 e^{-kt}$.

We can therefore work with the easily measured radioactivity instead of N.

Exponential decay

Note: No easy, accurate way to get k from this graph.

Mathematical interlude: the exponential function and natural logarithm

- e^x and $\ln x$ are inverse functions, i.e.

$$e^{\ln x} = x = \ln(e^x)$$

- $\ln(ab) = \ln a + \ln b$

- $\ln(a/b) = \ln a - \ln b$

- $\ln x = -\ln(1/x)$

Example: ^{35}S decay

^{35}S is a beta emitter. In one experiment, the following radioactivity measurements were obtained: $A = 4280\,\text{dpm}$ at $t = 0$, and $A = 3798\,\text{dpm}$ at $t = 15\,\text{d}$. Find k.

Note: dpm = disintegrations per minute

Answer: $k = 7.965 \times 10^{-3}\,\text{d}^{-1}$

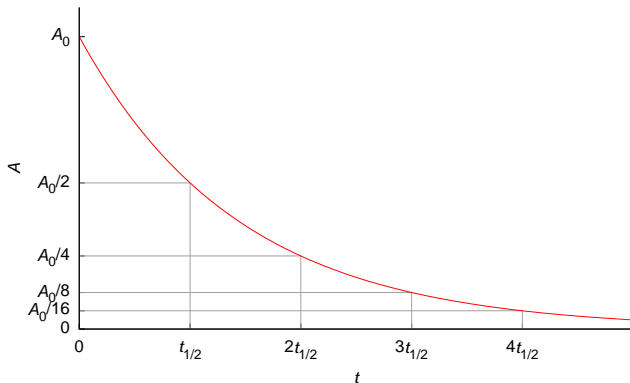What if we had two points, both at times different from zero?

- Physical laws do not depend on what point in time we arbitrarily label zero.
- Shift the time origin to the earlier of the two times.
- In other words, use Δt instead of t.

Half-life

$$\frac{A}{A_0} = e^{-kt}$$

- Note that the fraction by which A decreases in a fixed time t is independent of A_0.
- It should take the same amount of time to go from (e.g.) 1000 Bq to 500 Bq as it does to go from 200 Bq to 100 Bq.
- The time it takes for the number of radioactive atoms to be reduced by half is called the half-life, denoted $t_{1/2}$.

Half-life (continued)

At $t = t_{1/2}$, $\dfrac{A}{A_0} = \dfrac{1}{2}$.

$$\frac{A}{A_0} = e^{-kt}$$

$$\therefore \frac{1}{2} = e^{-kt_{1/2}}$$

$$\therefore \ln\left(\frac{1}{2}\right) = -kt_{1/2}$$

$$\therefore -\ln 2 = -kt_{1/2}$$

$$\therefore t_{1/2} = \frac{\ln 2}{k}$$

Two equivalent formulas

$$A = A_0 e^{-kt}$$

$$A = A_0 \left(\frac{1}{2}\right)^{t/t_{1/2}}$$

(The proof is elementary, but involves the change-of-base formula.)

Example: half-life of ^{35}S

We had previously found $k = 8.0 \times 10^{-3}\,\text{d}^{-1}$.

$$t_{1/2} = \frac{\ln 2}{k} = \frac{\ln 2}{8.0 \times 10^{-3}\,\text{d}^{-1}} = 87\,\text{d}$$

Why do we care about the half-life?

- Radioisotopes with long half-lives will be radioactive for a long time and pose a disposal problem.
- In medical imaging, we want radioisotopes with half-lives that are long enough for the imaging to be completed, but short enough not to become a long-term health hazard to the patient and his/her friends and relatives.
- Radioactive dating

^{14}C dating

- Percentage of ^{14}C in atmosphere fixed by a balance of its rate of production by cosmic-ray neutron bombardment and its rate of decay:

$$^{14}_{7}N + ^{1}_{0}n \longrightarrow ^{14}_{6}C + ^{1}_{1}H$$
$$^{14}_{6}C \longrightarrow ^{14}_{7}N + ^{0}_{-1}\beta$$
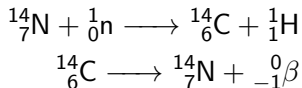
- Plants make sugars from atmospheric CO_2, so their percentage ^{14}C is the same as in the atmosphere.
- Animals eat plants or other animals, so they too have the same percentage ^{14}C as the atmosphere.
- At natural abundance, ^{14}C is responsible for 0.255 Bq of radioactivity per gram of total carbon.
- Half-life of ^{14}C: 5730 y

Example

A wooden tool has a radioactivity of 0.195 Bq per gram of carbon. How old is it?

$$t = \frac{1}{k} \ln \left(\frac{A_0}{A} \right) \qquad \text{(Derive)}$$

$$k = \frac{\ln 2}{t_{1/2}}$$

$$= \frac{\ln 2}{5730 \, \text{y}}$$

$$= 1.210 \times 10^{-4} \, \text{y}^{-1}$$

$$t = \frac{1}{1.210 \times 10^{-4} \, \text{y}^{-1}} \ln \left(\frac{0.255 \, \text{Bq}}{0.195 \, \text{Bq}} \right)$$

$$= 2218 \, \text{y}$$

Choosing an isotope

- All radioisotope dating methods are based on measuring either the radiation (as in ^{14}C dating) or the relative amounts of isotopes that are part of a decay chain.
- Eventually, the amount of a radioisotope drops to negligible levels. The isotope is not useful for dating items older than the time it takes for this to happen.
- How long this takes depends on
  - half-life
  - initial activity
- If we try to date very young objects, not enough decay has occurred to distinguish the decrease from natural variability in isotopic composition.
- For ^{14}C, the useful range is about 200–60 000 y ($\frac{1}{30}$–10 times the half-life).

Other isotopes used for dating

Isotope	$t_{1/2}$	Application(s)
^{235}U	7.038×10^8 y	} rocks (crosscheck)
^{238}U	4.468×10^9 y	
^{230}Th	$75\,380$ y	} sedimentary deposits (ratio)
^{231}Pa	$34\,300$ y	