Chemistry 1000 Lecture 4:
Kinetics of radioactive decay

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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).
  
  \[
  1 \text{ Bq} = 1 \text{ decay/s}
  \]
  
  \[
  A = \frac{\text{decays}}{\text{time}} = -\frac{\Delta N}{\Delta t}
  \]
  
  $\Delta N$ = change in the number of radioactive atoms in time $\Delta t$

- 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 $k$: 
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):

\[-A = \frac{dN}{dt} = -kN\]

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

\[\therefore \int_{N_0}^{N} \frac{dN}{N} = -k \int_{0}^{t} dt\]

\[\therefore \ln N \bigg|_{N_0}^{N} = -k \left. t \right|_{0}^{t}\]

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

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

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

\[\therefore N = N_0 e^{-kt}\]
Result:

\[ N = N_0 e^{-kt} \]  \hspace{1cm} (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 \( \text{exp} \).

**Note 1:** Equation (1) shows that \( N \) decays \textit{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: $^{35}\text{S}$ decay

$^{35}\text{S}$ 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 $\Delta t$ 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)

A sequence of horizontal lines labeled $A_0/16$, $A_0/8$, $A_0/4$, and $A_0/2$ decreases exponentially as $t$ increases by $t_{1/2}$ intervals. The graph shows the decay of radioactive material over time.
At \( t = t_{1/2} \), \( \frac{A}{A_0} = \frac{1}{2} \).

\[
\frac{A}{A_0} = e^{-kt}
\]
\[
\frac{1}{2} = e^{-kt_{1/2}}
\]
\[
\therefore \ln \left( \frac{1}{2} \right) = -kt_{1/2}
\]
\[
\therefore -\ln 2 = -kt_{1/2}
\]
\[
\therefore t_{1/2} = \frac{\ln 2}{k}
\]
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 $^{35}\text{S}$

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:

  $^{14}_7\text{N} + {}^0_0\text{n} \rightarrow ^{14}_6\text{C} + ^1_1\text{H}$

  $^{14}_6\text{C} \rightarrow ^{14}_7\text{N} + ^0_1\beta$

- 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?

\[ t = \frac{1}{k} \ln \left( \frac{A_0}{A} \right) \]  

(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

<table>
<thead>
<tr>
<th>Isotope</th>
<th>( t_{1/2} ) ( \times 10^n ) y</th>
<th>Application(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{235})U</td>
<td>7.038 \times 10^8 , y</td>
<td>rocks (crosscheck)</td>
</tr>
<tr>
<td>(^{238})U</td>
<td>4.468 \times 10^9 , y</td>
<td>sedimentary deposits (ratio)</td>
</tr>
<tr>
<td>(^{230})Th</td>
<td>75 380 , y</td>
<td></td>
</tr>
<tr>
<td>(^{231})Pa</td>
<td>34 300 , y</td>
<td></td>
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