Chemical Kinetics

- Thermodynamics can describe the final equilibrium position, but not how fast this situation will be achieved.

- Chemical kinetics is the science of the rates and mechanisms of chemical reactions.

- For a general reaction

\[ aA + bB \rightarrow cC + dD \]

the rate is defined as

\[ \frac{-1}{a} \frac{d[A]}{dt} = \frac{-1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt} \]

- The rate law for a reaction expresses the dependence of the rate on the concentrations of the reactants.
What does the reaction rate depend on?

The rate of a chemical reaction depends on five features of the reaction:

1. The **nature** of the reactants.

   (For example, ionic reactions may be very fast, breaking strong bonds may cause a slow reaction.)

2. The **effective concentrations** of reactants.

3. The **temperature**.

   (Most reactions go faster at higher temperature.)

4. The presence of a **catalyst**.

   (Usually a catalyst speeds up a reaction. A good example: enzymes.)

5. The **phase** of the reaction.

   (Solid, liquid, and gas phase reactions occur.)
Rate law expressions

- For some reactions the rate law can be expressed in the simple form

\[
\text{rate} = k \ [A]^m[B]^n
\]

where \( k = k(T) \) is the "rate constant" for the reaction. The exponents \( m \) and \( n \) are the orders of the reaction with respect to reactants \( A \) and \( B \), respectively. The overall order of the reaction is \( (m + n) \).

- It is important to understand that the rate law expression comes from experiment. It is not necessarily related to the stoichiometric expression for the reaction.

- Note that \( k \) will vary with temperature. The units of \( k \) will depend on the order of the reaction.

- Many reactions cannot be described by the simple rate law expression above.

- The rate law expression can help us to decide upon the mechanism of the reaction.
First Order reactions

- The rate law expression for a first-order reaction is

\[- \frac{d[A]}{dt} = k[A]\]

- Examples include nuclear decays, some isomerizations and some decompositions.

- To integrate the rate law expression we rearrange it:

\[\frac{d[A]}{[A]} = -k \, dt\]

Thus \[\int d[A]/[A] = -k \int dt.\]

- Integration from \([A]_0\) to \([A]\) and 0 to \(t\) yields

\[\ln[A] - \ln[A]_0 = -kt\]

So that

\[[A] = [A]_0 e^{-kt}\]
Carbon-14 Dating

- First proposed by the American chemist Willard Libby, Univ. of Chicago, in the 1950s. Awarded the Nobel Prize in Chemistry, 1960.

- Cosmic rays striking nitrogen atoms in the Earth's atmosphere cause the reaction

\[ {}^{14}\text{N} + {}^{1}\text{n} \rightarrow {}^{14}\text{C} + {}^{1}\text{H} \]

- The $^{14}\text{C}$ becomes incorporated into $\text{CO}_2$, which in turn is taken up by living plants.

- The $^{14}\text{C}$ decays by first-order kinetics

\[ {}^{14}\text{C} \rightarrow {}^{14}\text{N} + \text{e}^- \]

with a half-life of 5730 yr.

- So long as the plants are alive a steady-state of $^{14}\text{C}$ incorporation and decay is maintained, but upon death uptake of $^{14}\text{C}$ ceases.

- The age of an artifact can be estimated by measuring the relative amount of $^{14}\text{C}$ in the sample. Good for 1000-50,000 yr.
• Carbon has several isotopes with the following abundances and half-lives:

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Abundance</th>
<th>Half-life</th>
<th>Decay</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbon-9</td>
<td>0.1265 s</td>
<td>β⁺ 2α</td>
<td></td>
</tr>
<tr>
<td>carbon-10</td>
<td>19.2 s</td>
<td>β⁺</td>
<td></td>
</tr>
<tr>
<td>carbon-11</td>
<td>20.38 min</td>
<td>β⁺</td>
<td></td>
</tr>
<tr>
<td>carbon-12</td>
<td>98.89%</td>
<td>stable</td>
<td></td>
</tr>
<tr>
<td>carbon-13</td>
<td>1.11%</td>
<td>stable</td>
<td></td>
</tr>
<tr>
<td>carbon-14</td>
<td>ppm</td>
<td>5730 y</td>
<td>β⁻</td>
</tr>
<tr>
<td>carbon-15</td>
<td>2.449 s</td>
<td>β⁻</td>
<td></td>
</tr>
<tr>
<td>carbon-16</td>
<td>0.75 s</td>
<td>β⁻</td>
<td></td>
</tr>
</tbody>
</table>

• Since \( x = x_0 e^{-kt} \) we can calculate the age from the ratio \( x/x_0 \). The half-life is given by \( t_{1/2} = \ln 2/k_\), so \( k = \ln(2)/t_{1/2} = 0.693/5730 \text{ y} = 1.21\times10^{-4}/\text{y} \). Thus \( t = -\ln(x/x_0)/k \).

• Consider a sample that exhibits 63\% of the \(^{14}\text{C}\) radioactivity of a fresh sample. Then

\[
t = \left[ \frac{\ln(0.63)}{1.21\times10^{-4}} \right] \text{y} = 3820 \text{ y}
\]
Other Dating Techniques

• Uranium-238 has a half-life of $4.5 \times 10^9$ years. $^{238}\text{U}$ decays through several intermediates to form lead-206 ($^{206}\text{Pb}$).

---Assume that rocks start with only $^{238}\text{U}$ and no $^{206}\text{Pb}$. Then measure the ratio of $^{238}\text{U}/^{206}\text{Pb}$. Analysis of this gives the age of the rock if your assumption is correct.

---Note that “normal” lead is lead-208, which will be present if other processes caused lead in the rocks.

• Potassium-argon dating of rocks: When $^{40}\text{K}$ decays to $^{40}\text{Ar}$ in rocks the $^{40}\text{Ar}$ is trapped. Potassium-40 has a half-life of $1.25 \times 10^9$ years. Assuming all the $^{40}\text{Ar}$ detected comes from $^{40}\text{K}$ decay, one can date a rock sample.

Some other methods: Thermoluminescence, fission track dating, amino acid racemization, etc.
First-Order decay

- The half-life is the time it takes for one half of the initial material to disappear. It is given by $t_{1/2} = \ln(2)/k$.

  ![Graph showing the decay of A over time with half-life indicated]

  - To derive the $t_{1/2}$ formula plug in $[A] = 0.5[A]_0$ and solve for $t$

  - For a first-order decay the half-life is independent of the starting time.

- The most useful way to plot the data for this case is $\ln[A]$ vs. $t$:

  $\ln[A] = \ln[A]_0 - kt$

  ![Graph showing ln[A] vs. t with slope indicated]