A Radioactivity Example

\[ ^{14}_{6}\text{C} \rightarrow ^{14}_{7}\text{N} + e^- \]

Carbon-14 is unstable. It decays very slowly by a process called beta-decay.

A beta particle is an electron. It is ejected from the nucleus. In the process a neutron becomes a proton.

The rate that Carbon-14 decays is an inherent property of the nucleus. Thus the rate of decay is proportional to the number of \(^{14}\text{C}\) atoms present.

\[- \frac{d\left[^{14}\text{C}\right]}{dt} = k \left[^{14}\text{C}\right] \]

It is a perfect example of a first order reaction.

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

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

\[ \int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = -k \int_0^t dt \]

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

\[ \ln \frac{[A]_t}{[A]_0} = -kt \]

\[ [A]_t = [A]_0 e^{-kt} \]

when \([A]_t = 0.5 \ [A]_0\)

\[ 0.5 = e^{-kt} \]

\[ \ln 0.5 = -kt \]

\[ 0.693/k = t_{1/2} \]

For \(^{14}\text{C}\)

\[ t_{1/2} = 5730 \ \text{y} \]
A standard sample of Carbon from a modern day plant gave 15.3 counts per minute per gram of Carbon. A sample from an archeological site gave 4.5 counts per minute. How old is the sample?

For $^{14}$C

\[
\frac{0.693}{k} = t_{1/2}
\]

\[
\ln \left( \frac{[A]_t}{[A]_0} \right) = -kt
\]

\[
t_{1/2} = 5730 \text{ y}
\]

\[
k = \frac{0.693}{5730} \text{ yeats} = 1.21 \times 10^{-4} \text{ year}^{-1}
\]

\[
\ln \left( \frac{4.5}{15.3} \right) = -1.224 = -1.21 \times 10^{-4} \text{ year}^{-1} \times t
\]

\[
t = 10100 \text{ years}
\]

 Decomposition of $\text{N}_2\text{O}_5$ in $\text{CCl}_4$ solution

\[2\text{N}_2\text{O}_5 (\text{soln}) \rightarrow 4\text{NO}_2(\text{soln}) + \text{O}_2 (\text{g})\]

Rate determining step is:

\[
\begin{align*}
\text{NO}_2^\cdot & \overset{+}{\rightarrow} \text{NO}_2^+ + \text{O}_2^-
\end{align*}
\]

First order reaction
Second order reaction
\[ \frac{1}{[A]_t} - \frac{1}{[A]_0} = kt \]

First order reaction
\[ \ln[A]_t = -kt + \ln[A]_0 \]

2 \( \text{C}_4\text{H}_6(g) \rightarrow \text{C}_8\text{H}_{12}(g) \)

Predict the product
What is the order of the reaction?

1st order
\[ \ln[A]_t = -kt + \ln[A]_0 \]

2nd order
\[ \frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \]

Zero order
\[ -\frac{d[A]}{dt} = k[A]^0 = k \]
\[ d[A] = -k \, dt \]
\[ \int d[A] = -k \int dt \]
\[ [A]_t = -kt + [A]_0 \]
Zero order

\[ [A]_t = -kt + [A]_0 \]

The rate does not depend on any reactant!

For this to be true something else must be determining the rate.

A catalyst for example

\[ 2N_2O (g) \rightarrow 2N_2 (g) + O_2 (g) \]

The rate depends only on the surface area of the Pt not on the concentration of N₂O

Second order reaction

\[ \frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \]

First order reaction

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

Zero order reaction

\[ [A]_t = -kt + [A]_0 \]

Consider the famous reaction.

\[ A + B \rightarrow C + D \]

Assume the reaction in both directions is first order in each reactant

\[ \text{Rate}_{\text{forward}} = k_f [A][B] \]
\[ \text{Rate}_{\text{reverse}} = k_r [C][D] \]

High [A] or [B] favor fast forward reaction

High [C] or [D] favor fast reverse reaction

At some set of concentrations the rates will be equal.

When the forward and reverse reactions occur at the same rate there will be no change in concentrations.
\[
A + B \rightleftharpoons C + D
\]
This is equilibrium.
The forward and reverse rates are the same at equilibrium.
\[
\text{Rate}_{\text{forward}} = k_f [A][B] = \text{Rate}_{\text{reverse}} = k_r [C][D]
\]
\[
k_f [A][B] = k_r [C][D]
\]
\[
\frac{k_f}{k_r} = \frac{[C][D]}{[A][B]} = K_{\text{equil}}
\]

The equilibrium constant is determined by the relative forward and reverse rates.

The rate law does not necessarily reflect the stoichiometry of the reaction.

\[
\text{NO}_2(g) + \text{CO(g)} \rightarrow \text{NO(g)} + \text{CO}_2(g)
\]
Rate = \(k[\text{NO}_2]^2\)

What mechanism can explain this?

\[
\begin{align*}
\text{NO}_2(g) + \text{NO}_2(g) &\rightarrow \text{NO}_3(g) + \text{NO}(g) \\
\text{NO}_3(g) + \text{CO(g)} &\rightarrow \text{NO}_2(g) + \text{CO}_2(g)
\end{align*}
\]

Reactions that start with a fast equilibrium

\[
2\text{O}_3(g) \rightarrow 3\text{O}_2(g)
\]
Rate = \(k\frac{[\text{O}_3]^2}{[\text{O}_2]}\)

How can you explain this? Why is \([\text{O}_2]\) in the rate?
Energy distribution of molecules versus Temperature

\[ E_d - \frac{E_a}{RT} \]

As \(-E_a/RT\) approaches zero the Fraction of Collisions with Energy > \(E_a\) approaches unity.

This would happen at high T or low \(E_a\)
Fraction of Collisions with Energy > $E_a$:

$$e^{-E_a/RT}$$

- Pre-exponential factor.
- Fraction of collisions with proper steric orientation

Arrhenius Equation:

$$k = Ae^{-E_a/RT}$$

$$\ln(k) = -\frac{E_a}{RT} + \ln(A)$$

Arrhenius Equation:

$$k = Ae^{-E_a/RT}$$

$$\ln(k) = -\frac{E_a}{RT} + \ln(A)$$

Slope = $-\frac{E_a}{R}$

$E_a = -R \times (1.2 \times 10^4)K$

$E_a = 8.31J/K \times (1.2 \times 10^4)K$

$E_a = 100 \text{ kJ/mol}$

\[
\begin{array}{|c|c|c|c|c|}
\hline
\text{T (°C)} & \text{T (K)} & \frac{1}{T (K)} & \ln(k) & k (s^{-1}) \\
\hline
20 & 293 & 3.41 \times 10^{-3} & -10.82 & 2.0 \times 10^{-3} \\
30 & 303 & 3.30 \times 10^{-3} & -9.53 & 7.5 \times 10^{-3} \\
40 & 313 & 3.19 \times 10^{-3} & -8.22 & 2.7 \times 10^{-3} \\
50 & 323 & 3.10 \times 10^{-3} & -7.00 & 9.1 \times 10^{-4} \\
60 & 333 & 3.00 \times 10^{-3} & -5.84 & 2.9 \times 10^{-3} \\
\hline
\end{array}
\]

$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

$\ln(k_1) = -\frac{E_a}{RT_1} + \ln(A)$

$\ln(k_2) = -\frac{E_a}{RT_2} + \ln(A)$

$\ln(k_2/k_1) = \frac{E_a}{R}(\frac{1}{T_1} - \frac{1}{T_2})$

Assume $E_a = 100 \text{ kJ/mol}$ and $T = 300 K$

What temperature would be required to double the rate?

$$T_2 = \ ? \ K$$
\[
\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)
\]
Assume \( E_a = 100 \text{ kJ/mol} \) and \( T = 300 \text{ K} \)

\[
\ln(2) = \frac{10^5}{R} \left(\frac{1}{300} - \frac{1}{T_2}\right)
\]

\[
5.8 \times 10^{-5} = \frac{1}{300} - \frac{1}{T_2}
\]

\( T_2 = 305 \text{ K} \)

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**Catalysis**

A catalyst changes the mechanism of a reaction to one with a lower energy of activation.

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Try to find a new mechanism with a lower \( E_a \).

How do you do that? Use a catalyst.

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Amide hydrolysis

\[
\begin{align*}
\text{R} - \text{N} - \text{H} & \quad \text{H}_2\text{O} \\
\downarrow & \\
\text{H} & \quad \text{H} \\
\text{O} & \quad \text{H} \\
\end{align*}
\]

---

Water is too slow.

---

\[
\begin{align*}
\text{R} - \text{O} - \text{H} & \quad \text{R} - \text{O} - \text{H} \\
\downarrow & \\
\text{H} & \quad \text{H} \\
\text{O} & \quad \text{H} \\
\end{align*}
\]

---

\[
\begin{align*}
\text{R} - \text{N} - \text{H} & \quad \text{NH}_3\text{R} \\
\downarrow & \\
\text{H}_2\text{O} & \\
\end{align*}
\]

---

Water is too slow.

---

\[
\begin{align*}
\text{R} - \text{O} - \text{H} & \quad \text{R} - \text{O} - \text{H} \\
\downarrow & \\
\text{H} & \quad \text{H} \\
\text{O} & \quad \text{H} \\
\end{align*}
\]
Uncatalyzed reaction very slow.

Acid or base catalyzed reaction faster, but still requires high temperature and long time and it is unselective.

Enzymes can do it very fast at body temperature.

\[
\begin{align*}
\text{Carboxypeptidase-A Enzyme} \\
\text{Zn} \\
\end{align*}
\]

\[
\begin{align*}
\text{Carboxypeptidase-A Enzyme} \\
\end{align*}
\]

\[
\begin{align*}
S_N^2 \text{ reaction} \\
\frac{\text{Rate}}{d \text{t}} = \frac{-d [\text{CH}_3\text{Br}]}{d \text{t}} = k [\text{CH}_3\text{Br}] [\text{-OH}] \\
\text{This is a bimolecular reaction, first order in each reactant. Second order overall.} \\
\text{Can you integrate such an equation?} \\
\text{Sure, but it is too complicated for us.} \\
\text{So how can you study it?} \\
\end{align*}
\]

\[
\begin{align*}
\text{Rate} = & \frac{-d [\text{CH}_3\text{Br}]}{d \text{t}} = k [\text{CH}_3\text{Br}] [\text{-OH}] \\
\text{To study the effect of [CH}_3\text{Br} use a large excess of -OH. Thus [-OH] will be effectively constant.} \\
\text{If [-OH] >> [CH}_3\text{Br] then k [-OH] = k'} \\
\frac{-d [\text{CH}_3\text{Br}]}{d \text{t}} = k' [\text{CH}_3\text{Br}] \\
\text{Pseudo first order reaction in [CH}_3\text{Br]}
\end{align*}
\]
Rate = $\frac{-d [\text{CH}_3\text{Br}]}{d t} = k [\text{CH}_3\text{Br}] [\cdot \text{OH}]$

The to study the effect of [OH] use a large excess of CH₃Br. Now [CH₃Br] will be effectively constant.

If [CH₃Br] >> [·OH] then $k [\text{CH}_3\text{Br}] = k''$

$-\frac{d [\cdot \text{OH}]}{d t} = k'' [\cdot \text{OH}]$

Pseudo first order reaction in [·OH]