Differential and integrated rate laws

Consider A → B:  a) 0th Order

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

Differential rate law

\[d[A] = -k \, dt \quad \Rightarrow \quad \int d[A] = -k \int_0^t dt \]

\[[A](t) = [A]_0 - kt\]

Integrated rate law

b) 1st Order

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

Differential rate law

\[\int \frac{d[A]}{[A]} = -k \int_0^t dt \quad \Rightarrow \quad [A](t) = [A]_0 e^{-kt}\]

Integrated rate law

\[\ln[A](t) - \ln[A]_0 = \ln\left(\frac{[A](t)}{[A]_0}\right) = -kt\]
Differential and integrated rate laws of a second order reaction

c) 2nd Order

\[-\frac{d[A]}{dt} = k[A]^2\]

Differential rate law

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

Integrated rate law

\[
\frac{1}{[A](t)} = k t + \frac{1}{[A]_0}
\]

\[
[A](t) = \frac{[A]_0}{1 + k t [A]_0}
\]
The half-life of a reaction

Half-Life of a Reaction:
The time required for $[A]$ to drop by a factor of two

$0^{th}$ Order: $[A](t) = -kt + [A]_0$
$[A]_0/2 = -kt_{1/2} + [A]_0$

$kt_{1/2} = [A]_0 - [A]_0/2$
$\Rightarrow t_{1/2} = \frac{[A]_0}{2k}$

$1^{st}$ Order: $[A](t) = [A]_0 e^{-kt}$
$[A]_0/2 = [A]_0 e^{-kt_{1/2}}$

$e^{-kt_{1/2}} = 1/2$
$\Rightarrow t_{1/2} = \frac{\ln2}{k}$

Independent of $[A]_0$!

$2^{nd}$ Order: $\frac{1}{[A](t)} = kt + \frac{1}{[A]_0}$
$\frac{2}{[A]_0} = kt_{1/2} + \frac{1}{[A]_0}$
$kt_{1/2} = \frac{2}{[A]_0} - \frac{1}{[A]_0}$
$\Rightarrow t_{1/2} = \frac{1}{k[A]_0}$
# Summary of rate laws

## Differential Rate Law

### $0^{\text{th}}$ Order:
\[
- \frac{d[A]}{dt} = k
\]

### $1^{\text{st}}$ Order:
\[
- \frac{d[A]}{dt} = k[A]
\]

### $2^{\text{nd}}$ Order:
\[
- \frac{d[A]}{dt} = k[A]^2
\]

## Integral Rate Law

### $0^{\text{th}}$ Order:
\[
[A](t) = [A]_0 - kt
\]

### $1^{\text{st}}$ Order:
\[
[A](t) = [A]_0 e^{-kt}
\]

### $2^{\text{nd}}$ Order:
\[
\frac{1}{[A](t)} = kt + \frac{1}{[A]_0}
\]

## Half-Life

### $0^{\text{th}}$ Order:
\[
t_{\frac{1}{2}} = \frac{[A]_0}{2k}
\]

### $1^{\text{st}}$ Order:
\[
t_{\frac{1}{2}} = \frac{\ln2}{k}
\]

### $2^{\text{nd}}$ Order:
\[
t_{\frac{1}{2}} = \frac{1}{k[A]_0}
\]
Tricks to determine rate laws

Consider \( A \rightarrow B \):

- **0th Order:**
  \[
  [A](t) = -kt + [A]_0
  \]

- **1st Order:**
  \[
  \ln[A](t) = -kt + \ln[A]_0
  \]

- **2nd Order:**
  \[
  \frac{1}{[A](t)} = kt + \frac{1}{[A]_0}
  \]

Consider \( A + B \rightarrow C \):

- **2nd Order:**
  \[
  -\frac{d[A]}{dt} = k[A][B]
  \]

**BUT** by:

- a) choosing \([A]_0 = [B]_0\)
  \[
  \Rightarrow [A] = [B]!
  \]

- b) choosing \([A]_0 \ll [B]_0\)
  \[
  \Rightarrow [B] \approx \text{constant}!
  \]

\[
-\frac{d[A]}{dt} = k'[A]; \quad k' = k[B]_0
\]
Sample Problem:

Consider: \( \text{CH}_3\text{CH}_2\text{NO}_2 + \text{OH}^- \rightarrow \text{CH}_3\text{CHNO}_2^- + \text{H}_2\text{O} \)

Initially \( [\text{CH}_3\text{CH}_2\text{NO}_2] = [\text{OH}^-] = 5.00 \times 10^{-3} \text{ M} \). The concentration of hydroxide was then measured by monitoring the pH with the following result.

What is the order of the reaction? What is \( k \)?

<table>
<thead>
<tr>
<th>( t ) (min)</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>( [\text{OH}^-] ) (M)</td>
<td>5.00 \times 10^{-3}</td>
<td>2.6 \times 10^{-3}</td>
<td>1.7 \times 10^{-3}</td>
<td>1.3 \times 10^{-3}</td>
</tr>
<tr>
<td>( [\text{OH}^-]^{-1} )</td>
<td>200</td>
<td>385</td>
<td>588</td>
<td>769</td>
</tr>
</tbody>
</table>

The most reasonable initial guess for this reaction is:

\[
-\frac{d[\text{OH}^-]}{dt} = k [\text{OH}^-][\text{CH}_3\text{CH}_2\text{NO}_2] = k [\text{OH}^-]^2
\]

Good line (\( r = 0.9998 \)) \( \Rightarrow \) correct rate law

**slope** = \( k = 0.637 \text{ M}^{-1} \text{ s}^{-1} \)

\[
\frac{1}{[\text{OH}^-]} = kt + \frac{1}{[\text{OH}^-]_0}
\]