Kinetics II

Silberberg 2nd Ed, Chapter 16
www.chem.usyd.edu.au/hpage3.htm (login “chem”, passwd “chem@usyd”)

Any questions or requests - email to c.kepert@chem.usyd.edu.au
Rate (speed) of reaction = \( \frac{d(\text{concentration})}{d(\text{time})} \)
For \( aA + bB \rightarrow cC \ldots \),

\[
\text{Rate} = k \ [A]^x \ [B]^y \ \ldots
\]

where \( x, y \) can have any value (0, 1, \(-1/2\) \ldots).

Exponent of \([A]\) (ie value of \(x\))

\[
\Rightarrow \text{order of reaction with respect to A}
\]

\[
= 1, \text{ first order in A,}
\]

\[
= 2, \text{ second order in A,} \ldots
\]

\[
k = \text{rate coefficient (or “rate constant”)}
\]

Units of \( k \) depend on order of reaction
Elementary Reactions

* Occur in a single collision

* Have simple rate laws which follow stoichiometry:

\[ A \rightarrow \text{products} \quad \text{unimolecular} \quad \text{Rate} = k [A] \]

\[ \text{Cl}_2 \rightarrow \text{Cl} + \text{Cl} \]

\[ A + A \rightarrow \text{products} \quad \text{bimolecular} \quad \text{Rate} = k[A][A] \]

\[ \text{Cl} + \text{Cl} \rightarrow \text{Cl}_2 \]

\[ A + B \rightarrow \text{products} \quad \text{bimolecular} \quad \text{Rate} = k[A][B] \]

\[ \text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{Cl} \]
Example

For reaction $A \rightarrow \text{product}$,

Initial rates:

<table>
<thead>
<tr>
<th>initial $[A]$ / M</th>
<th>Rate / M s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>5.0</td>
</tr>
<tr>
<td>0.20</td>
<td>10.0</td>
</tr>
</tbody>
</table>
## Harder Example

For reaction $A + 3B \rightarrow \text{product}$

<table>
<thead>
<tr>
<th></th>
<th>initial [A] / M</th>
<th>initial [B] / M</th>
<th>initial rate R / M s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.10</td>
<td>1.0</td>
<td>5.0</td>
</tr>
<tr>
<td>2</td>
<td>0.14</td>
<td>1.0</td>
<td>10.0</td>
</tr>
<tr>
<td>3</td>
<td>0.14</td>
<td>0.5</td>
<td>5.0</td>
</tr>
</tbody>
</table>
For the reaction \{A \rightarrow \text{products}\} obeying the 1\textsuperscript{st}-order rate law:

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

- Solve this differential equation by integrating both sides:

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

\[
\ln[A(t)] = -kt + \ln[A(t = 0)]
\]

ie \[A(t)] = [A(t = 0)] e^{-kt}\]
**First Order: \( \ln[A] \) vs Time**

Plot of \( \ln[A] \) as function of time:

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

**Half-life:** time \( \left( t_{\frac{1}{2}} \right) \) for half of initial concentration to disappear
Half Life for a First Order Reaction

\[ [A(t_{1/2})] = \frac{1}{2} [A(t = 0)] \]

For 1st-order reactions we have the relation:

\[ [A(t)] = [A(t = 0)] e^{-kt} \]

\[ \iff \frac{1}{2} = \exp\left[-kt_{1/2}\right] \]

- Half Life is independent of initial concentration
- Solutions also exist for second-order reactions...
Half Life for a First Order Reaction

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>[A] (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.00</td>
</tr>
<tr>
<td>20</td>
<td>0.71</td>
</tr>
<tr>
<td>40</td>
<td>0.50</td>
</tr>
<tr>
<td>60</td>
<td>0.35</td>
</tr>
<tr>
<td>80</td>
<td>0.25</td>
</tr>
<tr>
<td>100</td>
<td>0.18</td>
</tr>
<tr>
<td>120</td>
<td>0.13</td>
</tr>
</tbody>
</table>
See Silberberg!

Plot of $[\text{N}_2\text{O}_5]$ vs. Time for Three Half-lives
Carbon-14

\[ ^{14}_{6}C \rightarrow ^{14}_{7}N + ^{0}_{-1}e \]
Mechanisms can be complex, but sometimes all steps are fast except one:

then slow step = rate-determining step
Suggested mechanism:

(1) \( \text{H}_2 + \text{ICl} \rightarrow \text{HI} + \text{HCl} \) slow

(2) \( \text{HI} + \text{ICl} \rightarrow \text{I}_2 + \text{HCl} \) fast

\[ \text{H}_2 + 2\text{ICl} \rightarrow \text{I}_2 + 2\text{HCl} \] net reaction

Rate (1) = \( k_1[\text{H}_2][\text{ICl}] \)

Rate (2) = \( k_2[\text{HI}][\text{ICl}] \)

\( \therefore \) Overall rate = \( k_1[\text{H}_2][\text{ICl}] \)

• Experiment: rate = \( k[\text{H}_2][\text{ICl}] \), supports assumed mechanism

• HI is an *intermediate*, it doesn’t appear in the overall reaction
Example

Fast reversible reaction followed by a slow step:

1. \(2\text{NO}(g) \leftrightarrow \text{N}_2\text{O}_2\ (g)\) \quad \text{fast equilibrium, } K
2. \(\text{N}_2\text{O}_2 \ (g) + \text{O}_2\ (g) \rightarrow 2\text{NO}_2\) \quad \text{slow (rate constant } k\text{)}

\[
2\text{NO}(g) + \text{O}_2\ (g) \rightarrow 2\text{NO}_2\ (g) \quad \text{net reaction}
\]

Rate = rate of slow step = \(k \ [\text{N}_2\text{O}_2][\text{O}_2]\)

From (1), with equilibrium constant, \(K = \frac{[\text{N}_2\text{O}_2]}{[\text{NO}] \ [\text{NO}]^2}\)

i.e. \([\text{N}_2\text{O}_2] = K [\text{NO}]^2\)

So rate = \(k \ [\text{N}_2\text{O}_2] \ [\text{O}_2] = k \ K \ [\text{NO}]^2 \ [\text{O}_2]\)

\[\Rightarrow \text{rate} = \text{constant} \times [\text{NO}]^2 \ [\text{O}_2]\]

consistent with observed rate law
Often: no simple solution to rate equations, solved coupled differential equations numerically.

Examples:

- oscillating reaction – iodate, malonic acid (CH$_2$(CO$_2$H)$_2$), H$_2$O$_2$
- ozone layer destruction by CFCs (chlorofluorocarbons): simplified mechanism is

\[
\begin{align*}
\text{CCl}_2\text{F}_2 & \xrightarrow{h\nu} \text{CCIF}_2 + \text{Cl} \\
\text{Cl} + \text{O}_3 & \rightarrow \text{ClO} + \text{O}_2 \\
\text{ClO} + \text{NO}_2 & \rightarrow \text{ClONO}_2 \\
\text{ClONO}_2 + \text{HCl} & \rightarrow \text{HNO}_3 + \text{Cl}_2 \\
\text{Cl}_2 & \xrightarrow{h\nu} 2\text{Cl}
\end{align*}
\]
Kinetics of the Slow Iodine Reaction

\[ 2\text{H}^+ + 3\text{I}^- + \text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{I}_3^- \]

Rate \(= \frac{\text{d}[\text{I}_3^-]}{\text{dt}} = k \times [\text{I}^-] \times [\text{H}_2\text{O}_2] \)

Why independent of \([\text{H}^+]?\)

What might the reaction mechanism (series of elementary reactions) be?