Chemical Kinetics

Thermodynamics – does a reaction take place?

Kinetics – how fast does a reaction proceed?

Chapter 14
**Chemical Kinetics**

*Reaction rate*: the *change* in the *concentration* of a reactant or a product with time (M/s).

**Reaction**: \( A \rightarrow B \)

\[
Rate = -\frac{\Delta [A]}{\Delta t}
\]

\( \Delta [A] = \text{change in concentration of A over time period} \Delta t \)

\[
Rate = \frac{\Delta [B]}{\Delta t}
\]

\( \Delta [B] = \text{change in concentration of B over time period} \Delta t \)
Chemical Kinetics

Reaction: $A \rightarrow B$

$Rate = -\frac{\Delta [A]}{\Delta t}$

$Rate = \frac{\Delta [B]}{\Delta t}$

Number of molecules

$t (s)$
The Rate of a Reaction

\[
\text{Br}_2(aq) + \text{HCOOH}(aq) \rightarrow 2\text{Br}^-(aq) + 2\text{H}^+(aq) + \text{CO}_2(g)
\]

393 nm light

Detector

\[
[\text{Br}_2] \propto \text{Absorption}
\]

\[
\Delta[\text{Br}_2] \propto \Delta \text{Absorption}
\]
\[ \text{Br}_2(\text{aq}) + \text{HCOOH}(\text{aq}) \rightarrow 2\text{Br}^- (\text{aq}) + 2\text{H}^+ (\text{aq}) + \text{CO}_2 (\text{g}) \]

**Average Rate**

\[
\text{Average Rate} = \frac{\Delta [\text{Br}_2]}{\Delta t} = \frac{[\text{Br}_2]_{\text{final}} - [\text{Br}_2]_{\text{initial}}}{t_{\text{final}} - t_{\text{initial}}} 
\]

*instantaneous rate* = rate for specific instance in time

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>[Br₂] (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.0120</td>
</tr>
<tr>
<td>50.0</td>
<td>0.0101</td>
</tr>
<tr>
<td>100.0</td>
<td>0.00846</td>
</tr>
<tr>
<td>150.0</td>
<td>0.00710</td>
</tr>
<tr>
<td>200.0</td>
<td>0.00596</td>
</tr>
<tr>
<td>250.0</td>
<td>0.00500</td>
</tr>
<tr>
<td>300.0</td>
<td>0.00420</td>
</tr>
<tr>
<td>350.0</td>
<td>0.00353</td>
</tr>
<tr>
<td>400.0</td>
<td>0.00296</td>
</tr>
</tbody>
</table>
Br₂(aq) + HCOOH(aq) → 2Br⁻(aq) + 2H⁺(aq) + CO₂(g)

Rates of the Reaction Between Molecular Bromine and Formic Acid at 25°C

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>[Br₂] (M)</th>
<th>Rate (M/s)</th>
<th>k = \frac{\text{rate}}{[\text{Br}_2]} (\text{s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.0120</td>
<td>4.20 × 10⁻⁵</td>
<td>3.50 × 10⁻³</td>
</tr>
<tr>
<td>50.0</td>
<td>0.0101</td>
<td>3.52 × 10⁻⁵</td>
<td>3.49 × 10⁻³</td>
</tr>
<tr>
<td>100.0</td>
<td>0.00846</td>
<td>2.96 × 10⁻⁵</td>
<td>3.50 × 10⁻³</td>
</tr>
<tr>
<td>150.0</td>
<td>0.00710</td>
<td>2.49 × 10⁻⁵</td>
<td>3.51 × 10⁻³</td>
</tr>
<tr>
<td>200.0</td>
<td>0.00596</td>
<td>2.09 × 10⁻⁵</td>
<td>3.51 × 10⁻³</td>
</tr>
<tr>
<td>250.0</td>
<td>0.00500</td>
<td>1.75 × 10⁻⁵</td>
<td>3.50 × 10⁻³</td>
</tr>
<tr>
<td>300.0</td>
<td>0.00420</td>
<td>1.48 × 10⁻⁵</td>
<td>3.52 × 10⁻³</td>
</tr>
<tr>
<td>350.0</td>
<td>0.00353</td>
<td>1.23 × 10⁻⁵</td>
<td>3.48 × 10⁻³</td>
</tr>
<tr>
<td>400.0</td>
<td>0.00296</td>
<td>1.04 × 10⁻⁵</td>
<td>3.51 × 10⁻³</td>
</tr>
</tbody>
</table>

Rate ∝ [Br₂]

Rate = k[Br₂]

\[ k = \frac{\text{Rate}}{[\text{Br}_2]} = \text{rate constant} \]

= 3.50 × 10⁻³ · s⁻¹

Nov. 2006

Shanghai Jiao Tong University
The Rate of a Reaction

$$2\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$$

$$PV = nRT$$

$$P = \frac{n}{V}RT = [O_2]RT$$

$$[O_2] = \frac{P}{RT}$$

$$\text{Rate} = \frac{\Delta [O_2]}{\Delta t} = \frac{1}{RT} \cdot \frac{\Delta P}{\Delta t}$$
The Rate of a Reaction

\[ 2\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g}) \]

An instantaneous rate at 400 min = 0.12 mmHg/min
Reaction Rates and Stoichiometry

\[2A \rightarrow B\]

Two moles of A disappear for each mole of B that is formed.

\[
\text{Rate} = -\frac{1}{2} \frac{\Delta [A]}{\Delta t} \quad \text{Rate} = \frac{\Delta [B]}{\Delta t}
\]

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

\[
\text{Rate} = -\frac{1}{a} \frac{\Delta [A]}{\Delta t} = -\frac{1}{b} \frac{\Delta [B]}{\Delta t} = \frac{1}{c} \frac{\Delta [C]}{\Delta t} = \frac{1}{d} \frac{\Delta [D]}{\Delta t}
\]
Reaction Rates and Stoichiometry

\[ \text{CH}_4(g) + 2\text{O}_2(g) = \text{CO}_2(g) + 2\text{H}_2\text{O}(g) \]

Write the rate expression, Rate=?

\[
\text{Rate} = -\frac{\Delta[\text{CH}_4]}{\Delta t} = -\frac{1}{2} \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{\Delta[\text{CO}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t}
\]
**The Rate Law**

\[ F_2(g) + 2ClO_2(g) \rightarrow 2FClO_2(g) \]

\[ \text{Rate} = k[F_2]^x \cdot [ClO_2]^y \]

<table>
<thead>
<tr>
<th><a href="M">F_2</a></th>
<th><a href="M">ClO_2</a></th>
<th>Initial Rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 0.10</td>
<td>0.010</td>
<td>1.2 \times 10^{-3}</td>
</tr>
<tr>
<td>2. 0.10</td>
<td>0.040</td>
<td>4.8 \times 10^{-3}</td>
</tr>
<tr>
<td>3. 0.20</td>
<td>0.010</td>
<td>2.4 \times 10^{-3}</td>
</tr>
</tbody>
</table>

Double \([F_2]\) at constant\([ClO_2]\), rate doubles
\[ \rightarrow x=1 \]

Quadruple \([ClO_2]\) at constant \([F_2]\), Rate quadruples
\[ \rightarrow y=1 \]

\[ \text{Rate} = k[F_2] \cdot [ClO_2] \]
The Rate Law

• Rate laws are always determined experimentally.

• Reaction order is always defined in terms of reactant (not product) concentrations.

• The order of a reactant is not related to the stoichiometric coefficient of the reactant in the balanced chemical equation.

\[ \text{Rate} = k[F_2][ClO_2]^1 \]

\[ F_2(g) + 2ClO_2(g) \rightarrow 2FClO_2(g) \]
The Rate Law

The Dependence of Rate on Concentration:

\[ \text{Rate} = k \ [\text{reactant 1}]^m \cdot [\text{reactant 2}]^n \]

- The reaction: \(m\)th order in reactant 1 and \(n\)th order in reactant 2.
- The overall order of reaction: \((m + n)\)
- A reaction can be zeroth order if \(m, n, \ldots\) are zero.
- The values of the exponents (orders) have to be determined experimentally. They are not simply related to stoichiometry.
- The rate constant \(k\) does not depend on concentration.
Problem

Determine the rate law and calculate the rate constant for the following reaction from the following data:

\[ \text{S}_2\text{O}_8^{2-}(aq) + 3\text{I}^-(aq) \rightarrow 2\text{SO}_4^{2-}(aq) + \text{I}_3(aq) \]

<table>
<thead>
<tr>
<th>Exp.</th>
<th>[S_2O_8^{2-}]</th>
<th>[I^-]</th>
<th>Initial Rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.08</td>
<td>0.034</td>
<td>2.2 x 10^{-4}</td>
</tr>
<tr>
<td>2</td>
<td>0.08</td>
<td>0.017</td>
<td>1.1 x 10^{-4}</td>
</tr>
<tr>
<td>3</td>
<td>0.16</td>
<td>0.017</td>
<td>2.2 x 10^{-4}</td>
</tr>
</tbody>
</table>

Rate = \( k \left[ \text{S}_2\text{O}_8^{2-} \right]^x \cdot \left[ \text{I}^- \right]^y \)

Double [I^-], rate doubles
Double [S_2O_8^{2-}], rate doubles
\( x = 1, y = 1 \)

\[ Rate = k \left[ \text{S}_2\text{O}_8^{2-} \right] \cdot \left[ \text{I}^- \right] \]

\[ k = \frac{\text{Rate}}{\left[ \text{S}_2\text{O}_8^{2-} \right]\left[ \text{I}^- \right]} = \frac{2.2 \times 10^{-4} \text{ M} / \text{s}}{(0.08 \text{ M}) \cdot (0.034 \text{ M})} = 0.08 \text{ M} / \text{s} \]
**First-Order Reactions**

\[ \frac{-\Delta[A]}{\Delta t} = k[A] \]

\[ \text{Rate} = \frac{\Delta[A]}{\Delta t} \quad \text{Rate} = k[A] \]

\[ k = \frac{\text{Rate}}{[A]} = \frac{M}{s} = \frac{1}{s} \]

\[ \nu_t = -\lim_{\Delta t \to 0} \frac{\Delta[A]}{\Delta t} = -\frac{d[A]}{dt} = k[A] \]

\[ -\frac{d[A]}{[A]} = kdt; \]

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

The reaction $2A \rightarrow B$ is first order in A with a rate constant of $2.8 \times 10^{-2} \text{ s}^{-1}$ at $80^0\text{C}$. How long will it take for A to decrease from $0.88 \text{ M}$ to $0.14 \text{ M}$?

Solution:

$$[A]_0 = 0.88 \text{ M} \quad [A] = 0.14 \text{ M}$$

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

$$t = -\frac{\ln[A]_t - \ln[A]_0}{k} = \frac{\ln([A]_0 /[A]_t)}{k}$$

$$= \frac{\ln(0.88M / 0.14M)}{2.8 \times 10^{-2} \text{ s}^{-1}} = 66 \text{ s}$$
**First-Order Reactions**

The *half-life* $t_{1/2}$:

the time required for the concentration of a reactant to decrease to half of its initial concentration.

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

$$t_{1/2} = \frac{\ln\left(\frac{[A]_0}{[A]_t}\right)}{k} = \frac{\ln\left(\frac{[A]_0}{2}\right)}{k} = \frac{\ln 2}{k} = 0.693/k$$
Problem

What is the half-life of $\text{N}_2\text{O}_5$ if it decomposes with a rate constant of $5.7 \times 10^{-4} \text{ s}^{-1}$?

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k} = \frac{0.693}{5.7 \times 10^{-4} \text{ s}^{-1}} = 1200 \text{ s} = 20 \text{ min}$$

How do you know decomposition is first order?

*First* Order reaction:

$$k = \frac{\text{Rate}}{[A]} = \frac{M}{s} = \frac{1}{s}$$

5.7 x $10^{-4}$ s$^{-1}$ units of $k$ (s$^{-1}$)
Second-Order Reactions

\[ A \rightarrow \text{Product} \]

\[ Rate = -\frac{\Delta [A]}{\Delta t} \quad Rate = k[A]^2 \]

\[ k = \frac{\text{Rate}}{[A]^2} = \frac{M/s}{M^2} = \frac{1}{M \cdot s} \]

\[ \nu_t = -\lim_{\Delta t \to 0} \frac{\Delta [A]}{\Delta t} = -\frac{d[A]}{dt} = k[A]^2 \]

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

\[ t_{1/2} = \frac{1}{k} \left( \frac{1}{[A]_0/2} - \frac{1}{[A]_0} \right) = \frac{1}{k \cdot [A]_0} \]
**Zero-Order Reactions**

\[ A \rightarrow \text{Product} \]

\[ \text{Rate} = -\frac{\Delta [A]}{\Delta t} = k \]

\[ k = \text{Rate} = M / s \]

\[ \nu_t = -\lim_{\Delta t \to 0} \frac{\Delta [A]}{\Delta t} = -\frac{d[A]}{dt} = k \]

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

\[ t_{1/2} = -\frac{([A]_0/2 - [A]_0)}{k} = \frac{[A]_0}{2k} \]
# Summary

**The Kinetics of Zero-Order, First-Order and Second-Order Reactions**

<table>
<thead>
<tr>
<th>Order</th>
<th>Rate Law</th>
<th>Equation</th>
<th>Half-Life</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>rate = ( k )</td>
<td>([A] = [A]_0 - kt)</td>
<td>( t_{\frac{1}{2}} = \frac{[A]_0}{2k} )</td>
</tr>
<tr>
<td>1</td>
<td>rate = ( k [A] )</td>
<td>( \ln[A] = \ln[A]_0 - kt)</td>
<td>( t_{\frac{1}{2}} = \frac{\ln 2}{k} )</td>
</tr>
<tr>
<td>2</td>
<td>rate = ( k [A]^2 )</td>
<td>( \frac{1}{[A]} = \frac{1}{[A]_0} + kt )</td>
<td>( t_{\frac{1}{2}} = \frac{1}{k[A]_0} )</td>
</tr>
</tbody>
</table>
Activation Energy

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

Exothermic Reaction

Endothermic Reaction
Temperature Dependence of the Rate Constant

\[ k = A \cdot \exp\left(-\frac{E_a}{RT}\right) \]  

(Arrhenius equation)

- \( E_a \): the activation energy (J/mol)
- \( R \): the gas constant (8.314 J/K\cdot mol)
- \( T \): the absolute temperature
- \( A \): the frequency factor

\[ \ln k = -\frac{E_a}{R} \cdot \frac{1}{T} + \ln A \]
Temperature Dependence of the Rate Constant

\[ \ln k = - \frac{E_a}{R} \cdot \frac{1}{T} + \ln A \]
Reaction Mechanisms

The overall progress of a chemical reaction can be represented at the molecular level by a series of simple elementary steps or elementary reactions.

Elementary step: any process that occurs in a single step.

The sequence of elementary steps that leads to product formation is the reaction mechanism.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

$N_2O_2$ is detected during the reaction!

Elementary step: \[ NO + NO \rightarrow N_2O_2 \]

+ Elementary step: \[ N_2O_2 + O_2 \rightarrow 2NO_2 \]

Overall reaction: \[ 2NO + O_2 \rightarrow 2NO_2 \]
Reaction Mechanisms

Intermediates: species that appear in a reaction mechanism but not in the overall balanced equation.

Elementary step: \[ \text{NO} + \text{NO} \rightarrow \text{N}_2\text{O}_2 \]

\[ + \text{ Elementary step: } \text{N}_2\text{O}_2 + \text{O}_2 \rightarrow 2\text{NO}_2 \]

Overall reaction: \[ 2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2 \]
Reaction Mechanisms

The number of molecules reacting in an elementary step.

Unimolecular reaction – elementary step with 1 molecule

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

Bimolecular reaction – elementary step with 2 molecules

\[ A + B \rightarrow \text{products} \quad \text{rate} = k [A][B] \]
\[ A + A \rightarrow \text{products} \quad \text{rate} = k [A]^2 \]

Termolecular reaction – elementary step with 3 molecules

• It is not common to see termolecular processes (statistically impossible).
Catalyst

A catalyst is a substance that increases the rate of a chemical reaction without itself being consumed.

\[ k = A \cdot \exp\left(-\frac{E_a}{RT}\right), \quad E_a \downarrow, k \uparrow \]

\[ E'_a < E_a \]

rate_{catalyzed} > rate_{uncatalyzed}
Catalyst

In *homogeneous catalysis*, the reactants and the catalysts are dispersed in a single phase, usually liquid.

- Acid catalysis
- Base catalysis

In *heterogeneous catalysis*, the reactants and the catalysts are in different phases.

- Haber synthesis of ammonia
- Catalytic converters
Homogeneous Catalysis:

\[ 2\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g) \text{ (slowly)} \]

- Hydrogen peroxide decomposes very slowly. In the presence of the bromide ion, the decomposition occurs rapidly:

\[ 2\text{H}_2\text{O}_2(\text{aq}) + \text{Br}^- \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g) \text{ (rapidly)} \]

\[ 2\text{Br}^- + \text{H}_2\text{O}_2 + 2\text{H}^+ \rightarrow \text{Br}_2 + 2\text{H}_2\text{O} \]

\[ \text{Br}_2 + \text{H}_2\text{O}_2 \rightarrow 2\text{Br}^- + 2\text{H}^+ + \text{O}_2 \]
Catalysis

Generally, catalysts operate by lowering the activation energy for a reaction.
Haber Process

\[ \text{Fe/Al}_2\text{O}_3/\text{K}_2\text{O} \text{ catalyst} \]

\[ \text{N}_2 (g) + 3\text{H}_2 (g) \xrightarrow{\text{Fe/Al}_2\text{O}_3/\text{K}_2\text{O catalyst}} 2\text{NH}_3 (g) \]
Enzyme Catalysis

Substrate + Enzyme → Enzyme-substrate complex → Products + Enzyme

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rate = \frac{\Delta [P]}{\Delta t}

rate = k [ES]
Enzyme Catalysis

Substrate

Enzyme

Enzyme-substrate complex

Enzyme

Products

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