Kinetics III

Silberberg 2nd Ed, Chapter 16

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Dr Kepert, Chem 1901
Kinetics Revision

Solving the 1\textsuperscript{st}-Order Rate Equation

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

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

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

Half Life, \( t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k} \)
Kinetics Revision cont’d

Reaction Mechanism
* Reactions can often be broken down into a number of individual steps known as *elementary reactions*.

\[
\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}
\]

\[
\begin{align*}
\text{Cl}_2 & \rightarrow 2\text{Cl} \\
\text{Cl} + \text{H}_2 & \rightarrow \text{HCl} + \text{H} \\
\text{H} + \text{Cl}_2 & \rightarrow \text{HCl} + \text{Cl} \\
2\text{Cl} & \rightarrow \text{Cl}_2
\end{align*}
\]

- unimolecular
- bimolecular

Rate-Determining Step
* Mechanisms can be complex, but sometimes all steps are fast except one:

then slow step = *rate-determining step*
**Example**

\[ H_2(g) + 2ICl(g) \rightarrow I_2(g) + 2HCl(g) \]

Suggested mechanism:

1. \( H_2 + ICl \rightarrow HI + HCl \) \hspace{1cm} \text{slow} \hspace{1cm} \text{rate constant } k_1
2. \( HI + ICl \rightarrow I_2 + HCl \) \hspace{1cm} \text{fast} \hspace{1cm} \text{rate constant } k_2

\[ H_2 + 2ICl \rightarrow I_2 + 2HCl \] \hspace{1cm} \text{net reaction}

Rate (1) \( = k_1[H_2][ICl] \)
Rate (2) \( = k_2[HI][ICl] \)

(1) is slow: rate determining step

\[ \therefore \text{Overall rate} = k_1[H_2][ICl] \]

- Experiment: rate \( = k[H_2][ICl] \), 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) \[ 2\text{NO}(g) \rightleftharpoons \text{N}_2\text{O}_2 (g) \quad \text{fast (equil. const.} \ K) \]

(2) \[ \text{N}_2\text{O}_2 (g) + \text{O}_2(g) \rightarrow 2\text{NO}_2 \quad \text{slow (rate constant} \ k) \]

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

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

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

\[ \Rightarrow [\text{N}_2\text{O}_2] = K [\text{NO}]^2 \]

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
**Understanding the Rate Equation**

\[ \text{Rate} = k \ [A] \ [B] \]

Q: Why do we multiply \([A]\) and \([B]\)?
Activation Energy, $E_a$

Reaction energy diagram
Transition State or Activated Complex

BrCH₃ + OH⁻ → Br⁻ + CH₃OH

TRANSITION STATE or ACTIVATED COMPLEX
• geometry through which system must pass between reactant and product
  ∴ higher energy than reactants or products
• not a stable molecule!
Transition State and Activation Energy

- Forward reaction is **EXOTHERMIC**, Reverse reaction is **ENDOTHERMIC**

BrCH$_3$+ OH$^-$

Br$^-$ + CH$_3$OH
See Silberberg!
Rate constants, $k$, have strong temperature dependence

**Arrhenius equation:**

$$k = Ae^{-E_a/RT}$$
Temperature Dependence of the Rate Constant

\[ k = A e^{-\frac{E_a}{RT}} \]

<table>
<thead>
<tr>
<th>Expt</th>
<th>[Ester]</th>
<th>[H₂O]</th>
<th>T(K)</th>
<th>Rate (mol/L·s)</th>
<th>k (L/mol·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.100</td>
<td>0.200</td>
<td>288</td>
<td>1.04×10⁻³</td>
<td>0.0521</td>
</tr>
<tr>
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<td>0.200</td>
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<td>2.02×10⁻³</td>
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</tr>
<tr>
<td>3</td>
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<td>0.200</td>
<td>308</td>
<td>3.68×10⁻³</td>
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<tr>
<td>4</td>
<td>0.100</td>
<td>0.200</td>
<td>318</td>
<td>6.64×10⁻³</td>
<td>0.332</td>
</tr>
</tbody>
</table>
Example

• Find the rate constants at 25 and 35 °C for a second order reaction with $A = 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and $E_{act} = 100 \text{ kJ mol}^{-1}$.

$$k = A \exp\left(-\frac{E_a}{RT}\right)$$

Exponent must be dimensionless, but units not consistent!

$$E_a = 100 \text{ kJ mol}^{-1} = 100 \times 10^3 \text{ J mol}^{-1}$$

$$k(25 ^\circ \text{C}) = 10^8 \text{ M}^{-1} \text{ s}^{-1} \exp\left\{\frac{-100 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times (25 + 273)\text{K}}\right\}$$
Understanding the “exp(−E_a/RT)” term in the Arrhenius Equation

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

- Consider a bimolecular collision A + B → products
  * must go via a transition state, therefore must have energy \( \geq E_a \)

\[ * \text{ (fraction of collisions with energy greater than } E_a \text{) } = e^{-E_a/RT} \]
Understanding the “exp(−E_a/RT)” term in the Arrhenius Equation
Understanding the “A” term in the Arrhenius Equation

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

\[ A = \left( \frac{\text{collision rate}}{\text{fraction of collisions with correct orientation to form transition state}} \right) \]

- For gases, collision frequency \( \approx 10^{30} \) collisions s\(^{-1}\)
- If each collision produced reaction, reaction rate \( \approx 10^6 \) M s\(^{-1}\)
- Experimental gas phase reaction rates \( \approx 10^{-4} \) M s\(^{-1}\)

\[ \therefore \text{Only a very small fraction of collisions lead to reaction} \]
The Importance of Molecular Orientation

\[ \text{F}_2 + \text{NO}_2 \rightarrow \text{F} + \text{NO}_2\text{F} \, ? \]
**Example**

**Q:** Assuming the activation energies are equal, predict which of the following reactions will occur at a higher rate at 50 ºC.

\[
\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \rightarrow \text{NH}_4\text{Cl}(\text{s})
\]

\[
\text{N(CH}_3\text{)}_3(\text{g}) + \text{HCl}(\text{g}) \rightarrow \text{NH(CH}_3\text{)}_3\text{Cl}(\text{s})
\]