Introduction to Chemical Kinetics

CHEM 102
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Chemical Kinetics

- Reaction rates
  - “How fast?”
- Reaction mechanisms
  - “How?”
- Answers to these questions depend on the path taken from reactants to products.
**Reaction Rates**

\[ \alpha A + \beta B \rightarrow \gamma C + \delta D \]

- Follow progress by measuring any one concentration:

\[
\frac{-1}{\alpha} \frac{\Delta [A]}{\Delta t}, \quad \frac{-1}{\beta} \frac{\Delta [B]}{\Delta t}, \quad \frac{1}{\gamma} \frac{\Delta [C]}{\Delta t}, \quad \frac{1}{\delta} \frac{\Delta [D]}{\Delta t}
\]

- Rates of change related by coefficients from balanced equation.

\[ 2 \text{NO}_2 \rightarrow 2 \text{NO} + \text{O}_2 \]

rate =

\[
-\frac{1}{2} \frac{\Delta [\text{NO}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta [\text{NO}]}{\Delta t} = \frac{\Delta [\text{O}_2]}{\Delta t}
\]
Factors Which Influence Rates

- Identity & form of reactants, products
  - $H_2 + I_2$ vs. $H_2 + Br_2$
  - solution vs. gas phase, etc.

- Concentrations of various species
  - usually reactants
  - sometimes products, other species

- Temperature
  - usually, faster at higher $T$
  - strong dependence

- Catalysts

Concentration Effects: Rate Laws

$\alpha A + \beta B \rightarrow \text{Products}$

- Empirically, usually find that
  
  $\text{Rate} = \dot{k}[A]^n[B]^m$

- $n =$ “order of reaction with respect to $A$”
- $m =$ “order of reaction with respect to $B$”
- $n + m =$ “overall order of reaction”
- $\dot{k} =$ rate constant $= \dot{k}(T)$
Example: rate of a redox reaction

\[ \text{Mg}^{2+} + 2 \text{H}^+ \rightarrow \text{Mg}^{2+} + 2 \text{H}_2 \]

Reaction Orders

- Order of a reaction can NOT be found by looking at a balanced equation!
  \[ \alpha A + \beta B \rightarrow \text{Products} \]
  \[ \text{Rate} = k [A]^n [B]^m \]
- In general:
  \( \alpha \) & \( n \), \( \beta \) & \( m \) are not necessarily equal — because this isn’t an elementary step
- Reaction order can only be found by experiments
Examples

\[2 \text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2\]
rate = \(k[\text{N}_2\text{O}_5]\)

- BUT

\[2 \text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2\]
rate = \(k[\text{NO}_2]^2\)

- CAN’T predict these from equations!

More Examples

\[\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}\]
rate = \(k[\text{H}_2][\text{I}_2]\)

- BUT

\[\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}\]
rate = \(\frac{k[\text{H}_2][\text{Br}_2]^{1/2}}{1 + k'[\text{HBr}][\text{Br}_2]^{-1}}\)
Finding rate laws, rate constants

“Method of Initial Rates”
- combine known amounts of reactants
- determine rate by measuring change in some concentration over a “short” time
- repeat with different initial concentrations
- find experimental rate law

Problem

\[
A + 2B \rightarrow \text{products}
\]

<table>
<thead>
<tr>
<th>Expt.</th>
<th>([A]_0)</th>
<th>([B]_0)</th>
<th>Initial Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.10</td>
<td>0.10</td>
<td>0.0032</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>0.20</td>
<td>0.0032</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>0.30</td>
<td>0.0128</td>
</tr>
</tbody>
</table>

- find rate law & rate constant, \(k\)
- (concentrations in M, rates in M/min)
Rates & Mechanisms

Experiments $\rightarrow$ Rate Law
Rate Law $\rightarrow$ Mechanism (?)

- MECHANISM: “The detailed molecular processes by which a chemical reaction proceeds.” A series of “elementary steps” which combine to give an observed net reaction.

Rate laws & mechanisms

- Start with overall reaction
- Guess some mechanism(s)
- Derive corresponding rate laws
- Compare with experiments
- Repeat as needed

* We need to relate rates of individual steps to the overall, observable rate laws.
**A reaction profile example**

A + B → C → D + E

1st step is rate-determining

**Elementary Steps**

- **ELEMENTARY STEP**: A chemical equation or reaction that describes a process as it occurs at the molecular level. A single reaction event which occurs in one simple atomic or molecular collision.

- Most reactions do not occur in a single elementary step.
Reactions vs. Elementary Steps

- Normal chemical eqs. tell us the overall stoichiometry of a reaction.
  \[ 2 \text{C}_8\text{H}_{18} + 25 \text{O}_2 \rightarrow 16 \text{CO}_2 + 18 \text{H}_2\text{O} \]

- Eq. for an elementary step looks just like a “normal” eq., but actually describes a simple molecular event.
  \[ \text{NO}_2 + \text{NO}_2 \rightarrow \text{N}_2\text{O}_4 \]

Reactions vs. Elementary Steps

- Not always easy to tell an elementary step from a (slightly) more complicated reaction
  \[ 2 \text{NO}_2 \rightarrow \text{N}_2\text{O}_4 \]
  \[ 2 \text{NO}_2 \rightarrow 2 \text{NO} + \text{O}_2 \]

- The first one is an elementary step, the second is not. You can’t really tell this from the equations.
Types of Elementary Reactions

- Unimolecular decomposition: one molecule falls apart: $A \rightarrow \text{Product(s)}$
- Bimolecular reaction: two reactant molecules collide: $A + B \rightarrow \text{Product(s)}$
- Termolecular reaction: three reactant molecules: $A + B + C \rightarrow \text{Product(s)}$
  (such steps rare in gas-phase and soln. rxns.)
- NO examples of more complex elementary reactions are known.

Rates of Elementary Steps

- For an elementary step, the rate law can be written from the equation.
- $A \rightarrow \text{Product(s)}$ rate $= k[A]$
- $A + B \rightarrow \text{Product(s)}$ rate $= k[A][B]$
- $2A \rightarrow \text{Product(s)}$ rate $= k[A]^2$
- $A + B + C \rightarrow \text{Product(s)}$ rate $= k[A][B][C]$
  (not for gas phase reactions)
- Can ONLY do this for an elementary step!
**Rate Determining Steps**

- If a single step in a reaction mechanism is much slower than the other steps, then the rate of the slow step is crucial in determining overall rate.

- The rate determining step (RDS) can be thought of as a “bottleneck” in the formation of products. Steps that follow the RDS have negligible effect on the overall rate of reaction.

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**A reaction profile example**

A + B → C → D + E

- 1st step is rate-determining
- “Reaction Coordinate”

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Example: rates & mechanisms

\[ 2 \text{NO}_2 \rightarrow 2 \text{NO} + \text{O}_2 \]

- Consider 2 mechanisms for this:
  - \[ \text{NO}_2 \rightarrow \text{NO} + \text{O} \quad \text{(slow)} \]
    \[ \text{O} + \text{NO}_2 \rightarrow \text{O}_2 + \text{NO} \quad \text{(fast)} \]
  - \[ 2 \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO} \quad \text{(slow)} \]
    \[ \text{NO}_3 \rightarrow \text{NO} + \text{O}_2 \quad \text{(fast)} \]

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Example: rates & mechanisms

- Experimental rate law is: \[ \text{rate} = \kappa [\text{NO}_2]^2 \]
  - \[ \text{NO}_2 \rightarrow \text{NO} + \text{O} \quad \text{(slow)} \]
    \[ \text{O} + \text{NO}_2 \rightarrow \text{O}_2 + \text{NO} \quad \text{(fast)} \]
    \[ \text{rate} = ? \]
  - \[ 2 \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO} \quad \text{(slow)} \]
    \[ \text{NO}_3 \rightarrow \text{NO} + \text{O}_2 \quad \text{(fast)} \]
    \[ \text{rate} = ? \]
Rate Laws *Can* Prove a Mechanism is Wrong but *Can’t* Prove one Right!

\[ 2 \text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2 \quad \text{rate} = k[\text{NO}]^2[\text{O}_2] \]

A single step mechanism?

\[ \begin{array}{c}
  \text{O} \\
  \text{N} \\
  \text{O} \\
  \text{O} \\
  \text{N} \\
  \text{O} \\
\end{array} \quad \begin{array}{c}
  \text{O} \\
  \text{N} \\
  \text{O} \\
  \text{O} \\
  \text{N} \\
  \text{O} \\
\end{array} \]

Rate Law is consistent.

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Rate Laws … Proof?

\[ 2 \text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2 \quad \text{rate} = k[\text{NO}_2]^2[\text{O}_2] \]

Two-step mechanism?

1. \( \text{NO} + \text{NO} \rightleftharpoons \text{N}_2\text{O}_2 \) (fast equilibrium)
2. \( \text{N}_2\text{O}_2 + \text{O}_2 \rightarrow 2\text{NO}_2 \) (slow)

\[ \begin{array}{c}
  \text{N} \\
  ^{218}\text{pm} \\
  \text{N} \\
  \text{O} \\
  \text{O} \\
\end{array} \]

Rate Law for this mechanism?
Mechanism & Rate

(1) NO + NO ⇌ N₂O₂ (fast equilibrium)
(2) N₂O₂ + O₂ → 2NO₂ (slow)

- rate = rate of slow step = \( k₂[N₂O₂][O₂] \)
- \( N₂O₂ \) is a reactive intermediate, **NOT** a reactant or a product. We should eliminate it from the rate law.

Reversible Step: 2 NO ⇌ N₂O₂

2 NO ⇌ N₂O₂ (fast)

- Rates of forward and backward reactions will quickly become equal.
- Set: rate forward = rate backward
  \( \dot{k}_f[NO]^2 = \dot{k}_r[N₂O₂] \)
- From this:
  \[ [N₂O₂] = (\dot{k}_f / \dot{k}_r) [NO]^2 \]
\[ 2 \text{NO}_2 + \text{O}_2 \rightarrow 2 \text{NO}_2 \text{, cont...} \]

\[ 2 \text{NO} \rightleftharpoons \text{N}_2\text{O}_2 \text{ (fast)} \]
\[ \text{N}_2\text{O}_2 + \text{O}_2 \rightarrow 2\text{NO}_2 \text{ (slow)} \]

- rate = rate of slow step = \( k_2 [\text{N}_2\text{O}_2] [\text{H}_2] \)
- \([\text{N}_2\text{O}_2] = \left( \frac{k_f}{k_r} \right) [\text{NO}]^2\)
- So:
  rate = \( k_2 [\text{N}_2\text{O}_2][\text{O}_2] = k_2 \left( \frac{k_f}{k_r} \right) [\text{NO}]^2[\text{O}_2] \)
  = \( k_{\text{observed}} [\text{NO}]^2[\text{O}_2] \)

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**Equilibrium:** \( 2 \text{NO} \rightleftharpoons \text{N}_2\text{O}_2 \)

The interconversion of products and reactants are an example of equilibrium

Set: rate forward = rate backward

\[ k_f [\text{NO}]^2 = k_r [\text{N}_2\text{O}_2] \]

The Equilibrium Constant, \( K_{eq} \) is defined as:

\[ \frac{k_f}{k_r} = \frac{[\text{N}_2\text{O}_2]}{[\text{NO}]^2} = \text{constant} = K_{eq} \]
Reversible Step: 2 NO ⇌ N₂O₂

2 NO  ⇌ N₂O₂ (fast)
- Rates of forward and backward reactions will quickly become equal.
- Set: rate forward = rate backward
  \[ k_f [NO]^2 = k_r [N₂O₂] \]
- From this:
  \[ [N₂O₂] = \left( \frac{k_f}{k_r} \right) [NO]^2 \]

2 NO₂ + O₂ ⇌ 2 NO₂, cont...

2 NO  ⇌ N₂O₂ (fast)
N₂O₂ + O₂ → 2NO₂ (slow)
- rate = rate of slow step = \( k_2 [N₂O₂][O₂] \)
- \[ [N₂O₂] = \left( \frac{k_f}{k_r} \right) [NO]^2 \]
- So:
  rate = \( k_2 [N₂O₂][O₂] = k_2 \left( \frac{k_f}{k_r} \right) [NO]^2 [O₂] \)
  = \( k_{observed} [NO]^2 [O₂] = k_2 K_{eq} [NO]^2 [O₂] \)