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:
  \[ \frac{1}{\alpha} \frac{\Delta[A]}{\Delta t}, \frac{1}{\beta} \frac{\Delta[B]}{\Delta t}, \frac{1}{\gamma} \frac{\Delta[C]}{\Delta t}, \frac{1}{\delta} \frac{\Delta[D]}{\Delta t} \]
- Rates of change related by coefficients from balanced equation.

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
  \[ \text{Rate} = k[A]^n[B]^m \]
- \( n = \) “order of reaction with respect to A”
- \( m = \) “order of reaction with respect to B”
- \( n + m = \) “overall order of reaction”
- \( k = \) rate constant = \( k(T) \)
**Example: rate of a redox reaction**

![Image of redox reaction example]

**Reaction Orders**

- Order of a reaction can NOT be found by looking at a balanced equation!
  
  \[
  \alpha A + \beta B \rightarrow \text{Products}
  \]
  
  Rate = \( k[A]^\alpha[B]^\beta \)

- 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**

1. \(2 \text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2\)
   
   \( \text{rate} = k[\text{N}_2\text{O}_5] \)

   - BUT

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

   - CAN’T predict these from equations!

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

   - BUT

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

**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 → Rate Law
Rate Law → 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

1st step is rate-determining

Energy

“Reaction Coordinate”

Reactions vs. Elementary Steps

- Normal chemical eqs. tell us the overall stoichiometry of a reaction.
  \[ 2 \text{C}_8\text{H}_{16} + 25 \text{O}_2 \rightarrow 16 \text{CO}_2 + 18 \text{H}_2\text{O} \]
- Eq. for an elementary step looks just like a “normal” eq., but actually describes a simple molecular event.
  \[ \text{NO}_2 + \text{NO}_2 \rightarrow \text{N}_2\text{O}_4 \]

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

- Not always easy to tell an elementary step from a (slightly) more complicated reaction
  \[
  \begin{align*}
  2 \text{NO}_2 & \rightarrow \text{N}_2\text{O}_4 \\
  2 \text{NO}_2 & \rightarrow 2 \text{NO} + \text{O}_2
  \end{align*}
  \]
- 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.
  - \( A \rightarrow \text{Product(s)} \) \( \text{rate} = k[A] \)
  - \( A + B \rightarrow \text{Product(s)} \) \( \text{rate} = k[A][B] \)
  - \( 2A \rightarrow \text{Product(s)} \) \( \text{rate} = k[A]^2 \)
  - \( A + B + C \rightarrow \text{Product(s)} \) \( \text{rate} = k[A][B][C] \)
    (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.

A reaction profile example

- **A + B \rightarrow C \rightarrow D + E**
  - 1st step is rate-determining
  - “Reaction Coordinate”

Example: rates & mechanisms

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

Example: rates & mechanisms

- experimental rate law is: \( \text{rate} = k[\text{NO}_2]^2 \)
  - \( \text{NO}_2 \rightarrow \text{NO} + \text{O} \) \( \text{(slow)} \)
    - \( \text{O} + \text{NO}_2 \rightarrow \text{O}_2 + \text{NO} \) \( \text{(fast)} \)
  - \( 2 \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO} \) \( \text{(slow)} \)
    - \( \text{NO}_2 \rightarrow \text{NO} + \text{O}_2 \) \( \text{(fast)} \)
    - 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?

$$\begin{array}{c}
\text{O} \quad \text{N} \\
\rightarrow \\
\text{O} \\
\downarrow \\
\text{O} \quad \text{N} \\
\text{O} \quad \text{N} \\
\end{array}$$

Rate Law is consistent.

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)

Rate Law for this mechanism?

Mechanism & Rate

(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)

- Rate = rate of slow step = $$k_2[\text{N}_2\text{O}_2][\text{O}_2]$$
- $$\text{N}_2\text{O}_2$$ is a reactive intermediate, NOT a reactant or a product. We should eliminate it from the rate law.

Reversible Step: $$2 \text{NO} \rightleftharpoons \text{N}_2\text{O}_2$$

$$2 \text{NO} \rightleftharpoons \text{N}_2\text{O}_2 \quad \text{(fast)}$$

- Rates of forward and backward reactions will quickly become equal.
- Set: rate forward = rate backward
  $$k_f[\text{NO}]^2 = k_r[\text{N}_2\text{O}_2]$$
- From this:
  $$[\text{N}_2\text{O}_2] = \left(\frac{k_f}{k_r}\right)[\text{NO}]^2$$

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: $2 \text{NO} \rightleftharpoons \text{N}_2\text{O}_2$  

2 NO $\rightleftharpoons$ N$_2$O$_2$ (fast)  
- Rates of forward and backward reactions will quickly become equal.  
- Set: rate forward = rate backward  
  $k_f[\text{NO}]^2 = k_r[\text{N}_2\text{O}_2]$  
- From this:  
  $[\text{N}_2\text{O}_2] = (k_f/k_r)[\text{NO}]^2$

2 NO + O$_2$ $\rightleftharpoons$ 2 NO$_2$, cont...  

2 NO $\rightleftharpoons$ N$_2$O$_2$ (fast)  
N$_2$O$_2$ + O$_2$ $\rightarrow$ 2NO$_2$ (slow)  
- rate = rate of slow step = $\dot{k}_2[\text{N}_2\text{O}_2][\text{O}_2]$  
- $[\text{N}_2\text{O}_2] = (k_f/k_r)[\text{NO}]^2$  
- So:  
  rate = $\dot{k}_2 [\text{N}_2\text{O}_2][\text{O}_2] = \dot{k}_2 (k_f/k_r)[\text{NO}]^2[\text{O}_2] = \dot{k}_\text{observed} [\text{NO}]^2[\text{O}_2] = \dot{k}_2 K_{eq}[\text{NO}]^2[\text{O}_2]$