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:

\[ \frac{d[A]}{dt}, \quad \frac{d[B]}{dt}, \quad \frac{d[C]}{dt}, \quad \frac{d[D]}{dt} \]

Rates of change related by coefficients from balanced equation.
\[ 2 \text{NO}_2 \rightarrow 2 \text{NO} + \text{O}_2 \]

rate = \[-\frac{1}{2} \frac{d[\text{NO}_2]}{dt} = \frac{1}{2} \frac{d[\text{NO}]}{dt} = \frac{d[\text{O}_2]}{dt} \]

**Factors That Influence Rates**
- Identity & form of reactants, products
  - \( \text{H}_2 + \text{I}_2 \) vs. \( \text{H}_2 + \text{Br}_2 \)
  - 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**

\[ \alpha \text{A} + \beta \text{B} \rightarrow \text{Products} \]

Empirically, usually find that

\[ \text{Rate} = \dot{k}[^{\alpha}\text{A}]^{\alpha}[^{\beta}\text{B}]^{\beta} \]

\( n = \) “order of reaction with respect to \( \text{A} \)”

\( m = \) “order of reaction with respect to \( \text{B} \)”

\( n + m = \) “overall order of reaction”

\( \dot{k} = \) rate constant = \( \dot{k}(T) \)
**Example: rate of a redox reaction**

![Graph showing reaction rates](image)

**Reaction Orders**

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

- In general:
  \[ \alpha \text{ & } n, \beta \text{ & } m \text{ are not necessarily equal} \]

- Reaction order can only be discovered in experiments

**Examples**

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

- 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!
**More Examples**

H₂ + I₂ → 2HI

rate = \( k[H₂][I₂] \)

BUT

H₂ + Br₂ → 2HBr

\[
\text{rate} = \frac{k[H₂][Br₂]^{1/2}}{1 + k'[HBr][Br₂]^{-1}}
\]

**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 → 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.

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**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.**

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**A reaction profile**

A + B → C → D + E

Energy

reactants
A + B

intermediate
C

products
D + E

“Reaction Coordinate”

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.

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**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.
  \[ \text{NO}_2 + \text{NO}_2 \rightarrow \text{N}_2\text{O}_4 \]

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**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.

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**Rates of Elementary Steps**

For an elementary step, the rate law can be written from the equation:

- \[ A \rightarrow \text{Product(s)} \text{ rate } = \kappa [A] \]
- \[ A + B \rightarrow \text{Product(s)} \text{ rate } = \kappa [A][B] \]
- \[ 2A \rightarrow \text{Product(s)} \text{ rate } = \kappa [A]^2 \]
- \[ A + B + C \rightarrow \text{Product(s)} \text{ rate } = \kappa [A][B][C] \]
  
  (not for gas phase reactions)

- Can ONLY write the rate expression for an elementary step!

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**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.