Physical Chemistry

Lecture 6
Mechanisms of chemical reactions

Chemical kinetics

- Understand the nature of reactions
  - Measure concentration changes with time
  - Determine effects of various parameters (e.g. pressure, temperature, relative concentration, presence of other chemical substances)
  - Explain observed changes in chemical terms
- Requires integration of theory of chemical action with experimental results
  - Development of a mechanism of reaction
  - Distinguish between possible mechanisms by comparison of prediction to observed results

Arrhenius theory

- Empirical equation of Arrhenius (van’t Hoff)
  - Useful parameterization of temperature-dependent rate constants
  - $A = \text{pre-exponential factor}$
  - $E_a = \text{activation energy}$
  - Often seen in empirical analysis of kinetic data
  - Activation energy related to the likelihood of a reactive event

Example Arrhenius plot

$\ln k(T) = \ln A - \frac{E_a}{RT}(\text{1})$

Non-Arrhenius behavior

- Arrhenius behavior is empirical
  - Modern chemical-reaction theory does not readily predict the Arrhenius equation
  - Surprising how often Arrhenius behavior is seen
  - Seen in analysis because it is simple
- Rate constants of some reactions do not obey Arrhenius’s simple equation
  - Example: decomposition of diacetylene
  - Indicates complexity of the chemical reaction

Elementary reactions

- Chemical reactions are often more complex than presented in the balanced equation
  - Do not always occur as a single step from initial state to final state
  - Order is not necessarily the stoichiometric coefficient
  - Some reactions do occur in a single step
  - Generally involve simple mono- or bimolecular interactions
  - May involve “unusual” species, i.e. species that are not thought of because they are not very stable
  - Order in elementary reactions is the stoichiometry number, which is called the molecularity

$H_2 + 2O \to H_2O_2 \quad v = k[H_2][O]^2$

$H + Br \to HBr \quad v = k[H][Br]$
Complex reactions

- Complex reactions are considered to be comprised of a series of elementary reactions.
- The simultaneous occurrence of these elementary reactions leads to an overall reaction mechanism.
- Example: reaction of hydrogen and bromine to produce HBr.

Elementary reaction mechanism

\[
\begin{align*}
H_2 + Br_2 & \rightarrow 2HBr \\
Br_2 & \rightarrow 2Br \\
H + Br_2 & \rightarrow HBr + Br \\
H + HBr & \rightarrow H_2 + Br \\
Br + Br & \rightarrow Br_2
\end{align*}
\]

Sequential two-step reaction

- Two subsequent first-order steps.
- Rate equations for both steps are integrable.

Parallel first-order reactions

- One reactant reacts along two different pathways.
- Consider both reactions to be of first order.
- Allows mathematical expressions for concentrations.
- At reaction end, both products are present.

Parallel reactions

- Ratio of final concentrations determined by the rate constants.
- Example: reactions of benzyl penicillin under acidic conditions.
  - Three parallel reactions.
  - Ratios of equilibrium product concentrations give ratios of rate constants.

Reversible reactions

- In kinetics, one often neglects steps considered inconsequential.
- Example: Reaction goes to completion; neglect reverse reaction.
- Can always postulate a reverse reaction to any reaction.
  - When reverse reaction is not inconsequential, it must be included.
  - Reversible first-order reactions can be solved mathematically.

Reversible reactions

- In principle, all reactions are reversible.
- In practice, for many reactions equilibrium lies at one extreme or the other.
  - Examples of equilibrium:
    - Chair – boat interchange of cyclohexane.
    - Monomer-dimer conversion.
    - Proflavin.
    - Carboxylic acid.

\[
\begin{align*}
\frac{[B]_{eq}}{[C]_{eq}} & = \frac{k_b}{k_c} \\
\frac{[C]_{eq}}{[B]_{eq}} & = \frac{k_c}{k_b}
\end{align*}
\]
Simple collision theory of gas-phase kinetics

- To participate in a bimolecular reaction, molecules must approach each other closely.
- SCT: gas-phase reaction rate proportional to collision frequency.
- SCT does not generally agree with experimental rates.
- Points out how to think about theory of chemical reactions.

![Relation of SCT parameters to Arrhenius parameters](image)

Experimental SCT and Arrhenius parameters

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Range</th>
<th>kA</th>
<th>Ea</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td>H + O2 + NO → HNO</td>
<td>200 – 750</td>
<td>24.67</td>
<td>16.6</td>
<td>0.505</td>
</tr>
<tr>
<td>H + NO → NO₂ + H₂</td>
<td>200 – 600</td>
<td>23.05</td>
<td>16.6</td>
<td>0.005</td>
</tr>
<tr>
<td>H + Br₂ + Br₂ → 2 Br₃</td>
<td>1000 – 1700</td>
<td>28.42</td>
<td>16.6</td>
<td>0.005</td>
</tr>
<tr>
<td>O + Cl₂ + 2 O₂</td>
<td>273 – 600</td>
<td>33.24</td>
<td>16.6</td>
<td>0.005</td>
</tr>
<tr>
<td>H + NO → N₂ + O</td>
<td>300 – 6000</td>
<td>23.27</td>
<td>16.6</td>
<td>0.005</td>
</tr>
<tr>
<td>CH₄ + Cl₂ → CH₃ + Cl₂</td>
<td>450 – 600</td>
<td>17.06</td>
<td>16.6</td>
<td>2.7 × 10⁻⁹</td>
</tr>
<tr>
<td>Br₂ + Br₂ + CO + O₂ + Br₂</td>
<td>273 – 273</td>
<td>19.3</td>
<td>29.3</td>
<td>2.0 × 10⁻¹</td>
</tr>
<tr>
<td>CO + O₂ → CO₂</td>
<td>2000 – 3000</td>
<td>21.97</td>
<td>21.84</td>
<td>6.8 × 10⁻¹</td>
</tr>
<tr>
<td>P₂ + Cl₂ + O → HOCl₂</td>
<td>50 – 500</td>
<td>16.05</td>
<td>29.3</td>
<td>5.8 × 10⁻¹</td>
</tr>
</tbody>
</table>

“Correcting” simple collision theory

- SCT neglects two features.
- Collision must be sufficiently energetic to cause reaction.
- Molecules must have proper orientation to allow reaction.
- Empirically add two factors to account for these features.
- p = static factor
- Eₜ = minimum energy for reaction.
- Like van der Waals’s improvement of the ideal-gas law.

Activated-complex theory

- Developed by H. Eyring, M. Evans, and M. Polanyi.
- Activated complex is a precursor to products.
- Exists in small amounts.
- Not seen, like a reactive intermediate.
- Can transform in two ways.
- Revert to reactants.
- Form products.
- Gives products by a first-order process.
- Can be thought of as a “decomposition”.
- Fast equilibrium between reactants and activated complex.

Relation of SCT parameters to Arrhenius parameters

- Many experimental data reported as Arrhenius behavior.
- Comparison with SCT necessary to connect theory and experiment.
- Predicts a temperature-dependent Arrhenius activation energy.
- Predicts a temperature-dependent Arrhenius pre-exponential factor.

Activated-complex mathematics

- Reaction velocity proportional to activated-complex concentration.
- Quasi-equilibrium between reactants and activated complex.
- Statistical mechanics defines disappearance rate constant of activated complex, T.
- Define the entropy and activation entropy of reaction.
- A means to parameterize the rate constant.
Eyring’s equation

- Activated-complex biomolecular rate constant, \( k_2 \), in terms of the parameters of the activated complex
  \[ k_2 = \frac{RT}{N_A C} \exp \left( \frac{\Delta S^* \gamma}{R} \right) \exp \left( -\frac{\Delta H^* \gamma}{RT} \right) \]

- Not Arrhenius-like behavior
  - Difficult to distinguish from Arrhenius behavior under many circumstances
- Another means to parameterize the rate constant
  - Can convert between Arrhenius parameters and Eyring parameters

Evaluation of Eyring parameters

- Evaluate by plotting \( \ln(k/T) \) versus \( 1/T \)
- Example:
  
  \[ \text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O} \]
- From slope and intercept:
  - \( \Delta H^* = 12.0 \text{ kJ/mol} \)
  - \( \Delta S^* = -33.2 \text{ J/K-mol} \)
- Alternative to Arrhenius parameters

Computer modeling of potential-energy surfaces

- Potential energy of configuration of molecules controls interaction
- Model time-dependent approach of molecules with (classical or quantum) simulation
- Example:
  - \( \text{D} + \text{H}_2 \rightarrow \text{HD} + \text{H} \)
- Several parameters:
  - Distances
  - Angles

Relation of Eyring and Arrhenius parameters

- Need to be able to convert between the two parameterizations of kinetic data
- Use differential of Eyring form to show relationships

<table>
<thead>
<tr>
<th>Phase/Molecularity</th>
<th>Activation Energy, ( E_a )</th>
<th>Pre-exponential factor, ( A )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution</td>
<td>( \Delta H^* + RT )</td>
<td>( \frac{RT}{N_A C} \exp \left( \frac{\Delta S^* \gamma}{R} \right) \exp \left( -\frac{\Delta H^* \gamma}{RT} \right) )</td>
</tr>
<tr>
<td>Gas, unimolecular</td>
<td>( \Delta H^* + RT )</td>
<td>( \frac{RT}{N_A C} \exp \left( \frac{\Delta S^* \gamma}{R} \right) \exp \left( -\frac{\Delta H^* \gamma}{RT} \right) )</td>
</tr>
<tr>
<td>Gas, bimolecular</td>
<td>( \Delta H^* + 2RT )</td>
<td>( \left( \frac{RT}{N_A C} \exp \left( \frac{\Delta S^* \gamma}{R} \right) \exp \left( -\frac{\Delta H^* \gamma}{RT} \right) \right)^2 )</td>
</tr>
<tr>
<td>Gas, termolecular</td>
<td>( \Delta H^* + 3RT )</td>
<td>( \left( \frac{RT}{N_A C} \exp \left( \frac{\Delta S^* \gamma}{R} \right) \exp \left( -\frac{\Delta H^* \gamma}{RT} \right) \right)^3 )</td>
</tr>
</tbody>
</table>

Computer simulation of gas-phase reactions

- Reactive encounters go through the reactive region
- Unreactive encounter goes to the reactive region and return in the same channel

Temperature and the Arrhenius model

- Why does the Arrhenius model work so well in many cases?
  - Empirical
  - Not predicted by the simplest theory
  - Not predicted by activated-complex theory
- Partial answer
  - Around room temperature, \( RT/2 \approx 1.2 \text{ kJ/mole} \)
  - \( RT/2 \) varies slowly with temperature compared to the exponential function
  - \( E_a \) tends to be much larger than \( RT/2 \) for many reactions
  - \( E_{\text{min}} \) and \( E_a \) both appear to be approximately constant
Simulation of a reactive event

- Follow the time course of the approach
- Atoms exchange partners
- Time scale is very short
- Repeat many times and measure fraction of times that reactive events happen

Summary

- Theories of simple reactions
  - Simple collision theory
  - Modified collision theory
  - Computer simulation
  - Activated-complex theory
- Parameterization of reaction dynamics
  - Arrhenius activation energy and pre-exponential factor
  - Equilibrium thermodynamic properties of activated complex from Eyring theory
  - Simple collision theory parameters