CHAPTER 14: Chemical Kinetics

- **Kinetics:**
  1. How fast do chemical reactions happen (Rate)?
  2. What are the detailed steps behind a chemical reaction (Mechanism)?
Introduction to Kinetics

5Fe²⁺(aq) + MnO₄⁻(aq) + 8H⁺(aq) → 5Fe³⁺(aq) + Mn²⁺(aq) + 4H₂O(l)

• What does the balanced chemical equation tell us?
  – Net summary of chemical reaction
  – Does not mean 5 irons combine with MnO₄⁻ and 8 protons simultaneously (collision of that many particles at once is highly improbable)

• What other information do we want to know?
  – Kinetics can provide different possible mechanisms of a reaction or the detailed steps involved in the overall reaction.
Kinetics: Rate of Reactions

• Kinetics can provide information about the amount of time required for a reaction (or step in a reaction) to occur i.e. the rate.

• What affects the rate of a reaction?
  – Chemical Concentrations
  – Temperature
  – Physical form of reactants (powder, solid, etc.)
  – Etc.
Defining Reaction Rates

1. Average Rate
2. Instantaneous Rate
3. Net Rate
Average Rate

• The average rate is the change in concentration divided by the change in time.

\[ \text{Average Rate} = \frac{\text{change in concentration}}{\text{change in time}} \]

• Units are frequently mol L\(^{-1}\)/s or mol L\(^{-1}\) s\(^{-1}\)

\[ \text{e.g. } \text{NO}_2(g) + \text{CO}(g) \rightarrow \text{NO}(g) + \text{CO}_2(g) \]

Could measure: \( \frac{[\text{NO}]_{\text{final}} - [\text{NO}]_{\text{initial}}}{t_{\text{final}} - t_{\text{initial}}} = \frac{\Delta[\text{NO}]}{\Delta t} \)

Could also look at [CO\(_2\)] or [NO\(_2\)] or [CO] instead.
Instantaneous Rate

• How fast is the reaction going right now?
• The rate of a reaction can change as a reaction progresses
  – e.g. start off fast and slow down, or vice versa, or etc.
• Average Rate ≠ Instantaneous Rate
• The slope or derivative of a concentration vs. time curve provides the instantaneous rate.

\[
\frac{d[\text{NO}]}{dt} \approx \frac{\Delta[\text{NO}]}{\Delta t}
\]

for small \( t \)

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Uniquely Defining Rate of Reaction

- What if $2\text{NO}_2(g) + \text{F}_2(g) \rightarrow 2\text{NO}_2\text{F}(g)$?

  $$-\frac{1}{2} \frac{\Delta [\text{NO}_2]}{\Delta t} = -\frac{\Delta [\text{F}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta [\text{NO}_2\text{F}]}{\Delta t}$$

- Divide by coefficients to obtain a uniquely defined “reaction rate”

- $\text{NO}_2\text{F}$ is appearing twice as fast as $\text{F}_2$ is disappearing, but the reaction rate is the same regardless of which compound is monitored.
Net Rate

- In equilibrium cases and reversible reactions, the reaction can go forward and backward.
- Net Rate = Forward Rate – Backward Rate
- For now assume K is large and the reaction essentially only goes in the forward direction.
Order of a Reaction

• How does the rate depend on concentration?
• Assuming only the forward reaction occurs, the rate frequently depends on the concentration of reactants raised to various powers.

\[ aA + bB \rightarrow cC + dD \]

Rate = \( k[A]^m[B]^n \) (exponents not necessarily a, b!!)

“Order” of reaction = m+n

• Note: m,n are often integer, but not always and can be zero. The reaction may not depend on the concentration of a reactant.
Example

Ammonium cyanate

\[ \text{NH}_4\text{CNO}(aq) \rightarrow \text{NH}_2\text{CONH}_2(aq) \]

<table>
<thead>
<tr>
<th>[NH₄CNO] (mol L⁻¹)</th>
<th>0.100</th>
<th>0.200</th>
<th>0.400</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate (mol L⁻¹ s⁻¹)</td>
<td>3.6x10⁻²</td>
<td>1.44x10⁻¹</td>
<td>5.76x10⁻¹</td>
</tr>
</tbody>
</table>

What is the order of the reaction and the rate expression with respect to NH₄CNO? What is the rate constant? What the rate if [NH₄CNO]=0.0500M?
Example
Example with Two Concentrations

sucrose(aq) + H2O(l) $\rightarrow$ fructose(aq) + glucose(aq) in acidic solution

• rate = $k[H^+][\text{sucrose}]$

• Note: H$^+$ doesn’t appear in the chemical equation, but it influences the rate!!

• What are the units of k here?
More with this Example

sucrose(aq) + H2O(l) → fructose(aq) + glucose(aq) in acidic solution

• rate = k[H⁺][sucrose]

• How is the rate affected by:
  a) cutting sucrose concentration in half (@ const pH)?
More with this Example

sucrose(aq) + H2O(l) → fructose(aq) + glucose(aq) in acidic solution

rate = k[H\textsuperscript{+}][sucrose]

b) keeping the sucrose concentration constant while lowering the pH from 1.5 to 0.5?
The Dependence of Concentration on Time

• First-order Reactions
  – e.g., decomposition of $\text{N}_2\text{O}_5$

$$\text{N}_2\text{O}_5(\text{g}) \rightarrow 2\text{NO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$$

$$\text{rate} = -\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = k[\text{N}_2\text{O}_5]$$

• What is we wanted $[\text{N}_2\text{O}_5]$ as a function of time?
• Hint: We know the derivative of $[\text{N}_2\text{O}_5]$ with respect to time.
The Dependence of Concentration on Time

- Integrate!
- Result: $[\text{N}_2\text{O}_5] = [\text{N}_2\text{O}_5]_0 e^{-kt}$
- By knowing the initial concentration and the rate constant we can calculate the concentration at anytime
- Also, $\ln [\text{N}_2\text{O}_5] = \ln [\text{N}_2\text{O}_5]_0 - kt$
- A plot of $\ln [\text{N}_2\text{O}_5]$ vs $t$ has slope equal to $-k$ and the intercept is $\ln [\text{N}_2\text{O}_5]_0$
Half-Life for First-order Reactions

- The “half-life” $t_{\frac{1}{2}}$ is the time it takes for $\frac{1}{2}$ of the reactant to decay.
- i.e., $t$ for which $[A] = \frac{[A]_0}{2}$
- From the 1st Order Equation:

$$
\ln[A] = \ln[A]_0 - kt_{\frac{1}{2}}
$$

$$
\ln\left(\frac{[A]_0}{2}\right) = \ln[A]_0 - kt_{\frac{1}{2}}
$$

$$
kt_{\frac{1}{2}} = \ln[A]_0 - \ln\left(\frac{[A]_0}{2}\right)
$$

$$
kt_{\frac{1}{2}} = \ln\left(\frac{[A]_0}{[A]_0/2}\right) = \ln(2)
$$

$$
t_{\frac{1}{2}} = \left(\frac{\ln 2}{k}\right) \approx \frac{0.6931}{k}
$$
Second-order Reaction

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

• The rate of the reaction above is observed to be second order.

\[ \text{rate} = -\frac{1}{2} \frac{\Delta[\text{NO}_2]}{\Delta t} = k[\text{NO}_2]^2 \]

• During the reaction two \( \text{NO}_2 \) collide to form \( \text{O}_2 \) and two \( \text{NO} \) molecules (mechanism)

• Based on the mechanism, it makes sense that the rate depends on \( [\text{NO}_2]^2 \)

• What is \( [\text{NO}_2] \) as a function of time?
Second-order Reaction

• Integrate: \[
\frac{\Delta[\text{NO}_2]}{\Delta t} = -2k[\text{NO}_2]^2
\]
\[
\frac{d[\text{NO}_2]}{dt} = -2k[\text{NO}_2]^2 \quad \text{for small } \Delta t
\]

• Result: \[
\frac{1}{[\text{NO}_2]} = 2kt + \frac{1}{[\text{NO}_2]_0}
\]

• A plot of \([1/\text{NO}_2]\) vs \(t\) has slope equal to \(2k\) and intercept \(1/[\text{NO}_2]_0\)

• Note: The above result of integration can be verified by differentiating the result to obtain the original expression.

• The half-life of a second-order reaction depends on initial concentrations. \(t_{1/2} = 1/(2k[\text{NO}_2]_0)\)
What do we do with this stuff?

• If we know the rate expression and concentrations at a given time $t$, then we can use concentration vs. time relationships to get the concentration at another time $t_2$.

• If we know the concentration at several times, we can figure out the order of the reaction.
  a) If a plot of $\ln[A]$ vs. $t$ is a straight line, then the reaction is first order.
  b) If a plot of $1/[A]$ vs. $t$ is a straight line, then the reaction is second order.
  c) If neither, then the reaction is 3rd order of possibly a combination of elementary reactions.

• The order of the reaction provides some insight into the mechanism.
Reaction Mechanisms

• The **mechanism** of a reaction is the sequence of **elementary steps** which make up the overall reaction.

• Each **elementary step** is a process occurring for a small (1-3) number of molecules, sometimes involving collisions between 2-3 molecules.
Examples of Elementary Reactions

1) **Unimolecular**: happens to one isolated molecule with excess energy (denoted by *)
   \[ \text{N}_2\text{O}_5^* \rightarrow \text{NO}_2 + \text{NO}_3 \text{ rate}=k[\text{N}_2\text{O}_5^*] \]

2) **Bimolecular**: involves collision between two molecules. The rate is obviously proportional to the concentration of the two reactants.
   \[ \text{NO}(g) + \text{O}_3(g) \rightarrow \text{NO}_2(g) + \text{O}_2(g) \text{ rate}=k[\text{NO}][\text{O}_3] \]

3) **Termolecular**:
   \[ \text{I} + \text{I} + \text{Ar} \rightarrow \text{I}_2 + \text{Ar} \text{ rate}=k[\text{I}]^2[\text{Ar}] \]
   simultaneous collision of 3 bodies is unlikely unless the concentrations are very high. Never see order $\geq 4$. 

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It’s Elementary, my dear Watson

• For an **elementary reaction**, the rate is just a constant times the concentrations of *all* reactants (raised to appropriate powers from the coefficients). This is **only** true for an elementary reaction!!

• The sequence of all elementary reactions is the reaction mechanism.
Example of a Mechanism

- The redox reaction between NO\(_2\) and CO:
  \[ \text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2 \]
- The overall reaction is made up of 2 bimolecular steps.
  1. \(\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO}\) (slow step)
  2. \(\text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2\) (fast step)
- Step 1: rate = \(k_1[\text{NO}_2]^2\)
- Step 2: rate = \(k_2[\text{NO}_3][\text{CO}]\)
- Step 1 + Step 2:
  \[2\text{NO}_2 + \text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{NO}_3 + \text{NO} + \text{CO}_2\]
  \[\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2\] original reaction
- \(\text{NO}_3\) is formed temporarily. It is an “intermediate”. 
Relationship between Rate Constants and Equilibrium Constants

- For a single elementary step, there is an easy connection between rate and equilibrium constants.
- e.g., \( \text{NO} + \text{O}_3 \rightleftharpoons \text{NO}_2 + \text{O}_2 \)
  
  Forward rate = \( k_1[\text{NO}][\text{O}_3] \)
  
  Backward rate = \( k_{-1}[\text{NO}_2][\text{O}_2] \)
  
- At equilibrium, the forward rate equals the backward rate.

\[
\frac{k_1[\text{NO}][\text{O}_3]}{[\text{NO}_2][\text{O}_2]} = \frac{k_1}{k_{-1}}
\]

\[
K = \frac{k_1}{k_{-1}}
\]

\( k_1 >> k_{-1} \) means big \( K \)

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Multiple Elementary Steps

- Treat each step separately and combine at end.

\[ \text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2 \]

1. \[ \text{NO}_2 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO} \]

2. \[ \text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2 \]

\[ k_1[\text{NO}][\text{O}_3] = k_{-1}[\text{NO}_2][\text{O}_2] \]

\[ k_2[\text{NO}_3][\text{CO}] = k_{-2}[\text{NO}_2][\text{CO}_2] \]

\[ K = \frac{[\text{NO}][\text{CO}_2]}{[\text{NO}_2][\text{CO}]} = \left( \frac{[\text{NO}_2][\text{CO}_2]}{[\text{NO}_3][\text{CO}]} \right) \left( \frac{[\text{NO}_3][\text{NO}]}{[\text{NO}_2]^2} \right) \]

\[ K = K_1K_2 \]

\[ K = \left( \frac{k_1}{k_{-1}} \right) \left( \frac{k_2}{k_{-2}} \right) \]

BIG K’s, \( K_{\text{eq}} \)

little k’s, k rates

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Mechanism and Rate

- Knowing the mechanism of a reaction helps us predict or understand the rate expression.
  \[2\text{NO}_2 + \text{F}_2 \rightarrow 2\text{NO}_2\text{F}\]

- A possible 2-step mechanism:
  1. \(\text{NO}_2 + \text{F}_2 \overset{k_1}{\rightarrow} \text{NO}_2\text{F} + \text{F}\)
  2. \(\text{NO}_2 + \text{F} \overset{k_2}{\rightarrow} \text{NO}_2\text{F}\) (sums to overall reaction)

  \[\text{rate} = k_1[\text{NO}_2][\text{F}_2]\]

- Why doesn’t \(k_2\) seem to matter?
- The 1\text{st} step must be much slower – it determines the rate!
- Elementary reaction 1 is the “rate limiting step”
Rate and Equilibrium

• Another example of the overall rate of a mechanism – rate determining (slow) step coupled with fast equilibrium.

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

(1) \[ \text{NO} + \text{NO} \xrightleftharpoons[k_1=k_k^-]{k_2} \text{N}_2\text{O}_2 \] (fast equilibrium)

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

• The slow step determines the rate.

\[ \text{rate} = k_2[\text{N}_2\text{O}_2][\text{O}_2] \]

• This rate equation is in terms of an \textit{intermediate} (which might be impossible to measure!)

• The equilibrium in (1) is useful. Since it is fast, it re-establishes equilibrium as \text{N}_2\text{O}_2 is consumed

\[ K = \left( \frac{k_1}{k_2} \right) = \frac{[\text{N}_2\text{O}_2]}{[\text{NO}]^2} \Rightarrow [\text{N}_2\text{O}_2] \approx K[\text{NO}]^2 \]

\[ \text{rate} = K k_2[\text{NO}]^2[\text{O}_2] \] (order = 3, but not termolecular mechanism)
Example Problem

$I^-(aq) + OCl^-(aq) \rightarrow Cl^-(aq) + OI^-(aq)$

has the mechanism:

$OCl^-(aq) + H_2O(l) \rightleftharpoons HOCl(aq) + OH^-(aq)$ (fast eq.)

$I^-(aq) + HOCl(aq) \rightleftharpoons HOI(aq) + Cl^-(aq)$ (fast eq.)

$OH^-(aq) + HOI(aq) \rightarrow H_2O(l) + OI^-(aq)$ (slow)

What is the rate expression?
Example Problem
Complication

• We can frequently write several different mechanisms. All of which might give the same predicted rate expression.
• Can’t always distinguish between possible mechanisms based on rate data!
• “A reaction mechanism can never be proved from an experimental rate law; it can only be disproved if it is inconsistent with the experimental behavior”
For Example

\[ \text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g}) \]
rate = \( k_{\text{obs}}[\text{H}_2][\text{I}_2] \)
simple bimolecular?

\[ \text{I}_2 + \text{M} \rightleftharpoons \text{I} + \text{I} + \text{M} \text{ (fast)} \]

\[ \text{H}_2 + \text{I} \rightleftharpoons \text{H}_2\text{I} \text{ (fast)} \]

\[ \text{H}_2\text{I} + \text{I} \rightarrow 2\text{HI} \text{ (slow)} \]
rate = \( k_3[\text{H}_2\text{I}][\text{I}] \)

\[ = k_3K_2K_1[\text{H}_2][\text{I}_2] \]

\[ \text{k}_{\text{obs}} \]

\text{not simple bimolecular!}
Chain Reactions

- Mechanisms with repeated steps – often involve radicals, seen in explosions, polymerizations …

\[ \text{CH}_4 + \text{F}_2 \rightarrow \bullet \text{CH}_3 + \text{HF} + \text{F}\bullet \quad \text{initiation} \]

\[ \bullet \text{CH}_3 + \text{F}_2 \rightarrow \text{CH}_3\text{F} + \text{F}\bullet \quad \text{propagation} \]

\[ \text{CH}_4 + \text{F}\bullet \rightarrow \bullet \text{CH}_3 + \text{HF} \quad \text{propagation} \]

\[ \bullet \text{CH}_3 + \text{F}\bullet + \text{M} \rightarrow \text{CH}_3\text{F} + \text{M} \quad \text{termination} \]

middle two steps keep it going and going!
Effect of Temperature on Reactions

- Gas molecules undergo $\sim 10^{10}$ collisions per second (kinetic theory of gases, Ch. 5)
- Reactions don’t go that fast – not every collision results in reaction. Why?
  a) Maybe colliding molecules are not lined up right to make bonds
  
  ![Chemical Diagram]
  
  “steric factor”
  b) Maybe the molecules don’t have enough energy to break bonds to react ("activation energy" $E_a$)
Energy for Reaction

• How would we give molecules more energy to react? Recall (Ch 5) connection between kinetic energy and temperature
• Increase temperature to give molecules more energy!
• Fraction of molecules in Boltzmann distribution with energies $> E_a$ goes as $e^{-E_a/RT}$ (approaches 1 or 100% as $T \to \infty$)
• Arrhenius found (1887) that

$$K = Ae^{-E_a/RT}$$

“pre-exponential factor” includes steric effects

activation energy
Potential Energy Curve

- Note: $E_a^{\text{rev}}$ for reverse reaction is $E_a + \Delta E_{\text{rxn}}$
- $E_a$ and $\Delta E_{\text{rxn}}$ are often expressed as $\Delta H$’s or $\Delta G$’s
- Usually, higher temp means more molecules go over the barrier. Not always true if “k” is not for an elementary reaction, but is a product of k’s as in multistep reactions.
Catalysis

• A catalyst is something that speeds up a chemical reaction by making a new mechanism available with a larger pre-exponential factor $A$ or a smaller activation energy $E_a$
• Present in small amounts most of the time, not consumed as a reactant
• Does not alter the thermodynamics ($\Delta H$, $\Delta G$) of a given reaction. (recall: for a state function like $H$ or $G$ the path taken does not matter)
• Often metals are used as catalysts (e.g. Pt for hydrogenation of C=C double bonds)
• Enzymes are examples of catalysts (inhibitors are opposite, blocking a mechanism)