Unit I - Kinetics - Chapters 13

LO 13.1 Define reaction rate and name factors which will affect the rate of a reaction. [Readings 13.1-13.2 Problems 1-9, 14, & 18]

What is a Rate
• Change in some quantity per unit time
• Average
Kinetics

The study of chemical reaction rates
Measures the change in concentration per unit time

\[ \text{Rate of reaction} = \frac{\Delta \text{concentration}}{\Delta \text{time}} \]

Introduction

Why chemists study rates:
To control chemical reactions
To give information about mechanisms

Factors that can effect the rate:
Concentration
Temperature
Particle Size
Catalyst

Concentration
Temperature

Physical State

Catalyst
13.2. Express and compare rates of chemical reactions in terms of the concentration changes of the reactants and products (or factors proportional to concentration) per unit time. [Readings 13.3 Problems 58, 59, & 60]

\[ 5\text{Br}^- + \text{BrO}_3^- + 6\text{H}^+ \rightarrow 3\text{Br}_2 + 3\text{H}_2\text{O} \]

Average rate \( \propto \)?
- \( \frac{-\Delta[\text{Br}^-]}{\Delta t} \)
- \( \frac{-\Delta[\text{BrO}_3^-]}{\Delta t} \)
- \( \frac{-\Delta[\text{H}^+]}{\Delta t} \)
- \( \frac{\Delta[\text{Br}_2]}{\Delta t} \)

Are rates equal?

5A + 2B \rightarrow C + 3D

Suppose that the rate with respect to B is 0.005M/hr
- What is the rate with respect to A?
- What is the rate with respect to C?
- What is the rate with respect to D?
LO 13.3 Given time concentration data, calculate the instantaneous rate for a particular reaction species. [Reading 13.3 problems 56, 57]

Example Reaction
The thermal decomposition of dinitrogen pentoxide to produce nitrogen dioxide and oxygen gases
\[ 2 \text{N}_2\text{O}_5 (g) \rightarrow 4 \text{NO}_2 (g) + \text{O}_2 (g) \]

Measuring rates as indirect measures of concentration
Evolution of gas (change in P)
Color (spectroscopic absorbance)
Electrical conductivity
Example Reaction

The thermal decomposition of dinitrogen pentoxide to produce nitrogen dioxide and oxygen gases

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

\[ \text{Rate of reaction} = \frac{\Delta \text{NO}_2}{\Delta \text{time}} \]

Concentration vs. Time Data

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>\text{N}_2\text{O}_5</th>
<th>\text{NO}_2</th>
<th>\text{O}_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0200</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>100</td>
<td>0.0149</td>
<td>0.0063</td>
<td>0.0016</td>
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<tr>
<td>200</td>
<td>0.0142</td>
<td>0.0115</td>
<td>0.0029</td>
</tr>
<tr>
<td>300</td>
<td>0.0120</td>
<td>0.0160</td>
<td>0.0040</td>
</tr>
<tr>
<td>400</td>
<td>0.0101</td>
<td>0.0197</td>
<td>0.0049</td>
</tr>
<tr>
<td>500</td>
<td>0.0086</td>
<td>0.0229</td>
<td>0.0057</td>
</tr>
<tr>
<td>600</td>
<td>0.0072</td>
<td>0.0256</td>
<td>0.0064</td>
</tr>
<tr>
<td>700</td>
<td>0.0061</td>
<td>0.0278</td>
<td>0.0070</td>
</tr>
</tbody>
</table>

Rate of Formation of NO\(_2\)

Rate Calculation

\[ \text{Rate} = \frac{0.0197M - 0.0160M}{400s - 300s} \]
\[ = 0.000037 M s^{-1} \]
Relating Rates in an equation

At what rate does N\textsubscript{2}O\textsubscript{5} disappear?

2 N\textsubscript{2}O\textsubscript{5} (g) $\longrightarrow$ 4 NO\textsubscript{2} (g) + O\textsubscript{2} (g)

\[ 0.000037 \text{ mol NO}_2/\text{s} \times \frac{2N_2O_5}{4NO_2} = 0.0000185 \text{ mol N}_2O_5/\text{s} \]

13.4. From experimental kinetics data, derive the rate law, the rate constant, and the order for a chemical reaction. [Readings 13.4 Problems 64, 65, 66, 67, 68, 69, 70, & 71]

Concentration dependence of rate: Rate Laws

Must be experimentally derived

Are not necessarily related to stoichiometry
The form of the Rate Law

Rxn:
3A + 2B $\rightarrow$ C + 2D

\[
Rate = -\frac{\Delta [A]}{\Delta t} = k[A]^x[B]^y
\]

[A] and [B] are initial concentrations

Definition of terms

• K = the rate constant
• Exponents - show how sensitive the rate is with respect to changes in concentration
• Exponents are not related to the stoichiometric coefficients

Reaction Order

A + 2B $\rightarrow$ 3C
Rate = k [A]^2 [B]
Reaction is second order in A
Reaction is first order in B
Reaction is (2+1) third order overall
5\text{Br}^– + \text{BrO}_3^– + 6\text{H}^+ \rightarrow 3\text{Br}_2 + 3\text{H}_2\text{O}

**THE RATE LAW**

\[
\text{Rate} = \frac{\Delta}{\Delta t} = k [\text{Br}^–]^x [\text{BrO}_3^–]^y [\text{H}^+]^z
\]

**Exptl. Data**

<table>
<thead>
<tr>
<th>([\text{Br}^–]_0)</th>
<th>([\text{BrO}_3^–]_0)</th>
<th>([\text{H}^+]_0)</th>
<th>Initial Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>0.1</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>0.1</td>
<td>2.0</td>
</tr>
<tr>
<td>3</td>
<td>0.1</td>
<td>0.2</td>
<td>2.0</td>
</tr>
<tr>
<td>4</td>
<td>0.1</td>
<td>0.1</td>
<td>4.0</td>
</tr>
<tr>
<td>5</td>
<td>0.1</td>
<td>0.3</td>
<td>9.0</td>
</tr>
</tbody>
</table>
Solving the Rate Law

1. Examine experimental data
2. Select two experiments which vary only one species
3. Solve the ratio of the two experiments to find exponents
4. Return to step 2 until all species have been solved
5. Solve for k

Exptl. Data

<table>
<thead>
<tr>
<th>[Br(^-)](_0)</th>
<th>[BrO(_3)(^-)](_0)</th>
<th>[H(^+)](_0)</th>
<th>Initial Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>1.0</td>
</tr>
<tr>
<td>2 0.2</td>
<td>0.1</td>
<td>0.1</td>
<td>2.0</td>
</tr>
<tr>
<td>3 0.1</td>
<td>0.2</td>
<td>0.1</td>
<td>2.0</td>
</tr>
<tr>
<td>4 0.1</td>
<td>0.1</td>
<td>0.2</td>
<td>4.0</td>
</tr>
<tr>
<td>5 0.1</td>
<td>0.1</td>
<td>0.3</td>
<td>9.0</td>
</tr>
</tbody>
</table>

The Exponents

- Experiments 1 and 2 to solve for x

\[
\frac{R_2}{R_1} = k \left( \frac{[Br^-]}{Br^-} \right)^x \left( \frac{[BrO_3^-]}{BrO_3^-} \right)^y \left( \frac{[H^+]}{H^+} \right)^z
\]
5Br⁻ + BrO₃⁻ + 6H⁺ → 3Br₂ + 3H₂₂

- k → rate constant
- Order of the reaction?
- Units of Rate and K?

\[
\text{Rate} = \frac{\Delta \left[ \right]}{\Delta t} = k \left[ \text{Br}^- \right] \left[ \text{BrO}_3^- \right] \left[ \text{H}^+ \right]^2
\]

13.5. Given the Initial Rate Law, concentrations, and the rate constant, determine the Rate. [Readings 13.4 Problems 62 & 63]

The Rate Law

The reaction:
2 NO(g) + 2 H₂(g) → N₂(g) + 2 H₂O(g)

The rate law is Rate = k[NO]² [H₂]
k = 1.23 M⁻² s⁻¹

What is the rate of the reaction when [NO] = 0.001 M and [H₂] = 0.005 M

What happens to the rate if:
a. [NO] is doubled
b. [H₂] is doubled
Review of the Rate Law

- Initial concentrations of reactants
- The rate of the reaction varies with initial concentrations
- The order of the reaction must be determined experimentally

Problems in measuring rates

- Rates change
- Need instantaneous rates
- Instantaneous rate at \( t=0 \) is defined as the initial rate

13.6. Use the Integrated Rate Law for a First Order Reaction to determine the concentration of a reaction species at some specified time [Reading 13.5 Problems 72, 73, 74, 75, 76, & 77]
**1\textsuperscript{ST} Order Reactions**

\[2\text{N}_2\text{O}_5 (\text{CCl}_4) \rightarrow 4\text{NO}_2 (\text{CCl}_4) + \text{O}_2 (\text{g})\]

rate = \(-\Delta [\text{N}_2\text{O}_5]/\Delta t = k [\text{N}_2\text{O}_5]\)

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**The Rate of Decomposition of Dinitrogen Pentoxide**

<table>
<thead>
<tr>
<th>Time, min</th>
<th>(\Delta t)</th>
<th>(\text{[N}_2\text{O}_5])</th>
<th>(\Delta [\text{N}_2\text{O}_5])</th>
<th>(\Delta [\text{N}_2\text{O}_5]/\Delta t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
<td>2.33</td>
<td>-0.25</td>
<td>1.36x10(^{-3})</td>
</tr>
<tr>
<td>184</td>
<td>0.25</td>
<td>2.08</td>
<td>-0.17</td>
<td>1.26x10(^{-3})</td>
</tr>
<tr>
<td>319</td>
<td>0.34</td>
<td>1.91</td>
<td>-0.24</td>
<td>1.16x10(^{-3})</td>
</tr>
<tr>
<td>526</td>
<td>0.34</td>
<td>1.67</td>
<td>-0.32</td>
<td>9.4x10(^{-4})</td>
</tr>
<tr>
<td>867</td>
<td>0.39</td>
<td>1.35</td>
<td>-0.24</td>
<td>7.2x10(^{-4})</td>
</tr>
<tr>
<td>1198</td>
<td>0.46</td>
<td>1.11</td>
<td>-0.24</td>
<td>5.7x10(^{-4})</td>
</tr>
<tr>
<td>1877</td>
<td>0.72</td>
<td>0.72</td>
<td>-0.39</td>
<td>4.7x10(^{-4})</td>
</tr>
</tbody>
</table>

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**Graph**

- X-axis: Time, min
- Y-axis: \([\text{N}_2\text{O}_5]\) concentration
- Data points labeled with corresponding values.
1ST Order Equations

\[ 2\text{N}_2\text{O}_5 (\text{CCl}_4) \rightarrow 4\text{NO}_2 (\text{CCl}_4) + \text{O}_2 (g) \]

\[-\Delta[\text{N}_2\text{O}_5]/\Delta t = k \ [\text{N}_2\text{O}_5] \]

\[ \ln [\text{N}_2\text{O}_5]_t = -kt + \ln [\text{N}_2\text{O}_5]_0 \]

\[ y = mx + b \]

Calculation Formula

\[ kt = \ln \frac{[\text{N}_2\text{O}_5]_0}{[\text{N}_2\text{O}_5]_t} \]

1st Order General Equation

For: \( A \rightarrow B \)

\[ kt = \ln \frac{[A]_0}{[A]_t} \]

\[ \begin{array}{c|c|c}
[A]_0 & t & [A]_t \\
\hline
1 & 0 & 1 \\
5 & 1 & 2 \\
10 & 1.5 & 3 \\
20 & 2 & 4 \\
50 & 4 & 5 \\
100 & 6 & 6 \\
200 & 8 & 7 \\
\end{array} \]
Problem

The decomposition of $N_2O_5$ in nitric acid is a first-order reaction. If it takes 4.26 minutes to decrease 2.56 mg of $N_2O_5$ to 2.50 mg. Find $k$ for the reaction.

Example

Hydrogen peroxide breaks down as a first order reaction as shown:

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

The rate constant at 20.0°C is $1.8 \times 10^{-5}$ s$^{-1}$

Given the initial concentration was 0.050M, what would the concentration be after 4.00 hrs.

13.7 For second order reaction, determine the rate constant and concentration after time. [Readings 13.5 Problems 78 & 79]
2nd Order Reactions

rate = k [A]^2

\[ \frac{1}{[A]}_t = kt + \frac{1}{[A]}_0 \]

\[ kt = \frac{1}{[A]}_t - \frac{1}{[A]}_0 \]

\[ t_{1/2} = \frac{1}{k [A]_0} \]

2nd Order Reactions

The rate constant for a second-order reaction is 0.47M\(^{-1}\)s\(^{-1}\). If the initial concentration of the reactant is 0.25 M, how much time would it take for the concentration to decrease to 0.15 M?

13.8 For first and second order reaction, determine the half-life for a chemical reaction from time/concentration data. [Readings 13.5 Problems 80, 81, 82, 83, 84, & 85]
Half-Life for 1st Order Reactions

\[ t = t_{1/2} \]

when \( [N_2O_5]_t = 1/2 \)
\( [N_2O_5]_o \)

\[ K \cdot t_{1/2} = 0.693 = \ln(2) \]

Problem

If \( k=0.00557/\text{min} \) for the decomposition of \( N_2O_5 \). What is the half-life for this compound?

Zero Order Reactions

rate = \( k \cdot [A]^o = k \)

\( [A]_t = - kt + [A]_o \)

\( kt = [A]_o - [A]_t \)

\( t_{1/2} = [A]_o / 2k \)
Using Half Lives

The half life for a 1st order reaction is 15.25 hours. How long would it take for a reaction to be 35% complete?

13.9. Use Collision and Transition State Theories to explain reaction rates. [Readings 13.6 Problems 33-41]

Collision Theory

Reactions occur because reactant molecules collide.

Collisions can cause the bonds of reactant molecules to break.

This allows the atoms to be arranged in new combinations therefore forming products.
Simplified collision theory:
The rate can be effected by factors that

1. Increase the number of effective collisions per unit time
2. Increase the force of collisions

Not all collisions are successful

Geometry of collisions

Threshold energies

Geometry of collisions
Threshold energies

Maxwell-Bolzman Distribution

Successful Collision
Maxwell-Boltzman Distribution

Energy Profile

Energy Profile
13.10. From a reaction profile, determine $\Delta H$ & $E_a$ for a chemical reaction. [Readings 13.6]
13.11. From kinetic data, determine the relationship between $E_a$, $k$, and the temperature of both catalyzed and uncatalyzed chemical reactions. [Readings 13.7 Problems 86, 87, 88, 90, 91, 92, & 93]
Rate Constant vs. Temperature

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Rate constant (k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>633</td>
<td>0.0000204</td>
</tr>
<tr>
<td>667</td>
<td>0.00012</td>
</tr>
<tr>
<td>710</td>
<td>0.000832</td>
</tr>
<tr>
<td>738</td>
<td>0.00263</td>
</tr>
</tbody>
</table>

Quantitative Temperature Dependence

The Arrhenius Equation

\[ k = A e^{-\frac{E_a}{RT}} \]

\[ \ln k = \ln (A e^{-\frac{E_a}{RT}}) \]

\[ \ln k = \ln A - \frac{E_a}{RT} \]
Calculation Formulas

General Form

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left[ \frac{1}{T_2} - \frac{1}{T_1} \right]$$

Calculating $E_a$

HI has a rate constant $k = 0.079 \text{ M}^{-1}\text{s}^{-1}$ at 500°C and $k = 0.24 \text{ M}^{-1}\text{s}^{-1}$. What is the activation energy for the decomposition of HI?
13.12 Determine the relationship between the rate law and the mechanism of a simple chemical reaction. [Readings 13.8 Problems 43, 44, 45, 46, 47, 48, 49, & 50]

Mechanism:

- A sequence of reaction steps
- Adding the reaction steps gives the overall reaction
- The overall reaction gives the stoichiometric reaction equation
- A reaction intermediate is formed in one step and consumed in the next (O in the previous example)
Mechanism:

• Reaction Mechanisms
  • Intermediates are not shown in the net equation for the complete reaction
  • In a multistep mechanism, one step is usually slower than the others.
  • This is the rate-determining step

Reaction Mechanisms

• The rate law for the rate-determining step is directly related to the rate law for the overall reaction
Rate Law and Mechanism

- The rate law for an individual step is directly related to the steps molecularity.
- Thus the exponent is equal to the coefficient in the step’s equation.
- NOT TRUE OF THE OVERALL EQUATION.

Unimolecular Reactions

- $A \rightarrow B + C$ single step
- Rate = $k[A]$ 
- Example: The decomposition of ozone
  - $O_3 \rightarrow O_2 + O$ slow step
  - $O_3 + O \rightarrow 2O_2$ fast step
  - $2O_3 \rightarrow 3O_2$

Bimolecular Reactions

Slow (rate determining) Step:
- $A + A \rightarrow$ products
- or
- $A + B \rightarrow$ products

Rate = $k[A]^2$ or
Rate = $k[A][B]$
2 NO₂ → 2NO + O₂  
rate_{exp} = k [NO₂]  
possible mechanism:  
(1) NO₂ → NO + O slow  
(2) O + NO₂ → O₂ + NO fast  

NO₂ + CO → NO + CO₂  
Possible Mechanism  

NO₂ + CO → NO + CO₂  
Alternate Possible Mechanism  

How can one choose the correct mechanism?
1.8. Explain the role of catalysts, what they are, how they work, and how they affect a reaction profile. [Readings 12.11 Problems 72, & 74]

A catalyst is a material added to the reactants which:

- Speeds up the reaction (doesn't cause reaction)
- Is part of the rate law
- Lowers $E_a$
- Makes an alternative mechanism possible
- Is not part of the stoichiometry of the reaction (is neither a reactant nor a product)

Heterogeneous catalysts