Chapter 14
Chemical Kinetics

• 14-1 Rates of Chemical Reactions
• 14-2 Reaction Rates and Concentrations
• 14-3 The Dependence of Concentrations on Time
• 14-4 Reaction Mechanisms
• 14-5 Reaction Mechanism and Rate Laws
• 14-6 Effect of Temperature on Reaction Rates
• 14-7 Kinetics of Catalysis
Chapter 14
Chemical Kinetics

• Thus far in the course, we have been using and talking about chemical reactions
  – Reactants, products, and how much is involved

• **Chemical Kinetics** deals with how fast a reaction proceeds
  – Kinetics = **Rates of Chemical Reactions**
  – And how to deduce reaction mechanisms from observed rates of reactions
  – Activation Energy
  – Catalysts
Chapter 14
Reaction Mechanisms

• Most reactions proceed not thru a single step but through a series of steps
• Each Step is called an elementary reaction
• Types of elementary Reactions
  1. Unimolecular (a single reactant)
     E.g., $A \rightarrow B + C$ (a decomposition)
  2. Bimolecular (most common type)
     E.g., $A + B \rightarrow \text{products}$
  3. Termolecular (less likely event)
     E.g., $A + B + C \rightarrow \text{products}$
Chapter 14
Chemical Kinetics

• Reaction Mechanism
  – is a detailed series of elementary steps and rates which are combined to yield the overall reaction
  – One goal of chemical kinetics is to use the observed rate to choose between several possible reaction mechanisms.
average reaction rate \( = \frac{\Delta [X]}{\Delta t} \)

units are \( \frac{\text{mol/L}}{\text{s}} = \frac{\text{mol}}{\text{L} \cdot \text{s}} = \text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1} \)

average rate \( = \frac{[X]_f - [X]_i}{t_f - t_i} = \frac{\Delta [X]}{\Delta t} \)

To measure rates we could monitor the disappearance of reactants or appearance of products

e.g., \( \text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2 \)
To measure rates we could monitor the disappearance of reactants or appearance of products

\[ 2\text{NO}_2 + \text{F}_2 \rightarrow 2\text{NO}_2\text{F} \]
Generalized Reaction

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

\[
\text{rate} = -\left( \frac{1}{a} \right) \frac{\Delta [A]}{\Delta t} = -\left( \frac{1}{b} \right) \frac{\Delta [B]}{\Delta t}
\]

\[
= +\left( \frac{1}{c} \right) \frac{\Delta [C]}{\Delta t} = \left( \frac{1}{d} \right) \frac{\Delta [D]}{\Delta t}
\]
Order of a Reaction

\[ N_2O_5 \xrightarrow{k} 2\text{NO}_2 + \frac{1}{2} \text{O}_2 \text{ decomposition} \]

e.g., \[ a\text{A} \rightarrow \text{products} \]

rate = \[ k[\text{A}]^n \]
\[
e^k \quad aA \rightarrow \text{products}
\]

\[
rate = k[A]^n
\]

n does not have to be an integer

n = 3/2 “three halves order” reaction

Note that n does not equal the coefficient of the reactant. It is related to the reaction mechanism and determined experimentally.
aA + bB $\xrightarrow{k}$ products

rate = $k[A]^m[B]^n$

Overall reaction order = $m + n$

$m^{th}$ order in [A]

$n^{th}$ order in [B]

as before

rate = $k[A]^m[B]^n$

$$= -\left(\frac{1}{a}\right) \frac{\Delta[A]}{\Delta t} = -\left(\frac{1}{b}\right) \frac{\Delta[B]}{\Delta t}$$
Example 14-2

At elevated temperatures, HI reacts according to the chemical equation

\[ \text{2HI} \rightarrow \text{H}_2 + \text{I}_2 \]

at 443°C, the rate of reaction increases with concentration of HI, as shown in this table.

<table>
<thead>
<tr>
<th>Data Point</th>
<th>[HI] (mol L(^{-1}))</th>
<th>Rate (mol L(^{-1}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.005</td>
<td>7.5 x 10(^{-4})</td>
</tr>
<tr>
<td>2</td>
<td>0.01</td>
<td>3.0 x 10(^{-3})</td>
</tr>
<tr>
<td>3</td>
<td>0.02</td>
<td>1.2 x 10(^{-2})</td>
</tr>
</tbody>
</table>

\(a\) Determine the order of the reaction with respect to HI and write the rate expression

\(b\) Calculate the rate constant and give its units

\(c\) Calculate the instantaneous rate of reaction for a [HI] = 0.0020M
\[
2\text{HI} \xrightarrow{k} \text{H}_2 + \text{I}_2
\]

\[
\text{rate}_1 = k([\text{HI}]_1)^n
\]
\[
\text{rate}_2 = k([\text{HI}]_2)^n
\]

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</tr>
<tr>
<td>3</td>
<td>0.02</td>
<td>1.2 \times 10^{-2}</td>
</tr>
</tbody>
</table>

\(a\) Determine the order of the reaction with respect to HI and write the rate expression

\[
\frac{\text{rate}_2}{\text{rate}_1} = \frac{k([\text{HI}]_2)^n}{k([\text{HI}]_1)^n}
\]

\[
\frac{3.0 \times 10^{-3}}{7.5 \times 10^{-4}} = \left(\frac{0.010}{0.0050}\right)^n
\]

\[
4 = (2)^n\]

\[
n = 2
\]

\[
\therefore \text{second order in HI and rate} = k[\text{HI}]^2 \quad \text{answer to part A}
\]
Example 14-2

b) Calculate the rate constant and give its units

\[ \text{rate} = k[\text{HI}]^2 \quad \text{answer to part A} \]

\[
k = \frac{\text{rate}}{[\text{HI}]^2} = \frac{7.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}}{(0.0050 \text{ mol L}^{-1})^2}
\]

\[ k = 30 \text{ L mol}^{-1} \text{ s}^{-1} \quad \text{answer to B} \]

Example 14-2

c) Calculate the instantaneous rate of reaction for a \([\text{HI}] = 0.0020\text{M}\)

\[ \text{rate} = k[\text{HI}]^2 \]

\[ = (30 \text{ L mol}^{-1} \text{ s}^{-1})(0.0020 \text{ mol L}^{-1})^2 \]

\[ = 1.2 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1} \quad \text{answer to C} \]
Similarly for two or more concentrations

\[ aA + bB \xrightarrow{k} \text{products} \]

\[
\text{rate} = k[A]^m [B]^n \quad \text{order is} \quad p = m + n
\]

units of \( k \) are \( \text{mol}^{-(p-1)} \text{L}^{(p-1)} \text{s}^{-1} \)

**Example**

\[ A + B \rightarrow C \]

<table>
<thead>
<tr>
<th>([A]) (\text{mol L}^{-1} \text{s}^{-1})</th>
<th>([B]) (\text{mol L}^{-1} \text{s}^{-1})</th>
<th>initial Rate (\text{mol L}^{-1} \text{s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1.0 \times 10^{-4})</td>
<td>(1.0 \times 10^{-4})</td>
<td>(2.8 \times 10^{-6})</td>
</tr>
<tr>
<td>(1.0 \times 10^{-4})</td>
<td>(3.0 \times 10^{-4})</td>
<td>(8.4 \times 10^{-6})</td>
</tr>
<tr>
<td>(2.0 \times 10^{-4})</td>
<td>(3.0 \times 10^{-4})</td>
<td>(3.4 \times 10^{-5})</td>
</tr>
</tbody>
</table>
For Example

\[ A + B \rightarrow C \]

\begin{align*}
\text{Initial Rate} & \quad \text{mol L}^{-1} \text{s}^{-1} \\
1.0 \times 10^{-4} & \quad 1.0 \times 10^{-4} & \quad 2.8 \times 10^{-6} \\
1.0 \times 10^{-4} & \quad 3.0 \times 10^{-4} & \quad 8.4 \times 10^{-6} \\
2.0 \times 10^{-4} & \quad 3.0 \times 10^{-4} & \quad 3.4 \times 10^{-5} \\
\end{align*}

\[ rate = k[A]^m [B]^n \]

1st When A is constant (1.0 \times 10^{-4}), B increases \times 3 and rate increases \times 3

\[ [B]^n = [B]^1 \]

\[ \therefore rate = k[A]^n [B]^1 \]
For Example

\[ A + B \rightarrow C \]

<table>
<thead>
<tr>
<th>[A]</th>
<th>[B]</th>
<th>\text{mol L}^{-1} \text{s}^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 \times 10^{-4}</td>
<td>1.0 \times 10^{-4}</td>
<td>2.8 \times 10^{-6}</td>
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<tr>
<td>2.0 \times 10^{-4}</td>
<td>3.0 \times 10^{-4}</td>
<td>3.4 \times 10^{-5}</td>
</tr>
</tbody>
</table>

\[
rate = k[A]^m [B]^1
\]

2\text{nd} When B is constant \((3.0 \times 10^{-4})\),

A increases \(X \ 2\) and rate increases \(X \ 4\)

\[
[A]^m = 4
\]

\[
[2]^2 = 4
\]

\[
m = 2
\]

\[
\therefore \ rate = k[A]^2[B]^1
\]
Can now solve for $k$

\[
\text{rate} = k[A]^2[B]^1
\]

\[
k = \frac{\text{rate}}{[A]^2[B]^1}
\]

\[
= \frac{2.8 \times 10^{-6}}{[1 \times 10^{-4}]^2[1 \times 10^{-4}]^1}
\]

\[
= 2.8 \times 10^6 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}
\]
14-3 The Dependence of Concentrations on Time

First Order Reactions

in general, for first order

$$ A \rightarrow \text{products} $$

rate \(= - \frac{\Delta [A]}{\Delta t} = k[A] \)

For now, just accept this important formula
Integrated Rate Law for a 1st Order Reaction

\[ [A] = [A]_0 e^{-kt} \]

If we take the ln of both sides

Recall \( y = mx + b \) or

\[ y = b + mx \]

A plot of \( \ln [A] \) vs \( t \) will be a straight line with the

\[ \text{Intercept} = \ln[A]_0 \]

\[ \text{Slope} = -k \]
\[ \ln[A] = \ln[A]_0 - kt \]

First Order Reaction

\[ \text{Slope} = -k \]

Intercept = \( \ln[N_2O_5]_0 \)

\[ \text{Slope} = -k = -1.72 \times 10^{-5} \text{ s}^{-1} \]
Second Order Reactions

In General, for second order

\[ 2 \text{A} \xrightleftharpoons[k]{} \text{products} \]

\[ \text{rate} = - \frac{1}{2} \frac{\Delta[A]}{\Delta t} = k[A]^2 \]

From calculus

Integrated Rate Law for a 2nd Order Reaction

\[ \frac{1}{[A]} = 2kt + \frac{1}{[A]_o} \]

equation for a straight line

\[ Y = mx + b \]
\[ \frac{1}{[\text{NO}_2]} \quad \text{(L mol}^{-1}) \]

\[ \text{Time (s)} \]

\[ 0 \quad 200 \quad 400 \quad 600 \quad 800 \quad 1000 \]

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

\( \text{Slope} = 2k \)

\[ \text{Concentration of } [\text{NO}_2] \quad (\text{mol L}^{-1}) \]

\[ 0.010 \quad 0.009 \quad 0.008 \quad 0.007 \quad 0.006 \quad 0.005 \]

\[ \text{Time (s)} \]

\[ 0 \quad 200 \quad 400 \quad 600 \quad 800 \quad 1000 \]
\[
\frac{1}{[A]} = 2kt + \frac{1}{[A]_o}
\]

Second Order Reaction

\[
\text{Slope} = 2k
\]
Summary

Integrated Rate Laws

First Order Reactions

\[ \ln[A] = \ln[A]_0 - kt \]

Second Order Reactions

\[ \frac{1}{[A]} = 2kt + \frac{1}{[A]_0} \]
In the real world, if we don’t know the order of the reaction $[A]^n$ plot both
Chapter 14-4
Reaction Mechanisms

- Most reactions proceed not thru a single step but through a series of steps
- Each Step is called an elementary reaction
- Types of elementary Reactions
  1. **Unimolecular** (a single reactant)
     E.g., $A \rightarrow B + C$ (a decomposition)
  2. **Bimolecular** (most common type)
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  3. **Termolecular** (less likely event)
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Chapter 14
Chemical Kinetics

• Reaction Mechanism
  – is a detailed series of elementary steps and rates which are combined to yield the overall reaction
  – One goal of chemical kinetics is to use the observed rate to chose between several possible reaction mechanisms.
1.) $\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO} \text{ (slow)}$

2.) $\text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2 \text{ (fast)}$

Notice that $\text{NO}_3$ is formed and consumed. This is called a reactive intermediate.

Notice also that:

Step 1 is bimolecular

Step 2 is bimolecular

Reactive intermediate is $\text{NO}_3$

**sum**

$$2\text{NO}_2 + \text{NO}_3 + \text{CO}$$

$$\rightarrow \text{NO}_3 + \text{NO} + \text{NO}_2 + \text{CO}_2$$

Overall:

$$\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2$$
Chemical Equilibrium

A direct connection exists between the equilibrium constant of a reaction that takes place in a sequence of steps and the rate constants in each step.

a.) at equil: forward rate = reverse rate
b.) $K_{eq} = \frac{k_f}{k_r}$

\[
\begin{align*}
\text{aA + bB} & \rightleftharpoons \text{cC + dD} \\
\text{Forward reaction rate} &= k_f [A]^a [B]^b \\
\text{Reverse reaction rate} &= k_r [C]^c [D]^d
\end{align*}
\]

1.) $k_f [A]^a [B]^b = k_r [C]^c [D]^d$

2.) \[ \frac{k_f}{k_r} = \frac{[C]^c [D]^d}{[A]^a [B]^b} = K_{eq} \]
A direct connection exists between the equilibrium constant of a reaction that takes place in a sequence of steps and the rate constants in each step.

\[ K_{eq} = \frac{k_f}{k_r} \quad \text{(sometimes} \ k_n / k_{-n}) \]

The book uses a general reaction to illustrate this principle.

\[ 2 \ A \ (g) + B \ (g) \leftrightarrow C \ (g) + D \ (g) \]

Suppose the reaction proceeds by the following two step mechanism

1.) \[ A \ (g) + A \ (g) \stackrel{k_1}{\leftrightarrow} A_2 \ (g) \]
   \[ \text{Rate}_1 = k_1[A]^2 \]
   \[ \text{Rate}_{-1} = k_{-1}[A_2] \]

2.) \[ A_2 \ (g) + B \ (g) \stackrel{k_2}{\leftrightarrow} C \ (g) + D \ (g) \]
   \[ \text{Rate}_2 = k_2[A_2][B] \]
   \[ \text{Rate}_{-2} = k_{-2}[C][D] \]

\[
K = K_1K_2 = \left( \frac{k_1}{k_{-1}} \right)\left( \frac{k_2}{k_{-2}} \right) = \frac{k_1}{k_{-1}} \cdot \frac{k_2}{k_{-2}}
\]

\[ K = \frac{[A_2][C][D]}{[A]^2[A_2][B]} = \frac{[C][D]}{[A]^2[B]} \]
14-5 Reaction Mechanism & Rate Laws

Typically with a reaction one of several elementary step reaction is the slowest step. This is called the Rate Determining Step (RDS)

Case #1: When the RDS occurs first, the first step is slow and determines the rate of the overall reaction.

1.) \( \text{NO}_2 + \text{F}_2 \rightarrow \text{NO}_2\text{F} + \text{F} \) (slow)

2.) \( \text{NO}_2 + \text{F} \rightarrow \text{NO}_2\text{F} \) (fast)

Step 1 is the RDS

rate = \( k_1[\text{NO}_2][\text{F}_2] \)
1. \( \text{NO}_2 + F_2 \xrightarrow{k_1} \text{NO}_2F + F \) (slow)

2. \( \text{NO}_2 + F \xrightarrow{k_2} \text{NO}_2F \) (fast)

Step 1 is the RDS

rate = \( k_1 [\text{NO}_2][F_2] \)
Case #2: When the RDS occurs after one or more Fast steps, mechanisms are often signaled by a reaction order greater than two. The slow step determines the overall rate of the reaction.

**Overall reaction**

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

3 molecule reaction. Is it A Termolecular or Bimolecular reactions? Three way collisions are rare. Try a two step mechanism.

1. \( \text{NO} + \text{NO} \xrightarrow{k_1} \text{N}_2\text{O}_2 \) (fast)
2. \( \text{N}_2\text{O}_2 + \text{O}_2 \xrightarrow{k_2} 2\text{NO}_2 \) (slow)

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

But \( \text{N}_2\text{O}_2 \) is a reactive intermediate
1. NO + NO $\xrightarrow{k_1} \text{N}_2\text{O}_2$ (fast) $\xleftarrow{k_{-1}}$

2. N$_2$O$_2$ + O$_2$ $\xrightarrow{k_2} 2\text{NO}_2$ (slow)

rate = $k_2[N_2O_2][O_2]$
1. \( \text{NO} + \text{NO} \xrightarrow{k_1} \text{N}_2\text{O}_2 \) (fast) 
\( \xleftarrow{k_{-1}} \) 
2. \( \text{N}_2\text{O}_2 + \text{O}_2 \xrightarrow{k_2} 2\text{NO}_2 \) (slow) 

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

Need to express [intermediates] in terms of other reactants

**forward rate** = \( k_1[\text{NO}]^2 \)

**reverse rate** = \( k_{-1}[\text{N}_2\text{O}_2] \)

at equilibrium

\[
k_1[\text{NO}]^2 = k_{-1}[\text{N}_2\text{O}_2]
\]

\[
K_1 = \frac{k_1}{k_{-1}} = \frac{[\text{N}_2\text{O}_2]}{[\text{NO}]^2}
\]

\[
\therefore [\text{N}_2\text{O}_2] = K_1[\text{NO}]^2
\]
\[ \begin{align*}
1.) & \quad \text{NO} + \text{NO} \xrightarrow{k_1} \text{N}_2\text{O}_2 \quad \text{(fast)} \\
& \quad \quad \xleftarrow{k_-1} \\
2.) & \quad \text{N}_2\text{O}_2 + \text{O}_2 \xrightarrow{k_2} 2\text{NO}_2 \quad \text{(slow)} \\
\text{rate} &= k_2[\text{N}_2\text{O}_2][\text{O}_2] \\
[\text{N}_2\text{O}_2] &= K_1[\text{NO}]^2
\end{align*} \]

Substituting for \([\text{N}_2\text{O}_2]\) in the rate expression above

\[ \text{rate} = k_2K_1[\text{NO}]^2[\text{O}_2] \]
1.) $\text{NO} + \text{NO} \xrightarrow{k_1} \text{N}_2\text{O}_2$ (fast)

$\text{N}_2\text{O}_2 \xleftarrow{k_{-1}} \text{NO} + \text{O}_2$

2.) $\text{N}_2\text{O}_2 + \text{O}_2 \xrightarrow{k_2} 2\text{NO}_2$ (slow)

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

$$\text{rate} = k_2 K_1 [\text{NO}]^2 [\text{O}_2]$$

Diagram:

- Energy
- Reaction Progress
- $\text{N}_2\text{O}_2 + \text{O}_2$
- $2\text{NO} + \text{O}_2$
- $2\text{NO}_2$
- Fast
- Slow
14-6 The Effect of Temperature on Reaction Rates

**Arrenhius Equation**

where

$E_a$ is the Activation energy

units are energy per mole

and

A is the "pre-exponential factor"

is a constant and has the units of k
Arrenhius Equation

\[ k = Ae^{-\frac{Ea}{RT}} \]

\[ y = mx + b \]

An Arrenhius Plot

Slope = \(-\frac{Ea}{R}\)
The Activation Energy ($E_a$) is the minimum collision energy that reactants must have in order to form products.
The Activation Energy ($E_a$) is the minimum collision energy that reactants must have in order to form products.

$$\Delta E = E_a^f - E_a^r$$
Chapter 14
Chemical Kinetics

• Catalyst
  – provides a lower energy path, but it does not alter the energy of the starting material and product
  – rather it changes the energy of the transition (s), in the reaction
  – A catalyst has no effect on the thermodynamics of the overall reaction

• Inhibitor
  – is a negative catalyst. It slows the rate of a reaction frequently by barring access to path of low Ea and thereby forcing the reaction to process by a path of higher Ea.
Kinetics of Catalysis

• A catalyst has no effect on the thermodynamics of the overall reaction
• It only provides a lower energy path
• Examples
  – Pt and Pd are typical catalysts for hydrogenation reactions (e.g., ethylene to ethane conversion)
  – Enzymes act as catalysts
• Phases
  – Homogenous catalysis – the reactants and catalyst are in the same catalyst (gas or liquid phase)
  – Heterogeneous catalysis – reaction occurs at the boundary of two different phases (a gas or liquid at the surface of a solid)
Chapter 14
Chemical Kinetics

• Example / exercise
  14-1, 14-2, 14-3, 14-4, 14-5,
  14-6, 14-7, 14-8, 14-9

• Problems
  7, 9, 11, 15, 19, 21, 23, 25, 37,
  41, 43, 45, 51, 53