Kinetics: Rates and Mechanisms of Chemical Reactions

14.1 Photochemical Smog (read on your own)

14.2 Reaction Rates

14.3 Effect of Concentration on Reaction Rate
   (The Rate Law and Its Components)

14.4 Reaction Mechanisms

14.5 Reaction Rates, Temperature, and the Arrhenius Equation

14.6 Catalysis: Speeding Up a Chemical Reaction
Factors That Affect Reaction Rate

1. Reactivity of the reactants

2. Reactant Contact
   a. homogeneous systems
      1. gas phase
      2. liquid phase
      3. solid phase
   b. heterogeneous systems
      1. rate $\propto$ area of phase interface

3. Concentrations of reactants (Rate Laws)

4. Temperature: As $T \Rightarrow$ reaction rate

5. Catalysts
Measurement and Expression of Reaction Rates

1. Measure the decrease in [reactant] as function of time, or
2. Measure the increase in [product] as function of time:

\[
\begin{array}{ccc}
\text{time, min} & 0 & 0.05 & 0.1 & 0.15 & 0.2 & 0.25 & 0.3 & 0.35 & 0.4 \\
\text{Concentration, M} & \text{[A]} & \text{[C]} & & & & & & & \\
\end{array}
\]
In general, for a reaction of the form
\[ aA + bB \rightarrow cC \]
the rate of reaction can be expressed as:

**NOTE:** Express Rate of reaction in terms of species with coefficient of 1.
Expressing Reaction Rate (cont’d)

3. Measure time it takes for a specific amount of reactant to be used, or, time it takes to produce a specific amount of a product.

⇒ shorter time = faster rate

Average Rate vs. Instantaneous Rate

Because rate of reaction depends on \[\text{reactant}\], as reactant is consumed and \[\text{reactant}\] ↓, then rate

\[\text{Average Rate:}\]

\[\text{Instantaneous Rate:}\]
Average Rate

\[ C_4H_9Cl(aq) + H_2O(l) \rightarrow C_4H_9OH(aq) + H^+(aq) + Cl^-(aq) \]
Instantaneous Rate: Rate at a Specific Point

\[ [\text{C}_4\text{H}_9\text{Cl}] \text{, M} \] vs. time, s
Instantaneous Rate

<table>
<thead>
<tr>
<th>time, s</th>
<th>Inst Rate, M/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$2.10 \times 10^{-4}$</td>
</tr>
<tr>
<td>50</td>
<td>$1.90 \times 10^{-4}$</td>
</tr>
<tr>
<td>100</td>
<td>$1.60 \times 10^{-4}$</td>
</tr>
<tr>
<td>200</td>
<td>$1.35 \times 10^{-4}$</td>
</tr>
<tr>
<td>300</td>
<td>$1.09 \times 10^{-4}$</td>
</tr>
<tr>
<td>400</td>
<td>$8.00 \times 10^{-5}$</td>
</tr>
<tr>
<td>500</td>
<td>$7.50 \times 10^{-5}$</td>
</tr>
<tr>
<td>800</td>
<td>$4.00 \times 10^{-5}$</td>
</tr>
</tbody>
</table>
Dependence of Rate on Reactant Concentration

[Graph showing the relationship between rate and reactant concentration]
The Rate Laws

Rate Law: mathematical expression relating the rate of a reaction to the reactant concentrations.

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

Rate Law:
Reaction Order

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

The exponents in the Rate Law are called the “reaction orders” in each of the reactants.

The example reaction is:
Notes about Rate Laws:

- Reaction order in any species usually is an integer or half (1/2, 3/2); can also be 0.

- Usually only reactants appear in Rate Law, but sometimes products do.

- Overall reaction order is sum of orders in each species.

- Rate Laws cannot be determined by inspection (i.e., cannot determine orders by knowing coefficients of balanced chemical equation).

- Rate Laws can be determined ONLY by:
Rate Laws: Examples

\[ 2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g) \quad \text{Rate} = k [N_2O_5] \]

\[ CH_3CHO(g) \rightarrow CH_4(g) + CO(g) \quad \text{Rate} = k [CH_3CHO]^{3/2} \]

\[ H_2O_2(aq) + 3I^-(aq) + 2H^+(aq) \rightarrow I^-_3(aq) + 2H_2O(l) \quad \text{Rate} = k [H_2O_2] [I^-] \]
Units of the Rate Constant, k

As we have seen, Rates are expressed in units of concentration per unit time, e.g., \( \text{M s}^{-1} \) or \( \text{M min}^{-1} \)

The units of k depend on Overall Reaction Order, so that Rate always comes out to be \( \text{M time}^{-1} \)

For a simple reaction \( aA \rightarrow bB \) or ANY other reaction:

<table>
<thead>
<tr>
<th>Overall Order</th>
<th>Rate Law</th>
<th>Units of Rate Constant k</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(^{st})</td>
<td>Rate =</td>
<td></td>
</tr>
<tr>
<td>2(^{nd})</td>
<td>Rate =</td>
<td></td>
</tr>
<tr>
<td>3(^{rd})</td>
<td>Rate =</td>
<td></td>
</tr>
<tr>
<td>etc...</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Determining Rate Laws Experimentally: The Isolation Method

Look at what happens to reaction rate when you change reactant concentrations one at a time, i.e., want to isolate the effect of each reactant.

So, carry out series of experiments under same conditions (e.g., T) but change one reactant concentration in each trial

Measure reaction rate for each trial, and deduce Rate Law

Note: Usually best to measure initial rate
Example 1: Determining a Rate Law

Determine the Rate Law of the reaction below, given the Rate vs. concentration data in the Table:

\[ A + 2B \rightarrow C \]

<table>
<thead>
<tr>
<th>Trial #</th>
<th>Initial [A]</th>
<th>Initial [B]</th>
<th>Initial Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.100 M</td>
<td>0.100 M</td>
<td>(5.50 \times 10^{-6} \text{ Ms}^{-1})</td>
</tr>
<tr>
<td>2</td>
<td>0.200</td>
<td>0.100</td>
<td>(2.20 \times 10^{-5})</td>
</tr>
<tr>
<td>3</td>
<td>0.400</td>
<td>0.100</td>
<td>(8.80 \times 10^{-5})</td>
</tr>
<tr>
<td>4</td>
<td>0.100</td>
<td>0.300</td>
<td>(1.65 \times 10^{-5})</td>
</tr>
<tr>
<td>5</td>
<td>0.100</td>
<td>0.500</td>
<td>(2.75 \times 10^{-5})</td>
</tr>
<tr>
<td>6</td>
<td>0.300</td>
<td>0.100</td>
<td>(4.95 \times 10^{-5})</td>
</tr>
</tbody>
</table>
The Integrated Rate Equations

1. Reactions that are 1st order overall.

Consider a reaction $aA \rightarrow B$ that is 1st order in $A$

Rearranging and integrating over the interval $t=0$ to $t=t$, (i.e., from $[A]_0$ to $[A]_t$):
First order reactions:

\[ aA \rightarrow B \]

![Graph 1](Image)

\[ \text{time, min} \]

\[ [A] \]

![Graph 2](Image)

\[ \ln [A]_t \]

\[ \text{time, min} \]
Half-life:
The time it takes to reduce reactant concentration to half its initial value.

First Order Reaction: Half-life = 120 s
Second Order Reactions \( aA \rightarrow B \)