Chapter 15: Phenomena

Phenomena: The reaction \( A(aq) + B(aq) \rightarrow C(aq) \) was studied at two different temperatures (298 K and 350 K). For each temperature the reaction was started by putting different concentrations of the 3 species that take part in the reaction into an otherwise empty container. The reaction rate was then measured. What patterns do you notice about the reaction rates? Can reaction rates be predicted?

Data Taken at 298 K

<table>
<thead>
<tr>
<th>Exp</th>
<th>([A])</th>
<th>([B])</th>
<th>([C])</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 M</td>
<td>1 M</td>
<td>1 M</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>1 M</td>
<td>0 M</td>
<td>1 M</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>1 M</td>
<td>1 M</td>
<td>0 M</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>0 M</td>
<td>1 M</td>
<td>1 M</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>0.5 M</td>
<td>2 M</td>
<td>1 M</td>
<td>200</td>
</tr>
<tr>
<td>6</td>
<td>1 M</td>
<td>3 M</td>
<td>0 M</td>
<td>10</td>
</tr>
<tr>
<td>7</td>
<td>2 M</td>
<td>1 M</td>
<td>1 M</td>
<td>800</td>
</tr>
<tr>
<td>8</td>
<td>4 M</td>
<td>1 M</td>
<td>1 M</td>
<td>3200</td>
</tr>
<tr>
<td>9</td>
<td>2 M</td>
<td>2 M</td>
<td>2 M</td>
<td>800</td>
</tr>
<tr>
<td>10</td>
<td>0.50 M</td>
<td>6 M</td>
<td>3 M</td>
<td></td>
</tr>
</tbody>
</table>

Data Taken at 350 K

<table>
<thead>
<tr>
<th>Exp</th>
<th>([A])</th>
<th>([B])</th>
<th>([C])</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 M</td>
<td>1 M</td>
<td>1 M</td>
<td>200</td>
</tr>
<tr>
<td>2</td>
<td>1 M</td>
<td>0 M</td>
<td>1 M</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>1 M</td>
<td>1 M</td>
<td>0 M</td>
<td>200</td>
</tr>
<tr>
<td>4</td>
<td>0 M</td>
<td>1 M</td>
<td>1 M</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>1 M</td>
<td>2 M</td>
<td>1 M</td>
<td>200</td>
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<tr>
<td>6</td>
<td>1 M</td>
<td>3 M</td>
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<td>2 M</td>
<td>1 M</td>
<td>1 M</td>
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<td>0.50 M</td>
<td>6 M</td>
<td>3 M</td>
<td></td>
</tr>
</tbody>
</table>

Chapter 15: Chemical Kinetics

Big Idea: The rates of chemical reactions are described by simple expressions that allow us to predict the composition of a reaction mixture at anytime. These expressions also suggest the steps in which the reaction takes place.

### Reaction Rates

- **Catalyst**: A substance that increases the reaction rate without being consumed in the reaction.
- **Homogeneous Catalyst**: A catalyst that is in the same phase as the reactants.
- **Heterogeneous Catalyst**: A catalyst that is in a different phase than the reactants.

### Reaction Rates

- **Reaction Rates**: The change in concentration of one of the reactants or products divided by the time interval over which the change takes place.

\[
\text{Rate} = \frac{\Delta R}{\Delta t}
\]

Note: Rates are always positive, therefore, since the reactants are consumed, a negative sign must be added to make the rate positive.

- **Average Rate of Consumption of R**: \( \frac{-\Delta R}{\Delta t} \)
- **Average Rate of Production of P**: \( \frac{\Delta P}{\Delta t} \)

**Unique Average Rate (UAR)**

\[
UAR = \frac{1 \Delta[A]}{a \Delta t} = \frac{1 \Delta[B]}{b \Delta t} = \frac{1 \Delta[C]}{c \Delta t}
\]

Note: Rates are always positive, therefore, since the reactants are consumed, a negative sign must be added to make the rate positive.

- **Instantaneous Rate of Reaction**: The best approximation to the rate at a single instant is obtained by drawing a line tangent to the plot of the concentration against time. The slope of the tangent line is called the instantaneous rate of the reaction.

- **Rate Law**: An equation expressing the instantaneous reaction rate in terms of the concentrations, at any instant, of the substances taking part in the reaction.

\[
\text{Rate} = k[A]^a[B]^b[C]^c
\]

Note: \( k \) is the rate constant and \( a, b, c \) are the orders of reaction.

Note: This form of the rate law is called the differential rate law.

Note: The units of rate are always different, therefore, the units of \( k \) will differ depending on the overall reaction order.

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**Thermo Review**

**Reaction Rates**

**Rate Laws**

**Concentration and Time**

**Reaction Mechanisms**

**Explaining Reaction Rate Factors**
Rate Laws

Things to know about the rate law:
- Rate laws can contain products, reactants, catalysts but usually only starting material.
- Rate laws do not contain intermediates.
- Rate laws can ONLY be determined experimentally.
- Orders do NOT correlate with coefficients in balanced equation!
- Orders can be an integers, zeros, fractions, positives, OR negatives!
- Each species has its own individual reaction order.
- The overall reaction order is the sum of the individual orders found in the reaction.

How to find the units of k

1) General Rate Law:
2) Order with respect to A:
3) Order with respect to B:
4) Order with respect to C:

<table>
<thead>
<tr>
<th>Experiment</th>
<th>[A]₀ (M)</th>
<th>[B]₀ (M)</th>
<th>[C]₀ (M)</th>
<th>Initial Rate (mol/L·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>6</td>
<td>4</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>6</td>
<td>2</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>40</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>6</td>
<td>2</td>
<td>20</td>
</tr>
</tbody>
</table>

1) General Rate Law:
2) Order with respect to A:
3) Order with respect to B:
4) Order with respect to C:

Determine the rate law: A + B + C → 2D

<table>
<thead>
<tr>
<th>Experiment</th>
<th>[A]₀ (M)</th>
<th>[B]₀ (M)</th>
<th>[C]₀ (M)</th>
<th>Initial Rate (mol/L·s)</th>
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<tr>
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<td>4</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>6</td>
<td>2</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>40</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>6</td>
<td>2</td>
<td>20</td>
</tr>
</tbody>
</table>

1) General Rate Law:
2) Order with respect to A:
3) Order with respect to B:
4) Order with respect to C:

Determining Order (long way)

- Step 1: Find two experiments in which the concentrations of everything, except one species, is held constant.
- Step 2: Divide the rate laws for these two experiments by each other.

Note: This will cancel out k and all other variables except for the order that you are trying to determine.

Math Note: \( \frac{d[A]}{dt} = k[A]^n \)

Step 3: Solve for order.

Math Note: It is sometimes useful to take the log of both sides of the equation. The \( \log(a^n) = n \log(a) \).
Chapter 15: Chemical Kinetics

Student Question

The rate law for the following reaction

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

was experimentally found to be in the form

\[ \text{rate} = k[\text{NO}]^x[\text{O}_2]^y \]

It was also found that when the NO concentration was doubled, the rate of the reaction increases by a factor of 4. In addition, when both the O\(_2\) and the NO concentration were doubled, the rate increases by a factor of 8. What is the reaction order of O\(_2\)?

a) 0th  b) 1st  c) 2nd  
d) 3rd  e) None of the above

---

Concentration and Time

- **Zero Order Integrated Rate Law**

1) \[ \text{Rate} = k \]

2) \[ \frac{dA}{dt} = k \]

3) \[ dA = -k dt \]

4) \[ \int_{[A]_0}^{[A]} dA = -k \int_0^t dt \]

- **First Order Integrated Rate Law**

1) \[ \int \frac{1}{x}dx = \ln x + \text{const} \]

2) \[ -\frac{dA}{dt} = k[A] \]

3) \[ \frac{1}{[A]} dA = -k dt \]

4) \[ \int_{[A]_0}^{[A]} \frac{1}{[A]} dA = -k \int_0^t dt \]

- **Second Order Integrated Rate Law**

1) \[ \text{Rate} = k[A]^2 \]

2) \[ \frac{dA}{dt} = k[A]^2 \]

3) \[ \frac{1}{[A]} dA = -k dt \]

4) \[ \int_{[A]_0}^{[A]} \frac{1}{[A]} dA = -k \int_0^t dt \]

---

The rate law for \( A + B \rightarrow C + D \) was only found to be dependent on \( A \). Using the following data determine the rate law and \( k \).

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>[A] (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.4</td>
</tr>
<tr>
<td>20</td>
<td>0.15</td>
</tr>
<tr>
<td>40</td>
<td>0.077</td>
</tr>
<tr>
<td>60</td>
<td>0.062</td>
</tr>
</tbody>
</table>
Calculate the concentration of N₂O after the first order decomposition:

\[ 2N_2O(g) \rightarrow 2N_2(g) + O_2(g) \]

The rate of decomposition of N₂O = k[N₂O].

The reaction has continued at 780ºC for 100. ms, and the initial concentration of N₂O was 0.20 M and \( k = 3.4 \text{ s}^{-1} \).

Concentration and Time

<table>
<thead>
<tr>
<th>[A] (M)</th>
<th>ln[A]</th>
<th>[A]⁻¹ (M⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.54</td>
<td>1.7</td>
<td>0.19</td>
</tr>
<tr>
<td>0.15</td>
<td>-1.9</td>
<td>6.7</td>
</tr>
<tr>
<td>0.077</td>
<td>-2.6</td>
<td>13</td>
</tr>
<tr>
<td>0.052</td>
<td>-3.0</td>
<td>19</td>
</tr>
</tbody>
</table>

**Half Life:** Time it takes for the concentration to drop to half the initial amount

0th Order

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

First Order

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

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

\[ t_{1/2} = \frac{\ln(2)}{k} \]

2nd Order

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

\[ \frac{1}{[A]} = kt_{1/2} + \frac{1}{[A]_0} \]

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

\[ t_{1/2} = \frac{1}{k[A]_0} \]
Chapter 15: Chemical Kinetics

Reaction Mechanisms

Student Question

Use the experimentally found rate laws given below to determine which reaction is most likely to occur in a single step.

Experimentally Found Rate Laws

a) \(2\text{NO}_2(g) + \text{F}_2(g) \rightarrow 2\text{NO}_2\text{F}(g)\) \(\text{rate} = k[\text{NO}_2][\text{F}_2]\)

b) \(\text{H}_2(g) + \text{Br}_2(g) \rightarrow 2\text{HBr}(g)\) \(\text{rate} = k[\text{H}_2][\text{Br}_2]\)

c) \(2\text{NO}(g) + 2\text{O}_2(g) \rightarrow 2\text{NO}_2(g) + \text{O}_2(g)\) \(\text{rate} = k[\text{NO}][\text{O}_2]^2\)

d) \(\text{NO}_2(g) + \text{CO}(g) \rightarrow \text{NO}(g) + \text{CO}_2(g)\) \(\text{rate} = k[\text{NO}_2][\text{CO}]\)

Consider the following hypothetical reaction:

\(\text{A} + 2\text{B} \rightarrow \text{E}\)

The mechanism for this reaction is:

1. \(\text{A} + \text{B} \rightarrow \text{C}\) (slow)
2. \(\text{B} + \text{C} \rightarrow \text{D}\) (fast)
3. \(\text{D} \rightarrow \text{E}\) (fast)

The rate law consistent with this mechanism is:

- a) \(\text{rate} = k[\text{A}][\text{B}]\)
- b) \(\text{rate} = k[\text{A}][\text{B}]\)
- c) \(\text{rate} = k[\text{A}]^2\)
- d) \(\text{rate} = k[\text{A}][\text{B}]^2\)
- e) None of the above

The reaction \(2\text{NO} + \text{Cl}_2 \rightarrow 2\text{NOCl}\) was experimentally found to have the rate law: \(\text{rate} = k[\text{Cl}_2][\text{NO}]^2\). Which mechanism could not be the correct mechanism?

- a) \(\text{Cl}_2 \rightarrow 2\text{Cl}\) (fast equilibrium)
- b) \(2\text{NO} + 2\text{Cl} \rightarrow 2\text{NOCl}\) (slow)
- c) \(2\text{NOCl} = \text{NOCl}_2 + \text{NOCl}\) (fast equilibrium)
- d) \(2\text{NO} + \text{Cl}_2 \rightarrow 2\text{NOCl}\)
- e) All of the above are possible mechanisms

Relating the Rate and Equilibrium Constants

At Equilibrium (\(\text{Rate}_{\text{forward}} = \text{Rate}_{\text{reverse}}\))

\[K = \frac{[\text{C}]}{[\text{A}][\text{B}]} = \frac{k_1[\text{A}][\text{B}]}{k_{-1}[\text{C}]}\]

\[K = \frac{k_1}{k_{-1}}\]
Multi Step Reactions With Unknown Speeds

- Step 1: Write an expression for the rate of formation of one of the final products (sometimes the product of interest is specified). If possible select a product that is only in 1 step.
- Step 2: Use the steady state approximation to solve for the concentration of intermediates.
- Step 3: Plug back into overall rate equation.

Student Question

Explaining Reaction Rate Factors

The rate constant for the second-order gas-phase reaction $\text{HO}(g) + \text{H}_2(g) \rightarrow \text{H}_2\text{O}(g) + \text{H}(g)$ varies with the temperature as shown here:

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Rate Constant (cm$^3$·mol$^{-1}$·s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>373</td>
<td>$1.1 \times 10^9$</td>
</tr>
<tr>
<td>473</td>
<td>$1.8 \times 10^9$</td>
</tr>
<tr>
<td>573</td>
<td>$2.2 \times 10^9$</td>
</tr>
<tr>
<td>673</td>
<td>$4.4 \times 10^7$</td>
</tr>
</tbody>
</table>

Determine the activation energy.

- a) $2.4 \times 10^5$
- b) $4.0 \times 10^3$
- c) $4.2 \times 10^4$
- d) None of the above

Collision Theory (Gases Only)

- Rate = Collision Frequency × Fraction with Sufficient Energy

How would we get collision frequency?
- Size of the molecules/atoms
- Average velocity of the molecules/atoms
- Concentration of molecules/atoms

How would we get fraction with sufficient energy?
- Boltzmann distribution

$\tilde{f}(u) = 4\pi \left( \frac{m}{2\pi k_B T} \right)^{3/2} u^2 e^{-E/k_B T}$

Collision Theory (Gases Only)

Problem: Although the rate has the right form (Arrhenius) it predicts a larger reaction rate than is found.

Solution: Sterics need to be taken into account.

$\ln(k) = -\frac{E_a}{RT} + \ln(A)$

$A = \text{Takes into account number of collisions and steric}$

Actuated Complex Theory (Solutions)

Big Idea: The rates of chemical reactions are described by simple expressions that allow us to predict the composition of a reaction mixture at anytime. These expressions also suggest the steps in which the reactions takes place.

Thermo Review
- Know the difference between thermo and kinetics
- Thermodynamics allows us to predict if a reaction will occur.
- Kinetics allows us to predict how fast a reaction will occur.
- Be able to draw reaction coordinates along with labeling reactants, products, intermediates, transition states, and activation energy. (80, 81, 82)

Reaction Rates
- Be able to explain how a catalyst can increase reaction rate. (84, 88)
Chapter 15: Chemical Kinetics

Take Away From Chapter 15

- **Reaction Rates (Continued)**
  - Be able to calculate the average rate of reaction of 1 species given the average rate of reaction of another species.
  - Be able to calculate the unique average rate of a reaction.

- **Rate Law**
  - Know that rate laws must be determined experimentally.
  - Be able to determine the order of a reaction and each individual species.
  - Be able to calculate rate law from experimental data. (17, 18, 19, 20, 21)

- **Concentration and Time**
  - Be able to use the integrated rate law to perform calculations. (41, 45, 46, 48)
  - 0th order: \[ \text{rate} = -k \text{[A]} \]
  - 1st order: \[ \text{rate} = -k \text{[A]} \]
  - 2nd order: \[ \text{rate} = -k \text{[A]}^2 \]

- **Explaining Reaction Rate Factors (continued)**
  - Surface Area
    - Know the ideas behind collision theory (gases).
    - Know the ideas behind activated complex theory (solutions).
  - Temperature
    - Know that most reactions follow Arrhenius behavior. (68, 73, 74, 65, 75, 77, 78)
    - \[ \ln(\text{rate}) = -\frac{E_a}{RT} + \text{constant} \]
    - \[ \ln(\text{rate}) = -\frac{E_a}{RT} + \text{constant} \]

- **Rate Law (Continued)**
  - Know that rate problems can be simplified when the concentration of 1 species is high and essentially unchanging (pseudo order reactions). (34, 37, 50)

- **Equilibrium**
  - Steady state approximation (65, 66)

- **Explaining Reaction Rate Factors**
  - Concentration
  - Catalyst
    - Be able to draw potential energy diagram of reactions
  - Temperature
    - Know that most reactions follow Arrhenius behavior. (68, 73, 74, 65, 75, 77, 78)
    - \[ \ln(\text{rate}) = -\frac{E_a}{RT} + \text{constant} \]
    - \[ \ln(\text{rate}) = -\frac{E_a}{RT} + \text{constant} \]