Chapter 16

Chemical Kinetics: The Study of Rates of Reaction & Mechanisms by Which Occur

Pharmacist/Pharmacokinetics – study of medicine’s rate of absorption, distribution, metabolism, and excretion.

Food Scientist – studies food’s rate of decay

Forensic Scientist – studies rate of body’s decomposition and how temperature, humidity, and oxygen affect rate of decay

Biolgist – studies rate of microorganism growth

Reaction Rates

Chemical Kinetics: study of how fast/slow (rate) a reaction occurs, and the mechanism by which it occurs.

Some reactions happen VERY quickly, while others happen VERY slowly. We observe how fast the reaction occurs. Balanced equation provides no information on rate of reaction.

Examples:

Rate of reaction=

Consider the theoretical reaction: \( aA \rightarrow bB \)

Write the expressions for…..

Rate of appearance of product =

Rate of disappearance of reactant =

\[ \text{NOTE: Pure product may never be obtained!!} \]
Sample Questions

1. Consider the following equation: \(2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)\)

   From the following experimental data calculate the rate of disappearance of \(N_2O_5\), and the rates of appearances of \(NO_2\) and \(O_2\), over the time intervals: 0-500 s, 500-1000 s, 1000-1500 s.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>([N_2O_5])</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.00</td>
</tr>
<tr>
<td>500</td>
<td>3.52</td>
</tr>
<tr>
<td>1000</td>
<td>2.48</td>
</tr>
<tr>
<td>1500</td>
<td>1.75</td>
</tr>
</tbody>
</table>

   Is the reaction rate constant?

   If not, what does it depend on?

   What is the difference between \(-\Delta [N_2O_5]/\Delta t\) and \(-d[N_2O_5]/dt\)?

2. In aqueous solutions, molecular bromine reacts with formic acid (HCOOH) as follows:

   \(Br_2(aq) + HCOOH (aq) \rightarrow 2Br^-(aq) + 2H^+(aq) + CO_2(g)\)

   From the following experimental data calculate the rate of disappearance of \(Br_2\), and the rate of appearances of \(Br^-\) and \(CO_2\), over the time intervals: 0-50 s, 50-100 s, and 100-150 s.

<table>
<thead>
<tr>
<th>Time(s)</th>
<th>([Br_2])</th>
<th>Time(s)</th>
<th>([Br^-])</th>
<th>Time(s)</th>
<th>([Br_2])</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.0120</td>
<td>150.0</td>
<td>0.00710</td>
<td>300.0</td>
<td>0.00420</td>
</tr>
<tr>
<td>50.0</td>
<td>0.0101</td>
<td>200.0</td>
<td>0.00596</td>
<td>350.0</td>
<td>0.00353</td>
</tr>
<tr>
<td>100.0</td>
<td>0.00846</td>
<td>250.0</td>
<td>0.00500</td>
<td>400.0</td>
<td>0.00296</td>
</tr>
</tbody>
</table>

Graphically:
1. 
2. 

Mathematically:
1. 
2. 

\[-d[A]/dt = -df(t)/dt\]
Relating Rates of Appearance and Disappearance

How related?

1. Consider the following reaction:
\[ \text{C}_3\text{H}_8(g) + 5\text{O}_2(g) \rightarrow 3\text{CO}_2 + 4\text{H}_2\text{O}(g) \]
If at a given moment \( \text{C}_3\text{H}_8 \) is reacting at rate of 0.400 mol L\(^{-1}\) s\(^{-1}\), what are the rates of formation of \( \text{CO}_2 \) and \( \text{H}_2\text{O} \)? What is the rate of disappearance of \( \text{O}_2 \)?

2. Hydrogen and nitrogen react to form ammonia according to the equation
\[ 3\text{H}_2(g) + \text{N}_2(g) \rightarrow 2\text{NH}_3(g) \]
If hydrogen is consumed at a rate of 0.50 M s\(^{-1}\), what is the rate at which nitrogen is consumed, and what is the rate at which ammonia is produced?

Rate Laws

The rate of a reaction is proportional to the concentrations of the different reactants raised to experimentally determined exponents.

A General Rate Law can be written for any reaction:
\[ \text{aA} + \text{bB} \rightarrow \text{products} \]

Rate =

Where:
\[ k = \text{specific rate constant} \]
1.
2.
3.
\( m \) and \( n \) are order of reaction with respect to each reactant
1.
### Rate Law Examples

1. The reaction: \( \text{NO}_2(g) + \text{CO}(g) \rightarrow \text{CO}_2(g) + \text{NO}(g) \) at 200°C is known to be second order in \( \text{NO}_2 \) and zeroth order in \( \text{CO} \).
   a. Write the rate law for this reaction.
   b. What is the overall reaction order for this reaction?
   c. What will happen to the reaction rate if the \([\text{NO}_2]\) is doubled?
   d. What will happen to the reaction rate if the \([\text{CO}]\) is halved?
   e. What are the units on \( k \)?

2. The gas-phase reaction of nitric oxide and bromine yields nitrosyl bromide:
   \[ 2\text{NO}(g) + \text{Br}_2(g) \rightarrow 2\text{NOBr}(g) \]
   The rate law is \( \text{rate} = k[\text{NO}][\text{Br}_2] \). What is the order of reaction with respect to each of the reactants, and what is the overall reaction order? What will happen to the reaction rate if \([\text{NO}]\) is tripled? if \([\text{Br}_2]\) is doubled? if \([\text{Br}_2]\) halved? What are the units of \( k \)?

3. Bromomethane is converted to methanol in an alkaline solution. The reaction is first order in each reactant.
   \[ \text{CH}_3\text{Br(aq)} + \text{OH}-(aq) \rightarrow \text{CH}_3\text{OH(aq)} + \text{Br}-(aq) \]
   a. Write the rate law. \( \text{rate} = k[\text{CH}_3\text{Br}][\text{OH}^-] \)
   b. How does the reaction rate change in the \( \text{OH}^- \) concentration is decreased by a factor of 5? \( \text{rate will decrease by a factor of 5} \)
   c. What is the change in rate if the concentration of both reactants are doubled? \( \text{rate will increase by a factor of 4} \)

### Factors That Affect the Reaction Rate

1.

2.

3.

4.

**Example:** Consider the heterogeneous reaction studied during **Exp #2:**

**Chemical Reaction Rates.**

**General Rxn:** \( \text{M(s)} + 2 \text{H}^+(aq) \rightarrow \text{M}^{2+}(aq) + \text{H}_2(g) \)

**Reaction Rate =**
Method of Initial Rates

*Experimental method used to determine orders of reaction (m,n) and k, and, as result, the rate law.*

*Best way to learn this method is by example….*

1. Use the method of initial rates to find the rate law for the following reaction:

\[
2 \text{ NOCl}(g) \rightarrow 2 \text{ NO}(g) + \text{ Cl}_2(g) \text{ at 27 } ^\circ\text{C}
\]

<table>
<thead>
<tr>
<th>[NOCl]</th>
<th>Initial Rate of Formation of NO</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.30 M</td>
<td>3.60 \times 10^{-9} \text{ M/s}</td>
</tr>
<tr>
<td>0.60 M</td>
<td>1.44 \times 10^{-8} \text{ M/s}</td>
</tr>
<tr>
<td>0.90 M</td>
<td>3.24 \times 10^{-8} \text{ M/s}</td>
</tr>
</tbody>
</table>

What is the value of the specific rate constant? How much will the rate of this reaction change if the initial concentration of NOCl is increased from 0.30 M to 1.2 M?

2. Find the rate law for the following reaction given the data shown below.

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

<table>
<thead>
<tr>
<th>[BrO$_3^-$]</th>
<th>[Br$^-$]</th>
<th>[H$^+$]</th>
<th>-d[BrO$_3^-$]/dt</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10 M</td>
<td>0.10 M</td>
<td>0.10 M</td>
<td>0.0012 M/s</td>
</tr>
<tr>
<td>0.20 M</td>
<td>0.10 M</td>
<td>0.10 M</td>
<td>0.0024 M/s</td>
</tr>
<tr>
<td>0.10 M</td>
<td>0.30 M</td>
<td>0.10 M</td>
<td>0.0035 M/s</td>
</tr>
<tr>
<td>0.20 M</td>
<td>0.10 M</td>
<td>0.15 M</td>
<td>0.0054 M/s</td>
</tr>
<tr>
<td>0.30 M</td>
<td>0.30 M</td>
<td>0.30 M</td>
<td>??</td>
</tr>
</tbody>
</table>

What is the value of the specific rate constant and what are its units? Calculate the rate of disappearance of BrO$_3^-$ for the last trial.
3. At 600 °C, acetone ($\text{CH}_3\text{COCH}_3$) decomposes to ketone ($\text{CH}_2\text{=C}=\text{O}$) and various hydrocarbons. Initial rate data are given below:

<table>
<thead>
<tr>
<th>Initial [CH$_3$COCH$_3$] (M)</th>
<th>Initial rate of decomposition of CH$_3$COCH$_3$ (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.0 x 10$^{-3}$ M</td>
<td>5.2 x 10$^{-5}$</td>
</tr>
<tr>
<td>9.0 x 10$^{-3}$ M</td>
<td>7.8 x 10$^{-5}$</td>
</tr>
</tbody>
</table>

a. Determine the rate law.
b. Calculate the value of the specific rate constant.
c. Calculate the initial rate decomposition when the initial acetone concentration is 1.8 x 10$^{-3}$ M.
d. How much will the reaction rate increase if the initial concentration of CH$_3$COCH$_3$ is increased from 6.0 x 10$^{-3}$ M to 2.4 x 10$^{-2}$ M.

4. Initial rate data at 25 °C are listed below for the reaction

$$\text{NH}_4^+(aq) + \text{NO}_2^-(aq) \rightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(l)$$

<table>
<thead>
<tr>
<th>Initial [NH$_4^+$] (M)</th>
<th>Initial [NO$_2^-$] (M)</th>
<th>Initial rate of consumption of nitrite (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.24 M</td>
<td>0.10 M</td>
<td>7.2 x 10$^{-5}$</td>
</tr>
<tr>
<td>0.12 M</td>
<td>0.10 M</td>
<td>3.6 x 10$^{-6}$</td>
</tr>
<tr>
<td>0.12 M</td>
<td>0.15 M</td>
<td>5.4 x 10$^{-6}$</td>
</tr>
</tbody>
</table>

a. What is the rate law? ($\text{rate} = k[\text{NH}_4^+][\text{NO}_2^-]$)
b. What is the value of the rate constant? (3.0 x 10$^{-4}$ M$^{-1}$ s$^{-1}$)
c. What is the initial rate when the initial concentrations are [NH$_4^+$]=0.39 M and [NO$_2^-$]=0.052 M? (6.1 x 10$^{-6}$ M s$^{-1}$)