Chapter 14: Chemical Kinetics

Homework:
Read Chapter 14 Work out sample/practice exercises in the sections,
Check for the MasteringChemistry.com assignment and complete before due date

Introduction to Kinetics:

Chemists generally want to know …

What happens? (Balanced equations)
To what extent does it happen? (Equilibrium)
The rate it happens and by what mechanism? (Kinetics)
Will the reaction spontaneously occur? (Thermodynamics)

KINETICS is the area of chemistry concerned with the RATE of a reaction; the variables that affect rate and the REACTION MECHANISM; the pathway by which a reaction occurs. Kinetic studies have environmental, biological and economic importance.

Kinetics will not tell us the extent of the reaction (Equilibrium) or whether the reaction spontaneously occurs under specified conditions (Thermodynamics).

Kinetic rates vary tremendously:

Methane combustion: (very fast reaction after a spark initiates the reaction)

\[
\text{CH}_4 (g) + 2 \text{O}_2(g) \rightarrow \text{CO}_2(g) + 2 \text{H}_2\text{O}(g) \quad \Delta H^\circ = -802.3 \text{ kJ/mol}
\]

Diamond combustion: (thankfully this does not occur at an observable rate)

\[
\text{C}_{\text{diamond}} + \text{O}_2(g) \rightarrow \text{CO}_2 (g) \quad \Delta H^\circ = -395.4 \text{ kJ/mol}
\]

(°) represents a value under standard state conditions: 25°C, 1 atm

Try this #1: Predict some variables that may influence the rate of reactions?
Factors that Affect Reaction Rates:

1. **Nature of the reactants** - periodic trends, physical state, surface area
   
   Examples…
   
   - Li, Na, K react with water at increasing rates
   - liquid gasoline burns slower that gas vapor
   - powders react faster than large pieces
   - dry solid reactants generally react slower than solutions of the same reactants

   **Try this #2: Form an explanation for each of these trends.**

2. **The concentration/pressures of the reactants**
   
   Examples…
   
   - higher concentrations or partial pressures of reactants generally speed a reaction
   - generally reaction rates slow over time

   **Try this #3: Form an explanation for each of these trends.**

At any time an instantaneous rate can be calculated from the negative slope of the tangent to the curve of time (x axis) verses reactant concentration (y axis) or the positive tangent to the time verses product concentration.

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**Figure 1**

Kinetic Graph
Rate of disappearance of the reactant and appearance of product

- **Concentration (M)**
- **Time (minutes)**
- **Reactant [M]**
- **Product [M]**
3. **The temperature at which the reaction occurs**

Example…

- as temperature increases the rate of reactants disappearing also increases
- as temperature drops the rate generally drops

**Try this #4: Form an explanation for this trend.**

4. **The presence of catalysts, enzymes, or inhibitors**

Examples…

- Catalysts alter the mechanism/pathway of the reaction. The activation energy is lowered and the steps in the reaction may vary from that without a catalyst. Enzymes are biological catalysts.

- Inhibitors alter the mechanism sometimes blocking an active site to slow or stop a reaction

**Try this #5: Form an explanation for this trend.**

**Reaction Rates:**

The speed of an event is its change over time. Similar to the speed of a car measured in miles per hour, a **reaction rate** is the concentration change over change in time, generally in Molarity/time

\[
\text{Rate} = \Delta [X] / \Delta t
\]

1. In slow reactions, samples can be taken of the reaction mixture after successive time intervals to determine rates.

2. In faster reactions, one can measure the change in a physical property, such as pressure if the number of moles of gas change or color by spectroscopy, some computer controlled spectroscopes can measure every picoseconds; \(1 \times 10^{-12}\) second
Hypothetical Reaction:
For the generic reaction…  \( aA + bB \rightarrow cC + dD \)
The amount is in Molarity \([X]\) or partial pressure in atmospheres \([P_x]\).
Change, \((\Delta)\), is always final minus initial
\( \text{Rate of disappearance of reactant} = \Delta[\text{reactant}] / \Delta\text{time} \) (negative answer)
\( \text{Rate of formation of product} = \Delta[\text{product}] / \Delta\text{time} \) (positive answer)

**Rate of Reaction** needs to be the same rate for all species in a balanced reaction, (Finish the equivalents for each reactant and product)

Try this #6:

\[
\text{Rate of Reaction} = -\frac{\Delta[A]}{a\Delta t} = \frac{\Delta[B]}{b\Delta t} = \frac{\Delta[C]}{c\Delta t} = \frac{\Delta[D]}{d\Delta t}
\]

Try this: #7 for the reaction… \( \text{H}_2 + 2 \text{ICl} \rightarrow \text{I}_2 + 2\text{HCl} \)

a) Write the terms for the Rate of Reaction for each reactant/product

\[
\text{Rate of Reaction} = \frac{-\Delta[A]}{a\Delta t} = \frac{\Delta[B]}{b\Delta t} = \frac{\Delta[C]}{c\Delta t} = \frac{\Delta[D]}{d\Delta t}
\]

b) Draw the expected graph with concentrations verses time beginning with 1M \( \text{H}_2 \) and 2 M ICl and no products initially.

c) If the rate of disappearance \( \text{H}_2 = -0.13\ M/s \) at a specific time, what is the value for the rate of formation of \( \text{HCl} \) during the same interval?

d) What is the generic reaction rate for that time interval?
**Rate Law Expression:**
For the generic reaction… \( a \ A + b \ B \rightarrow \text{products} \)
\[
\text{Rate} = k[A]^x[B]^y
\]
\( k = \text{Specific rate constant} \)
\( x, y = \text{orders, generally small positive integers, can be zero, fractions or negative} \)
\( k, x, y \) are experimentally determined
Concentrations of Reactants and Catalysts are in the rate law expression.
Rarely, Product concentration may be in a rate law expression.

**Specific rate constant**: Information on \( k \)
1. Its value is for a specific reaction represented by a balance equation
2. Its value will change if a catalyst is added
3. It is for a specific temperature and will change when Temp changes
4. Its units depend on the overall order.
   \[
   M^{(1-\text{overall order})} \text{ time}^{-1}
   \]
5. It does not change with concentration
6. It does not change with time
7. It is experimentally determined

**Orders**
1. Most common orders are 0, 1 and 2.
2. It is possible to have fractions such as \( \frac{1}{2} \)
3. On rare occasions the orders can be negative such as -1
4. Zero order reactant concentration has no affect on the rate as long as the reactant is present
5. First order reactant concentration is directly proportional to the rate.
   Doubling the concentration will double the rate.
6. The rate increases as a square of the second order reactant concentration.
   Doubling the concentration will quadruple the rate.
7. Overall order is the sum of all orders in the rate law expression.
Rate Law Expression:

Try this #8;

Determine the orders with respect to each reactant and the overall order for each.

Notice if rate law expression orders match the coefficients of the balanced reaction.

a) \[3\text{NO} (g) \rightarrow \text{N}_2\text{O} (g) + \text{NO}_2 (g)\]
   \[\text{Rate} = k[\text{NO}]^2\]

b) \[(\text{CH}_3)_3\text{CBr (aq)} + \text{OH}^{-1} (aq) \rightarrow (\text{CH}_3)_3\text{COH (aq)} + \text{Br}^{-1}\]
   \[\text{Rate} = k[(\text{CH}_3)_3\text{CBr}]\]

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

Try this #9: Given: \[2\text{NO} (g) + 2\text{H}_2 (g) \rightarrow 2\text{H}_2\text{O} (g) + \text{N}_2 (g)\]

The reaction is second order with NO and first order with respect to H\(_2\).

a) Write the rate law expression and determine the overall order.

b) Specify the units of the specific rate constant using time in seconds.

c) How does the reaction rate change if the NO concentration doubles? Triples?

d) How does the reaction rate change if both reactant concentrations are doubled?
**Rate Graphs:**

Determining Rate Law Expression from Experimental Data:

In order to determine orders and specific rate constant of a reaction, one may carry out a series of experiments (the minimum number is equal to the number of unknowns) in which initial rates are measured. It is best to design an experiment in which only one factor (concentration) is changed at a time. Do not confuse the rate of a reaction with the rate constant (k).

Try this #10:

The following rate data were obtained at 25°C for the reaction...

\[
2\text{NO (g)} + 2\text{H}_2\text{(g)} \rightarrow \text{N}_2\text{(g)} + 2\text{H}_2\text{O (g)} \quad \text{Rate} = k[\text{NO}]^x[\text{H}_2]^y
\]

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Initial [NO]</th>
<th>Initial [H\textsubscript{2}]</th>
<th>Rate forming N\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.10 M</td>
<td>0.10 M</td>
<td>1.23 x 10\textsuperscript{-3} M/s</td>
</tr>
<tr>
<td>2</td>
<td>0.10 M</td>
<td>0.20 M</td>
<td>2.46 x 10\textsuperscript{-3} M/s</td>
</tr>
<tr>
<td>3</td>
<td>0.20 M</td>
<td>0.10 M</td>
<td>4.92 x 10\textsuperscript{-3} M/s</td>
</tr>
<tr>
<td>4</td>
<td>?</td>
<td>0.30 M</td>
<td>8.00 x 10\textsuperscript{-3} M/s</td>
</tr>
</tbody>
</table>

Solve for the orders, overall order, the Rate Law Expression and the value and units of k (specific rate constant). First try estimation, then verify through algebra and logarithms. Determine the initial concentration of [NO] in expt 4.
Try this #11:

The following rate data were obtained at 25°C for the reaction...

\[ 2A + B + 2C \rightarrow D \quad \text{Rate} = k[A]^x[B]^y[C]^z \]

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Initial [A]</th>
<th>Initial [B]</th>
<th>Initial [C]</th>
<th>Rate forming D</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.34 M</td>
<td>0.16 M</td>
<td>0.12 M</td>
<td>1.4 x 10^{-2} M/min</td>
</tr>
<tr>
<td>2</td>
<td>0.34 M</td>
<td>0.32 M</td>
<td>0.24 M</td>
<td>2.8 x 10^{-2} M/min</td>
</tr>
<tr>
<td>3</td>
<td>0.34 M</td>
<td>0.16 M</td>
<td>0.35 M</td>
<td>1.4 x 10^{-2} M/min</td>
</tr>
<tr>
<td>4</td>
<td>0.68 M</td>
<td>0.32 M</td>
<td>0.49 M</td>
<td>5.6 x 10^{-2} M/min</td>
</tr>
<tr>
<td>5</td>
<td>0.50 M</td>
<td>0.50 M</td>
<td>0.20 M</td>
<td>?</td>
</tr>
</tbody>
</table>

Solve for the orders, overall order, the Rate Law Expression and the value and units of \( k \) as well as the initial rate of formation of \( D \) in expt. 5.
Try this #12:

The following rate data were obtained at 25°C for the reaction...

\[ 2 \text{SO}_2 (g) + \text{O}_2 (g) \rightarrow 2 \text{SO}_3 (g) \]

Rate = \( k[\text{SO}_2]^x[\text{O}_2]^y \)

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Initial [\text{SO}_2]</th>
<th>Initial [\text{O}_2]</th>
<th>Rate forming ( \text{SO}_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.30 M</td>
<td>0.20 M</td>
<td>1.2 \times 10^{-2} M/s</td>
</tr>
<tr>
<td>2</td>
<td>0.30 M</td>
<td>0.10 M</td>
<td>6.0 \times 10^{-3} M/s</td>
</tr>
<tr>
<td>3</td>
<td>0.60 M</td>
<td>0.20 M</td>
<td>4.8 \times 10^{-2} M/s</td>
</tr>
<tr>
<td>4</td>
<td>0.20 M</td>
<td>?</td>
<td>1.0 \times 10^{-2} M/s</td>
</tr>
<tr>
<td>5</td>
<td>0.35 M</td>
<td>0.15 M</td>
<td>?</td>
</tr>
<tr>
<td>6</td>
<td>?</td>
<td>0.05 M</td>
<td>5.0 \times 10^{-3} M/s</td>
</tr>
</tbody>
</table>

Solve for the orders, overall order, the Rate Law Expression, the value and units of \( k \), and fill in the blanks on the table.
Integrated Rate Equations:

Using calculus we can solve for new equations that relate concentration and time, allowing us to determine concentrations at a later time, how long in time it takes to reach a certain concentration and the time of its half life, $t_{1/2}$. For calculations in class we will simplify using only one reactant and assume the coefficient ($a$) is either 1 or incorporated into the constant.

**Zero order reactions**…

Rate of Reaction = $-\Delta[A]/a\Delta t$ and Rate = $k$

$-\Delta[A]/a\Delta t = k$ can be rearranged to $d[A] = -kt$

With calculus … $[A]_t = -kt + C$

Setting time to zero, solve for $C = [A]_0$

**our new equation** … $[A]_t = -kt + [A]_0$

For the half life, $t_{1/2}$,… $[A]_0/2 = -kt_{1/2} + [A]_0$

Rearranging we get… $t_{1/2} = [A]_0/2k$

Try this #13:

*Draw the straight line graph with concentration vs time.*

For zero order reactions: Each half life is $\frac{1}{2}$ the time of the previous one.
First order reactions…

Rate of Reaction = \(-\Delta[A]/a\Delta t\) and Rate = k[A]

\(-\Delta[A]/a\Delta t = k[A]\) can be rearranged to \(d[A]/[A]= - kdt\)

With calculus we then get… \(\ln[A]_t = -kt + C\)

Setting time to zero we solve for \(C = \ln[A]_0\)

**our new equation…** \(\ln[A]_t = -kt + \ln[A]_0\)

**Rearranged we also have…** \(\ln([A]_0/[A]_t) = kt\)

For the half life, \(t_{1/2}\)... \(\ln([A]_0/[A]_0/2) = kt_{1/2}\)

**Rearranging we get…** \(t_{1/2} = (\ln 2)/k\)

Try this #14:

*Draw the straight line graph with concentration vs time.*

For first order reactions: Each half life is the identical time of the previous one.
• **Second order reactions**…

Rate of Reaction = \(-\Delta[A]/\Delta t\) and \(\text{Rate} = k[A]^2\)

\(-\Delta[A]/\Delta t = k[A]^2\) can be rearranged to \(d[A]/[A]^2 = kdt\)

With calculus we then get… \(1/[A] = kt + C\)

Setting time to zero we solve for \(C = 1/[A]_0\)

**This gives us our new equation …**\(1/[A]_t = kt + 1/[A]_0\)

For the half life, \(t_{1/2},…\) \(1/[A/2]_0 = kt + 1/[A]_0\)

**Rearranging we get…** \(t_{1/2} = 1/(k[A]_0)\)

**Try this #15:**

*Draw the straight line graph with concentration vs time.*

For second order reactions: Each half life is twice the time of the previous one.
Solving Problems Using the Integrated Rate Equations:

Try this #16:

Cyclopropane, an anesthetic, decomposes to propane as follows…

\[
\text{CH}_2 \quad / \quad \text{CH}_2 = \text{CH}_2 (g)
\]

The reaction is first order with respect to cyclopropane with \( k = 9.2 \, \text{s}^{-1} \) at 1000°C.

a) Calculate the half-life of the reaction.

b) How much of a 3.00 g sample of cyclopropane remains after 0.50 sec at 1000°C

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Try this #17:

The half-life for the first order reaction…

\[
\text{CS}_2 (g) \rightarrow \text{CS} (g) + \text{S} (g)
\]

is 688 hrs at 1000°C

a) Calculate the specific rate constant value and units.

b) Calculate the amount of a 3.0 g sample of CS\(_2\) remaining after 48 hours.
Try this #18:

Acetaldehyde decomposes to methane and carbon monoxide as follows…

\[
\text{CH}_3\text{CHO} \ (g) \rightarrow \text{CH}_4 \ (g) + \text{CO} \ (g) \quad \text{at } 527^\circ \text{C}
\]

Its rate law expression is … \( \text{Rate} = k[\text{CH}_3\text{CHO}]^2 \)

The specific rate constant at 527°C is… \( k = 2.0 \times 10^{-2} \ \text{M}^{-1}\text{hr}^{-1} \)

a) What is the order with respect to acetaldehyde?

b) What is the half-life if 0.10 mole of CH₃CHO is injected into an empty 1.0 L vessel at 527°C?

c) How many moles of CH₃CHO remain after 200 hrs?

d) What percent of CH₃CHO remains after 200 hours?

e) What is the half-life if 0.10 mole of CH₃CHO is injected into an empty 10.0 L vessel at 527°C?

f) How many moles of CH₃CHO remain after 200 hrs?

g) What percent of CH₃CHO remains after 200 hours?
Try this #19:

Concentration verses time data for the thermal decomposition of ethylbromide is given below…  \( \text{C}_2\text{H}_5\text{Br} \rightarrow \text{C}_2\text{H}_4 + \text{HBr} \) at 700 K

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>([\text{C}_2\text{H}_5\text{Br}]_0)</th>
<th>(\ln[\text{C}_2\text{H}_5\text{Br}]_0)</th>
<th>(1/[\text{C}_2\text{H}_5\text{Br}]_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.00 M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.82 M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.67 M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.55 M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.45 M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.37 M</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) Fill in the table above.
b) Use graphs to determine the order of the reaction and the specific rate constant
c) Calculate the time of the first half life.
Try this #20:

Concentration verses time data for the decomposition of NO₂ is given below…

\[ 2 \text{NO}_2 (\ g) \rightarrow 2 \text{NO} (\ g) + \text{O}_2 (\ g) \] at 500 K

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>[NO₂]</th>
<th>ln[NO₂]</th>
<th>1/[ NO₂]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.00 M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.36 M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.27 M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.18 M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>0.12 M</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) Fill in the table
b) Use graphs to determine the order and the specific rate constant value and units.

c) What is the time required to reach 0.45M [NO₂]
Temperature and Rate:

**Arrhenius Equation: Temperature and Rate**

Reaction rates increase as temperature increases. The specific rate constant, \( k \), is temperature dependent and will change as the temperature changes.

**Arrhenius Equation…** \[ k = Ae^{-\frac{E_a}{RT}} \]

\( R \) is the gas constant 8.314 J/mol K and \( T \) is temperature in Kelvin.

The constant \( A \) is related to (z) the collision frequency and (p) the fraction of collisions with proper orientation to react. This \( A \) constant is not significantly affected by temperature.

\( e^{-\frac{E_a}{RT}} \) is a mathematical calculation of (f) the fraction of collisions with the minimum energy (activation energy, \( E_a \)) required to react.

We can rearrange the Arrhenius equation to be more useful by taking the natural log of both sides…

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

This is a straight line equation of the style … \( y = mx + b \)

If we graph \( \ln k \) vs \( 1/T \) (or \( T^{-1} \)) and take two points we can rearrange the equation into the following form that will help to solve activation energy, \( E_a \)…

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

**Try this #21:**

The specific rate constant, \( k \), for the decomposition of \( \text{N}_2\text{O} \…\]

\[ 2 \text{N}_2\text{O} (g) \rightarrow 2 \text{N}_2 (g) + \text{O}_2 (g) \]

at 300°C is \( 2.6 \times 10^{-11} \text{ s}^{-1} \) and at 330°C, \( k \) is \( 2.1 \times 10^{-10} \text{ s}^{-1} \).

a) Solve for the activation energy, \( E_a \), of the reaction.

b) Prepare a reaction coordinate diagram given \( \Delta H_{rxn} = -164.1 \text{ kJ} \)
Temperature and Rate Expanded:

We learned reaction rates increase as temperature increases.

Arrhenius Equation… \( k = A e^{-E_a/RT} \)

can be rearranged to… \( \ln k = -E_a/RT + \ln A \)

or… \( \ln (k_1/k_2) = (E_a/R)(T_2^{-1} - T_1^{-1}) \)

Now we will look for the explanation and where this equation comes from using the collision theory model.

For the single step reaction…

\[
\text{NO (g) + Cl}_2\text{ (g)} \rightarrow \text{NOCl (g) + Cl (g)}
\]

at 25 °C, \( k = 4.9 \times 10^{-6} \text{ 1/(M s)} \)

at 35°C, \( k = 1.5 \times 10^{-5} \text{ 1/(M s)} \)

With just 10°C change the rate of this reaction more than triples. The question for you is… “What causes this dramatic change in specific rate constant?”

For an explanation we have the Collision Model which is based on the kinetic molecular theory of gases.

Collision Model:

Effective collisions must…

1. Possess at least the minimum energy necessary to rearrange outer electrons in breaking and forming new ones (the activation energy, \( E_a \)).

   Example: CH₄ will not combust with air at room temperature without a spark to ignite the reaction.

2. Have proper orientations (steric factor, \( p \)) toward each other at the time of the collision.

   Example: For the reaction…NO (g) + Cl₂ (g) \( \rightarrow \) NOCl (g) + Cl (g)

   if the Cl₂ collides with the N side of NO no reaction will take place, Cl₂ must collide with the O in the NO molecule to react.
In the Arrhenius Equation, \( A = Zp \) (frequency factor) and \( f = e^{-Ea/RT} \).

The collision frequency, \( Z \), is how often particles collide. This is directly proportional to the root mean squared speed, \( \mu_{\text{rms}} \). From the kinetic molecular theory found with gas laws in Chem 1A, we learned that \( \mu_{\text{rms}} = \sqrt{\frac{3RT}{\text{Molecular weight}}} \). As the temperature increases we know molecules move faster and will collide a bit more frequently.

**Do the math** for the root mean squared speed of NO or Cl\(_2\) at 25°C and 35°C to show this 10°C rise has less than a 2% increase in collision frequency (speed).

Does \( Z \) noticeably affect the specific rate constant as the temperature changes to account for the tripling affect on rate we saw in the NO and Cl\(_2\) example?

\( p = \) fraction of collisions with proper orientation (steric factor), independent of Temp.

\( f = \) fraction of collisions with the **activation energy** required for success. This energy allows the particles to create an **activated complex** at the height of the energy profile. This factor is greatly affected by small temperature changes.

**Thermal Energy Distribution**

As temperature increases, the fraction of molecules with enough energy to surmount the activation energy barrier also increases.
Try this #22:

Using the same NO and Cl₂ example and given that \( f = e^{E_a/RT} \) and given the activation energy is 85 kJ/mol

a) solve for \( f \) at 25°C and at 35°C
b) Does this account for \( k \) being about 3 times larger?

Transition State:

Energy profile diagrams show the reaction pathway (reactants \( \rightarrow \) products) verses energy. At the peak of a profile the activation energy has been added and an unstable, high energy intermediate is formed (activated complex) in which bonds are partially broken/formed.

*Draw a sample energy profile diagram...*
Mechanisms:

Reaction Mechanisms and Catalysts:
We have learned to determine orders and rate laws. Now we will use this information to determine the pathway of a reaction. Reaction Mechanisms are the step-by-step pathway by which a reaction occurs. These may be a single step or a series of elementary steps. The slowest step is rate determining.

Example of rate determining step: Two people are working together in writing 100 handwritten invitations for a large surprise party. One writes the card containing all the information on time, location, what to bring, a small personal note etc. (assume an average of 2 minutes per card). The second person places the card into an envelope, adds the stamp and sticks on addresses for both the return and the recipient (assume an average of 20 seconds per card).

What is the rate determining step?
How long will it take to finish the 100 invitations?

Items to Consider when determining Reaction Mechanisms/Catalysts

- Does the reaction occur in one elementary step?
  Reaction orders of the reactants match coefficients and no catalyst.

- Is this a multistep reaction?
  Slowest step is rate determining. Orders in the rate law expression are based on the slow step. The separate elementary reactions within a multi-step reaction add together to give the overall reaction.

- What is the molecularity of the steps in the reaction?
  Unimolecular reactions have one reactant that will change or decompose. Bimolecular reactions have two particles collide and react. Termolecular reactions have three particles collide to react and are generally slow since all particles need to collide with proper orientation and the minimum energy for the reaction to occur. Uni and bi-molecular reactions are much more favorable than termolecular.

- Is a reaction intermediate involved?
  Reaction Intermediates are substances that are created in an elementary step and then consumed in a later step. Reaction Intermediates are never part of a rate law expression.
• Is a homogeneous catalyst involved?

Homogeneous Catalysts are first used during an elementary step and then reformed in a later step of a multi-step reaction mechanism. A homogeneous catalyst is in the same phase as the other reactants. A catalyst is neither a reactant nor product, but is identified in the overall reaction by writing the substance above the reaction arrow. Homogeneous catalysts always show up in the rate law expression.

• Is a heterogeneous catalyst involved?

Heterogeneous Catalysts are generally a solid surface that adsorbs reactants, activates/diffuse (i.e. splits an O\textsubscript{2} to 2 O atoms adsorbed to the surface of the catalyst), reacts and then desorbs off the catalyst. The speed of the reaction is dependent on the surface area of the catalyst.
Orders in a Rate Law Expression assist in identifying the slow step. Only reactants, catalysts and rarely products are in the expression.

Does a slow step follow a fast equilibrium step which creates a Reaction Intermediate? The rate law expression must be calculated using the forward and reverse reaction of the equilibrium step in addition to the slow step to eliminate the Intermediate from the rate law.

Enzymes are biological catalysts. Specific reactant molecules are substrates, the site where the enzyme reaction occurs is the active site. Substrates bind very specifically to an active site in a lock-and-key model.

Practice problems with Reaction Mechanisms and Catalysts:
Try this #23:

The reaction mechanism for a reaction is as follows…

Step 1 \( \text{O}_3 \ (g) + \text{NO}_2 \ (g) \rightarrow \text{NO}_3 \ (g) + \text{O}_2 \ (g) \) slow

Step 2 \( \text{NO}_3 \ (g) + \text{NO}_2 \ (g) \rightarrow \text{N}_2\text{O}_5 \ (g) \) fast

Write the overall reaction.

Identify the molecularity of each step.

Identify all that apply: reactants, products, catalysts, [reaction intermediates]

What is the rate law expression for this mechanism?
Try this #24:
The reaction mechanism for a reaction is as follows…

Step 1  \( \text{Cl (g) + O}_3\text{(g)} \rightarrow \text{ClO (g) + O}_2\text{(g)} \)  \( \text{slow} \)
Step 2  \( \text{ClO (g) + O (g)} \rightarrow \text{Cl (g) + O}_2\text{(g)} \)  \( \text{fast} \)

Write the overall reaction.

Identify the molecularity of each step.

Identify all that apply:  reactants, products, catalysts, [reaction intermediates]

What is the rate law expression for this mechanism?

Try this #25:
The reaction mechanism for a reaction is as follows…

Step 1  \( 2 \text{NO (g) + O}_2\text{(g)} \rightarrow 2 \text{NO}_2\text{(g)} \)  \( \text{slow} \)
Step 2  \( 2 [\text{NO}_2\text{(g) + SO}_2\text{(g)} \rightarrow \text{NO (g) + SO}_3\text{(g)}] \)  \( \text{fast} \)

What is the overall reaction?

Identify the molecularity of each step.

Identify all that apply:  reactants, products, catalysts, [reaction intermediates]

What is the rate law expression for this mechanism?
Try this #26:

The reaction mechanism for a reaction is as follows...

Step 1 \[ 2 \text{NO} \text{(g)} \leftrightharpoons \text{N}_2\text{O}_2 \text{(g)} \] fast equilibrium
Step 2 \[ \text{N}_2\text{O}_2 \text{(g)} + \text{H}_2 \text{(g)} \rightarrow \text{N}_2 \text{O} \text{(g)} + \text{H}_2\text{O} \text{(g)} \] slow
Step 3 \[ \text{N}_2\text{O} \text{(g)} + \text{H}_2 \text{(g)} \rightarrow \text{N}_2 \text{(g)} + \text{H}_2\text{O} \text{(g)} \] fast

What is the overall reaction?

Identify the molecularity of each step.

Identify all that apply: reactants, products, catalysts, [reaction intermediates]

What is the rate law expression for this mechanism?

Try this #27:

The reaction mechanism for a reaction is as follows...

Step 1 \[ \text{I}_2 \text{(g)} \leftrightharpoons 2 \text{I} \text{(g)} \] fast equilibrium
Step 2 \[ \text{H}_2 \text{(g)} + \text{I} \text{(g)} \leftrightharpoons \text{H}_2\text{I} \text{(g)} \] fast equilibrium
Step 3 \[ \text{H}_2\text{I} \text{(g)} + \text{I} \text{(g)} \rightarrow 2 \text{HI} \text{(g)} \] slow

What is the overall reaction?

Identify the molecularity of each step.

Identify all that apply: reactants, products, catalysts, [reaction intermediates]

What is the rate law expression for this mechanism?
Try this #28:

Postulate a mechanism… (try to create more than one)
Using experimental data and chemical intuition come up with a couple of possible mechanisms that fit.
Overall reaction… NO\textsubscript{2} (g) + CO (g) \rightarrow NO (g) + CO\textsubscript{2} (g) at 255°C
Rate = k[NO\textsubscript{2}]\textsuperscript{2}
Identify the molecularity of each step.
Identify all that apply: reactants, products, catalysts, [reaction intermediates]
Two possible answers to Try this #28:

Postulate 1…
Step 1 2 NO₂ (g) → N₂O₄ (g)  
Step 2 N₂O₄ (g) + CO (g) → NO (g) + CO₂ (g) + NO₂ (g)  

Postulate 2…
Step 1 2 NO₂ (g) → NO₃ (g) + NO (g)  
Step 2 NO₃ (g) + CO (g) → CO₂ (g) + NO₂ (g)

Both postulates fit the overall reaction and the rate law expression. The difference is that different reaction intermediates (N₂O₄, NO₃) are formed. Further experimentation can check what intermediate may show up during the reaction. We find that NO₃ is formed during the reaction so postulate 2 seems to be most probable pathway.

Try this #29:

Given…
Overall reaction: 2 NO₂Cl (g) → 2 NO₂ (g) + Cl₂ (g)
Rate = k[NO₂Cl]
Can this be a single step reaction?

Postulate a mechanism using experimental data and chemical intuition come up with a mechanism that fits.
Identify the molecularity of each step.
Identify all that apply: reactants, products, catalysts, [reaction intermediates]
Try this #30:
Given…
Overall reaction: \( 2 \text{NO}_2 (g) + \text{F}_2 (g) \rightarrow 2 \text{NO}_2\text{F} (g) \)
Rate = \( k[\text{NO}_2][\text{F}_2] \)
Can this be a single step reaction?
Postulate a mechanism using experimental data and chemical intuition come up with a mechanism that fits.
Identify the molecularity of each step.
Identify all that apply: reactants, products, catalysts, [reaction intermediates]

Try this #31:
Given…
Overall reaction: \( 2 \text{H}_2\text{O}_2 (aq) \rightarrow 2 \text{H}_2\text{O} (l) + \text{O}_2 (g) \)
Rate = \( k[\text{H}_2\text{O}_2][\text{I}^{-1}] \)
\( \text{I}^{-1} \) is a catalyst, step one is slow, \( \text{IO}^{-1} \) is a reaction intermediate.
Step one must occur 2 times before step 2 reacts (similar to step 2 in the example 3).
Postulate a mechanism using experimental data and chemical intuition come up with a mechanism that fits.
Identify the molecularity of each step.
Identify all that apply: reactants, products, catalysts, [reaction intermediates]
**Answers to try this:**

6a) Rate of Reaction \(- \Delta [H]/\Delta t = -\Delta [ICl]/2\Delta t = \Delta [I_2]/\Delta t = \Delta [HCl]/2\Delta t\)

6b) similar to Figure 1, but with 4 lines

6c) +0.26 M/s

6d) +0.13 M/s

7a) Rate is second order with respect to NO and overall

7b) Rate is first order with respect to (CH\textsubscript{3})\textsubscript{3}CBr and zero order with OH\textsuperscript{-1} and first order overall

7c) Rate is second order with respect to NO, first order with respect to O\textsubscript{2} and third order overall

9a) Rate = k[NO]\textsuperscript{2}[H\textsubscript{2}] overall it is 3\textsuperscript{rd} order

9b) M\textsuperscript{-2}s\textsuperscript{-1}

9c) if [NO] doubles the rate is 4 times faster. When [NO] triples it is 9 times faster

9d) 8 times faster

10) Rate is second order with respect to [NO], first order with respect to [H\textsubscript{2}] and third order overall, \(\text{Rate} = k[NO]^2[H_2], k = 1.23 \text{ M}^2\text{s}^{-1}\), [NO] for expt 4 = 0.147M

11) Rate is first order with respect to [A], first order with respect to [B], zero order with [C] and second order overall, \(\text{Rate} = k[A][B], k = 0.26 \text{ M}^{-1}\text{s}^{-1}\), Rate of formation of D for expt. 5 = 6.5 x 10\textsuperscript{-2} M/min

12) Rate is second order with respect to [SO\textsubscript{2}], first order with respect to [O\textsubscript{2}] and third order overall, \(\text{Rate} = k[SO_2]^2[O_2], k = 0.67 \text{ M}^2\text{s}^{-1}\), [O\textsubscript{2}] for expt 4 = 0.375 M, Rate of formation of SO\textsubscript{3} in expt. 5 = 1.2 x 10\textsuperscript{-2} M/s, [SO\textsubscript{2}] for expt 6 = 0.39 M

16) a) 0.075 sec, b) 0.030 g

17) a) 1.01 x 10\textsuperscript{-3} hr\textsuperscript{-1}, b) 2.86 g

18) a) second, b) \(t_1/2 = 500\) hrs, c) 0.071 mol, d) 71%, e) \(t_1/2 = 5000\) hrs, f) 0.096 mol, g) 96%

19) a) fill the table, b) the reaction is first order, k = 0.20 min\textsuperscript{-1}, c) \(t_1/2 = 3.5\) min

20) a) fill the table, b) second order, \(k = 0.92 \text{ M}^{-1}\text{min}^{-1}\), c) 1.3 min

21) a) 200 kJ/mol, b) draw diagram

22) a) 25°C, \(f = 1.3 x 10^{-15}\) and at 35°C, \(f = 3.9 x 10^{-15}\), b) yes