CHEMICAL KINETICS: THE RATES AND MECHANISMS OF CHEMICAL REACTIONS

Chemical kinetics is the study of the speed or rate of a reaction under various conditions. Spontaneity is also important AND a spontaneous reaction does NOT imply a rapid reaction. The changing of diamond into graphite is spontaneous but so slow that it is not detectable even in a lifetime. A mechanism is a sequence of events at the molecular level that controls the speed and outcome of the reaction.

FACTORS THAT AFFECT REACTION RATES

The following conditions affect the speed of a chemical process:

1. **Nature of the reactants**--Some reactant molecules react in a hurry, others react very slowly.

   Pointers:
   - **Physical state**—gasoline (l) vs. gasoline (g); K$_2$SO$_4$ (s) + Ba(NO$_3$)$_2$ (s) → no rxn.; while both of these in the aqueous state react.
   - **Chemical identity**—What is reacting? Usually ions of opposite charge react very rapidly. Usually, the more bonds between reacting atoms in a molecule, the slower the reaction rate. Substances with strong bonds (larger bond energies) will react much more slowly. Examples: metallic sodium reacts much faster with water than metallic calcium. Oxidation of methane can be increased with an increase in temperature; photosynthesis is very slow and changes very little with an increase in temperature.

2. **Concentration of reactants**—more molecules, more collisions.

3. **Temperature**—heat >em up & speed >em up; the faster they move, the more likely they are to collide.

   - An increase in temperature produces more successful collisions that are able to overcome the needed activation energy, therefore, a general increase in reaction rate with increasing temperature.
   - In fact, a general rule of thumb is that a 10$^\text{°C}$ increase in temperature will double the reaction rate.
   - * This actually depends on the magnitude of the Ea* and the temperature range.

4. **Catalysts**—accelerate chemical reactions but are not themselves transformed.

   - Biological catalysts are proteins called enzymes.
   - A catalyst is a substance that changes the rate of reaction by altering the reaction pathway. Most catalysts work by lowering the activation energy needed for the reaction to proceed, therefore, more collisions are successful and the reaction rate is increased.
   - Remember! The catalyst is not part of the chemical reaction and is not used up during the reaction.* (May be homogeneous or heterogeneous catalysts.) Ex. H$_2$O$_2$ decomposes relatively slowly into H$_2$O and O$_2$; however; exposure to light accelerates this process AND with the help of MnO$_2$, it goes extremely FAST!! Note: A catalyst lowers the activation energy barrier. Therefore, the forward and reverse reactions are both accelerated to the same degree.
   - * (Some homogeneous catalysts actually appear in the rate law because their concentration affects the reaction. Ex. NO catalyzing O$_3$)

4. **Surface area of reactants**—exposed surfaces affect speed.

   - Except for substances in the gaseous state or solution, reactions occur at the boundary, or interface, between two phases.
   - The greater surface area exposed, the greater chance of collisions between particles, hence, the reaction should proceed at a much faster rate. Ex. coal dust is very explosive as opposed to a piece of charcoal. Solutions are ultimate exposure!
THE COLLISION THEORY OF REACTION RATES

- Particles must collide.
- Only two particles may collide at one time.
- Proper orientation of colliding molecules so that atoms in the can come in contact with each other to become products.
- The collision must occur with enough energy to overcome the electron/electron repulsion of the valence shell electrons of the reacting species and must have enough energy to transform translational energy into vibrational energy in order to penetrate into each other so that the electrons can rearrange and form new bonds.
- This new collision product is at the peak of the activation energy hump and is called the activated complex or the transition state. At this point, the activated complex can still either fall to reactants or to products.
- With all of these criteria met, the reaction may proceed in the forward direction. Amazing that we have reactions occurring at all!

12.1 CHEMICAL REACTION RATES

The speed of a reaction is expressed in terms of its rate, some measurable quantity is changing with time.

The rate of a chemical reaction is measured by the decrease in concentration of a reactant or an increase in concentration of a product in a unit of time.

\[
\text{Rate} = \frac{\text{change in concentration of a species}}{\text{time interval}}
\]

When writing rate expressions, they can be written in terms of reactants disappearance or products appearance.

* Rate is not constant, it changes with time. Graphing the data of an experiment will show an average rate of reaction. You can find the instantaneous rate by computing the slope of a straight line tangent to the curve at that time.
**Reaction Rate**—expressed as the $\Delta$ in concentration of a reagent per unit time or $\Delta[A]/\Delta t$

- Focus either on the disappearance of reactants or the appearance of products.
  - Rate of $\Delta$ of a reactant is always **negative**
  - Rate of $\Delta$ of a product is always **positive**

Consider:

$$2 \text{NO}_2(g) \rightarrow 6 \text{O}_2(g) + 2 \text{NO}(g)$$

Oxygen can appear only half as rapidly as the nitrogen dioxide disappears.

NO appears twice as fast as oxygen appears.

Calculate the AVERAGE rate at which $[\text{NO}_2]$ changes in the first 50.0 seconds:

$$\text{RATE} = \frac{\Delta [\text{NO}_2]}{\Delta t} = \frac{[0.0079] - [0.0100]}{50.0 \text{ s}}$$

$$= -[-4.2 \times 10^{-5} \text{ mol/L Xsec}]$$

$$= 4.2 \times 10^{-5} \text{ mol/L Xsec or M X s}^{-1}$$

**Note that the rate is NOT constant but decreases with time.** The rates given below are **average** rates.

<table>
<thead>
<tr>
<th>$-\frac{\Delta [\text{NO}_2]}{\Delta t} \times 10^{-5}$</th>
<th>Time period (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2</td>
<td>0 $\square$ 50</td>
</tr>
<tr>
<td>2.8</td>
<td>50 $\square$ 100</td>
</tr>
<tr>
<td>2.0</td>
<td>100 $\square$ 150</td>
</tr>
<tr>
<td>1.4</td>
<td>150 $\square$ 200</td>
</tr>
<tr>
<td>1.0</td>
<td>200 $\square$ 250</td>
</tr>
</tbody>
</table>

To find the value of the rate at a particular time, the **instantaneous rate**, compute the slope of a line tangent to the curve at that point. Why the negative on $\text{NO}_2$?

**Relative Rates**: We can consider the appearance of products along with the disappearance of reactants. The reactant's concentration is declining, the products is increasing. Respect the algebraic sign AND respect the stoichiometry. [divide the rate of change in concentration of each reactant by its stoichiometric coefficient in the balanced chem. eqn. and this is foolproof and a breeze!]

Thus,...

"rate of reaction $= -\frac{1\Delta[\text{NO}_2]}{\Delta t} = \frac{1\Delta[\text{NO}]}{\Delta t} = \Delta[\text{O}_2]"
2 Δtime  2 Δtime Δtime

Of course you can change these once the ratio is set. You might prefer -1 : +1 : +2

Relative Rates from the balanced equation:
Using the coefficients from the balanced equation, students should be able to give relative rates. For example: \( 4 \text{PH}_3(g) \rightarrow \text{P}_4(g) + 6 \text{H}_2(g) \)

Initial rate rxn. = \(-\frac{1}{4} \left[ \frac{\Delta[\text{PH}_3]}{\Delta t} \right]\) = \(\frac{1}{6} \left[ \frac{\Delta[\text{H}_2]}{\Delta t} \right]\)

**Exercise**
What are the *relative* rates of change in concentration of the products and reactant in the decomposition of nitrosyl chloride, NOCl?

\( 2 \text{NOCl}_2(g) \rightarrow 2 \text{NO}_2(g) + \text{Cl}_2(g) \)

### 12.2 RATE LAWS: AN INTRODUCTION

Reactions are reversible. So far, we’ve only considered the forward reaction. The reverse is equally important. When the rate of the forward = the rate of the reverse we have EQUILIBRIUM! To avoid this complication we will discuss reactions soon after mixing—initial reaction rates, and not worry about the buildup of products and how that starts up the reverse reaction.

**Initial reaction rates**—begin with pure reactants, mix thoroughly, then measure speed of rxn. over time
"presence of products can alter results dramatically and lead to confusing results. We’ll be talking initial reaction rates throughout our discussions!
"Rate = \(k[\text{NO}_2]^n\) = \(-\frac{\Delta[\text{NO}_2]}{\Delta t}\)

**Rate expression or rate law** is the relation between reaction rate and the concentrations of reactants given by a mathematical equation.

### CONCENTRATION AND REACTION RATE:

**THE RATE LAW OR RATE EXPRESSION**: Rates generally depend on reactant concentrations. To find the exact relation between rate and concentration, we must do some experiments and collect information.

\(a\text{A} + b\text{B} \rightarrow x\text{X}\)

"where C is a catalysts, the rate expression will always have the form:

Initial rxn rate = \(k[A]^m[B]^n[C]^p\)

\(k = \text{rate constant}\)

\([A] = \text{concentration of reactant A}\)

\([B] = \text{concentration of reactant B}\)
[C] = concentration of the catalyst--won't see this too often in AP
m = order of reaction for reactant A
n = order of reaction for reactant B
p = order of reaction for the catalyst C

Exponents can be zero, whole numbers or fractions AND MUST BE DETERMINED BY EXPERIMENTATION!!

THE RATE CONSTANT, k

- temperature dependent & must be evaluated by experiment.
- Example: rate = k[Pt(NH₃)₂Cl₂]
- and k is 0.090/hr, therefore when [ion] = 0.018 mol/L
  - rate = (.0090/hr)(0.018 mol/L) = 0.0016 mol/(L·hr)

ORDER OF A REACTION

- order with respect to a certain reactant is the exponent on its concentration term in the rate expression
- order of the reaction is the sum of all the exponents on all the concentration terms in the expression
- DETERMINATION OF THE RATE EXPRESSION
  
aA + bB 6 xX
  
- initial rate = k[A]₀ᵐ[B]ⁿ₀
- the little subscript Ao@ means original.

1. **Zero order**: The change in concentration of reactant has no effect on the rate.
   - These are not very common.
   - General form of rate equation: Rate = k

2. **First order**: Rate is directly proportional to the reactants concentration; doubling [rxt], doubles rate. These are very common! Nuclear decay reactions usually fit into this category.
   - General form of rate equation: Rate = k [A]

3. **Second order**: Rate is quadrupled when [rxt] is doubled and increases by a factor of 9 when [rxt] is tripled etc. These are common, particularly in gas-phase reactions.
   - General form of rate equation: Rate = k [A]²

4. Fractional orders are rare!
   - Ex. rate = k[A]₀ᵐ[B]ⁿ₀
     - If m = 0 ; reaction is zero order with respect to A
     - If m = 1 ; reaction is 1st order with respect to A
     - If m = 2 ; reaction is 2nd order with respect to A
     - If n = 0 ; reaction is zero order with respect to B
     - If n = 1 ; reaction is 1st order with respect to B
     - If n = 2 ; reaction is 2nd order with respect to B
Adding the orders of each reactant gives the *overall order* of the reaction.

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>Initial Rate (\text{mol/(LXhr)})</th>
<th>Initial concentration ([A]_0)</th>
<th>Initial concentration ([B]_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(0.50 \times 10^{-2})</td>
<td>0.50</td>
<td>0.20</td>
</tr>
<tr>
<td>2</td>
<td>(0.50 \times 10^{-2})</td>
<td>0.75</td>
<td>0.20</td>
</tr>
<tr>
<td>3</td>
<td>(0.50 \times 10^{-2})</td>
<td>1.00</td>
<td>0.20</td>
</tr>
<tr>
<td>4</td>
<td>(1.00 \times 10^{-2})</td>
<td>0.50</td>
<td>0.40</td>
</tr>
<tr>
<td>5</td>
<td>(1.50 \times 10^{-2})</td>
<td>0.50</td>
<td>0.60</td>
</tr>
</tbody>
</table>

Since the rate stays the same regardless of the concentration of \([A]\), it is zero order with respect to \(A\). However, the rate doubles with a doubling of \([B]\) and triples with a tripling of \([B]\). This indicates the rate is first order with respect to \([B]\).

**Summary:** Initial reaction rate = \(k[A]_o[B]_o^{1/2} = k[B]_o^{1/2}\)

The overall reaction rate = \(1 + 0 = 1^{\text{st}}\) order overall.

Now . . . . .

Use a set of the data to calculate \(k\):

\[
0.0050 \text{ mol/(LXhr)} = k[0.20 \text{ mol/L}]^{1/2}
\]

\[
k = 2.5 \times 10^{-2} \text{ /hr}
\]

You should get the same value with any set of data!

Ugly algebraic method is sometimes necessary:

rate 1 = \(k[\text{reactant}]^m [\text{reactant}]^n\)
rate 2 \(k[\text{reactant}]^m [\text{reactant}]^n\)

Select a trial where one reactant concentration is held constant SO THAT IT CANCELS; the \(k\)’s will also cancel

Using trials 1 & 4:

\[
0.50 \times 10^{-2} = k[0.50]^m [0.20]^n \quad \text{so…} \quad \frac{1}{2} = [\frac{1}{2}]^n \quad \text{and} \quad \therefore \ n \text{ must be ONE to make that true!}
\]

\[
1.00 \times 10^{-2} = k[0.50]^m [0.40]^n
\]

**Exercise**

In the following reaction, a Co-Cl bond is replaced by a Co-OH₂ bond.

\[
[\text{Co(NH}_3\text{)}_5\text{Cl}]^{2+} + \text{H}_2\text{O} \rightarrow \text{[Co(NH}_3\text{)}_5\text{H}_2\text{O}]^{3+} + \text{Cl}^{-}
\]

Using the data below, find the value of \(m\) in the rate expression and calculate the value of \(k\).

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Initial Concentration of [Co(NH₃)₅Cl]²⁺ (mol/L)</th>
<th>Initial rate (mol/(LXmin))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(1.0 \times 10^{-3})</td>
<td>(1.3 \times 10^{-7})</td>
</tr>
<tr>
<td>2</td>
<td>(2.0 \times 10^{-3})</td>
<td>(2.6 \times 10^{-7})</td>
</tr>
<tr>
<td>3</td>
<td>(3.0 \times 10^{-3})</td>
<td>(3.9 \times 10^{-7})</td>
</tr>
<tr>
<td>4</td>
<td>(1.0 \times 10^{-3})</td>
<td>(1.3 \times 10^{-7})</td>
</tr>
</tbody>
</table>
Exercise 12.1
The reaction between bromate ions and bromide ions in acidic aqueous solution is given by the equation:

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

The table below gives the results of four experiments. Using these data, determine the orders for all three reactants, the overall reaction order, and the value of the rate constant. What is the value of \( k \)? What are the units of \( k \)?

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Initial [BrO(_3)^-]</th>
<th>Initial [Br(^-)]</th>
<th>Initial [H(^+)]</th>
<th>Measured initial rate (mol/L ( \cdot ) s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>8.0 ( \times ) 10(^{-4} )</td>
</tr>
<tr>
<td>2</td>
<td>0.20</td>
<td>0.10</td>
<td>0.10</td>
<td>1.6 ( \times ) 10(^{-3} )</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>0.20</td>
<td>0.10</td>
<td>3.2 ( \times ) 10(^{-3} )</td>
</tr>
<tr>
<td>4</td>
<td>0.10</td>
<td>0.10</td>
<td>0.20</td>
<td>3.2 ( \times ) 10(^{-3} )</td>
</tr>
</tbody>
</table>

TWO TYPES OF RATE LAW

! **differential rate law**—expresses how the rate depends on concentration (most common & what we’ve been doing!)

! **integrated rate law**—expresses how the concentrations depend on time

12.3 DETERMINING THE FORM OF THE RATE LAW—experimental convenience

Note the shape of this curve! It will save you time in the future!
Write the relative rate expression:

Write the differential rate law [expression]:

12.4 INTEGRATED RATE LAW: CONCENTRATION/TIME RELATIONSHIPS
When we wish to know how long a reaction must proceed to reach a predetermined concentration of some reagent, we can construct curves or derive an equation that relates concentration and time.

GRAPHICAL METHODS FOR DISTINGUISHING FIRST AND SECOND ORDER REACTIONS

first order:                                         second order:
\[ \ln[A] = -kt + \ln[A]_o \]                          \[ \frac{1}{[A]} = kt + \frac{1}{[A]_o} \]
\[ y = ax + b \]                                        \[ y = ax + b \]
" ln[reactant] vs. time \( \Delta \) straight line for \textbf{first order} in that reactant & since \( a = -k \) the slope of the line is \textit{negative}.
" \( \frac{1}{[\text{reactant}]} \) vs. time \( \Delta \) straight line for \textbf{second order} in that reactant since \( a = k \) the slope is \textit{positive}.

Using the graphing calculator: Set up your calculator so that time is always in \( L1 \) and the \( y \)-list is alphabetical!

- \( L1 \) \( \Delta \) time (\( x \) variable throughout!)
- \( L2 \) \( \Delta \) concentration \( [A] \) straight line = zero order
- \( L3 \) \( \Delta \) ln concentration \( \ln[A] \) straight line = first order
- \( L4 \) \( \Delta \) reciprocal concentration \( \frac{1}{[A]} \) straight line = second order

Run 3 linear regressions one each for \( L1,L2; L1,L3; L1,L4 \) and see which has the best \( \bar{r} \) [linear regression correlation coefficient in big people language!] Paste the best one into \( y= \) by hitting \( \Psi \subseteq \) to get the command back on the screen, then “fix” it to read LinReg \{the combination that was the best regression\}. Next, hit ‘\( \mathbf{\square} \)’ to Y-VARS then \( \mathbf{\Psi} \). If you were successful, you’ll see LinReg(\( ax + b \)) \( L1 \), \( L \)-whichever you chose, \( Y1 \) displayed on your screen.

The order of the reaction is 0; 1; 2 respectively for each combination.

*\( \text{slope} \) = \( k \) \& Rate = \( k[\text{rxt.}]^{\text{order}} \)

Next, since linear, NEVER, EVER FORGET: \( y = mx + b \) (TI uses an \( Aa@ \) instead of an \( Am@ \))

If \( L1,L3 \) was your best \( \bar{r} \) then, the reaction is first order and

\[ y = mx + b \] becomes
\[ \ln \text{[conc.]} = k \text{ (DO use the proper sign for k here!)}t + \ln \text{[conc.]}_o \]

Do the same substitutions into \( y = mx + b \) for the other formats!
Exercise 12.2
The decomposition of $\text{N}_2\text{O}_5$ in the gas phase was studied at constant temperature.

$$2\, \text{N}_2\text{O}_5 (\text{g}) \rightarrow 4\, \text{NO}_2 (\text{g}) + \text{O}_2 (\text{g})$$

The following results were collected:

<table>
<thead>
<tr>
<th>$[\text{N}_2\text{O}_5]$</th>
<th>Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1000</td>
<td>0</td>
</tr>
<tr>
<td>0.0707</td>
<td>50</td>
</tr>
<tr>
<td>0.0500</td>
<td>100</td>
</tr>
<tr>
<td>0.0250</td>
<td>200</td>
</tr>
<tr>
<td>0.0125</td>
<td>300</td>
</tr>
<tr>
<td>0.00625</td>
<td>400</td>
</tr>
</tbody>
</table>

Determine the rate law and calculate the value of $k$.

Once you have the CORRECT equation for the reaction’s rate law in your calculator so that it can draw the CORRECT linear regression line… You can display the graph, make sure your plot 1 is ON and then set it up to read the CORRECT axes. Check the max and min x-values that zoom 9 assigned to the window. You can now solve for any concentration EXACTLY between those max and min values. What if your window doesn’t have the proper time range? CHANGE IT!

To solve, display your graph by hitting $\sigma$. Next hit $\psi \rho$ to get to calculate then choose $\Sigma$ which is “value”. Now your screen has the graph displayed AND in the lower left corner an $x=$ with a flashing cursor. Just enter the time you want the concentration for and voila!

Exercise 12.3
Using the data given in Ex. 12.2 above, calculate $[\text{N}_2\text{O}_5]$ at 150 s after the start of the reaction.

Calculate the $[\text{N}_2\text{O}_5]$ at the following times:

- 200 s
- 400 s
- 600 s
- 1,000 s
! HALF-LIFE AND REACTION RATE FOR FIRST ORDER REACTIONS, $t_{1/2}$
"the time required for one half of one of the reactants to disappear.
"$[A] = 2[A]_o$ or $[A] = 2$ so... $\ln \frac{[A]}{[A]_o} = k t_2$ and... $\ln 2 = t_2$\[A]_o[\[A]_o/2
"Rearrange, evaluate $\ln 2$ and solve for $t_2$ and you get
$t_2 = \frac{0.693}{k}$
"“Half life is INDEPENDENT OF ORIGINAL CONCENTRATION for 1st order!!!

Exercise 12.4
A certain first-order reaction has a half-life of 20.0 minutes.
a. Calculate the rate constant for this reaction.

b. How much time is required for this reaction to be 75% complete?

! HALF-LIFE AND REACTION RATE FOR SECOND ORDER REACTIONS, $t_{1/2}$
"the time required for one half of one of the reactants to disappear.
"$[A] = 2[A]_o$ or $[A] = 2$ so... $\frac{1}{[A]_o} = k t_2 + \frac{1}{[A]_o/2}$
"Rearrange,
$$\frac{2}{[A]_o} - \frac{1}{[A]_o} = k t_2$$
$$k t_2 = \frac{1}{[A]_o}$$ solve for $t_2$, $t_2 = \frac{1}{k[A]_o}$ for a 2nd order rxn.

Exercise
The rate constant for the first order transformation of cyclopropane to propene is $5.40 \times 10^{-2}$/hr. What is the half-life of this reaction? What fraction of the cyclopropane remains after 51.2 hours? What fraction remains after 18.0 hours?
Exercise
For the reaction of \((\text{CH}_3)_3\text{CBr}\) with \(\text{OH}^-\),

\[(\text{CH}_3)_3\text{CBr} + \text{OH}^- \rightarrow (\text{CH}_3)_3\text{COH} + \text{Br}^-\]

The following data were obtained in the laboratory.

<table>
<thead>
<tr>
<th>TIME (s)</th>
<th>([(\text{CH}_3)_3\text{CBr}] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.100</td>
</tr>
<tr>
<td>30</td>
<td>0.074</td>
</tr>
<tr>
<td>60</td>
<td>0.055</td>
</tr>
<tr>
<td>90</td>
<td>0.041</td>
</tr>
</tbody>
</table>

Plot these data as \(\ln [(\text{CH}_3)_3\text{CBr}] \) versus time. Sketch your graph.

Is the reaction first order or second order? What is the value of the rate constant?
Exercise 12.5
Butadiene reacts to form its dimer according to the equation

\[ 2 \text{C}_4\text{H}_6 (g) \rightarrow \text{C}_8\text{H}_{12} (g) \]

The following data were collected for this reaction at a given temperature:

<table>
<thead>
<tr>
<th>[C₄H₆]</th>
<th>Time (± 1 s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01000</td>
<td>0</td>
</tr>
<tr>
<td>0.00625</td>
<td>1000</td>
</tr>
<tr>
<td>0.00476</td>
<td>1800</td>
</tr>
<tr>
<td>0.00370</td>
<td>2800</td>
</tr>
<tr>
<td>0.00313</td>
<td>3600</td>
</tr>
<tr>
<td>0.00270</td>
<td>4400</td>
</tr>
<tr>
<td>0.00241</td>
<td>5200</td>
</tr>
<tr>
<td>0.00208</td>
<td>6200</td>
</tr>
</tbody>
</table>

a. What is the order of this reaction? Explain. Sketch your graph as part of your explanation. Write the rate law expression:

b. What is the value of the rate constant for this reaction?

c. What if the half-life for the reaction under the conditions of this experiment?
HALF-LIFE AND REACTION RATE FOR ZERO ORDER REACTIONS, $t_{1/2}$

"the time required for one half of one of the reactants to disappear, BUT
Rate = $k[A]_0^0 = k$ (a big fat 1) = $k$
Integrated rate law is $[A] = -kt + [A]_0$

" $[A] = 2[A]_0$ or $\frac{[A]}{[A]_0} = 2$ so...

$\frac{[A]_0}{2} = -kt_2 + [A]_0$

$k\ t_2 = \frac{[A]_0}{2k} \text{ solve for } t_2, \ t_2 = \frac{[A]_0}{2k}$ for a ZERO order rxn.

Zero-order reactions are most often encountered when a substance such as a metal surface or an enzyme is required for the reaction to occur. The enzyme or catalyst may be come saturated and therefore an increase in the [reactant/substrate] has no effect on the rate.

INTEGRATED RATE LAWS FOR REACTIONS WITH MORE THAN ONE REACTANT

! Must [still] be determined by experiment! But we use a technique called “swamping”.

! Flood the reaction vessel with high concentrations of all but one reactant and perform the experiment. The reactants at high concentrations like say, 1.0 M compared to the reactant with a low concentration say, 1.0 x $10^{-3}$ M, stay the same.

" “In English”—the rate is now dependent on the concentration of the little guy since the big guy’s aren’t changing, therefore the rate = $k'$ [little guy]

" We now re-write the rate as a pseudo-rate-law and $k'$ is a pseudo-rate-constant

This is what is happening in the Crystal Violet lab!

A SUMMARY:
12.6 REACTION MECHANISMS
The sequence of bond-making and bond-breaking steps that occurs during the conversion of reactants to products.

! Must be determined by experiment! Must agree with overall stoichiometry AND the experimentally determined rate law!

ELEMENTARY STEPS
" **molecularity** -- number of molecules that participate in an atomic rearrangement
" unimolecular: involves one reactant molecule

" bimolecular: involves a collision between two reactant molecules

" termolecular: simultaneous collision between three reactant molecules [**very rare!**]

! RATE EXPRESSIONS FOR ELEMENTARY STEPS -- the rate expression cannot be predicted from overall stoichiometry. The rate expression of an elementary step is given by the product of the rate constant and the concentrations of the reactants in the step.

<table>
<thead>
<tr>
<th>ELEMENTARY STEP</th>
<th>MOLECULARITY</th>
<th>RATE EXPRESSION</th>
</tr>
</thead>
<tbody>
<tr>
<td>A6 products</td>
<td>unimolecular</td>
<td>rate = ( k[A] )</td>
</tr>
<tr>
<td>A + B 6 products</td>
<td>bimolecular</td>
<td>rate = ( k[A][B] )</td>
</tr>
<tr>
<td>A + A 6 products</td>
<td>bimolecular</td>
<td>rate = ( k[A]^2 )</td>
</tr>
<tr>
<td>2 A + B 6 products*</td>
<td>termolecular*</td>
<td>rate = ( k[A]^2[B] )</td>
</tr>
</tbody>
</table>

THE PHYSICAL SIGNIFICANCE OF RATE EXPRESSIONS FOR ELEMENTARY STEPS
" the more molecules the more collisions, the faster the rate
" the faster the molecules are moving, the more likely they will collide, the faster the rate

MOLECULARITY AND ORDER
" an **elementary step** is a reaction whose rate law can be written from its molecularity
" NOT true of the overall reaction order!

**Exercise**
Nitrogen oxide is reduced by hydrogen to give water and nitrogen,

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

and one possible mechanism to account for this reaction is

\[
2 \text{NO}(\text{g}) \rightleftharpoons \text{N}_2\text{O}_2(\text{g})
\]

\[
\text{N}_2\text{O}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow 6 \text{N}_2\text{O}(\text{g}) + \text{H}_2\text{O}(\text{g})
\]

\[
\text{N}_2\text{O}(\text{g}) + \text{H}_2(\text{g}) \rightarrow 6 \text{N}_2(\text{g}) + \text{H}_2\text{O}(\text{g})
\]

What is the molecularity of each of the three steps? Show that the sum of these elementary steps is the net reaction.
REACTION MECHANISMS AND RATE EXPRESSIONS

" determined by experiment
" the rate of the overall reaction is limited by, and is exactly equal to, the combined rates of all elementary steps up to and including the slowest step in the mechanism
" the slowest step is the rate determining step
" reaction intermediate--produced in one step but consumed in another.
" catalyst--goes in, comes out unharmed and DOES NOT show up in the final rxn.

Exercise 12.6
The balanced equation for the reaction of the gases nitrogen dioxide and fluorine is

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

The experimentally determined rate law is

\[ \text{Rate} = k [\text{NO}_2][\text{F}_2] \]

A suggested mechanism for the reaction is

\[ \text{NO}_2 + \text{F}_2 \rightarrow \text{NO}_2\text{F} + \text{F} \quad \text{Slow} \]

\[ \text{F} + \text{NO}_2 \rightarrow \text{NO}_2\text{F} \quad \text{Fast} \]

Is this an acceptable mechanism? That is, does it satisfy the two requirements? Justify.

12.7 A MODEL FOR KINETICS
Generally reactions occur more rapidly at higher temperatures than at lower temps. The rate generally doubles for every 10 K rise in temperature. It's an exponential increase!

TRANSITION STATE THEORY

" energy barrier must be overcome
" reaction energy diagram [humpy diagrams]
" transition state energy--max of rxn. E diagram
" activated complex--deformed molecules in their transition state, formed at the E\text{is}--unstable, can go either way!
" Activation energy, E*, Ea--energy a reacting molecule must absorb from its environment in order to react.
Kinetics and net energy of reaction.

\[ \Delta E \approx \Delta H \]
--a thermodynamic quantity

Collision Theory

Assumes molecules must collide in order to react!
Hindered by concentration, temperature and geometry--# of effective collisions

The Effect of Temperature of Reaction Rate: Arrhenius Equation

\[ k = \text{reaction rate constant} = Ae^{\frac{-E_a}{RT}} \]

\[ R \text{ is the “energy” R or } 8.31 \times 10^{-3} \text{kJ/KXmol} \]
\[ A \text{ is the frequency factor units of } \text{L/(mol X s)} \text{ & depends on the frequency of collisions and the fraction of these that have the correct geometry--# of effective collisions} \]
\[ e^{\frac{-E_a}{RT}} \text{ is always less than 1 and is the fraction of molecules having the minimum energy required for reaction} \]

*Notice in the equation: As "Ea" increases, "k" gets smaller and thus, the rate would decrease. Also, notice that as "T" goes up, "k" increases and so the rate would also increase.

Applying the laws of logarithms, taking the natural log of both sides, ln, we can rewrite the equation.

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

Rewrite in the form of an equation for a straight line, we get;

\[ \ln k = - \frac{E_a}{R} \frac{1}{T} + \ln [A] \]

Taking this equation, plot 1/T vs. ln [k], and get a straight line. From the straight line, find the slope and then find the activation energy.

\[ \text{slope} = - \frac{E_a}{R} \text{ so ... } E_a = - ( R ) ( \text{slope} ) \]
OR find $E_a$ from data given mathematically:

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

"used to calculate
- value of activation energy from temperature dependence of the rate constant
- rate constant for a given temp. if the $E^*$ [also known as $E_a$] and A factor are known

Example - Arrhenius
Calculate the activation energy for the following set of data:

<table>
<thead>
<tr>
<th>$T$ (EC)</th>
<th>$k$ (l/mol·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>$1.4 \times 10^{-3}$</td>
</tr>
<tr>
<td>13</td>
<td>$2.9 \times 10^{-3}$</td>
</tr>
<tr>
<td>24</td>
<td>$6.2 \times 10^{-3}$</td>
</tr>
<tr>
<td>33</td>
<td>$1.2 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

C. Points to remember!!
1. $E_a$ is smaller; $k$ is greater; the reaction is faster.
2. $E_a$ is greater; $k$ is smaller; the reaction is slower.

Exercise
The colorless gas dinitrogen tetroxide decomposes to the brown gas NO$_2$ in a first order reaction with a value of $k$ of $4.5 \times 10^3$/s at 274K. If $k$ is $1.00 \times 10^4$/s at 283K, what is the energy of activation?
Exercise 12.7
The reaction
\[ 2 \text{N}_2\text{O}_5 (g) \rightarrow 4 \text{NO}_2 (g) + \text{O}_2 (g) \]
was studied at several temperatures and the following values of \( k \) were obtained:

<table>
<thead>
<tr>
<th>( k ) (s(^{-1}))</th>
<th>( T ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0 ( \times ) 10(^{-5})</td>
<td>20</td>
</tr>
<tr>
<td>7.3 ( \times ) 10(^{-5})</td>
<td>30</td>
</tr>
<tr>
<td>2.7 ( \times ) 10(^{-4})</td>
<td>40</td>
</tr>
<tr>
<td>9.1 ( \times ) 10(^{-4})</td>
<td>50</td>
</tr>
<tr>
<td>2.9 ( \times ) 10(^{-3})</td>
<td>60</td>
</tr>
</tbody>
</table>

Calculate the value of \( E_a \) for this reaction. Sketch your graph.

Exercise 12.8
The gas-phase reaction between methane and diatomic sulfur is given by the equation
\[ \text{CH}_4 (g) + 2 \text{S}_2 (g) \rightarrow \text{CS}_2 (g) + 2 \text{H}_2\text{S} (g) \]
At 550° C the rate constant for this reaction is 1.1 M\(^{-1}\)s\(^{-1}\) and at 625° C the rate constant is 6.4 M\(^{-1}\)s\(^{-1}\). Using these values, calculate \( E_a \) for this reaction.
12.8 CATALYSIS

Alter the mechanism so the activation energy barrier can be lowered.

! Catalysts are not altered during the reaction—they serve to lower the activation energy and speed up the reaction by offering a different pathway for the reaction.

! \( E \) is NOT changed for the process.

! Biological catalysts are enzymes—proteins with specific shapes. ATP synthetase is the most important enzyme in the human body!

**HETEROGENEOUS CATALYST**—different phase than reactants, usually involves gaseous reactants adsorbed on the surface of a solid catalyst.

! Adsorption—refers to the collection of one substance on the surface of another.

! Absorption—refers to the penetration of one substance into another; water is absorbed by a sponge.

! Hydrogenation of unsaturated hydrocarbons—especially important in converting unsaturated fats [oils] into saturated fats [solids like Crisco].

! C=C bonds are converted into C-C bonds by adding a pair of hydrogens “across the double bond.”

! A simple example of hydrogenation involves ethylene:

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{C} & \quad \text{C} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H}
\end{align*}
\]

ethene (ethylene)

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{C} & \quad \text{C} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H}
\end{align*}
\]

ethane

This reaction uses a solid catalyst in the form of Pt, Pd, or Ni. The hydrogen and ethylene adsorb on the catalyst surface where the reaction occurs. The catalyst allows for metal-hydrogen interactions that weaken the strong H-H bonds and facilitate the reaction. Typically involves 4 steps:

1. Adsorption and activation of the reactants
2. Migration of the adsorbed reactants on the surface
3. Reaction of the adsorbed substances
4. Escape, or desorption, of the products

Catalytic converters are also heterogeneous catalysts. They have been placed in automobiles since 1974. [I know! You weren’t born yet! Don’t rub it in.] Gasoline containing lead RUINS the catalytic converter in your car!
HOMOGENEOUS CATALYST—exists in the same phase as the reacting molecules.

Freons or chlorofluorocarbons [CFC’s] were used until recently as refrigerants and as propellants in aerosol cans. Freon-12 (CCl₂F₂) is relatively inert and thus remains in the environment for a long time. Eventually they migrate upward into the upper atmosphere and are decomposed by high-energy light. Among the decomposition products are chlorine atoms:

\[
\text{CCl}_2\text{F}_2(\text{g}) \xrightarrow{\text{light}} \text{CCIF}_2(\text{g}) + \text{Cl}(\text{g})
\]

These chlorine atoms can catalyze the decomposition of ozone:

\[
\begin{align*}
\text{Cl}(\text{g}) + \text{O}_3(\text{g}) & \rightarrow \text{ClO}(\text{g}) + \text{O}_2(\text{g}) \\
\text{O}(\text{g}) + \text{ClO}(\text{g}) & \rightarrow \text{Cl}(\text{g}) + \text{O}_2(\text{g}) \\
\text{O}(\text{g}) + \text{O}_3(\text{g}) & \rightarrow 2 \text{O}_2(\text{g})
\end{align*}
\]

READ THE LAST COUPLE OF PAGES OF THIS CHAPTER FOR SOME GREAT DESCRIPTIVE STUFF! (That translates into multiple choice points!)