Chapter 30

Chemical Kinetics
Chemists have three fundamental questions in mind when they study chemical reactions: 1.) What happens? 2.) How fast does it happen? 3.) What extent does it happen?

This chapter deals with the second question - speed or rate of a reaction which is called Chemical Kinetics.

Chemical reactions require varying lengths of time for completion.
30.1 Reaction Rates

- This reaction rate depends on the characteristics of the reactants and products and the conditions under which the reaction is run.
- By understanding how the rate of a reaction is affected by changing conditions, one can learn the details of what is happening at the molecular level (mechanism or steps required for reaction).

$$2A + B \rightarrow C + D$$

reaction may be more complicated than it appears

1.) $A + A \rightarrow A_2$
2.) $A_2 + B \rightarrow C + D$

Overall: $2A + B \rightarrow C + D$
Reaction Rates

• The questions posed in this chapter that we will answer are:
  – How is the rate of a reaction measured?
  – How do you express the relationship of rate to the variables affecting the rate?
  – What conditions will affect the rate of a reaction?
  – What happens on a molecular level during a chemical reaction?
Reaction Rates

- **Chemical kinetics** is the study of reaction rates, how reaction rates change under varying conditions (how fast reactants consumed and products are formed), and what molecular events occur during the overall reaction (mechanism – pathway or series of steps for reaction).
Definition of Reaction Rate

• The **reaction rate** is a positive quantity that expresses how the concentration of a reactant or product changes with time.
Where “-” for reactants is to keep rate positive:

Δ[R] will be a negative number: (smaller # - larger #)

Rate produced equals rate consumed; [ ] means molarity

Negative (-) means consumed; positive (+) means produced

Note: could look at it as absolute value of rate and get positive #
Definition of Reaction Rates

• Consider the gas-phase decomposition of dinitrogen pentoxide.

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

Rate of formation of oxygen \[ = \frac{\Delta[\text{O}_2]}{\Delta t} \]

– This equation gives the average rate over the time interval, \( \Delta t \).

– If \( \Delta t \) is short, you obtain an \textbf{instantaneous rate}, that is, the rate at a particular instant.
In the reaction

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

The concentration of $O_2$ increases over time. You obtain the instantaneous rate from the slope of the tangent at the point of the curve corresponding to that time.
When the time changes from 4200 s to 4800 s, the average rate has slowed to $5 \times 10^{-7}$ mol/(L·s).

Thus, the rate of a reaction decreases as the reaction proceeds.

When the time changes from 600 s to 1200 s, the average rate is $2.5 \times 10^{-6}$ mol/(L·s).
Definition of Reaction Rates

• Note that the rate decreases as the reaction proceeds.
• Rate is time dependent. It decreases as reaction mixture runs out of reactants. Naturally conc less for reactants therefore less collisions and slower formation of products (smaller probability for collision/reaction)
• Rate is dependent on time and conc therefore rate is changing over time; not constant for whole rxn.
• Over any particular time there is a certain concentration of reactants and a particular rate.
• Reactions occur as the result of collisions between reactant molecules; higher conc, greater probability of collisions, faster rxn.
• As reactants are consumed, their conc drop, collisions occur less frequently, reaction rate decreases, eventually going to zero when all reactants are consumed.
Definition of Reaction Rates

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

- Because the amounts of products and reactants are related by stoichiometry, any substance in the reaction can be used to express the rate.

Rate of decomposition of \( \text{N}_2\text{O}_5 \) = \( -\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} \)

- Note the negative sign. This results in a positive rate as reactant concentrations decrease.
We are describing the same rate just in terms of consumed or produced (half full or half empty glass – same quantity of liquid). However, the rates of production (products) and consumption (reactants) are equal but on a per mol basis.

Rate of consumption = Rate of production
on per mol basis
The rate of decomposition of $\text{N}_2\text{O}_5$ and the formation of $\text{O}_2$ are easily related.

Since two moles of $\text{N}_2\text{O}_5$ decompose for each mole of $\text{O}_2$ formed, the rate of the decomposition of $\text{N}_2\text{O}_5$ is twice the rate of the formation of $\text{O}_2$. Using double; therefore rate of consumption doubles and must account for it.
HW 5  

More generally, for a reaction \(aA + bB \rightarrow cC + dD\)

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

Ex. Given consumption rate of \(N_2\) is 0.10 M/min, what is the consumption rate of \(H_2\)? Want to know \(\Delta[H_2]\)

\[ N_2 (g) + 3H_2 (g) \rightarrow 2NH_3 (g) \]

\[ \text{rate} = \frac{-\Delta[N_2]}{\Delta t} = \frac{-\Delta[H_2]}{3\Delta t} \]

\[ \text{rate} = \frac{(-0.10 \text{ M/min})}{3\Delta t} = -0.01 \text{ M/min} \]

\[ \text{rate} = \frac{(3)(0.10 \text{ M/min})}{\Delta t} = \frac{0.30 \text{ M/min}}{\Delta t} \]

\[ -0.30 \text{ M/min} = \frac{\Delta[H_2]}{\Delta t} \]

Note: could do problem using mol to mol ratio

HW absolute value to simplify

Rate always positive# by definition

Rate = 0.30 M/min

Submit answer as positive – rate positive #

Negative just stating consumed
Experimental Determination of Reaction Rates

• To obtain the rate of a reaction you must determine the concentration of a reactant or product during the course of the reaction.

  – One method for slow reactions is to withdraw samples from the reaction vessel at various times and analyze them.
  – More convenient are techniques that continuously monitor the progress of a reaction based on some physical property of the system.
Experimental Determination of Reaction Rates

• Gas-phase partial pressures is one way:
  – Manometer readings provide the concentration of species during the course of the reaction based on partial pressures.

• Colorimetry is another way:
  – species that absorbs near uv light; The intensity of the absorption is proportional to [species], and you can use the absorption rate to determine the reaction rate.
30.2 Relationship between Rate and Concentration

- Experimentally, it has been found that the rate of a reaction depends on the concentration of certain reactants (not always all reactants) as well as catalysts.

  - Let’s look at the reaction of nitrogen dioxide with fluorine to give nitryl fluoride.

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

  - The rate of this reaction has been observed to be proportional to the concentration of nitrogen dioxide.
Dependence of Rate on Concentration

- When the concentration of nitrogen dioxide is doubled, the reaction rate doubles. (linear effect)
  - The rate is also proportional to the concentration of fluorine; doubling the concentration of fluorine also doubles the rate. (linear effect)
  - We need a mathematical expression to relate the rate of the reaction to the concentrations of the reactants.
30.2.1 Rate Law

- A rate law is an equation that relates the rate of a reaction to the concentration of reactants (and catalyst) raised to various powers. 

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

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

- The rate constant, \( k \), is a proportionality constant in the relationship between rate and concentrations. (proportional not equal without constant)
Dependence of Rate on Concentration

- As a more general example, consider the reaction of substances A and B to give D and E.

\[ aA + bB \xrightarrow{C} dD + eE \quad \text{C} = \text{catalyst} \]

  - You could write the rate law in the form \((\text{reactants/catalyst})^p\)

\[ \text{Rate} = k[A]^m[B]^n[C]^p \]

  - The exponents \(m\), \(n\), and \(p\) are frequently, but not always, integers. They must be determined experimentally and cannot be obtained by simply looking at the balanced equation.
30.2.2 Reaction Order

• Reaction Order

  – The reaction order with respect to a given reactant species equals the exponent of the concentration of that species in the rate law, as determined experimentally.

\[
\text{Rate} = k \, [\text{NO}_2]^1[\text{F}_2]^1
\]

  note: typically if 1st order “1” not written

  – The overall order of the reaction equals the sum of the orders of the reacting species in the rate law.

\[
\text{Overall} = 1 + 1 = 2^{\text{nd}}
\]
Dependence of Rate on Concentration

• Reaction Order

– Consider the reaction of nitric oxide with hydrogen according to the following equation.

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

– The experimentally determined rate law is

\[ \text{Rate} = k[\text{NO}]^2[\text{H}_2] \]

– Thus, the reaction is second order in NO, first order in \( H_2 \), (not 2 as in eq – molecular eq, not elementary eq based on collisions) and third order overall.
Dependence of Rate on Concentration

- **Reaction Order**
  - Although reaction orders frequently have whole number values (particularly 1 and 2), they can be **fractional**.
  - **Zero** and **negative** orders are also possible.
  - The concentration of a reactant with a zero-order dependence has **no effect** on the rate of the reaction.

1.) \[ A + A \rightarrow A_2 \] (slow; this step dictates rate of rxn)

2.) \[ A_2 + B \rightarrow C + D \] (fast)

Overall: \[ 2A + B \rightarrow C + D \] \[ \text{rate} = k[A]^2 \]

Note: B is zero order, not part of rate law because not part of slowest step
30.2.3 Determining the Rate Law

• Determining the Rate Law.
  – One method for determining the order of a reaction with respect to each reactant is the method of initial rates.
  – It involves running the experiment multiple times, each time varying the concentration of only one reactant and measuring its initial rate.
  – The resulting change in rate indicates the order with respect to that reactant.
Dependence of Rate on Concentration
• Determining the Rate Law.
  – If doubling the concentration of a reactant has a doubling effect on the rate, then one would deduce it was a first-order dependence. (same change to conc occurs to rate - power of one – linear - $2C \rightarrow 2^1R = 2R$
  
  – If doubling the concentration had a quadrupling effect on the rate, one would deduce it was a second-order dependence. (the square occurs to the rate as opposed to change in conc. $2C \rightarrow 2^2R = 4R$

  – A doubling of concentration that results in an eight-fold increase in the rate would be a third-order dependence. (the cubed occurs to the rate as opposed to the change in conc $2C \rightarrow 2^3R = 8R$

HW 6

  – If doubling the concentration had no effect on the rate, one would deduce it was a zero-order dependence. $2C \rightarrow 2^0R = R$
### Ex. A + B → C

rate = \( k [A]^x [B]^y \)

<table>
<thead>
<tr>
<th>Exp</th>
<th>[A]</th>
<th>[B]</th>
<th>rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

\[
\text{rate}_2 = \frac{k [A]^x [B]^y}{\text{rate}_1} = \frac{k [A]^x [B]^y}{\frac{1 M/s}{1 M/s} \left( \frac{2 M}{1 M} \right)^y} = \frac{8 M/s}{1 M/s} = \left( \frac{1 M}{1 M} \right)^x \left( \frac{2 M}{1 M} \right)^y = 8 = 2^y
\]

\[
y = \frac{\log 8}{\log 2} = 3
\]

\[
x = \frac{\log 1}{\log 2} = 0
\]

\[
\text{rate} = 1 \, \text{M}^{-2} \, \text{s}^{-1} [B]^3
\]
A Problem to Consider

• Iodide ion is oxidized in acidic solution to triiodide ion, I$_3^-$, by hydrogen peroxide.

\[ \text{H}_2\text{O}_2(aq) + 3\text{I}^-(aq) + 2\text{H}^+(aq) \rightarrow \text{I}_3^-(aq) + 2\text{H}_2\text{O}(l) \]

– A series of four experiments were run at different concentrations, and the initial rates of I$_3^-$ formation were determined.

– From the following data, obtain the reaction orders with respect to H$_2$O$_2$, I$^-$, and H$^+$.

– Calculate the numerical value of the rate constant, k.

\[ \text{rate} = k \left[ \text{H}_2\text{O}_2 \right]^x \left[ \text{I}^- \right]^y \left[ \text{H}^+ \right]^z \]
A Problem to Consider

<table>
<thead>
<tr>
<th>Initial Concentrations (mol/L)</th>
<th>Initial Rate [mol/(L·s)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2\text{O}_2 )</td>
<td>( \text{I}^- )</td>
</tr>
<tr>
<td>Exp. 1</td>
<td>0.010</td>
</tr>
<tr>
<td>Exp. 2</td>
<td>0.020</td>
</tr>
<tr>
<td>Exp. 3</td>
<td>0.010</td>
</tr>
<tr>
<td>Exp. 4</td>
<td>0.010</td>
</tr>
</tbody>
</table>

Comparing Experiment 1 and Experiment 2, you see that when the \( \text{H}_2\text{O}_2 \) concentration doubles (with other concentrations constant), the rate doubles.

This implies a **first-order dependence with respect to \( \text{H}_2\text{O}_2 \).**

\[
\frac{2.30 \times 10^{-6} \text{ M/s}}{1.15 \times 10^{-6} \text{ M/s}} = \frac{k (0.020 M)^x (0.010 M)^y (0.00050 M)^z}{k (0.010 M)^x (0.010 M)^y (0.00050 M)^z}
\]

\[
2 = 2^x
\]

\[
\log 2 = x \log 2
\]

\[
x = 1
\]
A Problem to Consider

<table>
<thead>
<tr>
<th>Initial Concentrations (mol/L)</th>
<th>Initial Rate [mol/(L·s)]</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>H₂O₂</td>
</tr>
<tr>
<td>Exp. 1</td>
<td>0.010</td>
</tr>
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</tr>
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<td>0.010</td>
</tr>
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<td>Exp. 4</td>
<td>0.010</td>
</tr>
</tbody>
</table>

- Comparing Experiment 1 and Experiment 3, you see that when the I⁻ concentration doubles (with other concentrations constant), the rate doubles.
- This implies a first-order dependence with respect to I⁻.

\[
\frac{2.30 \times 10^{-6} \text{ M/s}}{1.15 \times 10^{-6} \text{ M/s}} = \frac{k (0.010 \text{ M})^1 (0.020 \text{ M})^y (0.000050 \text{ M})^z}{k (0.010 \text{ M})^1 (0.010 \text{ M})^y (0.000050 \text{ M})^z}
\]

\[
2 = 2^y
\]

\[
\log 2 = y \log 2
\]

\[
y = 1
\]
A Problem to Consider

<table>
<thead>
<tr>
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<th>Initial Rate [mol/(L·s)]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2$</td>
<td>$I^-$</td>
</tr>
<tr>
<td>Exp. 1</td>
<td>0.010</td>
</tr>
<tr>
<td>Exp. 2</td>
<td>0.020</td>
</tr>
<tr>
<td>Exp. 3</td>
<td>0.010</td>
</tr>
<tr>
<td>Exp. 4</td>
<td>0.010</td>
</tr>
</tbody>
</table>

Comparing Experiment 1 and Experiment 4, you see that when the $\text{H}^+$ concentration doubles (with other concentrations constant), the rate is unchanged.

This implies a zero-order dependence with respect to $\text{H}^+$.

\[
\frac{\text{exp 4}}{\text{exp 1}}: \quad \frac{1.15 \times 10^{-6} \, \text{M/s}}{1.15 \times 10^{-6} \, \text{M/s}} = \frac{k \, (0.010 \, \text{M})^1 \, (0.010 \, \text{M})^1 \, (0.00100 \, \text{M})^z}{k \, (0.010 \, \text{M})^1 \, (0.010 \, \text{M})^1 \, (0.00050 \, \text{M})^z}
\]

\[
1 = 2^z \\
\log 1 = z \log 2 \\
z = 0
\]

\[
\text{Rate} = k[\text{H}_2\text{O}_2][I^-]
\]
A Problem to Consider

Initial Concentrations (mol/L)

<table>
<thead>
<tr>
<th>Exp.</th>
<th>H₂O₂</th>
<th>I⁻</th>
<th>H⁺</th>
<th>Initial Rate [mol/(L·s)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp. 1</td>
<td>0.010</td>
<td>0.010</td>
<td>0.00050</td>
<td>1.15 x 10⁻⁶</td>
</tr>
<tr>
<td>Exp. 2</td>
<td>0.020</td>
<td>0.010</td>
<td>0.00050</td>
<td>2.30 x 10⁻⁶</td>
</tr>
<tr>
<td>Exp. 3</td>
<td>0.010</td>
<td>0.020</td>
<td>0.00050</td>
<td>2.30 x 10⁻⁶</td>
</tr>
<tr>
<td>Exp. 4</td>
<td>0.010</td>
<td>0.010</td>
<td>0.00100</td>
<td>1.15 x 10⁻⁶</td>
</tr>
</tbody>
</table>

Rate = k[H₂O₂ ][I⁻]

- You can now calculate the rate constant by substituting values from any of the experiments. Using Experiment 1 (can use any) you obtain:

\[ 1.15 \times 10^{-6} \text{ M s}^{-1} = k \times (0.010\text{M})^1 \times (0.010\text{M})^1 \]
A Problem to Consider

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</table>

\[ k = \frac{1.15 \times 10^{-6} \text{Ms}^{-1}}{0.010M \times 0.010M} = 1.2 \times 10^{-2} M^{-1}s^{-1} \]

\[ \text{Rate} = 1.2 \times 10^{-2} M^{-1}s^{-1}[H₂O₂][I⁻] \]

HW 7
Units on $k$, $M^n$ time$^{-1}$ are very important because it helps to inform you about the overall order of the reaction:

**Overall Order Rxn**

Zero – rate ($Mt^{-1}$) = $k$

therefore units on $k$ must be $M$ time$^{-1}$

1$^{st}$ - rate ($Mt^{-1}$) = $k$ [A]

therefore units on $k$ must be time$^{-1}$

2$^{nd}$ – rate ($Mt^{-1}$) = $k$ [A]$^2$

therefore units on $k$ must be $M^{-1}$time$^{-1}$

3$^{rd}$ – rate ($Mt^{-1}$) = $k$ [A]$^3$

therefore units on $k$ must be $M^{-2}$time$^{-1}$

pattern, **sum of $k$ units = overall order**

Ex 1. $k$ is $M^{-5}s^{-1}$ ; What is overall order?

- sum of $k$ units = overall order

- (-5 -1) = 6$^{th}$ overall order

Ex 2. rate = $k$ [A] [B]$^2$ ; What are the units on $k$?

We know $k$ units are $M^n$ time$^{-1}$ and sum of $k$ units ($n$ -1) = - overall order

n -1 = -3 where n = -2

$k$ units: $M^{-2}$ time$^{-1}$
30.3 Concentration and Time

- A rate law simply tells you how the rate of reaction changes as reactant concentrations change.
  - A more useful mathematical relationship would show how a reactant concentration changes over a period of time. More important to know the relationship between conc and time than conc and rate.
Change of Concentration with Time

– Using calculus we can transform a rate law into a mathematical relationship between concentration and time called the integrated rate equation (we will skip the derivation).

– This provides a **graphical method** for determining rate laws.
30.3.1 First Order Integrated Rate Law

• First-Order Integrated Rate Law
• For the simple case of one reactant and coeff of one

\[ A \rightarrow \text{products} \]

– You could write the rate law in the form

\[
\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]
\]
Concentration-Time Equations

• First-Order Integrated Rate Law

  Using calculus, you get the following equation.

\[
\ln \left( \frac{[A]_t}{[A]_o} \right) = -kt
\]

- Here \([A]_t\) is the concentration of reactant A at time \(t\), and \([A]_o\) is the initial concentration.
- The ratio \([A]_t/[A]_o\) is the fraction of A remaining at time \(t\).
Eq allows you to calculate conc A at any time t or vice versa.

To help remember the equations (will give you three), let's place the equation in a more useful form that is easier to remember.

Definition of logs: mult-add, divide - subtract; therefore

\[
\ln \frac{[A]_t}{[A]_o} = -kt
\]

\[
\ln [A]_t - \ln [A]_o = -kt
\]

We stated that this could be used for a graphical method therefore we rearranged in this manner for the equation of a straight line

\[
y = mx + b
\]

\[
\ln [A]_t = -kt + \ln [A]_o
\]
Graphing Kinetic Data

- This means if you plot $\ln[A]_t$ versus time, you will get a straight line for a first-order reaction. You will always get straight line if the reaction is 1st order but will not get a straight line if the reaction is not a 1st order reaction. You plot $\ln [A]_t$ on the y axis (dependent variable - measured variable) vs the time on the x axis (independent variable - one you have control). The slope (rise/run) of the line gives you the -k (rate constant): $m = -k$

- Note: know units on k from the information we discussed about k units vs overall order of rxn - time$^{-1}$
Figure: A plot of $\ln [N_2O_5]$ versus time.

A Problem to Consider

The decomposition of \( \text{N}_2\text{O}_5 \) to 2 mols NO\(_2\) and 0.5 mols O\(_2\) has a rate constant of \( 4.80 \times 10^{-4} \) s\(^{-1}\). If the initial concentration of \( \text{N}_2\text{O}_5 \) is \( 1.65 \times 10^{-2} \) mol/L, what is the concentration of \( \text{N}_2\text{O}_5 \) after 825 seconds?
The decomposition of $\text{N}_2\text{O}_5$ to 2 mols $\text{NO}_2$ and 0.5 mols $\text{O}_2$ has a rate constant of $4.80 \times 10^{-4} \text{ s}^{-1}$. If the initial concentration of $\text{N}_2\text{O}_5$ is $1.65 \times 10^{-2} \text{ mol/L}$, what is the concentration of $\text{N}_2\text{O}_5$ after 825 seconds?

Substituting the given information we obtain:

\[
\ln [N_2O_5]_t = -kt + \ln [N_2O_5]_o
\]

\[
\ln [N_2O_5]_t = -[(4.80 \times 10^{-4} \text{ s}^{-1}) \times (825 \text{ s})] + \ln (1.65 \times 10^{-2} \text{ M})
\]

\[
\ln [N_2O_5]_t = -0.396 + -4.104 = -4.500
\]

\[
[N_2O_5]_t = e^{-4.500} \quad \text{2nd ln} = e^x
\]

\[
[N_2O_5]_t = 0.0111 \text{ M}
\]
Another ex: The decomposition of $\text{N}_2\text{O}_5$ to $2\text{NO}_2$ and $0.5\text{O}_2$ has a rate constant of $4.80 \times 10^{-4}$ s$^{-1}$. What time is required for the concentration of $\text{N}_2\text{O}_5$ to drop from 0.160 to 0.100 M?

\[
\ln [\text{N}_2\text{O}_5]_t = -kt + \ln [\text{N}_2\text{O}_5]_o
\]

\[
\ln [\text{N}_2\text{O}_5]_t - \ln [\text{N}_2\text{O}_5]_o = -kt
\]

\[
\ln [0.100M]_t - \ln [0.160M]_o = -4.80 \times 10^{-4} \text{ s}^{-1} \times t
\]

\[
-2.303 - (-1.833) = -4.80 \times 10^{-4} \text{ s}^{-1} \times t
\]

\[
-0.470 = -4.80 \times 10^{-4} \text{ s}^{-1} \times t
\]

\[
979 \text{ s} = \frac{-0.470}{-4.80 \times 10^{-4} \text{ s}^{-1}} = t
\]

HW 9
30.3.2 Zero and Second Order Integrated Rate Law

• Zero-Order Integrated Rate Law
  – The Zero-Order Integrated Rate Law equation is:
    \[ A \rightarrow \text{products} \quad \text{rate} = k [A]^o = k \]
    \[ [A]_t = -kt + [A]_o \]
  – Note just like 1st order except drop ln
  – \( m = -k; \) units M/s; \( \text{graph} = [A]_t \text{ vs } t \text{ line slope} = \backslash \)
  – Straight line only if zero order
Concentration-Time Equations

• Second-Order Integrated Rate Law
  – You could write the rate law in the form
    
    \[ \text{rate} = k[A]^2 \]
    
    \[ \frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \]
    
    \[ m = k; \text{ units } M^{-1} \text{ s}^{-1}; \text{ graph } = 1/[A]_t \text{ vs } t \quad \text{line slope } = / \]
    
    – Straight line only if second order

HW 10
30.4 Half-life of a Reaction

- The **half-life** \( t_{1/2} \) of a reaction is the time required for the reactant concentration to decrease to one-half of its initial value.

  - For a first-order reaction, the half-life is independent of the initial concentration of reactant.
  
  - One half-life is the amount time needed for reactant to decrease by one-half, meaning \([A]_t = 1/2 [A]_0\). Substituting into the first-order concentration-time equation, we can derive the eq:
30.4.1 First Order Half-life

\[ \ln\left( \frac{[A]_t}{[A]_o} \right) = -kt \]

At half-life, \([A]_t = \frac{1}{2} [A]_o\)

- Solving for \(t_{1/2}\) we obtain:

\[ \ln\left( \frac{1/2[A]_o}{[A]_o} \right) = -kt \]

\[ \ln\left( \frac{1}{2} \right) = -kt \]

\[-0.693 = -kt\]

\[ 0.693 = \frac{t_{1/2}}{k} \]

- Basically means is \(t_{1/2} = 2\) min and initial conc = 0.160M and wait 2 min, conc = 0.080M; at 4 min (another 2 min - 2 \(t_{1/2}\)'s) conc = 0.040M.
30.4.2 Zero and Second Order Half-life

- For a second-order reaction, half-life depends on the initial concentration and becomes larger as time goes on ([A] decreasing over time and reaction slows down therefore longer time needed for half to be consumed).
  - Again, assuming that $[A]_t = \frac{1}{2}[A]_o$ after one half-life, it can be shown that:
    \[
    \frac{1}{[A]_t} = kt + \frac{1}{[A]_o}
    \]
    \[
    t_{\frac{1}{2}} = \frac{1}{k[A]_o}
    \]
  - Each succeeding half-life is twice the length of its predecessor due to decrease in [A].
Zero Order Half-life

• For Zero-Order reactions, the half-life is dependent upon the initial concentration of the reactant and becomes shorter as the reaction proceeds ([A] in numerator - linear effect).

  – Again, assuming that \([A]_t = \frac{1}{2}[A]_o\) after one half-life, it can be shown that:

\[
A_t = -kt + A_o
\]

\[
t_{\frac{1}{2}} = \frac{A_o}{2k}
\]

\[
\frac{1}{2}[A]_o = -kt + [A]_o
\]

\[
1/2[A]_o - [A]_o = -kt
\]

\[
-A_o = -kt
\]

\[
\frac{2}{[A]_o} = -kt
\]

\[
\frac{[A]_o}{2k} = t_{\frac{1}{2}}
\]
Half-life

- Sulfuryl chloride, $\text{SO}_2\text{Cl}_2$, decomposes in a reaction to $\text{SO}_2$ and $\text{Cl}_2$.

$$\text{SO}_2\text{Cl}_2 (g) \rightarrow \text{SO}_2 (g) + \text{Cl}_2 (g)$$

- At 320 °C, the rate constant is $2.20 \times 10^{-5} \text{ s}^{-1}$. What is the half-life of $\text{SO}_2\text{Cl}_2$ vapor at this temperature?

- Substitute the value of $k$ into the relationship between $k$ and $t_{1/2}$.

$$t_{\frac{1}{2}} = \frac{0.693}{k} = \frac{0.693}{2.20 \times 10^{-5} \text{ s}^{-1}} = 3.15 \times 10^4 \text{ s}$$

HW 11
## 30.5 Summary of Equations

<table>
<thead>
<tr>
<th>Order</th>
<th>rate Law</th>
<th>Integrated rate eq</th>
<th>linear plot</th>
<th>( t_{1/2} )</th>
<th>k units</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>( \text{rate}=k )</td>
<td>([A]_t = -kt + [A]_o)</td>
<td>([A]_t \text{ vs } t)</td>
<td>([A]_o)</td>
<td>(M \text{ time}^{-1})</td>
</tr>
<tr>
<td>1</td>
<td>( \text{rate}=k[A] )</td>
<td>(\ln[A]_t = -kt + \ln[A]_o)</td>
<td>(\ln[A]_t \text{ vs } t)</td>
<td>(0.693)</td>
<td>(\text{time}^{-1})</td>
</tr>
<tr>
<td>2</td>
<td>( \text{rate}=k[A]^2 )</td>
<td>(\frac{1}{[A]} = kt + \frac{1}{[A]_o})</td>
<td>(\frac{1}{[A]} \text{ vs } t)</td>
<td>(\frac{1}{k[A]_o})</td>
<td>(M^{-1} \text{ time}^{-1})</td>
</tr>
</tbody>
</table>
30.6 Collision Theory

- Rate constants vary with temperature. Consequently, the actual rate of a reaction is very temperature dependent.

- Why the rate depends on temperature can be explained by collision theory.
Collision Theory

• **Collision theory** assumes that for a reaction to occur, reactant molecules must collide with the proper orientation and sufficient energy, meaning not every collision forms product.

  - Must have proper orientation for effective collision
  - Rxn: \( \text{CO} + \text{NO}_2 \rightarrow \text{CO}_2 + \text{NO} \)
  - OC collides \( \text{NO}_2 \) nothing, but OC collides ONO form \( \text{CO}_2 \) and leave NO

• The minimum energy of collision required for two molecules to react is called the **activation energy**, \( E_a \).
Transition-State Theory

- Molecules are held together by strong chemical bonds. Only if the colliding molecules are moving very rapidly will the kinetic energy be large enough to supply the energy required to break these bonds. Molecules with small kinetic energies bounce off one another without reacting. As a result, only a small fraction of collisions are effective.

- For every reaction there is a certain minimum energy that molecules must possess for collisions to be effective (activation energy). This is a energy barrier and must be overcome by the KE of moving molecules when they collide for a reaction to occur. The larger the activation energy, the slower the reaction; least likely collisions will be effective.
Potential-Energy Diagrams for Reactions

- We can illustrate this graphically by plotting the potential energy of a reaction versus time.

Note: higher the $E_a$, the slower the reaction and the slowest step in multi step reaction will have largest $E_a$.
Figure: Potential-energy curve for the endothermic reaction of nitric oxide and chlorine.
Figure: Potential-energy curve for an **exothermic** reaction.

30.6.1 Factors that Affect Reaction Rates

What variables affect reaction rate and activational energy?

- Concentration of reactants.
- Concentration of a catalyst
- Temperature at which the reaction occurs.
- Surface area of a solid reactant or catalyst.
Factors Affecting Reaction Rates

• Concentration of reactants.
  
  - More often than not, the rate of a reaction increases when the concentration of a reactant is increased (unless zero order meaning reactant is not part of rate determining step).
  
  - Increasing the population of reactants increases the likelihood of a successful collision (increase probability for collision and reaction to occur).
Factors Affecting Reaction Rates

• 2nd factor: Concentration of a catalyst.

  - A catalyst is a substance that increases the rate of a reaction without being consumed in the overall reaction.
  - The catalyst generally does not appear in the overall balanced chemical equation (although its presence may be indicated by writing its formula over the arrow).

\[ 2H_2O_2(aq) \xrightarrow{HBr(aq)} 2H_2O(l) + O_2(g) \]
Factors Affecting Reaction Rates

- Catalyst could change form along the way for reaction but at the end of the reaction will be the same amount and form as it started ($X \rightarrow XY \rightarrow X$).

- A catalyst speeds up reactions by reducing the “activation energy” needed for successful reaction.

- A catalyst may also provide an alternative mechanism, or pathway, that results in a faster rate.
Catalysts

• A **catalyst** is a substance that provides a good “environment” for a reaction to occur, thereby increasing the reaction rate without being consumed by the reaction.

  – To avoid being consumed, the catalyst must participate in at least one step of the reaction and then be regenerated in a later step.
Catalysts

Ex.

1.) \(R + S \rightarrow T\)  
   R and S consumed, T produced

2.) \(T + U \rightarrow W + S\)  
   T & U consumed, W & S produced

\(R + U \rightarrow W\)

T intermediate – produced then consumed

S catalyst – consumed then produced later. Notice not part of overall balanced equation; however, actually present in final composite of final product. Think of it as consumed and produced. If you do this, there would be W and S left after the reaction.

- Catalyst presence increases the rate of reaction by lowering the activation energy, \(E_a\). (speeds up reaction)
Catalysts

• **Homogeneous catalysis** is the use of a catalyst in the same phase as the reacting species.

  – The oxidation of sulfur dioxide using nitric oxide as a catalyst is an example where all species are in the gas phase.

\[
2\text{SO}_2(g) + \text{O}_2(g) \xrightarrow{\text{NO(g)}} 2\text{SO}_3(g)
\]
Catalysts

- **Heterogeneous catalysis** is the use of a catalyst that exists in a different phase from the reacting species, usually a solid catalyst in contact with a liquid or gaseous solution of reactants.

  - Such surface catalysis is thought to occur by chemical adsorption of the reactants onto the surface of the catalyst.
  - Adsorption is the attraction of molecules to a surface.
Enzyme Catalysis

- biological organisms have catalysis called Enzymes. This accounts for many of the body's functions. Without it we would not exist.
Factors Affecting Reaction Rates

• 3rd affect: Temperature at which a reaction occurs.
  – Usually reactions speed up when the temperature increases (more energy into system; therefore, more KE to overcome $E_a$ have more effective collisions).
  – Temp also causes molecules to move faster and cause collisions to occur more often, increasing probability of effective collisions happening more often.
  – Temp has no effect on lowering $E_a$, just gives more molecules the energy needed to overcome it thereby speeding up reaction.
  – A good “rule of thumb” is that reactions approximately double in rate with a 10 °C rise in temperature. (This is why store food in refrigerator – slow down reaction rate of spoiling food – decrease energy, less effective collisions).
Factors Affecting Reaction Rates

- 4th factor: Surface area of a solid reactant or catalyst.
  - Because the reaction occurs at the surface of the solid, the rate increases with increasing surface area.
  - Wood burns faster chopped into smaller pieces rather than logs.

HW 12
30.7 Reaction Mechanisms

Even though a balanced chemical equation may give the ultimate result of a reaction (stoich, not based on collisions), what actually happens in the reaction **may take place in several steps.**

- This “pathway” the reaction takes is referred to as the **reaction mechanism.**
- The individual steps in the larger overall reaction are referred to as **elementary reactions (based on collisions).**

1.) \( A + A \rightarrow A_2 \) **elementary rxn**

2.) \( A_2 + B \rightarrow C + D \) **elementary rxn**

Overall: \( 2A + B \rightarrow C + D \) **molecular rxn**
30.7.1 Rate Laws for Elementary Steps

Consider the reaction of nitrogen dioxide with carbon monoxide.

$$\text{NO}_2(g) + \text{CO}(g) \rightarrow \text{NO}(g) + \text{CO}_2(g)$$

- This reaction is believed to take place in two steps.

1.) $$\text{NO}_2(g) + \text{NO}_2(g) \rightarrow \text{NO}_3(g) + \text{NO}(g)$$ (elementary reaction)  
   Step 1 (slow)

2.) $$\text{NO}_3(g) + \text{CO}(g) \rightarrow \text{NO}_2(g) + \text{CO}_2(g)$$ (elementary reaction)  
   Step 2 (fast)

overall) $$\text{NO}_2(g) + \text{CO}(g) \rightarrow \text{NO}(g) + \text{CO}_2(g)$$

rate = $$k [\text{NO}_2]^2$$
Molecularity

- We can classify reactions according to their **molecularity**, that is, the number of molecules that must collide for the elementary reaction to occur.
  - A **unimolecular** reaction involves only one reactant molecule. \[ A \rightarrow P \]
  - A **bimolecular** reaction involves the collision of two reactant molecules. \[ A + A \rightarrow P \]
    \[ A + B \rightarrow P \]
  - A **termolecular** reaction requires the collision of three reactant molecules. (very rare) \[ A + B + C \rightarrow P \]
    \[ 2A + B \rightarrow P \]
Molecularity

Higher molecularities are rare because of the small statistical probability that four or more molecules would all collide at the same instant.
Rate Equations for Elementary Reactions

• Since a chemical reaction may occur in several steps, there is no easily stated relationship between its overall reaction and its rate law.

• However, for elementary reactions, the rate is proportional to the concentrations of all reactant molecules involved.

Rate laws can be written directly from balanced elementary reactions.
Rate Equations for Elementary Reactions

• For example, consider the generic equation below.

\[ A \rightarrow \text{products} \]

The rate is dependent only on the concentration of A since elementary rxn; that is,

\[ \text{Rate} = k[A] \]
Rate Equations for Elementary Reactions

• However, for the reaction

\[ A + B \rightarrow \text{products} \]

the rate is dependent on the concentrations of both A and B since elementary rxn

\[ \text{Rate} = k[A][B] \]
Rate Equations for Elementary Reactions

• For a termolecular reaction

\[ A + B + C \rightarrow \text{products} \]

the rate is dependent on the populations of all three participants since elementary rxn.

\[ \text{Rate} = k[A][B][C] \]
Rate Equations for Elementary Reactions

• Note that if two molecules of a given reactant are required, it appears twice in the rate law. For example, the reaction

\[ 2A + B \rightarrow \text{products} \]

would have the rate law:

\[ \text{Rate} = k[A]^2[B] \]
Rate Equations for Elementary Reactions

- So, in essence, for an elementary reaction, the coefficient of each reactant becomes the power to which it is raised in the rate law for that reaction. (ONLY for ELEMENTARY RXNS or STEPS in MECHANISM)
  - Note that many chemical reactions occur in multiple steps and it is, therefore, impossible to predict the rate law based solely on the overall reaction.
Rate Laws and Mechanisms

• Consider the reaction below.

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

- Experiments performed with this reaction show that the rate law is

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

slowest elementary step determines actual rate law

- The reaction is first order with respect to each reactant, even though the coefficient for NO\(_2\) in the overall reaction is 2. Molecular equation not elementary rxn.
30.7.2 Rate-Determining Step

- This implies that this reaction is not an elementary reaction but rather the result of multiple steps.

- In multiple-step reactions, one of the elementary reactions in the sequence is often slower than the rest.

  - The overall reaction cannot proceed any faster than this slowest rate-determining step.
Rate-Determining Step

- Our previous example occurs in two elementary steps where the first step is much slower.

\[
\begin{align*}
\text{NO}_2(g) + F_2(g) & \xrightarrow{k_1} \text{NO}_2F(g) + F(g) \quad \text{(slow)} \\
\text{NO}_2(g) + F(g) & \xrightarrow{k_2} \text{NO}_2F(g) \quad \text{(fast)} \\
2 \text{NO}_2(g) + F_2(g) & \rightarrow 2 \text{NO}_2F(g)
\end{align*}
\]

\[
\text{Rate} = k[\text{NO}_2][F_2]
\]

Note: F is intermediate in this reaction, produced then consumed.
Rate-Determining Step

Since the overall rate of this reaction is determined by the slow step, it seems logical that the observed rate law is:

\[ \text{Rate} = k_1[\text{NO}_2][\text{F}_2]. \]

\[
\text{NO}_2(g) + \text{F}_2(g) \xrightarrow{k_1} \text{NO}_2\text{F}(g) + \text{F}(g) \quad \text{(slow)}
\]
In a mechanism where the first elementary step is the rate-determining step, the overall rate law is simply expressed as the elementary rate law for that slow step. This is why sometimes zero order for reactants; they were not part of slow step.

A more complicated scenario occurs when the rate-determining step contains a reaction intermediate as part of slowest step and is not part of balanced molecular equation.
Rate-Determining Step

• Mechanisms with an Initial Fast Step
  – The rate-determining step of a mechanism contains a reaction intermediate that does not appear in the overall reaction.
  – The experimental rate law, however, can be expressed only in terms of substances that appear in the overall reaction (must eliminate intermediates).
Rate-Determining Step

• Consider the reduction of nitric oxide with \( \text{H}_2 \). — A proposed mechanism is:

\[
2\text{NO} \xrightleftharpoons[\text{k}_1]{\text{k}_-1} \text{N}_2\text{O}_2
\]

\[
\text{N}_2\text{O}_2 + \text{H}_2 \xrightarrow{\text{k}_2} \text{N}_2\text{O} + \text{H}_2\text{O}
\]

\[
\text{N}_2\text{O} + \text{H}_2 \xrightarrow{\text{k}_3} \text{N}_2 + \text{H}_2\text{O}
\]

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

— It has been experimentally determined that the rate law is \( \text{Rate} = k [\text{NO}]^2[\text{H}_2] \)
The rate-determining step (step 2 in this case) generally outlines the rate law for the overall reaction.

\[ \text{Rate} = k_2 [N_2O_2][H_2] \]

(Rate law for the rate-determining step)

- As mentioned earlier, the overall rate law can be expressed only in terms of substances represented in the overall reaction and cannot contain reaction intermediates.

- It is necessary to re-express this proposed rate law after eliminating \([N_2O_2]\).

- We can do this by looking at the first step, which is fast and establishes equilibrium.
Rate-Determining Step

\[ 2\text{NO} \xrightleftharpoons[k_1]{k_{-1}} \text{N}_2\text{O}_2 \]

- At equilibrium, the forward rate and the reverse rate are equal \((R_f = R_r)\).
  \[ R_f = k_1[\text{NO}]^2 \quad \text{and} \quad R_r = k_{-1}[\text{N}_2\text{O}_2] \]

\[ k_1[\text{NO}]^2 = k_{-1}[\text{N}_2\text{O}_2] \]

- Therefore, \[ [\text{N}_2\text{O}_2] = \left( \frac{k_1}{k_{-1}} \right)[\text{NO}]^2 \]
- If we substitute this into our proposed rate law we obtain:
Rate-Determining Step

\[
\begin{align*}
N_2O_2 + H_2 & \xrightarrow{k_2} N_2O + H_2O \\
\text{Rate} &= k_2[N_2O_2][H_2] \\
[N_2O_2] &= \left(\frac{k_1}{k_{-1}}\right)[NO]^2
\end{align*}
\]

\[
\text{Rate} = \frac{k_2k_1}{k_{-1}}[NO]^2[H_2]
\]

- If we replace the constants \((k_2k_1/k_{-1})\) with \(k\), we obtain the observed rate law:

\[
\text{Rate} = k[NO]^2[H_2]
\]