



Lecture (4)

Chemical Kinetics Orders

Chemical kinetics is the study of chemical reactions via their rates. Studying the concentration dependence of reaction rates gives information about the reaction mechanism.

Reaction Rates

A **reaction rate** is the speed in which a reactant is consumed or a product is produced within a chemical reaction.

$$\text{rate} = v = \frac{d\xi}{dt} \quad \xi - \text{extent of reaction} \quad \xi = \frac{n_i - n_{i,0}}{\nu}$$

For a general reaction $aA + bB \rightarrow cC + dD$ in the solution phase,

$$\text{rate} = v = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

Example:

Consider the reaction $2 \text{NO}_2 (\text{g}) \rightarrow \text{N}_2\text{O}_4 (\text{g})$

$$\text{rate} = v = -\frac{1}{2} \frac{d[\text{NO}_2]}{dt} = \frac{d[\text{N}_2\text{O}_4]}{dt}$$

That is, NO_2 disappears twice as fast as N_2O_4 appears.

Introduction to Rate Laws

Mathematical expression are sought so that the reaction rate can be predicted from known the concentration of reactants. That is, $v \propto f([A], [B], [C] \dots)$

The true expression can be very complicated. Simple expressions are desired and are quite often found.

First-order reactions

For a **first-order reaction**, the rate is proportional to the concentration of reactant $v \propto [A]$

- The proportionality constant is called the **rate constant**, k .

$$v = k[A]$$

- The rate constant is the same for a given reaction at a given temperature. It is independent of the concentration of any chemical species.



Second-order reactions

For a **second-order reaction**, the rate is proportional to the square of the concentration of reactant or to the concentration of two reactants.

$$v = k[A]^2 \quad v = k[A][B]$$

Zeroth-order reactions

For a **zero-order reaction**, the rate is not related to the concentration of reactant.

$$v = k$$

Experimental Techniques

The experimental apparatus used to study kinetics must address two concerns.

- 1.) The reactants must mix in a timely way.
- 2.) The amount of reactant must be able to be monitored.

Real-time

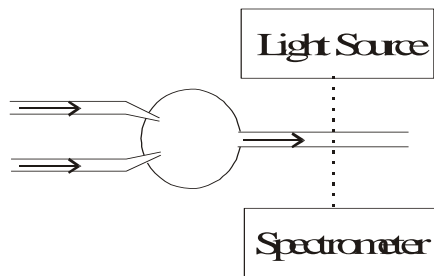
Mix solutions together and monitor concentrations of bulk solution as time evolves.
Time scale on the order of 1 sec.

Quenching

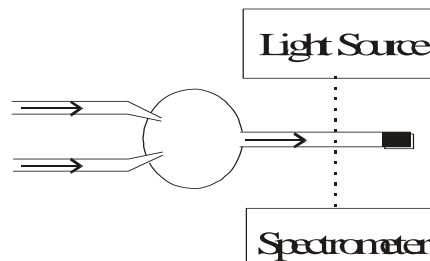
Mix solutions together, then stop reaction (quench) and analyze solution.
Time scale on the order of 1 sec.

Flow Techniques

Continuous flow



Stopped flow



uses much less reactant

Time scale on the order of 1s to 1 ms



- ability to mix solutions is the limiting factor

Relaxation

Make sudden changes in the environment of a system at equilibrium and measure how the system responds.

- 1967 Nobel Prize (Manfred Eigen)

Variables that are commonly disturbed.

1. temperature
2. pressure
3. electric field

Time scale is 1 ms to 1 μ s.

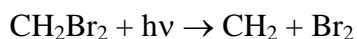
Flash Photolysis

Uses laser pulses of light to examine reaction. First a **pump pulse** is used to input the energy needed to start a reaction. A **probe pulse** then is used to measure the absorbance of product. The reaction rate is measured by doing a series of experiments that varies the time interval between the pump and the probe.

- 1967 Nobel Prize (R. G. W. Norrish, George Porter)
- 1999 Nobel Prize (Ahmed Zewail)

Time scale is 1 μ s to 100 as (10^{-16} s)

Consider the examining the dynamics of the photodissociation of methylene bromide.

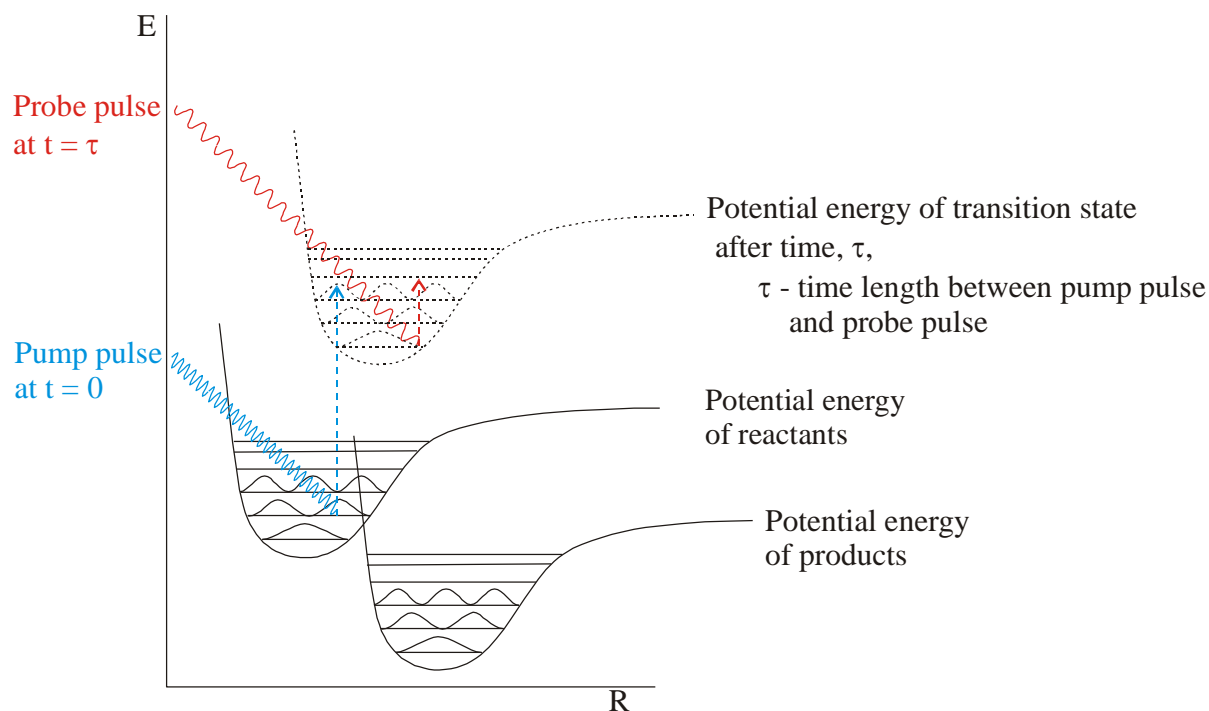


We can determine the mode of dissociation using “**pump-probe**” femtosecond spectroscopy.



To use “pump-probe” spectroscopy on transition states, we need to use two laser pulses.

1. Pump pulse activates the reaction.
 - after the pump pulse hits the molecule, the electrons and nuclei start their rearrangement to the transition state.
 - even though the transition state is unstable, it does have a particular arrangement of electrons and nuclei and means it has its own potential energy surface with various vibrational levels.
2. Probe pulse analyses the structure of the transition state and length of time needed to make the transition state.
 - The time delay, τ , between the pump pulse and the probe pulse is varied to measure the formation time of the transition state and its lifetime.
 - As the absorption of the pulse increases, more of the molecules as have formed the transition state.
 - As the absorption of the pulse decreases, more of the molecules as have progressed past the transition state.
 - The frequency of the probe pulse is varied to find the structure of the transition state.
 - Since different transition states will absorb different frequency of light, we can discover, upon analysis, what the transition state may look like.



Determining Rate Laws

All rate laws must be experimental determined. For such a determination, the reaction rate must be measured as a function of reactant concentration.

Method of Initial Rates

- 1.) Assume that the rate law has the following form: $v = k[A]^m[B]^n[C]^p \dots$
- 2.) Measure the initial rate when the reactants are mixed for a number of trials using different concentrations.
- 3.) Rewrite the assumed rate law as $\ln v = \ln k + m \ln [A] + n \ln [B] + p \ln [C] + \dots$
- 4.) Plot $\ln v$ versus $\ln [A]$, etc... to find reaction orders and rate constants.

Integrated Rate Laws

First-order

$$v = k[A] \Rightarrow \frac{d[A]}{dt} = -k[A]$$



$$\begin{aligned}\frac{d[A]}{dt} &= -k[A] \Rightarrow \frac{d[A]}{[A]} = -k dt \Rightarrow \int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -\int_0^t k dt \Rightarrow \ln \frac{[A]}{[A]_0} = -k t \\ \Rightarrow [A] &= [A]_0 e^{-kt}\end{aligned}$$

Note that plot of $\ln [A]$ vs. t is linear.

First-order half-life

$$\begin{aligned}\ln \frac{[A]}{[A]_0} &= -k t \Rightarrow \ln \frac{\frac{1}{2}[A]_0}{[A]_0} = -k t_{\frac{1}{2}} \Rightarrow \ln \frac{1}{2} = -k t_{\frac{1}{2}} \\ -\ln 2 &= -k t_{\frac{1}{2}} \Rightarrow t_{\frac{1}{2}} = \frac{\ln 2}{k}\end{aligned}$$

Example: ^{14}C has a half-life of 5730 years. The activity of carbon in living beings is 12.5 counts per minute per gram. A bone is found on an archeological dig and found to have an activity of 10.5 counts per minute per gram. Estimate the age of the bone.

$$\ln \frac{[A]}{[A]_0} = -k t \Rightarrow t = -\frac{1}{k} \ln \frac{[A]}{[A]_0}$$

Calculate the rate constant from the half-life.

$$t_{\frac{1}{2}} = \frac{\ln 2}{k} \Rightarrow k = \frac{\ln 2}{t_{\frac{1}{2}}} = \frac{\ln 2}{5730 \text{ yr}} = 1.21 \times 10^{-4} \text{ yr}^{-1}$$

Note to calculate the time we don't explicitly need the concentration of carbon. We only need the ratio of concentrations. If we find some ratio equivalent to the concentration ratio, we can use it. Note the activity is proportional to the concentration. Thus a ratio of activities is equal to a ratio of concentrations.



$$t = -\frac{1}{k} \ln \frac{[A]}{[A]_0} = -\frac{1}{1.21 \times 10^{-4} \text{ yr}^{-1}} \ln \frac{10.5 \text{ counts} \cdot \text{min}^{-1} \cdot \text{g}^{-1}}{12.4 \text{ counts} \cdot \text{min}^{-1} \cdot \text{g}^{-1}} = 1380 \text{ yr}$$

The 1380 years is time elapsed thus the age of the bone is $2000 - 1380 = 620 \text{ A.D.}$

Second-order (homogeneous)

$$\begin{aligned} v &= k[A]^2 \Rightarrow \frac{d[A]}{dt} = -k[A]^2 \\ \frac{d[A]}{dt} &= -k[A]^2 \Rightarrow \frac{d[A]}{[A]^2} = -k dt \Rightarrow \int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = -\int_0^t k dt \Rightarrow -\frac{1}{[A]} - \left(-\frac{1}{[A]_0}\right) = -k t \\ \Rightarrow \frac{1}{[A]} &= \frac{1}{[A]_0} + k t \end{aligned}$$

Example: The reaction $2A \rightarrow P$ has a second-order rate constant of $5.20 \times 10^{-4} \text{ M}^{-1} \cdot \text{s}^{-1}$. Calculate the time required for the concentration of A to change from 0.315 M to 0.044 M.



$$\frac{1}{[A]} = \frac{1}{[A]_0} + k t \Rightarrow \frac{\frac{1}{[A]} - \frac{1}{[A]_0}}{k} = t$$

$$\Rightarrow t = \frac{\frac{1}{0.044 \text{ M}} - \frac{1}{0.315 \text{ M}}}{5.20 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}} = \frac{23 \text{ M}^{-1} - 3.18 \text{ M}^{-1}}{5.20 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}} = \frac{20 \text{ M}^{-1}}{5.20 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}} = 38000 \text{ s} = 10.4 \text{ hr}$$

Second-order half-life

$$\frac{1}{[A]} = \frac{1}{[A]_0} + k t \Rightarrow \frac{1}{\frac{1}{2}[A]_0} = \frac{1}{[A]_0} + k t_{\frac{1}{2}} \Rightarrow \frac{2}{[A]_0} - \frac{1}{[A]_0} = k t_{\frac{1}{2}} \Rightarrow \frac{1}{[A]_0} = k t_{\frac{1}{2}}$$

$$\Rightarrow t_{\frac{1}{2}} = \frac{1}{k[A]_0}$$

Second-order (heterogeneous)

$$v = k[A][B] \Rightarrow \frac{d[A]}{dt} = -k[A][B] = -k([A]_0 - x)([B]_0 - x)$$

Define x as $x = [A]_0 - [A]$

$$x = [A]_0 - [A] \Rightarrow [A] = [A]_0 - x \quad \text{and} \quad \frac{d[A]}{dt} = -\frac{dx}{dt}$$

$$\frac{d[A]}{dt} = -k[A][B] \Rightarrow \frac{dx}{dt} = k([A]_0 - x)([B]_0 - x) \Rightarrow \int_0^x \frac{dx}{([A]_0 - x)([B]_0 - x)} = -\int_0^t k dt$$

To do this integral, we must use the technique of partial fractions.



$$\frac{1}{([A]_0 - x)([B]_0 - x)} = \frac{C}{([A]_0 - x)} + \frac{D}{([B]_0 - x)}$$

$$\begin{aligned} 1 &= C([B]_0 - x) + D([A]_0 - x) \Rightarrow 1 = C[B]_0 + D[A]_0 - (C + D)x \\ &\Rightarrow 1 = C[B]_0 + D[A]_0 \quad \text{and} \quad 0x = -(C + D)x \\ 0x &= -(C + D)x \Rightarrow 0 = -(C + D) \Rightarrow C = -D \\ &\Rightarrow 1 = C[B]_0 - C[A]_0 \Rightarrow C = \frac{1}{[B]_0 - [A]_0} \end{aligned}$$

$$\int_0^x \frac{dx}{([A]_0 - x)([B]_0 - x)} = -\int_0^t k dt \Rightarrow \frac{1}{[B]_0 - [A]_0} \left[\int_0^x \frac{dx}{([A]_0 - x)} - \int_0^x \frac{dx}{([B]_0 - x)} \right] = -\int_0^t k dt$$

$$\int_0^x \frac{dx}{([A]_0 - x)} \Rightarrow \text{Let } z = ([A]_0 - x) \Rightarrow dz = -dx$$

$$\Rightarrow \int_{z_0}^z -\frac{dz}{z} = -\ln\left(\frac{z}{z_0}\right) = -\ln\left(\frac{[A]_0 - x}{[A]_0 - 0}\right) = \ln\left(\frac{[A]_0}{[A]_0 - x}\right)$$

$$\Rightarrow \int_0^x \frac{dx}{([A]_0 - x)} = \ln\left(\frac{[A]_0}{[A]_0 - x}\right)$$

$$\frac{1}{[B]_0 - [A]_0} \left[\int_0^x \frac{dx}{([A]_0 - x)} - \int_0^x \frac{dx}{([B]_0 - x)} \right] = \frac{1}{[B]_0 - [A]_0} \left[\ln\left(\frac{[A]_0}{[A]_0 - x}\right) - \ln\left(\frac{[B]_0}{[B]_0 - x}\right) \right] = k t$$

$$\Rightarrow \frac{1}{[B]_0 - [A]_0} \ln\left(\frac{[A]_0([B]_0 - x)}{([A]_0 - x)[B]_0}\right) = \frac{1}{[B]_0 - [A]_0} \ln\left(\frac{[A]_0[B]}{[A][B]_0}\right) = k t$$

Collision Theory of Reactions

Most reactions occur because of collisions between reactant molecules.

Not all collisions yield products.

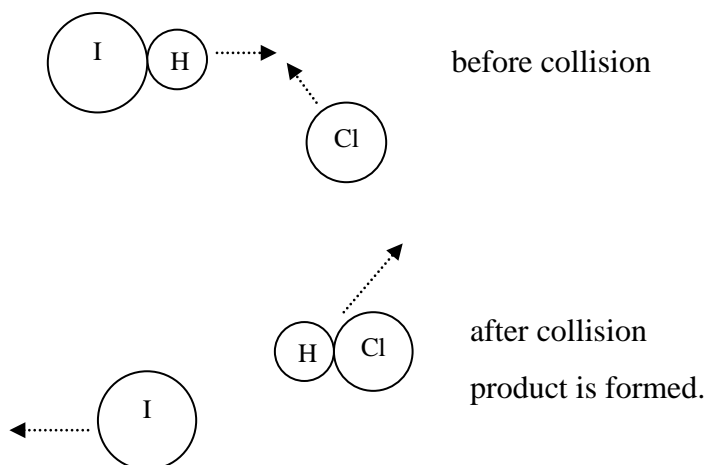
For products to be formed, the molecules in the collision must:

- 1) have enough kinetic energy
 - Molecules must be moving fast enough when they collide to make products.
 - At higher temperatures, molecules have increased speeds.
 - Increased temperature tends to increase reaction rate by increasing kinetic energy of collision.
- 2.) be oriented correctly
 - Not all collisions with enough energy form products.
 - Molecules must also be in correct position

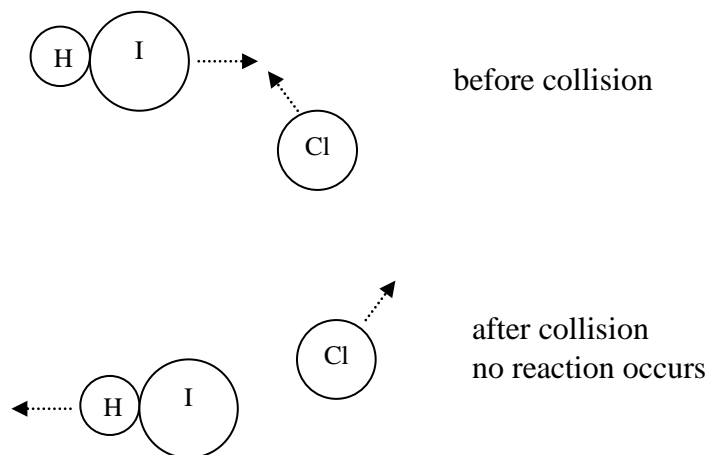


Illustration: $\text{Cl (g)} + \text{HI (g)} \rightarrow \text{HCl (g)} + \text{I (g)}$

Correct collision orientation



Incorrect collision orientation



Activation Energy

Consider reaction $\text{A} + \text{B} \rightarrow \text{C} + \text{D}$

From an energy point of view, the reaction occurs because C and D have less energy than A and B.

However, molecules must collide in order to react.

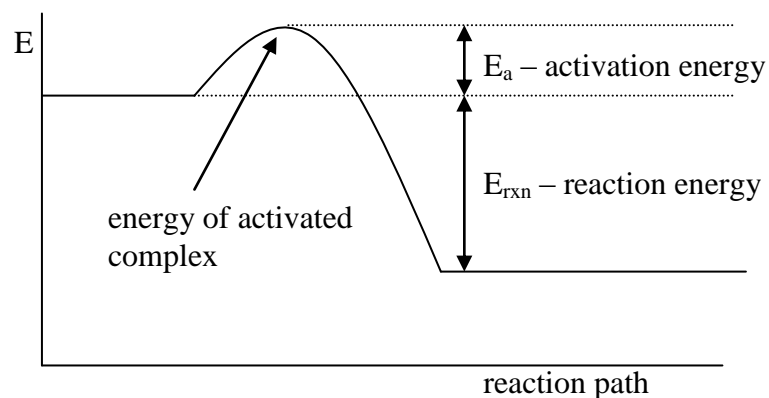
- Thus energy must be inputted.

The energy input necessary for a reaction to proceed is called the **activation energy**.

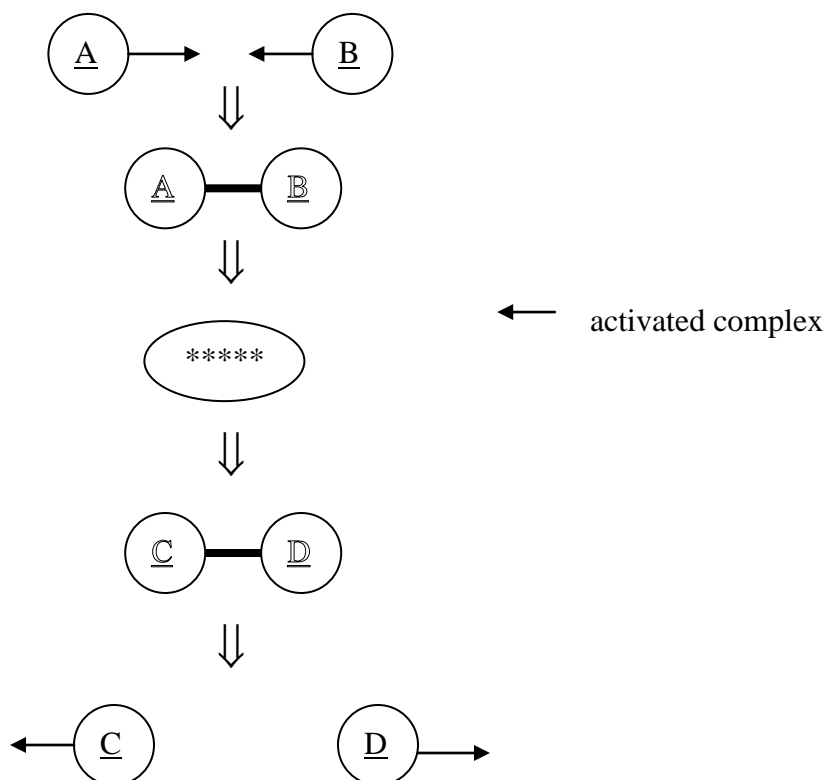
Reaction Energy Diagram



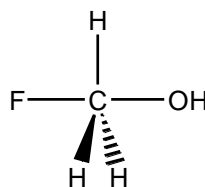
Consider the energetics of the reaction $A \rightarrow B$



Consider the creation of the activated complex within the collision model.



The activated complex is an unstable yet temporarily bound collection of atoms. Thus the activated complex has the highest energy. Graphically, the energy of the activated complex is at the top reaction energy diagram. Below would be the activated complex for the reaction of methyl alcohol with HF to form methyl fluoride.





ARRHENIUS EQUATION

Rate constant is related to kinetic energy and geometry.

$$k = A \cdot e^{-\frac{E_a}{RT}} \quad \begin{array}{l} A - \text{frequency (geometric) factor} \\ E_a - \text{activation energy} \end{array}$$

E_a is measure of the kinetic energy of the particle needed to coerce reaction.

A is measure of how the collision orientation affects the reaction.

For a typical reaction, a plot of the rate constant versus temperature yields an exponential curve.

An exponential curve is more difficult to interpret than a straight line. We would like to manipulate the Arrhenius equation so that it looks like $y = b + m \cdot x$

$$\begin{aligned} k &= A \cdot e^{-\frac{E_a}{RT}} \Rightarrow \ln k = \ln \left(A \cdot e^{-\frac{E_a}{RT}} \right) = \ln A + \ln \left(e^{-\frac{E_a}{RT}} \right) \\ \ln k &= \ln A - \frac{E_a}{RT} = \ln A - \frac{E_a}{R} \cdot \frac{1}{T} \\ \ln k &\Leftrightarrow y \quad \frac{E_a}{R} \Leftrightarrow m \quad \frac{1}{T} \Leftrightarrow x \end{aligned}$$

Thus a plot of $\ln k$ versus $1/T$ should yield a straight line with the y-intercept being $\ln A$ and the slope being $-E_a/R$.

If the plot of $\ln k$ versus $1/T$ is not linear, one can define a temperature-dependent activation energy from the slope of the curve. That is,

$$E_a = RT^2 \frac{d \ln k}{dT} = -R \frac{d \ln k}{d \left(\frac{1}{T} \right)}$$

Example: A sample of milk kept at 25 °C is found to sour 40 times as rapidly as when it is kept at 4 °C. Estimate the activation energy for the process.

The tricky part of the problem is to realize that we need to set up a ratio of Arrhenius equations under two sets of conditions.

$$\frac{k_1 = A \cdot e^{-\frac{E_a}{RT_1}}}{k_2 = A \cdot e^{-\frac{E_a}{RT_2}}} \Rightarrow \frac{k_1}{k_2} = \frac{e^{-\frac{E_a}{RT_1}}}{e^{-\frac{E_a}{RT_2}}} = e^{-\frac{E_a}{RT_1} - \left(-\frac{E_a}{RT_2} \right)} = e^{-\frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)}$$



To make bookkeeping easier, let the conditions at 25 °C be labeled 1 and those at 4 °C be labeled 2.

The ratio k_1/k_2 is 40.

Now we can solve for E_a .

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

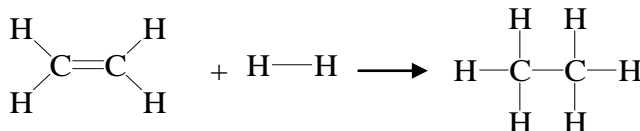
$$E_a = -\frac{R \ln \left(\frac{k_1}{k_2} \right)}{\frac{1}{T_1} - \frac{1}{T_2}} = -\frac{8.314 \text{ J} \times \ln(40)}{\frac{1}{298 \text{ K}} - \frac{1}{277 \text{ K}}} = \frac{8.314 \text{ J}}{2.54 \times 10^{-4} \text{ K}^{-1}} \times 3.69 = 121000 \text{ J} = 121 \text{ kJ}$$

CATALYSIS

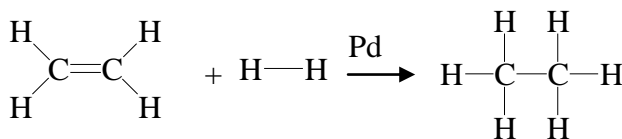
Catalyst – A substance that increases reaction rate while remaining unchanged.

- Catalysts generally lower activation energy.
- Catalysts also may place reactant molecules in optimal position for a collision
- Enzymes are biological catalysts.

Example:

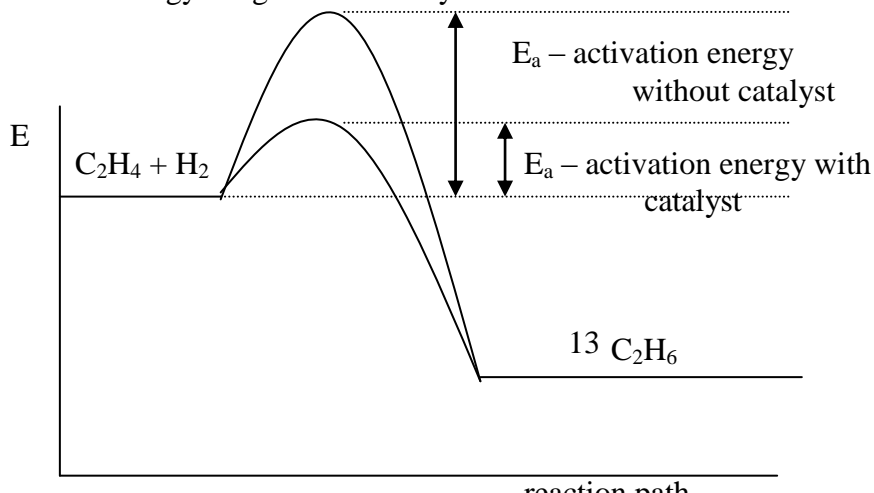


Without catalyst, reaction is very slow.



With palladium catalyst, reaction is fast.

Reaction Energy Diagram for Catalysis





homogeneous catalysis – catalyst is the same phase as the reaction

heterogeneous catalysis – catalyst is different phase than the reaction

Most heterogeneous catalysts are solids. Reactant **adsorb** on surface to permit a more favorable collision orientation.

Catalysts are usually responsible for zeroth-order reaction mechanism.

Once catalytic sites are saturated, increasing concentration of reactant is ineffective.

Reaction Mechanisms

A **reaction mechanism** answers the following questions

- What types of collisions are necessary for reaction to occur?
- What is relative order of collisions steps?

Mechanism information is not necessarily found from stoichiometry of reaction.



** The rate law of a prospective mechanism must be compared to the experimental rate law. **

Elementary reaction – single step involving the collision of two (rarely three) molecules or decomposition of a single molecule

Almost all elementary reactions are **unimolecular** or **bimolecular**.

The rate law for an elementary reaction always has the form, $v = k[A]^m[B]^n$

m, n are the **partial orders**

m + n is the **molecularity** of the reaction

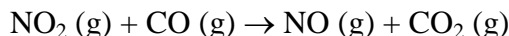
Elementary rate laws

heterogeneous bimolecular reaction $A + B \rightarrow P$ $v = k[A][B]$

homogeneous bimolecular reaction $A + A \rightarrow P$ $v = k[A]^2$

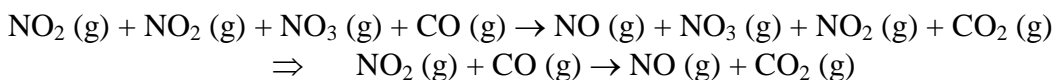
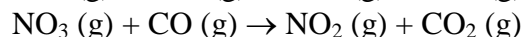
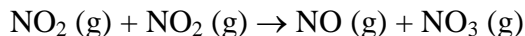
unimolecular reaction $A \rightarrow P$ $v = k[A]$

Example:



It is known that NO_2 does not directly collide with CO to form products.

The following is the reaction mechanism:



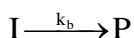
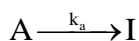
Note elementary reactions add together to form original reaction.

$\text{NO}_3 (\text{g})$ was formed during the reaction, but it did not remain to become a product.

NO_3 is an **intermediate**.

From the mechanism, one can use the elementary rate laws to find an overall rate expression.

Consider the simple mechanism of $A \rightarrow P$



$$\frac{d[A]}{dt} = -k_a [A] \Rightarrow [A] = [A]_0 e^{-k_a t}$$



$$\frac{d[I]}{dt} = -k_b [I] + k_a [A]$$

$$\frac{d[P]}{dt} = k_b [I]$$

$$\Rightarrow \frac{d[I]}{dt} = -k_b [I] + k_a [A]_0 e^{-k_a t}$$

To solve for [I], we need to use differential equations (more next semester),

If $y' + Py = Q$, then $y = e^{-Pt} \left[\int Q e^{Pt} dt + c \right]$

Thus

$$[I] = e^{-k_b t} \left[\int k_a [A]_0 e^{-k_a t} e^{k_b t} dt + c \right] = \frac{e^{-k_b t} k_a [A]_0 e^{-k_a t} e^{k_b t}}{k_b - k_a} + c e^{-k_b t} = \frac{k_a [A]_0}{k_b - k_a} e^{-k_a t} + c e^{-k_b t}$$

$$[I]_0 = 0 \Rightarrow 0 = \frac{k_a [A]_0}{k_b - k_a} \cdot 1 + c \cdot 1 \Rightarrow c = -\frac{k_a [A]_0}{k_b - k_a}$$

$$[I] = \frac{k_a [A]_0}{k_b - k_a} e^{-k_a t} - \frac{k_a [A]_0}{k_b - k_a} e^{-k_b t} = \frac{k_a [A]_0}{k_b - k_a} (e^{-k_a t} - e^{-k_b t})$$

$$\frac{d[P]}{dt} = k_b [I] \Rightarrow [P] = \int \frac{k_a k_b [A]_0}{k_b - k_a} (e^{-k_a t} - e^{-k_b t}) dt$$

$$[P] = \frac{k_a k_b [A]_0}{k_b - k_a} \left(-\frac{1}{k_a} e^{-k_a t} - \frac{1}{k_b} e^{-k_b t} + c \right) = \frac{[A]_0}{k_b - k_a} (k_a e^{-k_b t} - k_b e^{-k_a t} + k_a k_b c)$$

$[P]_0 = 0$ therefore,

$$0 = \frac{[A]_0}{k_b - k_a} (k_a \cdot 1 - k_b \cdot 1 + k_a k_b c) \Rightarrow c = -\frac{k_b - k_a}{k_b k_a}$$

Thus the overall rate law is

$$[P] = \frac{[A]_0}{k_b - k_a} (k_a e^{-k_b t} - k_b e^{-k_a t} + (k_b - k_a))$$

This is a simple mechanism! Yikes!!

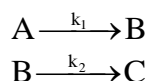
Approximations for finding the rate laws of complex reactions

1) *Rate-determining step*

If through experiment or chemical intuition, a rate-determining step can be established, then finding the rate law of the mechanism is simple.



Example: Find the rate for the reaction mechanism below, if $k_2 \gg k_1$.



If $k_2 \gg k_1$, then $A \rightarrow B$ is the rate-determining step.

$$\text{Then } \frac{d[C]}{dt} = -\frac{d[A]}{dt} \quad -\frac{d[A]}{dt} = -k[A] \Rightarrow [A] = [A]_0 e^{-k_1 t}$$

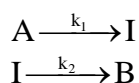
Consider that we can account for all the mass in the reaction via the following mass balance equation $[C] = [A]_0 - [A]$

$$\text{Then } [C] = [A]_0 - [A]_0 e^{-k_1 t} = [A]_0 (1 - e^{-k_1 t})$$

2) Steady-state approximation

Assume that intermediates have constant concentration.

Example: Find the rate law for the mechanism below using the steady-state approximation.



$$\frac{d[A]}{dt} = -k_1 [A]$$

$$\frac{d[I]}{dt} = -k_2 [I] + k_1 [A]$$

$$\frac{d[B]}{dt} = k_2 [I]$$

$$\text{Assume } \frac{d[I]}{dt} = 0 \Rightarrow -k_2 [I] + k_1 [A] = 0 \Rightarrow [I] = \frac{k_1}{k_2} [A]$$

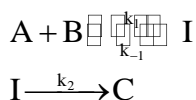
$$\frac{d[B]}{dt} = k_2 [I] = \frac{k_2 k_1}{k_2} [A] = k_1 [A] = k_1 [A]_0 e^{-k_1 t}$$

$$\frac{d[B]}{dt} = k_1 [A]_0 e^{-k_1 t} \Rightarrow [B] = \int k_1 [A]_0 e^{-k_1 t} dt = -[A]_0 e^{-k_1 t} + c$$

$$[B]_0 = 0 \text{ therefore, } 0 = -[A]_0 \cdot 1 + c \Rightarrow c = [A]_0$$

$$[B] = -[A]_0 e^{-k_1 t} + [A]_0 = [A]_0 (1 - e^{-k_1 t})$$

Example: Find the rate law for the following reaction mechanism using the steady state approximation.





$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = -k_1[A][B] + k_{-1}[I]$$

$$\frac{d[I]}{dt} = -k_{-1}[I] + k_1[A][B] - k_2[I]$$

$$\frac{d[C]}{dt} = k_2[I]$$

Steady-state approximation implies that $\frac{d[I]}{dt} = 0$

$$0 = -k_{-1}[I] + k_1[A][B] + k_2[I] \Rightarrow [I] = \frac{k_1}{k_{-1} + k_2}[A][B]$$

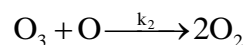
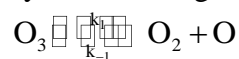
$$\frac{d[C]}{dt} = k_2[I] = \frac{k_2 k_1}{k_{-1} + k_2}[A][B]$$

$$v = \frac{d[A]}{dt} = -k_1[A][B] + k_{-1} \frac{k_1}{k_{-1} + k_2}[A][B] = -k_1[A][B] \left(\frac{k_2}{k_{-1} + k_2} \right)$$

3) *Equilibrium approximation*

Assume that the products and reactants within an elementary step are in equilibrium.

Example: Find the rate law for ozonolysis, assuming that the mechanism is the following

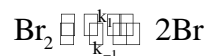


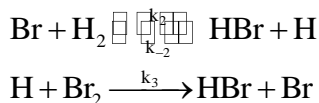
Assume the elementary step is in equilibrium

$$k_1[O_3] = k_{-1}[O_2][O] \Rightarrow [O] = \frac{k_1[O_3]}{k_{-1}[O_2]}$$

$$\frac{1}{2} \frac{d[O_2]}{dt} = k_2[O_3][O] = k_2[O_3] \frac{k_1[O_3]}{k_{-1}[O_2]} = \frac{k_2 k_1 [O_3]^2}{k_{-1} [O_2]}$$

Summary Example: Consider the reaction $H_2 + Br_2 \rightarrow 2 HBr$. Find the rate law for the following mechanism:





$$\begin{aligned} \frac{d[\text{Br}_2]}{dt} &= -k_3[\text{H}][\text{Br}_2] - k_1[\text{Br}_2] + k_{-1}[\text{Br}]^2 \\ \frac{d[\text{Br}]}{dt} &= -k_{-1}[\text{Br}]^2 + k_1[\text{Br}_2] - k_2[\text{H}_2][\text{Br}] + k_{-2}[\text{HBr}][\text{H}] + k_3[\text{H}][\text{Br}_2] \\ \frac{d[\text{H}_2]}{dt} &= -k_2[\text{H}_2][\text{Br}] + k_{-2}[\text{HBr}][\text{H}] \\ \frac{d[\text{H}]}{dt} &= k_2[\text{H}_2][\text{Br}] - k_{-2}[\text{HBr}][\text{H}] - k_3[\text{H}][\text{Br}_2] \\ \frac{d[\text{HBr}]}{dt} &= k_2[\text{H}_2][\text{Br}] - k_{-2}[\text{HBr}][\text{H}] + k_3[\text{H}][\text{Br}_2] \end{aligned}$$

Assume that the concentration of the intermediates doesn't change (steady-state approximation).

$$\frac{d[\text{Br}]}{dt} = 0 \qquad \frac{d[\text{H}]}{dt} = 0$$

$$\begin{aligned} \frac{d[\text{Br}]}{dt} = 0 &\Rightarrow k_{-1}[\text{Br}]^2 + k_2[\text{H}_2][\text{Br}] = k_1[\text{Br}_2] + k_{-2}[\text{HBr}][\text{H}] + k_3[\text{H}][\text{Br}_2] \\ \frac{d[\text{H}]}{dt} = 0 &\Rightarrow k_2[\text{H}_2][\text{Br}] = k_{-2}[\text{HBr}][\text{H}] + k_3[\text{H}][\text{Br}_2] \end{aligned}$$

Combining the above equations yields

$$k_{-1}[\text{Br}]^2 = k_1[\text{Br}_2] \Rightarrow [\text{Br}] = \left(\frac{k_1[\text{Br}_2]}{k_{-1}} \right)^{\frac{1}{2}}$$

From $\frac{d[\text{H}]}{dt} = 0$ equation

$$[\text{H}] = \frac{k_2[\text{H}_2][\text{Br}]}{k_{-2}[\text{HBr}] + k_3[\text{Br}_2]} = \frac{k_2[\text{H}_2] \left(\frac{k_1[\text{Br}_2]}{k_{-1}} \right)^{\frac{1}{2}}}{k_{-2}[\text{HBr}] + k_3[\text{Br}_2]} = k_2 \left(\frac{k_1}{k_{-1}} \right)^{\frac{1}{2}} \frac{[\text{H}_2][\text{Br}_2]^{\frac{1}{2}}}{(k_{-2}[\text{HBr}] + k_3[\text{Br}_2])}$$

$$v = \frac{d[\text{H}_2]}{dt} = -k_2[\text{H}_2][\text{Br}] + k_{-2}[\text{HBr}][\text{H}]$$



$$\begin{aligned}
 v &= \frac{d[H_2]}{dt} = -k_2[H_2] \left(\frac{k_1[Br_2]}{k_{-1}} \right)^{\frac{1}{2}} + k_{-2}[HBr] k_2 \left(\frac{k_1}{k_{-1}} \right)^{\frac{1}{2}} \frac{[H_2][Br_2]^{\frac{1}{2}}}{(k_{-2}[HBr] + k_3[Br_2])} \\
 &= k_2[H_2] \left(\frac{k_1[Br_2]}{k_{-1}} \right)^{\frac{1}{2}} \left[-1 + \frac{k_{-2}[HBr]}{(k_{-2}[HBr] + k_3[Br_2])} \right] = k_2[H_2] \left(\frac{k_1[Br_2]}{k_{-1}} \right)^{\frac{1}{2}} \left[\frac{-k_3[Br_2]}{(k_{-2}[HBr] + k_3[Br_2])} \right] \\
 &= -k_2 k_3 \left(\frac{k_1}{k_{-1}} \right)^{\frac{1}{2}} \left[\frac{[H_2][Br_2]^{\frac{3}{2}}}{(k_{-2}[HBr] + k_3[Br_2])} \right]
 \end{aligned}$$

Enzyme Kinetics

The kinetics of most enzymes are modeled using the **Michaelis-Menton mechanism**



Simplifying assumptions

- 1.) [S] is large
- 2.) $ES \rightarrow E + P$ is rate-determining step
- 3.) [P] is small
- 4.) $E + S \rightleftharpoons ES$ is in equilibrium

$$\frac{d[ES]}{dt} = -k_{-1}[ES] - k_2[ES] + k_1[E][S] = 0$$

$$\Rightarrow [ES] = \frac{k_1[E][S]}{k_{-1} + k_2}$$

$$\text{From mass balance } [E]_0 = [E] + [ES] \Rightarrow [E] = [E]_0 - [ES]$$

$$[ES] = \frac{k_1([E]_0 - [ES])[S]}{k_{-1} + k_2} \Rightarrow (k_{-1} + k_2)[ES] - k_1[ES][S] = k_1[E]_0[S]$$

$$[ES] = \frac{k_1[E]_0[S]}{k_{-1} + k_2 + k_1[S]}$$

$$v = \frac{d[P]}{dt} = k_2[ES] = \frac{k_1 k_2 [E]_0 [S]}{k_{-1} + k_2 + k_1 [S]} = \frac{k_1 k_2 [E]_0 [S]}{k_1 \left(\frac{k_{-1} + k_2}{k_1} + [S] \right)} = \frac{k_2 [E]_0 [S]}{\left(\frac{k_{-1} + k_2}{k_1} + [S] \right)}$$

$$\text{For convenience, define } K_m = \frac{k_{-1} + k_2}{k_1} \text{ and } V_{\max} = k_2 [E]_0$$

$$v = \frac{k_2 [E]_0 [S]}{\frac{k_{-1} + k_2}{k_1} + [S]} = \frac{V_{\max} [S]}{K_m + [S]}$$

Notes:

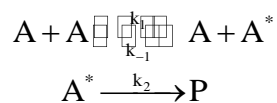
At low substrate concentration (that is $K_m \gg k_1[S]$), kinetics are first-order

At high substrate concentration (that is $K_m \ll k_1[S]$), kinetics are zeroth-order



Unimolecular Reactions

Lindemann-Hinshelwood mechanism



$$\frac{d[A]}{dt} = -k_1[A]^2 + k_{-1}[A][A^*]$$

$$\frac{d[A^*]}{dt} = k_1[A]^2 - k_{-1}[A][A^*] - k_2[A^*]$$

$$\frac{d[P]}{dt} = k_2[A^*]$$

Assume steady-state

$$\frac{d[A^*]}{dt} = 0 \Rightarrow k_1[A]^2 - k_{-1}[A][A^*] - k_2[A^*] = 0 \Rightarrow [A^*] = \frac{k_1[A]^2}{k_{-1}[A] + k_2}$$

$$v = \frac{d[P]}{dt} = k_2[A^*] = \frac{k_1 k_2 [A]^2}{k_{-1}[A] + k_2}$$

Notes:

At high pressure (concentration), reaction is first-order.

At low pressure, reaction is second-order.