

These Notes are to **SUPPLEMENT** the Text, They do NOT Replace reading the Text Book Material. Additional material that is in the Text Book will be on your tests! To get the most information, **READ THE CHAPTER** prior to the Lecture, bring in these lecture notes and make comments on these notes. These notes alone are NOT enough to pass any test!

Note: For my lectures and class (aq) for aqueous is assumed.

Note: The reactions in this chapter go to completion, Ch 16 are reactions at equilibrium

Phenolphthalein is an indicator used in the titration of acid and a base.

pH < 8 = colorless (neutral to acidic), pH > 12 (basic) color is pink

Species	H ₃ In ⁺	H ₂ In	In ²⁻	In(OH) ³⁻
Structure				
pH	<0	0-8.2	8.2-12.0	>12.0
Conditions	strongly acidic	acidic or near-neutral	basic	strongly basic
Color	orange	colorless	pink to fuchsia	colorless
Image				

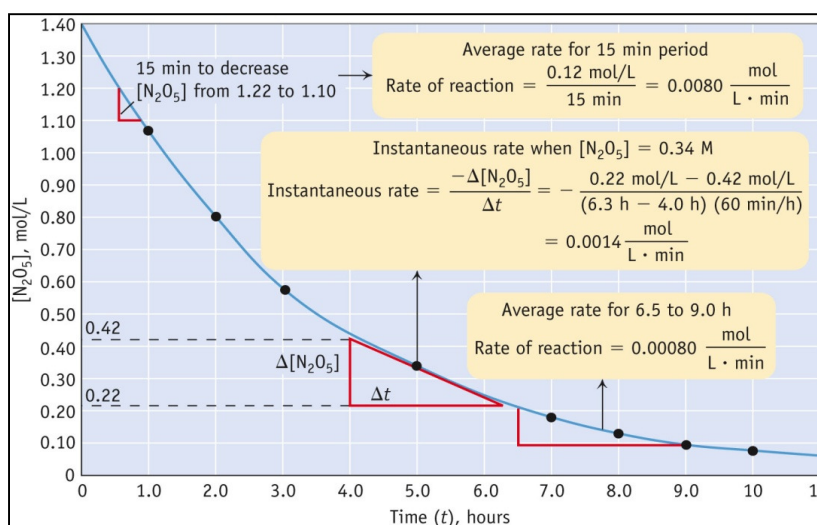
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From Wikipedia

Chemical Kinetics is the study of Rates of Chemical Reactions

Reaction Mechanism is the detailed pathway taken by atoms and molecules as a reaction proceeds.

15.1 Rates of Reaction = Change in Concentration / Change in Time = $\Delta[\text{concentration}] / \Delta \text{time}$



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You will notice for this reaction, the rate of reaction changes with time

1. **Initial Rate** is the rate at Time = 0, (hard to measure), use a Tangent

2. **Average Rate of Reaction** – measure 2 quantities (conc & time), $\text{Rate}_{\text{avg}} = \Delta\text{Conc} / \Delta\text{Time}$

Rate of loss of N₂O₅ = $-\Delta[\text{N}_2\text{O}_5] / \Delta t$

Rate_{avg} of loss of N₂O₅ for time 45 min to 60 min = $-(1.10 - 1.22) \text{ mol/L} / (55 - 40) \text{ min} = 0.0080 \text{ mol} / \text{L min} = 8.0 \times 10^{-3} \text{ mol} / \text{L min}$

Rate_{avg} of loss of N₂O₅ for time 6.5 to 9.0 hrs = $-(0.10 - 0.22) \text{ mol/L} / (540 - 390) \text{ min} = 0.00080 \text{ mol/L min} = 8.0 \times 10^{-4} \text{ mol/L min}$

Instantaneous Rate of Reaction = Tangent line to Conc / Time curve, measure slope of the line

Note $\text{Rate}_{\text{inst}}$ for [N₂O₅] at time = 5.0 hrs = 0.0014492 = **1.4 x 10⁻³ mol/L min**

Since the plot does not show a straight line, the rate of reaction is not constant, the rate of reaction changes as the reaction progresses. In the beginning, $\text{Rate}_{\text{Decom}} \text{N}_2\text{O}_5$ is fast ($8.0 \times 10^{-3} \text{ mol} / \text{L min}$), later it slows ($8.0 \times 10^{-4} \text{ mol/L min}$).

For This Reaction: $\text{N}_2\text{O}_5 \rightarrow 2 \text{NO}_2 + \frac{1}{2} \text{O}_2$

Rate of decomp of N₂O₅ = $\frac{1}{2} * \text{Rate of formation of NO}_2 = 2 * \text{Rate of formation of O}_2$
 $-\Delta[\text{N}_2\text{O}_5] / \Delta t = \frac{1}{2} \Delta[\text{NO}_2] / \Delta t = 2 \Delta[\text{O}_2] / \Delta t$

Rate of formation of NO₂ = $2 * \text{Rate of decomp of N}_2\text{O}_5$
 $\Delta[\text{NO}_2] / \Delta t = 2 - \Delta[\text{N}_2\text{O}_5] / \Delta t$

Rate of formation of O₂ = $\frac{1}{2} * \text{Rate of decomp of N}_2\text{O}_5$
 $\Delta[\text{O}_2] / \Delta t = \frac{1}{2} - \Delta[\text{N}_2\text{O}_5] / \Delta t$

Example 15.1 $4 \text{PH}_3 (\text{g}) \rightarrow \text{P}_4 (\text{g}) + 6 \text{H}_2 (\text{g})$

Rate of decomp of PH₃ = $4 * \text{the Rate of formation of P}_4 = \frac{6}{4} * \text{the Rate of formation of H}_2$
 $-\Delta[\text{PH}_3] / \Delta t = 4 * \Delta[\text{P}_4] / \Delta t = \frac{6}{4} \Delta[\text{H}_2] / \Delta t$

15.2 Reaction Conditions and Rate

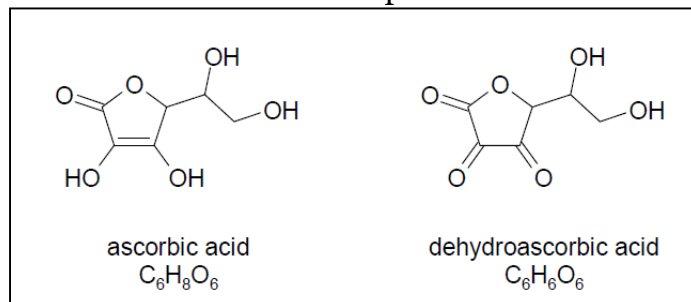
Effect of Concentration and Temperature (ROT increase temp 10° C = doubles rate)

Determine the amount of Vit C in a sample. H₂O₂ + Iodide, Ascorbic Acid, Starch

1. $\text{H}_2\text{O}_2 + 2 \text{I}^- + 2 \text{H}_3\text{O}^+ \rightarrow 4 \text{H}_2\text{O} + \text{I}_2$ Slow Reaction, generates Iodine

Iodine, then reacts with the Vitamin C (Ascorbic Acid) [Fast Reaction] until all of the Vitamin C is used up. Then the excess I₂ reacts with the Starch to form a blue-black complex.

2. $\text{H}_2\text{O} + \text{I}_2 + \text{C}_6\text{H}_8\text{O}_6 \rightarrow \text{C}_6\text{H}_6\text{O}_6 + 2 \text{H}_3\text{O}^+ + 2 \text{I}^-$ Fast Reaction
I₂⁻ + Starch → Blue Black Complex



Experimental:

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Chapter 15

Moles of Vit C

X moles

Less than X moles

X moles, solution heated

Time for all Vit C to be used up (soln turns blue-black)

51 seconds

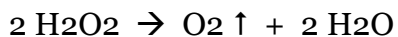
1 min 33 sec

56 seconds

1. If the concentration of a reactant is increased, the reaction rate will often increase
2. If the temperature is raised, the reaction rate will increase (ROT – 10°C increase will double the reaction rate)

Catalyst are substances that accelerate a reaction but are not consumed.

Surface area also affects reaction rate, the smaller the particles, the larger the surface area, the faster the reaction rate.

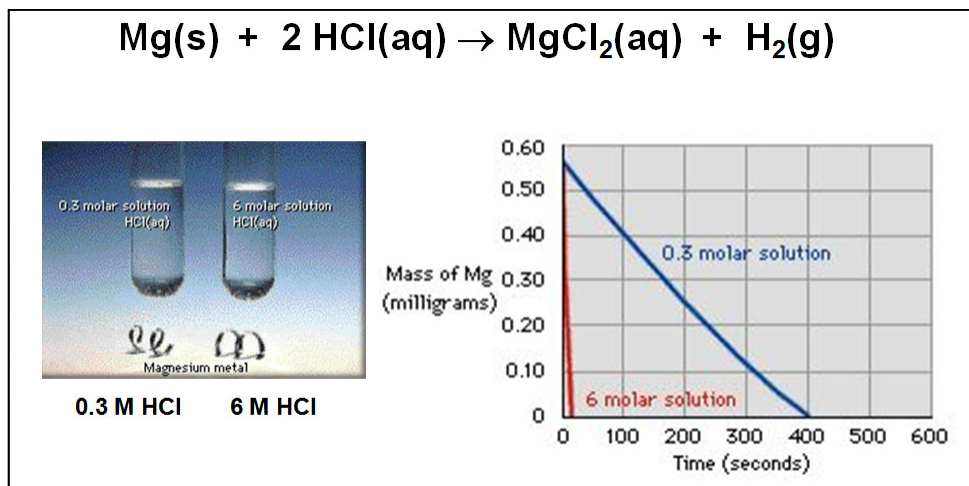


Reaction is very slow (a bottle of Hydrogen Peroxide can sit on your shelf for a year), but add a pinch of MnO_2 and the reaction is very fast.



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15.3 Effect of Concentration on Reaction Rate



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Refer to previous data above, Rate Equations



At $[\text{N}_2\text{O}_2] = 0.34 \text{ mol/L}$, $\text{Rate}_{\text{inst}} = 0.0014 \text{ mol/L min}$

At $[\text{N}_2\text{O}_2] = 0.68 \text{ mol/L}$, $\text{Rate}_{\text{inst}} = 0.0028 \text{ mol/L min}$

Doubling the concentration doubles the reaction rate

So Rate of Reaction $\propto [\text{N}_2\text{O}_2]$

Rate Equations:

$$\text{Rate of Reaction} = -\Delta(\text{N}_2\text{O}_2) / \Delta t = + (1/2) \Delta(\text{NO}_2) / \Delta t = 2 \Delta(\text{O}_2) / \Delta t = k [\text{N}_2\text{O}_2]$$

k = rate constant

General form of Rate Equation: $aA + bB \rightarrow xX$ Rate of Reaction = $k [A]^m [B]^n$
k, m, n are determined by experiment!

Order of a Reaction

Order = particular reactant is the **exponent** of a components concentration
 Overall Reaction Order = sum of all exponents of concentration

A reaction order can be zero, or positive integer and fractional number.

Order	Name	Rate Law
0	zeroth	rate = $k[A]^0 = k$
1	first	rate = $k[A]$
2	second	rate = $k[A]^2$
0.5	one-half	rate = $k[A]^{1/2}$
1.5	three-half	rate = $k[A]^{3/2}$
0.667	two-thirds	rate = $k[A]^{2/3}$

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$2 \text{NO} (g) + 2 \text{H}_2 (g) \rightarrow \text{N}_2 (g) + 2 \text{H}_2\text{O} (g)$
 is experimentally found to be **first order** in H_2 and **third order** in NO

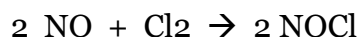
a) Write the rate law.
 Rate(Ms^{-1}) = $k [\text{H}_2] [\text{NO}]^3$

b) What is the overall order of the reaction?
 Overall order = $1 + 3 = 4$ "4th order"

c) What are the units of the rate constant?
 $\text{Rate} = \frac{\text{M}}{\text{s}} = k \times \text{M} \times \text{M}^3 = k \times \text{M}^4$ $k = \frac{\text{M}}{\text{s} \times \text{M}^4} = \underline{\underline{\text{M}^{-3} \text{s}^{-1}}}$

Slide

Experimental Determination of Rate Constant:



Experiment	[NO] mol/L	[Cl ₂] mol/L	Rate mol/L s
1	0.250	0.250	1.43×10^{-6}
2	0.500	0.250	5.72×10^{-6}
3	0.250	0.500	2.86×10^{-6}
4	0.500	0.500	11.4×10^{-6}

Compare:

1 - 2	[Cl ₂] is constant	[NO] is doubled	Rate increases by 4
1 - 3	[Cl ₂] is doubled	[NO] is constant	Rate doubles
1 - 4	[Cl ₂] is doubled	[NO] is doubled	Rate = $2 * 4 = 8$

Rate	$1/2$	1	2	4	Change of rate between two measurements
M	-1	0	1	2	Exponent of concentration

Reaction Rate Constant = $K = [\text{NO}]^m * [\text{Cl}_2]^n = [\text{NO}]^2 * [\text{Cl}_2]^1$

If you double the concentration of one component and the reaction rate doubles, then K is directly proportional to [x] or [x]¹. See 1-3 above.

Units for Rate Constant, k

First Order	$k = 1/\text{time}$
Second Order	$k = \text{L}/\text{mol time}$
Zero Order	$k = \text{mol} / \text{L time}$

Determining Rate Equation $\text{CH}_3\text{COOCH}_3 + \text{OH}^- \rightarrow \text{CH}_3\text{CO}_2^- + \text{CH}_3\text{OH}$

Experiment	$[\text{CH}_3\text{COOCH}_3]$ mol/L = M	$[\text{OH}^-]$ mol/L	Initial Rate mol/L s at 25°C	
1	0.050	0.050	0.0034	
2	0.050	0.10	0.0069	Rate Doubles
3	0.10	0.10	0.0137	Rate Doubles

See Rate/M chart above,

2 → 3 Conc doubles, rate is 2 x, exponent is 1 $[\text{CH}_3\text{COOCH}_3]^1$
 1 → 2 Cond doubles, rate is 2 x, exponent is 1 $[\text{OH}^-]^1$

$$\text{Reaction Rate} = k * [\text{CH}_3\text{COOCH}_3]^1 * [\text{OH}^-]^1$$

$$k = \text{Reaction Rate} / [\text{CH}_3\text{COOCH}_3]^1 * [\text{OH}^-]^1$$

$$= 0.0034 \text{ mol/Ls} / (0.050 \text{ mol/L} * 0.050 \text{ mol/L}) = 1.36 \text{ L/mol s}$$

$$= 0.0069 \text{ mol/Ls} / (0.050 \text{ mol/L} * 0.10 \text{ mol/L}) = 1.38 \text{ L/mol s}$$

$$= 0.0137 \text{ mol/Ls} / (0.10 \text{ mol/L} * 0.10 \text{ mol/L}) = 1.37 \text{ L/mol s}$$

Note: Overall reaction is 2nd order. k units are second order units

SEE SLIDE

EXAMPLE: The reaction,

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

is experimentally found to be *first order* in H_2 and *third order* in NO

a) Write the rate law.

$$\text{Rate}(\text{Ms}^{-1}) = k [\text{H}_2] [\text{NO}]^3$$

b) What is the overall order of the reaction?

Overall order = 1 + 3 = 4 “4th order”

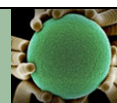
c) What are the units of the rate constant?

$$\text{Rate} = \frac{\text{M}}{\text{s}} = k \times \text{M} \times \text{M}^3 = k \times \text{M}^4 \quad k = \frac{\text{M}}{\text{s} \times \text{M}^4} = \underline{\underline{\text{M}^{-3} \text{s}^{-1}}}$$

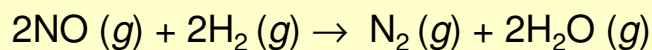
Rate = k [A]^x [B]^y If the rate doubles when [A] doubles and [B] stays the same the order is 1

Another way to do it!

Determining Reaction Order: *The Method of Initial Rates*



The reaction of nitric oxide with hydrogen at 1280 ° C is as follows:

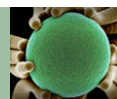


From the following experimental data, determine the rate law and rate constant.

Trial	[NO] _o (M)	[H ₂] _o (M)	Initial Rate (Mmin ⁻¹)
1	0.0100	0.0100	0.00600
2	0.0200	0.0300	0.144
3	0.0100	0.0200	0.0120

Trial 1 to Trial 3, [NO] is constant, [H₂] is doubled, rate is doubled, rate is \propto to [H₂]¹

Determining Reaction Order: *The Method of Initial Rates*



Similarly for x: $\text{Rate}(\text{M}/\text{min}) = k [\text{NO}]^x [\text{H}_2]^y$

$$\frac{\text{Rate}(2)}{\text{Rate}(1)} = \frac{k [\text{NO}]_{(2)}^x [\text{H}_2]_{(1)}^y}{k [\text{NO}]_{(1)}^x [\text{H}_2]_{(2)}^y}$$

$$\frac{0.144}{0.00600} = \frac{k \cancel{[0.0200]}^x [0.0300]}{k \cancel{[0.0100]}^x [0.0100]}$$

$$24 = (2)^x \times (3)$$

$$(2)^x = 8$$

$$x \log(2) = \log(8) \quad x = 3$$

There are other examples in your book, go over them!

15.4 Concentration-Time Relationships

MEMORIZE TABLE 15.1

Table 15.1 Characteristic Properties of Reactions of the Type "R → Products"

Order	Rate Equation	Integrated Rate Equation	Straight-Line Plot	Slope	k Units
0	$-\Delta[R]/\Delta t = k[R]^0$	$[R]_0 - [R]_t = kt$	$[R]_t$ vs. t	$-k$	mol/L · time
1	$-\Delta[R]/\Delta t = k[R]^1$	$\ln ([R]_t/[R]_0) = -kt$	$\ln [R]_t$ vs. t	$-k$	1/time
2	$-\Delta[R]/\Delta t = k[R]^2$	$(1/[R]_t) - (1/[R]_0) = kt$	$1/[R]_t$ vs. t	k	L/mol · time

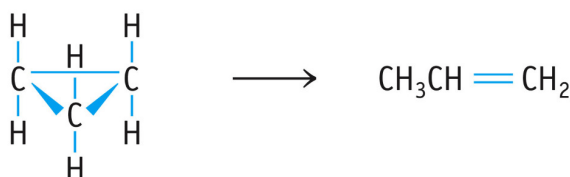
1. First Order Reactions $\ln ([R]_t) / ([R]_0) = -kt$ k units = 1 / time

Reaction Rate = k is directly proportional to $[R]^1$

$R =$ conc at time t and zero $R_t/R_0 =$ fraction of reactant that remains = < 1

Note: k is independent of concentration – use any units of concentration

Example 15.5 Cyclopropane → Propene at 500 °C $k = 2.42 \text{ h}^{-1}$



How long will it take for 0.050 mol/L to drop to 0.010 mol/L?

$$\ln ([R]_t) / ([R]_0) = -kt \quad \text{solve for } t$$

$$\ln ([0.010 \text{ M}] / [0.050 \text{ M}]) = -(2.42 \text{ h}^{-1}) t$$

$$t = -\ln (0.20) / 2.42 \text{ h}^{-1} = 0.665 \text{ h} = 0.67 \text{ h (rounded to 2 SD).}$$

2. Second Order Reactions $1 / [R]_t - 1 / [R]_0 = kt$ k units = L / mol time

Example 15.7 $\text{HI (g)} \rightarrow \frac{1}{2} \text{H}_2 \text{(g)} + \frac{1}{2} \text{I}_2 \text{(g)}$ is 2nd order, $k = 30. \text{ L/mol min}$ at 443 °C

How long will it take $[\text{HI}]$ to drop from 0.010 M to 0.0050 M?

$$1 / [R]_t - 1 / [R]_0 = kt \quad \text{solve for } t$$

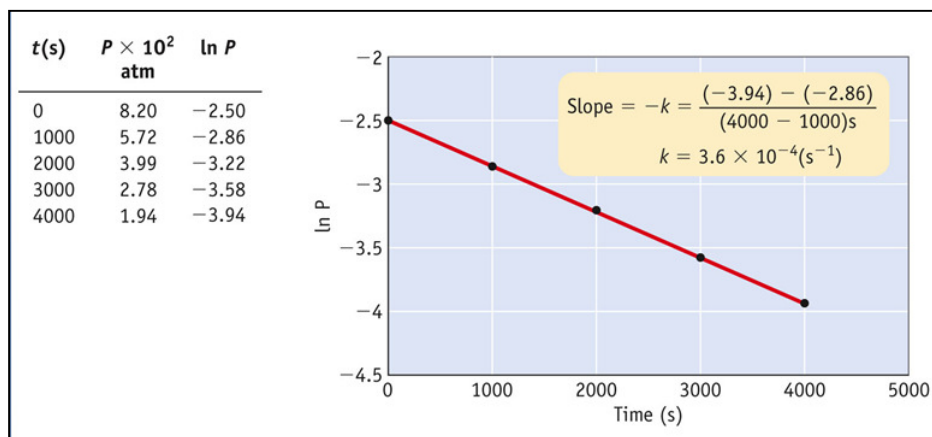
$$(1 / 0.0050 \text{ mol/L}) - (1 / 0.010 \text{ mol/L}) = 30. \text{ L/Mol min} * t$$

$$t = 3.3 \text{ min}$$

3. Zero Order Reactions $[R]_0 - [R]_t = kt$ k units = mol / L sec

Graphic Methods to determine Reaction Order and Rate Constant (See 15.1 above):

Plot data as a straight line	Y	=	mX	+	B
Zero Order	$[R]_t$	=	$-kt$	+	$[R]_0$
First Order	$\ln [R]_t$	=	$-kt$	+	$\ln [R]_0$
Second Order	$1 / [R]_t$	=	$+kt$	+	$1 / [R]_0$



See plot 15.6 of $\ln [\text{CH}_3\text{N}_2\text{CH}_3]$ is a straight line = **First Order**

Half Life / First Order Reactions, Half life = $t_{1/2}$ is used when dealing with 1st order reactions

$$t_{1/2} = 0.693 / k \quad \text{***** Note } t_{1/2} \text{ is independent of concentration}$$

Azomethane above has $k = 3.6 \times 10^{-4} / \text{s}$ What is it's half life?

$$t_{1/2} = 0.693 / k = 0.693 / 3.6 \times 10^{-4} / \text{s} = 1.9 \times 10^3 \text{ s} = 32. \text{ min}$$

Example 15.9, p 688 Radon-222 gas (^{222}Rn) $t_{1/2} = 3.8$ days.

How much will remain after 30 days starting with 4.0×10^{13} atoms

$$k = 0.693 / t_{1/2} = 0.693 / 3.8 \text{ days} = 0.18 / \text{day}$$

From the Integrated Rate Equation:

$$\ln ([\text{R}]_t / [\text{R}]_0) = -kt = \ln ([\text{R}]_t / 4.0 \times 10^{13} \text{ atoms}) = -(0.18 / \text{day}) * 30 \text{ day} = -5.5$$

$$[\text{R}]_t / 4.0 \times 10^{13} \text{ atoms} = e^{-5.5} = 0.0042$$

$$[\text{R}]_t = 4.0 \times 10^{13} \text{ atoms} * 0.0042 = 1.68 \times 10^{11} \text{ atoms} = 1.7 \times 10^{11} \text{ atoms}$$

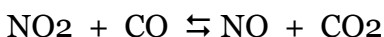
15.5 Microscopic View of Reaction Rates, Collision theory of reaction rates:

- Concentration and Reaction Rates
 - Reacting molecules must collide with one another
 - Double the concentration of one reactant, you will double the number of collisions
- Temperature and Reaction Rates
 - Reacting molecules must collide with sufficient energy to initiate a reaction
 - Increase temp, the reaction occurs more rapidly. It increases the average energy of the molecules
 - Lower the temp will slow down the reaction
 - Remember ROT – increase the temp of a reaction by 10 °C and you will double the reaction rate!
 - Increase temp increases the reaction rate by increasing the fraction of molecules with enough activation energy.
- Activation Energy = E_a
 - Molecules require a minimum amount of energy to react

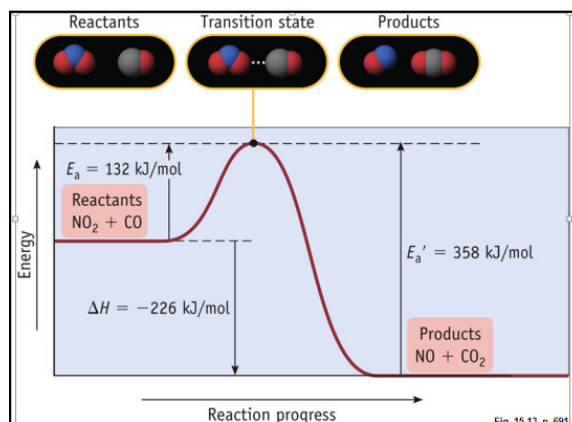
Throw volleyball over a net, need to give it sufficient energy to go over the net



Transition State – the number of molecules reaches a maximum energy, as such it cannot be isolated. At the Transition State, the reaction can go either way forward or reverse.



Peak is Transition State, reaction is Exothermic



4. Molecules must collide in an orientation that can lead to a reaction, Reactant molecules must come together in correct orientation

- 1 molecule collides, than comes apart – can happen
- 2 molecules collide – can happen
- 3 molecules must collide – rare for 3 things to collide at once

Arrhenius Equation

$$\text{Rate Constant} = k = A e^{-E/RT}$$

$$R = 8.314510 \times 10^{-3} \text{ kJ / K mol}$$

A = frequency factor = # of collisions with correct geometry and is temp dependant

$e^{-E/RT}$ = fraction of molecules with minimum energy for reaction and is < 1

$$\ln k = \mathbf{Ea/R} (1/T) + \ln A$$

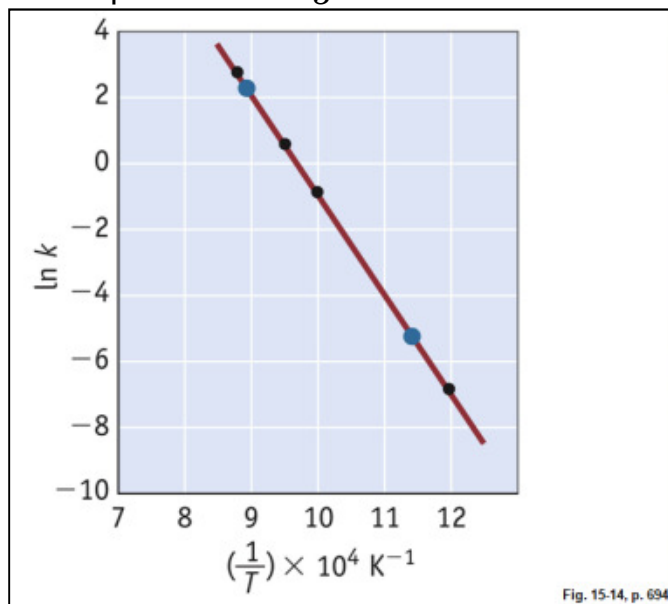
Plot of a straight line!

$$y = \mathbf{m} \quad x \quad + \quad b$$

Note m = slope of the line

Example 15.10 $2 \text{N}_2\text{O} (\text{g}) \rightarrow 2 \text{N}_2 (\text{g}) + \text{O}_2 (\text{g})$

Experiment	Temp (K)	k (L/mol s)
1	1125	11.59
2	1053	1.67
3	1001	0.380
4	838	0.0011



Slope = $-3.0 \times 10^4 \text{ K}$ = $-\text{E}_a/\text{R}$

E_a = $-3.0 \times 10^4 \text{ K} * 8.31 \times 10^{-3} \text{ kJ/K mol} = 2.493 \times 10^2 = \mathbf{2.5 \times 10^2 \text{ kJ/mol}}$

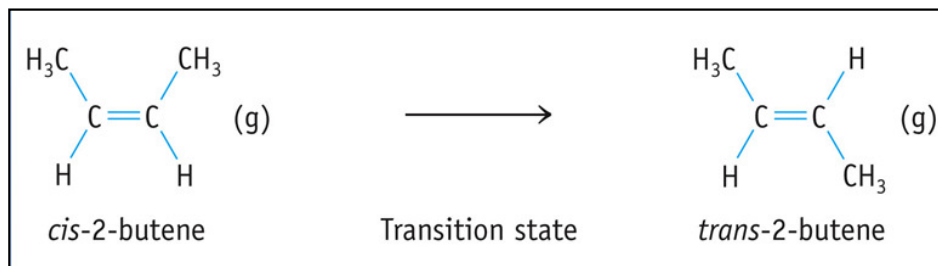
E_a is determined if we know k at two temperatures: $\ln k_2/k_1 = -\text{E}_a/\text{R} * [1/\text{T}_2 - 1/\text{T}_1]$

STUDENTS: Re-solve the above reaction using 2 temperatures.

STUDENTS: Example 15.11, calculate E_a

Effects of Catalysts on Reaction Rate

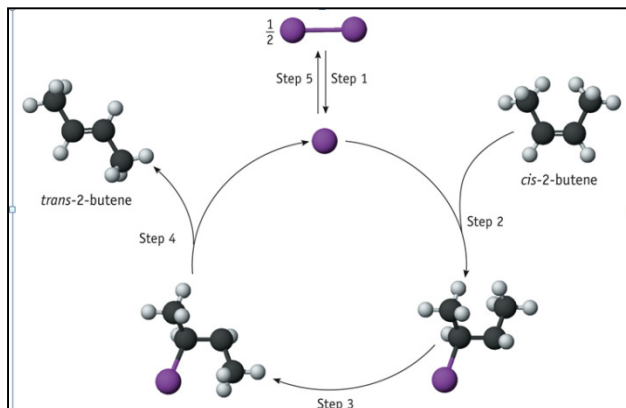
cis-2-butene \rightarrow trans-2-butene with an I₂ catalyst



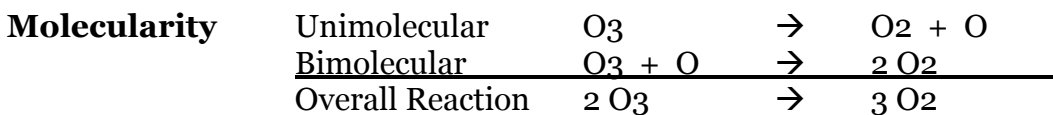
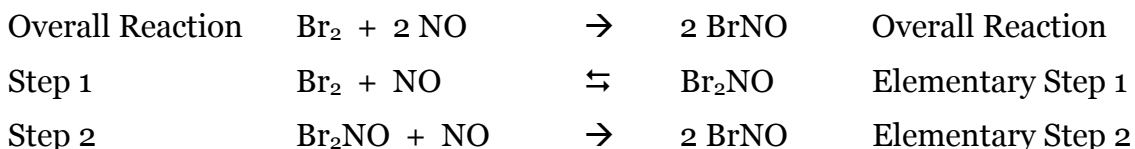
E_a = large 264 kJ/mol because a π bond is broken

But if you add I₂ it runs faster Ea = large 150 kJ/mol Rate = k [cis-2-butene] [I₂]^{1/2}

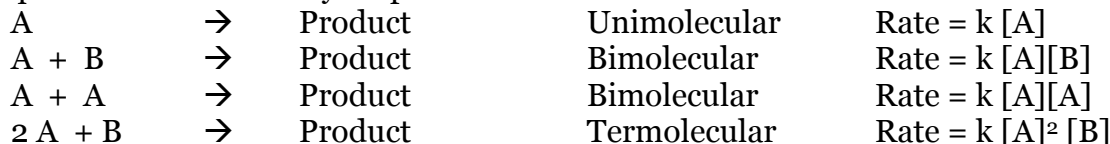
The Ea is lower because the mechanism is changed. Generates Reaction Intermediates



15.6 Reaction Mechanism, Chemical Reactions occur in steps

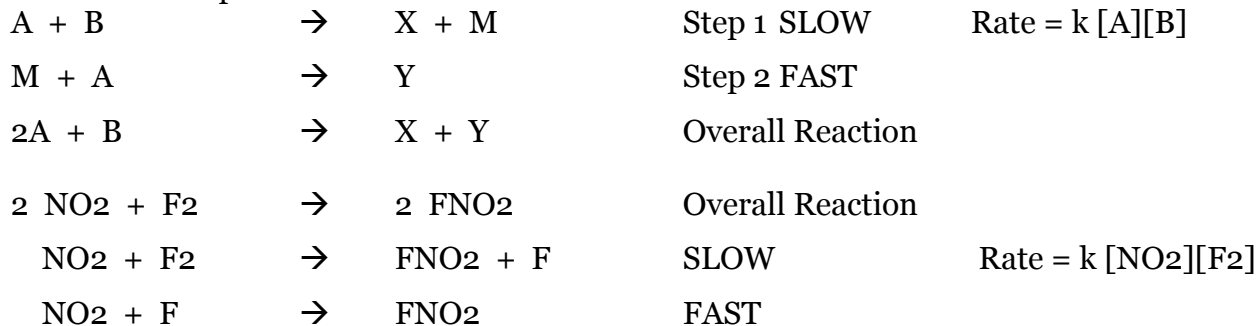


Rate Equation for Elementary Steps



Reaction Mechanisms and Rate Equations

Rate Determining Step – products of a reaction can never be produced at a rate faster than the rate of the slowest step

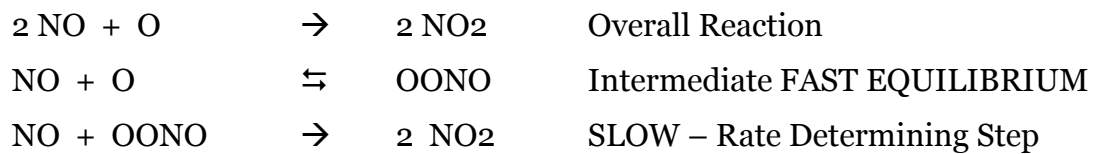


EXAMPLE 15.13 Students need to understand this principle

Enzymes are Nature's Catalyst and increase reaction rates 10⁷ to 10¹⁴ times

Reaction Mechanism with Equilibrium

A fast initial step gives an intermediate, then a slower step to produce product.



So rate = $k_2 [\text{NO}] [\text{OONO}]$