

Kinetics

- The study of reaction rates.
- Spontaneous reactions are reactions that will happen - but we can't tell how fast.
- Diamond will spontaneously turn to graphite – eventually.
- Reaction mechanism- the steps by which a reaction takes place.

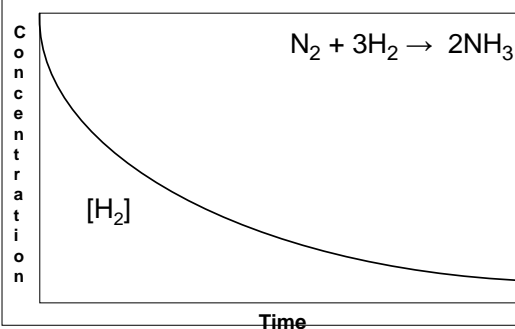
Review- Collision Theory

- Particles have to collide to react.
- Have to hit hard enough
- Things that increase this increase rate
- High temp – faster reaction
- High concentration – faster reaction
- Small particles = greater surface area means faster reaction

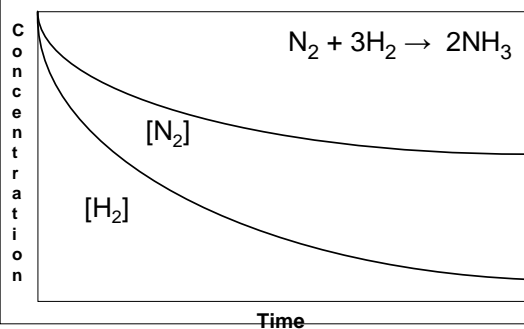
Reaction Rate

- Rate = $\frac{\text{Conc. of A at } t_2 - \text{Conc. of A at } t_1}{t_2 - t_1}$
- Rate = $\frac{\Delta[A]}{\Delta t}$
- Change in concentration per unit time
- For this reaction
- $\text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3$

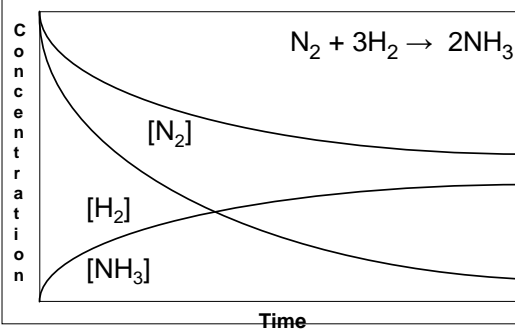
- As the reaction progresses the concentration H_2 goes down



- As the reaction progresses the concentration N_2 goes down 1/3 as fast



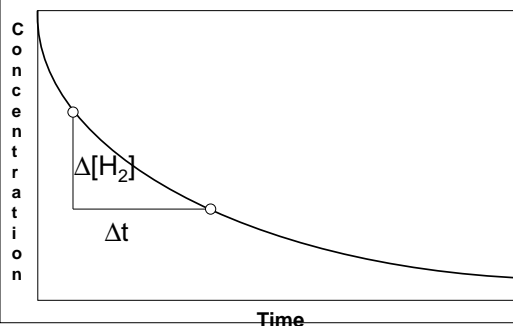
- As the reaction progresses the concentration NH_3 goes up 2/3 times



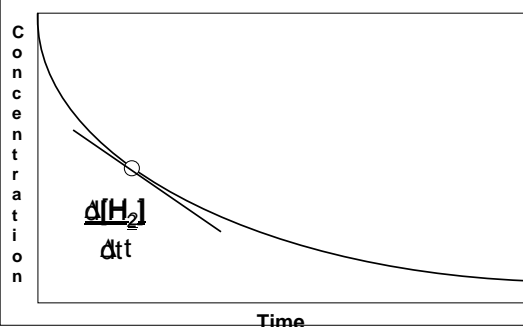
Calculating Rates

- Average rates are taken over long intervals
- Instantaneous rates are determined by finding the slope of a line tangent to the curve at any given point because the rate can change over time
- Derivative.

- Average slope method



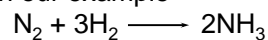
- Instantaneous slope method.



Defining Rate

- We can define rate in terms of the disappearance of the reactant or in terms of the rate of appearance of the product.

- In our example



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

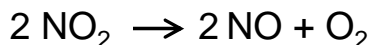
- $\frac{\Delta[NH_3]}{\Delta t} = \frac{-2\Delta[N_2]}{\Delta t}$

Rate Laws

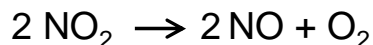
- Reactions are reversible.
- As products accumulate they can begin to turn back into reactants.
- Early on the rate will depend on only the amount of reactants present.
- We want to measure the reactants as soon as they are mixed.
- This is called the Initial rate method.

Rate Laws

- Two key points
- The concentration of the products do not appear in the rate law because this is an initial rate.
- The order (exponent) must be determined experimentally,
- can't be obtained from the equation



- You will find that the rate will only depend on the concentration of the reactants. (Initially)
- Rate = $k[\text{NO}_2]^n$
- This is called a rate law expression.
- k is called the rate constant.
- n is the order of the reactant -usually a positive integer.



- The rate of appearance of O_2 can be said to be.
- Rate' = $\frac{\Delta[\text{O}_2]}{\Delta t} = k'[\text{NO}_2]$
- Because there are 2 NO_2 for each O_2
- Rate = 2 x Rate'
- So $k[\text{NO}_2]^n = 2 \times k'[\text{NO}_2]^n$
- So $k = 2 \times k'$

Types of Rate Laws

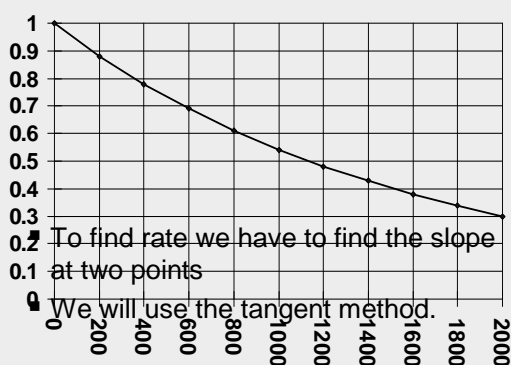
- Differential Rate law - describes how rate depends on concentration.
- Integrated Rate Law - Describes how concentration depends on time.
- For each type of differential rate law there is an integrated rate law and vice versa.
- Rate laws can help us better understand reaction mechanisms.

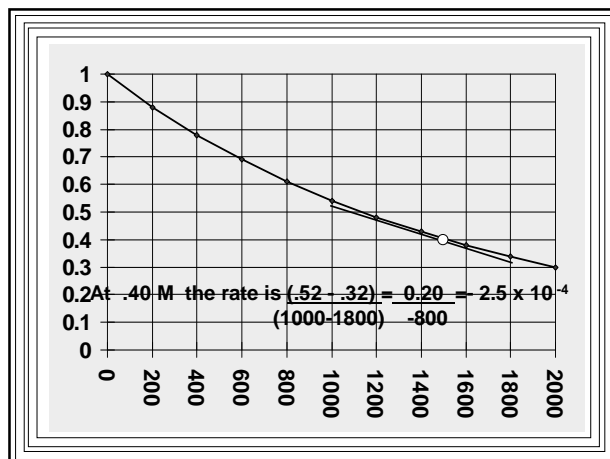
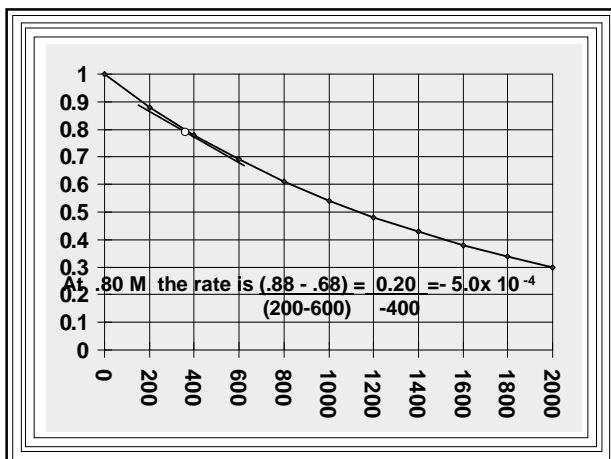
Determining Rate Laws

- The first step is to determine the form of the rate law (especially its order).
- Must be determined from experimental data.
- For this reaction
 $2 \text{N}_2\text{O}_5 (\text{aq}) \rightarrow 4\text{NO}_2 (\text{aq}) + \text{O}_2(\text{g})$
- The reverse reaction won't play a role because the gas leaves

$[\text{N}_2\text{O}_5]$ (mol/L)	Time (s)
1.00	0
0.88	200
0.78	400
0.69	600
0.61	800
0.54	1000
0.48	1200
0.43	1400
0.38	1600
0.34	1800
0.30	2000

Now graph the data





- Since the rate at twice as fast when the concentration is twice as big the rate law must be..
- First power
- Rate = $\frac{-\Delta[\text{N}_2\text{O}_5]}{\Delta t} = k[\text{N}_2\text{O}_5]^1 = k[\text{N}_2\text{O}_5]$
- We say this reaction is first order in N_2O_5
- The only way to determine order is to run the experiment.

- ### The method of Initial Rates
- This method requires that a reaction be run several times.
 - The initial concentrations of the reactants are varied.
 - The reaction rate is measured just after the reactants are mixed.
 - Eliminates the effect of the reverse reaction.

- ### An example
- For the reaction

$$\text{BrO}_3^- + 5 \text{Br}^- + 6\text{H}^+ \longrightarrow 3\text{Br}_2 + 3 \text{H}_2\text{O}$$
 - The general form of the Rate Law is

$$\text{Rate} = k[\text{BrO}_3^-]^n[\text{Br}^-]^m[\text{H}^+]^p$$
 - We use experimental data to determine the values of n,m,and p

Initial concentrations (M)			Rate (M/s)
BrO_3^-	Br^-	H^+	
0.10	0.10	0.10	8.0×10^{-4}
0.20	0.10	0.10	1.6×10^{-3}
0.20	0.20	0.10	3.2×10^{-3}
0.10	0.10	0.20	3.2×10^{-3}

Now we have to see how the rate changes with concentration

Integrated Rate Law

- Expresses the reaction concentration as a function of time.
- Form of the equation depends on the order of the rate law (differential).
- Changes $\text{Rate} = \frac{\Delta[A]^n}{\Delta t}$
- We will only work with $n=0, 1, \text{ and } 2$

First Order

- For the reaction $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$
- We found the Rate = $k[\text{N}_2\text{O}_5]^1$
- If concentration doubles rate doubles.
- If we integrate this equation with respect to time we get the Integrated Rate Law
- $\ln[\text{N}_2\text{O}_5] = -kt + \ln[\text{N}_2\text{O}_5]_0$
- \ln is the natural \ln
- $[\text{N}_2\text{O}_5]_0$ is the initial concentration.

First Order

- General form $\text{Rate} = \Delta[A] / \Delta t = k[A]$
- $\ln[A] = -kt + \ln[A]_0$
- In the form $y = mx + b$
- $y = \ln[A]$ $m = -k$
- $x = t$ $b = \ln[A]_0$
- A graph of $\ln[A]$ vs time is a straight line.

First Order

- By getting the straight line you can prove it is first order
- Often expressed in a ratio

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Half Life

- The time required to reach half the original concentration.
- If the reaction is first order
- $[A] = [A]_0/2$ when $t = t_{1/2}$

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$$\ln(2) = kt_{1/2}$$

Half Life

- $t_{1/2} = 0.693 / k$
- The time to reach half the original concentration does not depend on the starting concentration.
- An easy way to find k

- The highly radioactive plutonium in nuclear waste undergoes first-order decay with a half-life of approximately 24,000 years. How many years must pass before the level of radioactivity due to the plutonium falls to 1/128th (about 1%) of its original potency?

Second Order

- Rate = $-\Delta[A]/\Delta t = k[A]^2$
- integrated rate law
- $1/[A] = kt + 1/[A]_0$
- $y = 1/[A]$ $m = k$
- $x = t$ $b = 1/[A]_0$
- A straight line if $1/[A]$ vs t is graphed
- Knowing k and $[A]_0$ you can calculate $[A]$ at any time t

Second Order Half Life

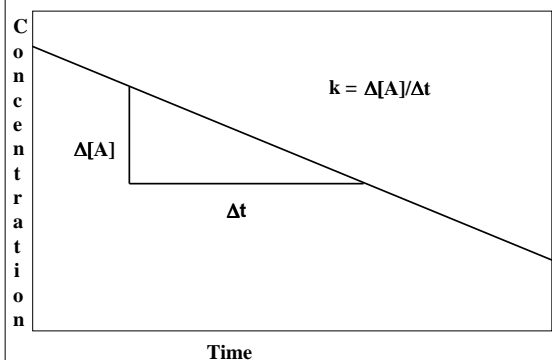
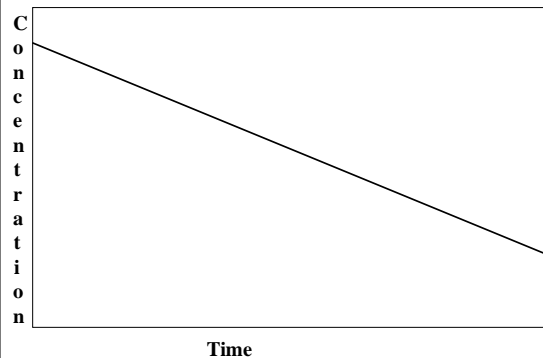
$$[A] = [A]_0 / 2 \text{ at } t = t_{1/2}$$

Zero Order Rate Law

- Rate = $k[A]^0 = k$
- Rate does not change with concentration.
- Integrated $[A] = -kt + [A]_0$
- When $[A] = [A]_0 / 2$ $t = t_{1/2}$
- $t_{1/2} = [A]_0 / 2k$

Zero Order Rate Law

- Most often when reaction happens on a surface because the surface area stays constant.
- Also applies to enzyme chemistry.



Summary of Rate Laws

More Complicated Reactions

- $\text{BrO}_3^- + 5 \text{Br}^- + 6\text{H}^+ \rightarrow 3\text{Br}_2 + 3 \text{H}_2\text{O}$
- For this reaction we found the rate law to be
- $\text{Rate} = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$
- To investigate this reaction rate we need to control the conditions

$$\text{Rate} = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$$

- We set up the experiment so that two of the reactants are in large excess.
- $[\text{BrO}_3^-]_0 = 1.0 \times 10^{-3} \text{ M}$
- $[\text{Br}^-]_0 = 1.0 \text{ M}$
- $[\text{H}^+]_0 = 1.0 \text{ M}$
- As the reaction proceeds $[\text{BrO}_3^-]$ changes noticeably
- $[\text{Br}^-]$ and $[\text{H}^+]$ don't

$$\text{Rate} = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$$

- This rate law can be rewritten
- $\text{Rate} = k[\text{BrO}_3^-][\text{Br}^-]_0[\text{H}^+]_0^2$
- $\text{Rate} = k[\text{Br}^-]_0[\text{H}^+]_0^2[\text{BrO}_3^-]$
- $\text{Rate} = k'[\text{BrO}_3^-]$
- This is called a pseudo first order rate law.
- $k = \frac{k'}{[\text{Br}^-]_0[\text{H}^+]_0^2}$

Reaction Mechanisms

- The series of steps that actually occur in a chemical reaction.
- Kinetics can tell us something about the mechanism
- A balanced equation does not tell us how the reactants become products.

Reaction Mechanisms

- $2\text{NO}_2 + \text{F}_2 \longrightarrow 2\text{NO}_2\text{F}$
- $\text{Rate} = k[\text{NO}_2][\text{F}_2]$
- The proposed mechanism is
- $\text{NO}_2 + \text{F}_2 \longrightarrow \text{NO}_2\text{F} + \text{F}$ (slow)
- $\text{F} + \text{NO}_2 \longrightarrow \text{NO}_2\text{F}$ (fast)
- F is called an intermediate. It is formed then consumed in the reaction

Reaction Mechanisms

- Each of the two reactions is called an elementary step.
- The rate for a reaction can be written from its molecularity.
- Molecularity is the number of pieces that must come together.
- Elementary steps add up to the balanced equation

- Unimolecular step involves one molecule - Rate is first order.
- Bimolecular step - requires two molecules - Rate is second order
- Termolecular step - requires three molecules - Rate is third order
- Termolecular steps are almost never heard of because the chances of three molecules coming into contact at the same time are miniscule.

Molecularity and Rate Laws

- | | |
|--|--|
| ▪ $\text{A} \longrightarrow \text{products}$ | Rate = $k[\text{A}]$ |
| ▪ $\text{A} + \text{A} \longrightarrow \text{products}$ | Rate = $k[\text{A}]^2$ |
| ▪ $2\text{A} \longrightarrow \text{products}$ | Rate = $k[\text{A}]^2$ |
| ▪ $\text{A} + \text{B} \longrightarrow \text{products}$ | Rate = $k[\text{A}][\text{B}]$ |
| ▪ $\text{A} + \text{A} + \text{B} \longrightarrow \text{Products}$ | Rate = $k[\text{A}]^2[\text{B}]$ |
| ▪ $2\text{A} + \text{B} \longrightarrow \text{Products}$ | Rate = $k[\text{A}]^2[\text{B}]$ |
| ▪ $\text{A} + \text{B} + \text{C} \longrightarrow \text{Products}$ | Rate = $k[\text{A}][\text{B}][\text{C}]$ |

How to get rid of intermediates

- They can't appear in the rate law.
- Slow step determines the rate and the rate law
- Use the reactions that form them
- If the reactions are fast and irreversible the concentration of the intermediate is based on stoichiometry.
- If it is formed by a reversible reaction set the rates equal to each other.

Formed in reversible reactions

- $2 \text{NO} + \text{O}_2 \longrightarrow 2 \text{NO}_2$
- Mechanism
- $2 \text{NO} \rightleftharpoons \text{N}_2\text{O}_2$ (fast)
- $\text{N}_2\text{O}_2 + \text{O}_2 \longrightarrow 2 \text{NO}_2$ (slow)
- $\text{rate} = k_2[\text{N}_2\text{O}_2][\text{O}_2]$
- $k_1[\text{NO}]^2 = k_{-1}[\text{N}_2\text{O}_2]$ (equilibrium)
- $\text{Rate} = k_2 (k_1 / k_{-1}) [\text{NO}]^2 [\text{O}_2]$
- $\text{Rate} = k [\text{NO}]^2 [\text{O}_2]$

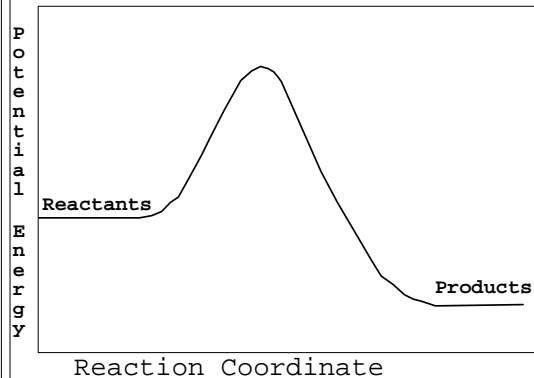
Formed in fast reactions

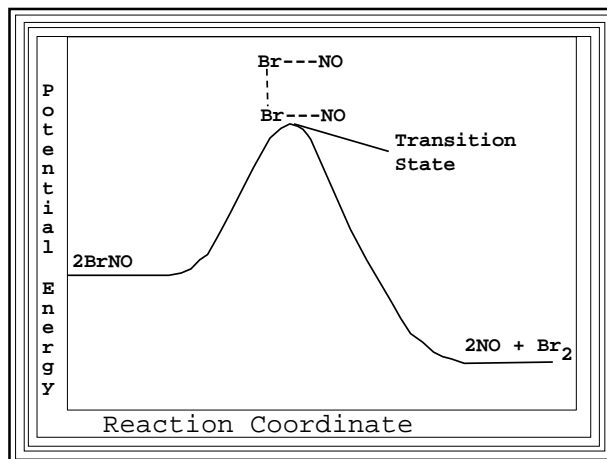
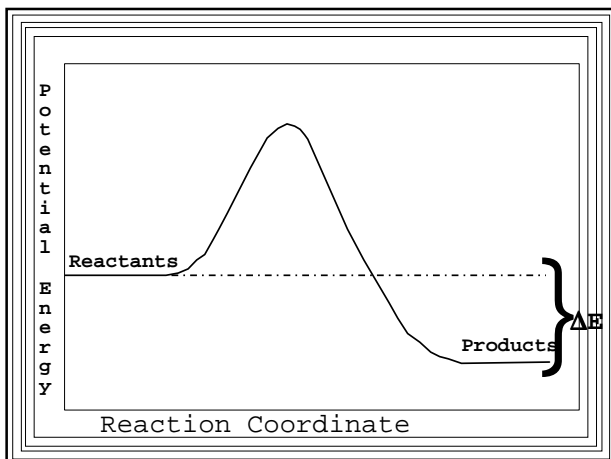
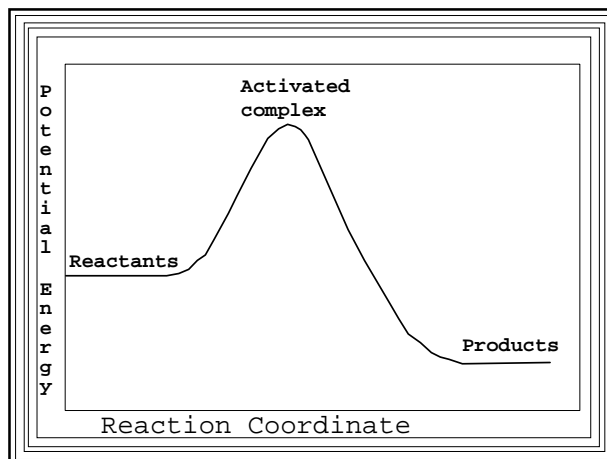
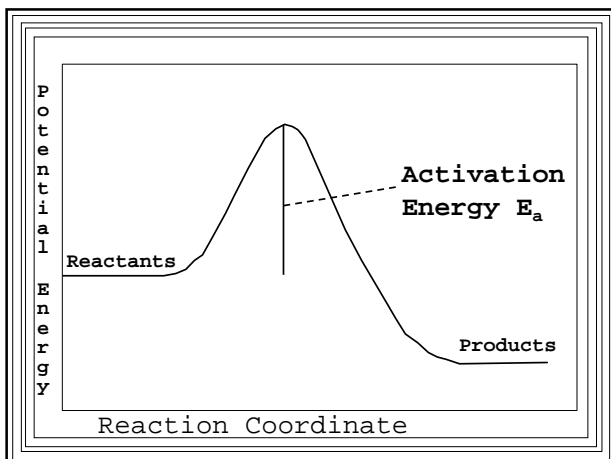
- $2 \text{IBr} \longrightarrow \text{I}_2 + \text{Br}_2$
- Mechanism
- $\text{IBr} \longrightarrow \text{I} + \text{Br}$ (fast)
- $\text{IBr} + \text{Br} \longrightarrow \text{I} + \text{Br}_2$ (slow)
- $\text{I} + \text{I} \longrightarrow \text{I}_2$ (fast)
- $\text{Rate} = k[\text{IBr}][\text{Br}]$ but $[\text{Br}] = [\text{IBr}]$ because the first step is fast
- $\text{Rate} = k[\text{IBr}][\text{IBr}] = k[\text{IBr}]^2$

- $2 \text{NO}_2\text{Cl} \rightarrow 2 \text{NO}_2 + \text{Cl}_2$
(balanced equation)
- $\text{NO}_2\text{Cl} \rightarrow \text{NO}_2 + \text{Cl}$ (slow)
- $\text{NO}_2\text{Cl} + \text{Cl} \rightarrow \text{NO}_2 + \text{Cl}_2$ (fast)

Collision theory

- Molecules must collide to react.
- Concentration affects rates because collisions are more likely.
- Must collide hard enough.
- Temperature and rate are related.
- Only a small number of collisions produce reactions.





Terms

- Activation energy - the minimum energy needed to make a reaction happen.
- Activated Complex or Transition State - The arrangement of atoms at the top of the energy barrier.

Arrhenius

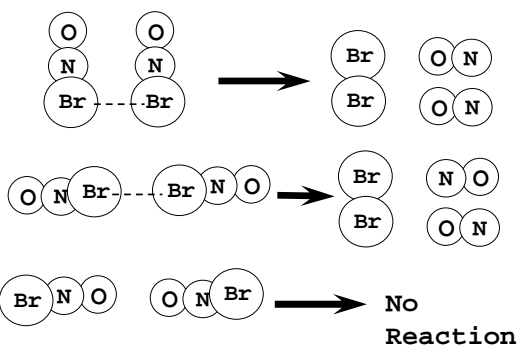
- Said the at reaction rate should increase with temperature.
- At high temperature more molecules have the energy required to get over the barrier.
- The number of collisions with the necessary energy increases exponentially.

Arrhenius

- Number of collisions with the required energy = $ze^{-E_a/RT}$
- z = total collisions
- e is Euler's number (inverse of \ln)
- E_a = activation energy
- R = ideal gas constant (in J/K mol)
- T is temperature in Kelvin

Problem with this

- Observed rate is too small
- Due to molecular orientation- they have to be facing the right way
- written into equation as p the steric factor.



Arrhenius Equation

- $k = zpe^{-E_a/RT} = Ae^{-E_a/RT}$
- A is called the frequency factor = zp
- k is the rate constant
- $\ln k = -(E_a/R)(1/T) + \ln A$
- Another line !!!!
- $\ln k$ vs $1/T$ is a straight line
- With slope E_a/R so we can find E_a
- And intercept $\ln A$

- A reaction is found to have a rate constant of $8.60 \times 10^{-1} \text{sec}^{-1}$ at 523 K and an activation energy of 120.8 kJ/mol. What is the value of the rate constant at 270 K?

Which statement is true concerning the plot of rate constants at various temperatures for a particular reaction?

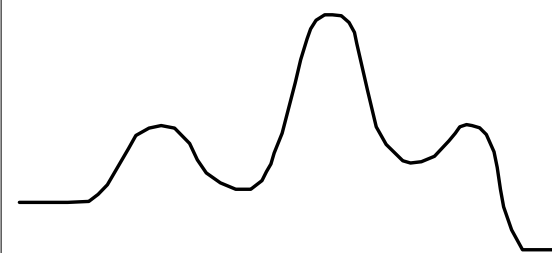
- A steep slope of the $\ln k$ versus $1/T$ plot is indicative of small changes in the rate constant for a given increase in temperature.
- Different sections of the $\ln k$ versus $1/T$ plot show different E_a values.
- The plot of k versus T shows a linear increase in k as the temperature increases.
- A steep slope of the $\ln k$ versus $1/T$ plot is indicative of a large E_a .
- The y-intercept of the $\ln k$ versus $1/T$ plot is the E_a value for that reaction

Activation Energy and Rates

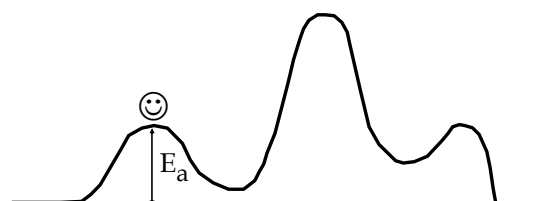
The final saga

Mechanisms and rates

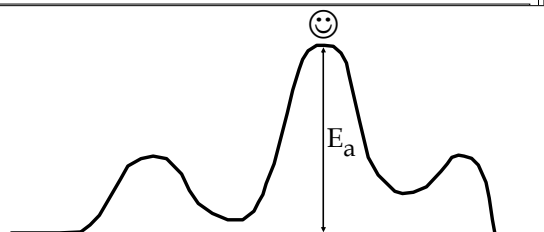
- There is an activation energy for each elementary step.
- Activation energy determines k .
- $k = Ae^{-E_a/RT}$
- k determines rate
- Slowest step (rate determining) must have the highest activation energy.



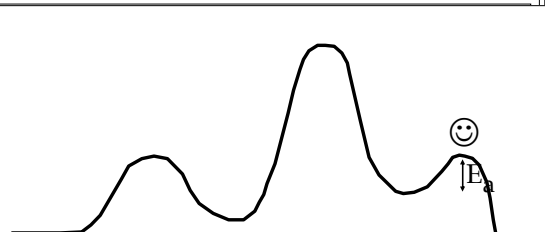
- This reaction takes place in three steps



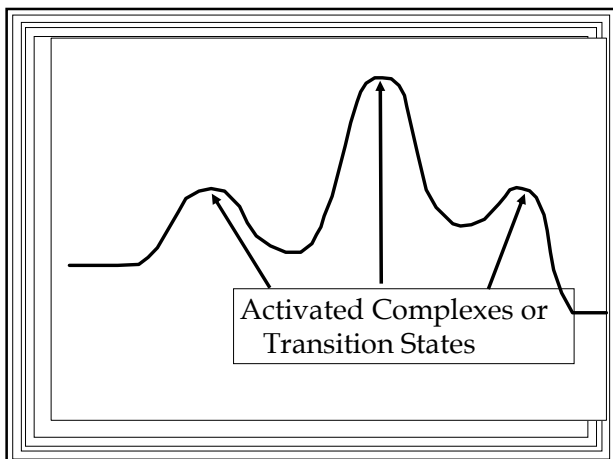
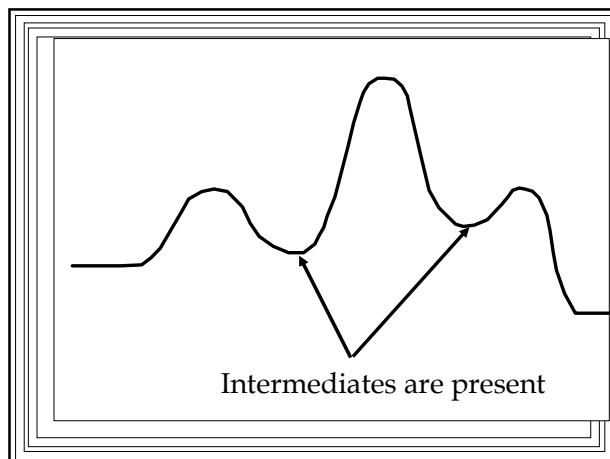
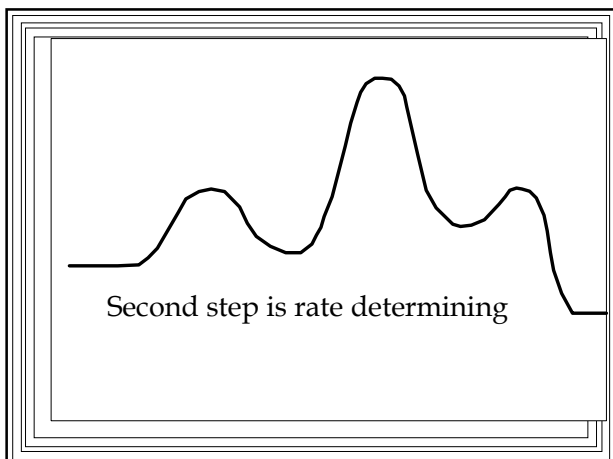
First step is fast
Low activation energy



Second step is slow
High activation energy



Third step is fast
Low activation energy

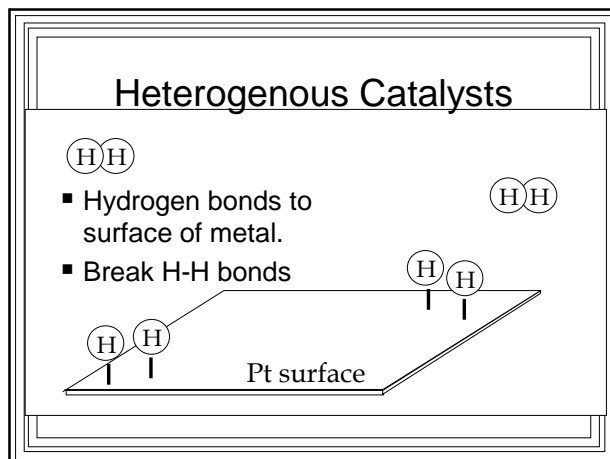


Catalysts

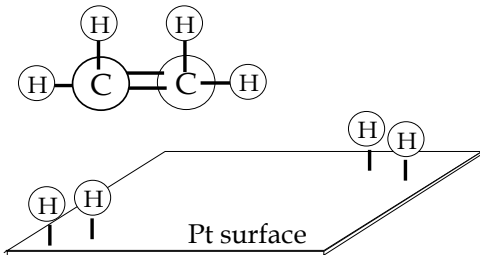
- Speed up a reaction without being used up in the reaction.
- Enzymes are biological catalysts.
- Homogenous Catalysts are in the same phase as the reactants.
- Heterogeneous Catalysts are in a different phase as the reactants.

How Catalysts Work

- Catalysts allow reactions to proceed by a different mechanism - a new pathway.
- New pathway has a lower activation energy.
- More molecules will have this activation energy.
- Does not change ΔE
- Show up as a reactant in one step and a product in a later step

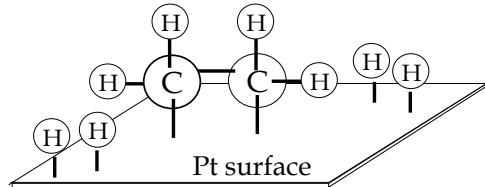


Heterogenous Catalysts



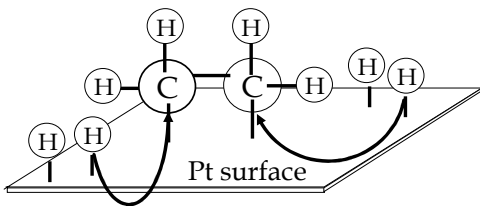
Heterogenous Catalysts

- The double bond breaks and bonds to the catalyst.

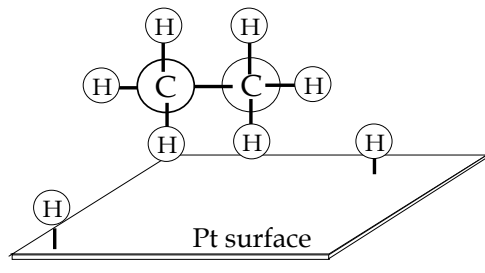


Heterogenous Catalysts

- The hydrogen atoms bond with the carbon



Heterogenous Catalysts



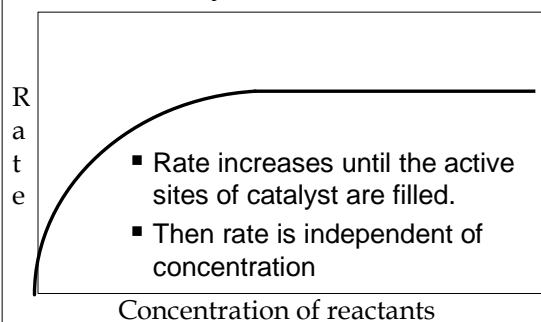
Homogenous Catalysts

- Chlorofluorocarbons (CFCs) catalyze the decomposition of ozone.
- Enzymes regulating the body processes. (Protein catalysts)

Catalysts and rate

- Catalysts will speed up a reaction but only to a certain point.
- Past a certain point adding more reactants won't change the rate.
- Zero Order

Catalysts and rate.



The
End