

## 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

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

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## 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.

- ▶ 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.

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

## How to get rid of intermediates

- ▶ 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

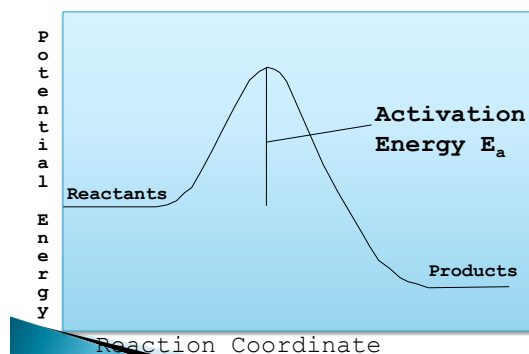
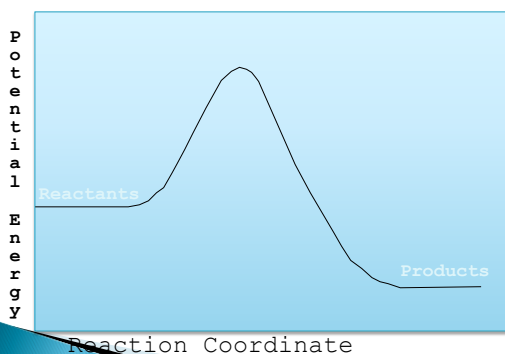
- ▶  $2 \text{NO} + \text{O}_2 \rightarrow 2 \text{NO}_2$
- ▶ Mechanism
- ▶  $2 \text{NO} \leftrightarrow \text{N}_2\text{O}_2$  (fast)
- ▶  $\text{N}_2\text{O}_2 + \text{O}_2 \rightarrow 2 \text{NO}_2$  (slow)
- ▶  $\text{rate} = k_2[\text{N}_2\text{O}_2][\text{O}_2]$
- ▶  $k_1[\text{NO}]^2 = k_{-1}[\text{N}_2\text{O}_2]$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

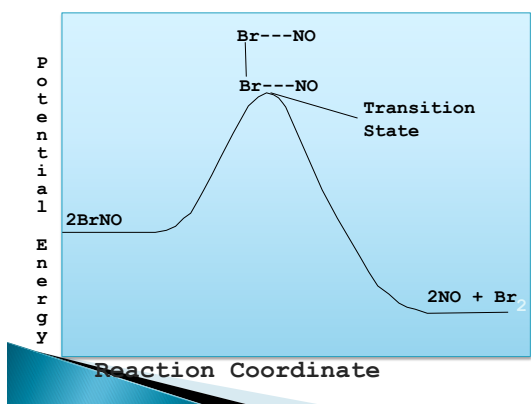
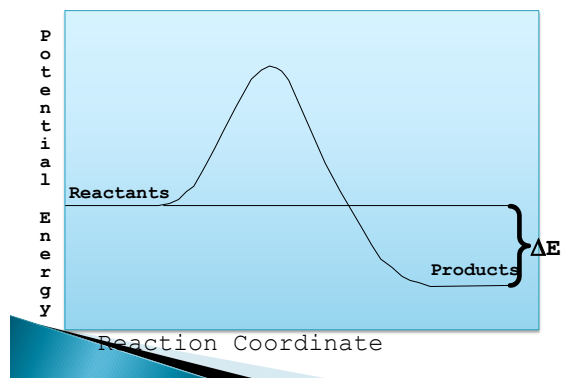
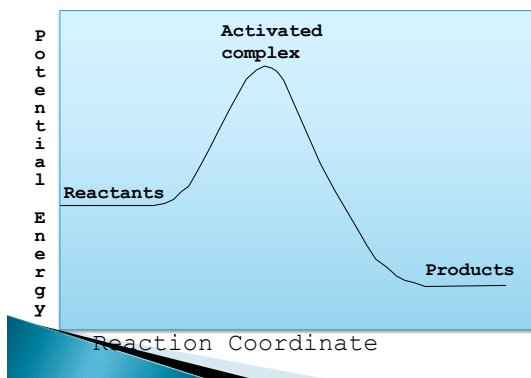
## Formed in fast reactions

- ▶  $2 \text{IBr} \rightarrow \text{I}_2 + \text{Br}_2$
- ▶ Mechanism
- ▶  $\text{IBr} \rightarrow \text{I} + \text{Br}$  (fast)
- ▶  $\text{IBr} + \text{Br} \rightarrow \text{I} + \text{Br}_2$  (slow)
- ▶  $\text{I} + \text{I} \rightarrow \text{I}_2$  (fast)
- ▶  $\text{Rate} = k[\text{IBr}][\text{Br}]$  but  $[\text{Br}] = [\text{IBr}]$
- ▶  $\text{Rate} = k[\text{IBr}][\text{IBr}] = k[\text{IBr}]^2$

## 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

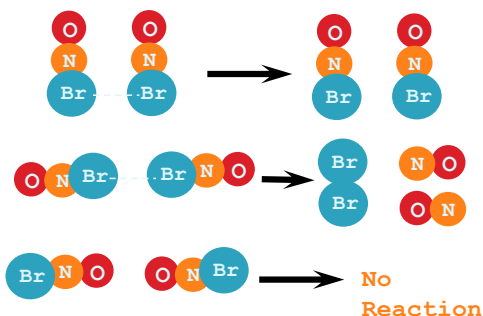
- ▶ Said the at reaction rate should increase with temperature.
- ▶ At high temperature more molecules have the energy required to get over the barrier.
- ▶ The number of collisions with the necessary energy increases exponentially.

## Arrhenius

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

## Problems

- Observed rate is less than the number of collisions that have the minimum energy.
- Due to Molecular orientation
- written into equation as  $p$  included in  $A$  the steric factor.

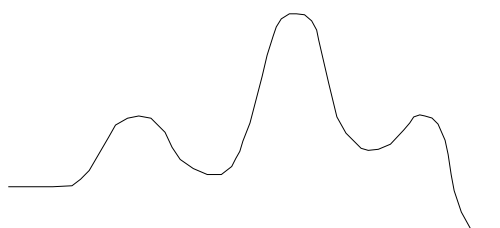


## Arrhenius Equation

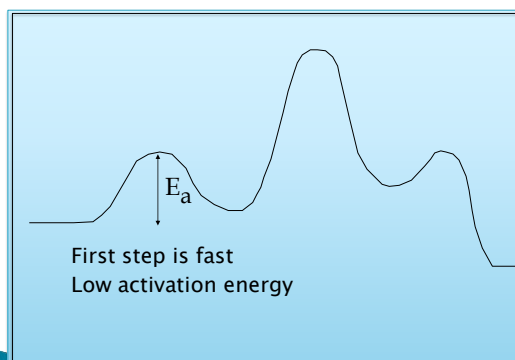
- $k = zpe^{-E_a/RT} = Ae^{-E_a/RT}$
- $A$  is called the frequency factor =  $zp$
- $\ln k = -(E_a/R)(1/T) + \ln A$
- Another line !!!!
- $\ln k$  vs  $1/T$  is a straight line

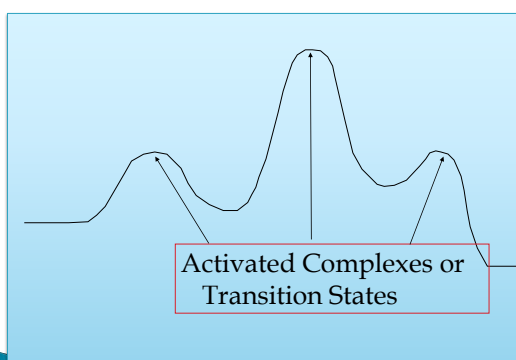
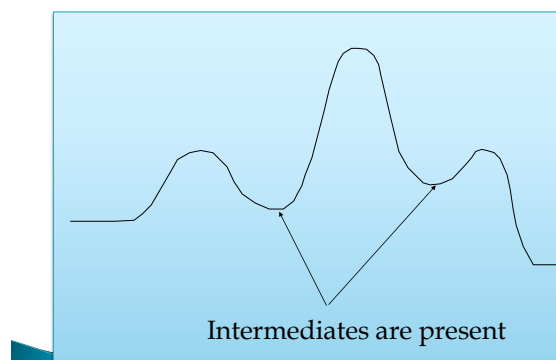
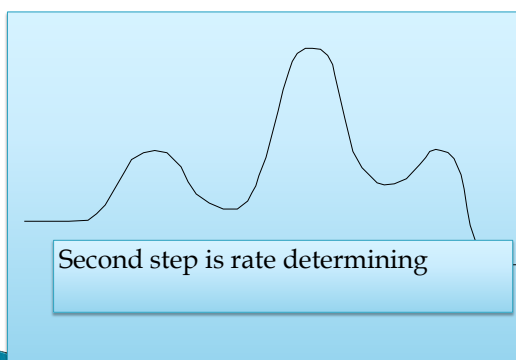
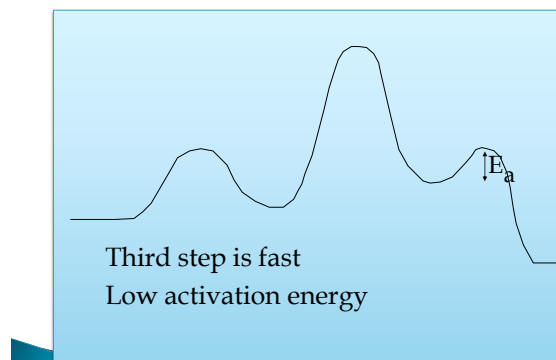
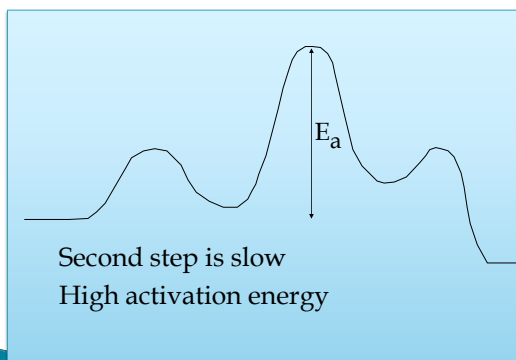
## Mechanisms and rates

- 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





## 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.

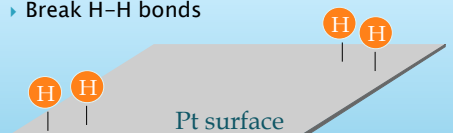
## How Catalysts Work

- ▶ 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.
- ▶ Do not change  $\Delta E$

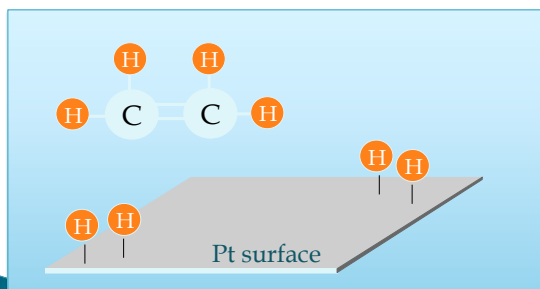
## Heterogenous Catalysts



- ▶ Hydrogen bonds to surface of metal.
- ▶ Break H-H bonds

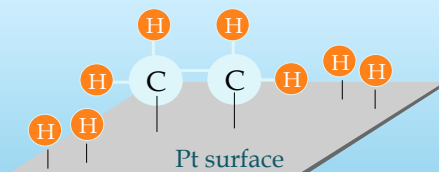


## Heterogenous Catalysts



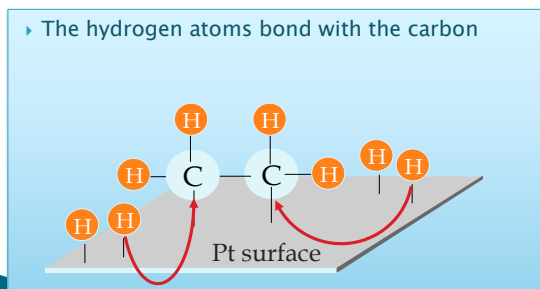
## Heterogenous Catalysts

- ▶ The double bond breaks and bonds to the catalyst.

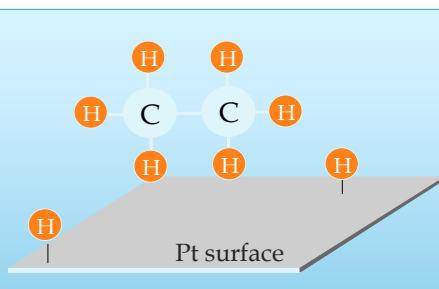


## Heterogenous Catalysts

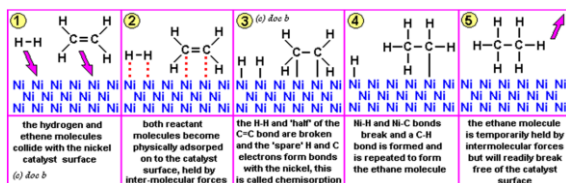
- ▶ The hydrogen atoms bond with the carbon



## Heterogenous Catalysts



## Heterogeneous Catalyst



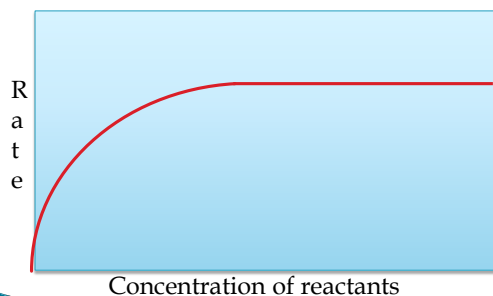
## Homogenous Catalysts

- ▶ Chlorofluorocarbons 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.



## When will you suggest a mechanism for a reaction?

- ▶ When the rate law is not equal to the law of mass action it implies that the reaction does not take place in a single step hence a mechanism should be suggested to satisfy the rate law if known.

## What are elementary steps in a mechanism?

- ▶ In a multi step reaction the single steps involved are called the elementary steps.
- ▶ The different elementary steps should add up to represent the actual reaction.

## What are reactive intermediates?

- ▶ Reactive intermediates are molecules, atoms or ions formed as a result of molecular interaction of the reactants or the cleavage of the covalent bonds in them. (the F atom in the above reaction is a reactive intermediate with high energy and looking for ways to stabilize ASAP)

## How can you identify a catalyst from a multistep reaction?

- ▶ Catalyst will appear as a reactant and will be produced on one or the other step. Since catalyst is always regenerated at the end of the reaction it should not appear when all the elementary steps are added up.

## What happens to the reactive intermediates in a reaction involving a multi step reaction?

- ▶ The reactive intermediates in the elementary steps have very short existence and high energy and usually they change rapidly into other products and will not be present in the final equation as they will cancel out in the subsequent elementary steps.

## Why is the slowest step an important step in determining the rate of the reaction?

- ▶ The elementary steps that involve cleavage of covalent bonds in aqueous solutions require large amount of energy and hence are slow reactions. **Energy of activation** is high. The quantity of products formed depends on the rate of the slowest step or RDS. The reactive intermediates are formed in the slow steps and hence the rate of reaction of the intermediate does not alter the rate of the reaction.

## Contd.....

- ▶ Elementary steps which are slow are the rate determining steps- hence rate law is written using this step. (The reactive intermediates are high energy species and hence will change quickly into other products rather fast and such elementary steps will usually be faster than the rate determining steps.)