

## Law of Mass Action

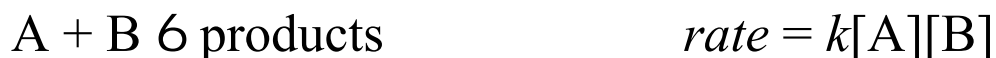
- L For any elementary reaction, the rate law expression for that step is proportional to the concentration of each reactant such that the molecularity determines the overall order.

### Rate Law Expressions for Elementary Reactions

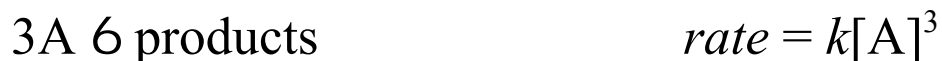
Unimolecular: one-body processes



Bimolecular: two-body collisions



Termolecular : three-body collisions (low probability)



## Concept of the Rate Determining Step

- L In many cases, one step in the proposed mechanism may be significantly slower than others.
  - U Such a step is called a *rate determining step*, because the overall reaction rate can be no faster than the rate at that step.
  - U The overall rate expression must be equivalent to the rate expression at the rate determining step.
- ( We can always write down the rate expression for the rate determining step, using the Law of Mass Action
- ; The rate determining step may involve concentrations of species that are created temporarily and then destroyed in the course of the mechanism, called *reaction intermediates*.
- K In order to make the comparison with the experimentally observed rate law expression, an equivalent expression in terms of *observable* reactants (*not* reaction intermediates) must be derived from the rate-determining step's rate expression.

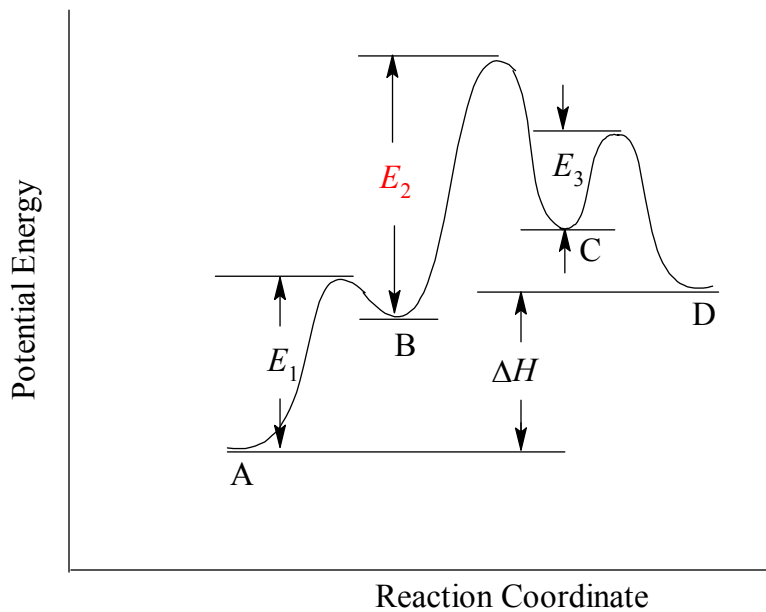
# Arrhenius Plot for a Hypothetical Reaction A → D

## Proceeding by a Three-Step Mechanism

Mechanism (**Step 2 rate determining**):

I	A → B	fast	rate <sub>1</sub> = k <sub>1</sub> [A]	) H <sub>1</sub> > 0			
II	B → C	slow	rate <sub>2</sub> = k <sub>2</sub> [B]	) H <sub>2</sub> > 0			
III	C → D	fast	rate <sub>3</sub> = k <sub>3</sub> [C]	) H <sub>3</sub> < 0			
<table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 30%;">A → D</td> <td style="width: 30%; text-align: center;">Rate / rate<sub>2</sub></td> <td style="width: 40%; text-align: right;">) H<sub>rxn</sub> &gt; 0</td> </tr> </table>					A → D	Rate / rate <sub>2</sub>	) H <sub>rxn</sub> > 0
A → D	Rate / rate <sub>2</sub>	) H <sub>rxn</sub> > 0					

Arrhenius Plot:



$$E_2 \gg E_1 > E_3$$

$$k_2 \ll k_1 < k_3$$

## **Requirements of a Plausible Proposed Mechanism**

1. The sum of the proposed steps of the mechanism must add to give the stoichiometry of the overall reaction.
2. The mechanism's derived rate law expression must be capable of being expressed in terms of the same observable reactant (and sometimes product) species as the experimentally observed rate law expression.
3. The reactant (and sometimes product) species' concentration dependencies (i.e., their orders) must be the same in both the proposed mechanism's rate law and the experimental rate law.

## Observed Rate and Proposed Mechanism

Overall Reaction:



Experimentally Determined Rate Law:

$$\text{Rate} = k_{\text{obs}}[\text{I}^-][\text{H}_2\text{O}_2]$$

Proposed Mechanism:



Derived Rate Law Expression for Mechanism:

$$\text{Rate} = \text{rate}_1 = k_1[\text{I}^-][\text{H}_2\text{O}_2] \quad (k_1 = k_{\text{obs}})$$

## Observed Rate and Proposed Mechanism

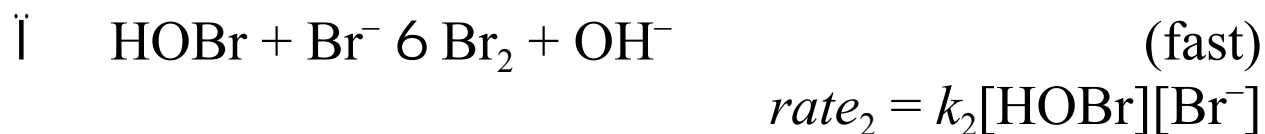
Overall Reaction:



Experimentally Determined Rate Law :

$$\text{Rate} = k_{\text{obs}}[\text{Br}^-][\text{H}^+][\text{H}_2\text{O}_2]$$

Proposed Mechanism:



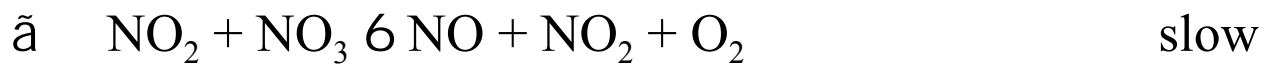
Derived Rate Law Expression for Mechanism:

$$\text{Rate} = \text{rate}_1 = k_1[\text{H}^+][\text{Br}^-][\text{H}_2\text{O}_2] \quad (k_1 = k_{\text{obs}})$$

**Proposed Mechanism for**  
 $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$

$$\text{Rate} = k_{\text{obs}}[\text{N}_2\text{O}_5]$$

Proposed mechanism:



Rate expressions from molecularity:

â  $rate_1 = k_1[\text{N}_2\text{O}_5] \quad rate_{-1} = k_{-1}[\text{NO}_2][\text{NO}_3]$

ã  $rate_2 = k_2[\text{NO}_2][\text{NO}_3]$  7 Rate determining

ä  $rate_3 = k_3[\text{NO}_3][\text{NO}]$

Therefore:

$$\text{Rate} = rate_2 = k_2[\text{NO}_2][\text{NO}_3]$$

; But  $\text{NO}_3$  is an unobservable reaction intermediate.

## Deriving an Expression for [NO<sub>3</sub>]

Step  $\hat{a}$  is a dynamic equilibrium, so

$$rate_1 = rate_{-1}$$

$$k_1[\text{N}_2\text{O}_5] = k_{-1}[\text{NO}_2][\text{NO}_3]$$

Solving for [NO<sub>3</sub>] gives

$$[\text{NO}_3] = \frac{k_1 [\text{N}_2\text{O}_5]}{k_{-1} [\text{NO}_2]}$$

Substituting into expression for  $rate_2$ :

$$Rate = k_2[\text{NO}_2] \frac{k_1 [\text{N}_2\text{O}_5]}{k_{-1} [\text{NO}_2]} = \frac{k_1 k_2}{k_{-1}} [\text{N}_2\text{O}_5]$$

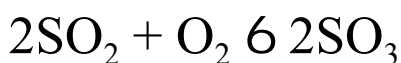
( Same as observed rate law if  $k_1 k_2 / k_{-1} = k_{\text{obs}}$

## Catalyst

- A catalyst is a substance that alters the rate of a reaction.
  - ┆ Most often a catalyst increases the reaction rate (*promoter*), but some catalysts slow the rate (*inhibitor*).
- A catalyst participates in the mechanism, offering an alternative path from reactants to products.
  - ┆ A catalyst that increases the rate lowers the overall activation energy of the reaction.
- A catalyst is usually not consumed in the course of the overall reaction.
  - ┆ The amount of catalyst at the beginning of the reaction is the same as that at the end of the reaction.
- A catalyst is *not* a reaction intermediate.
  - ┆ It is not produced and consumed in the course of the reaction.

## Mechanisms of SO<sub>2</sub> Oxidation Without and With NO Catalyst

Overall Reaction:



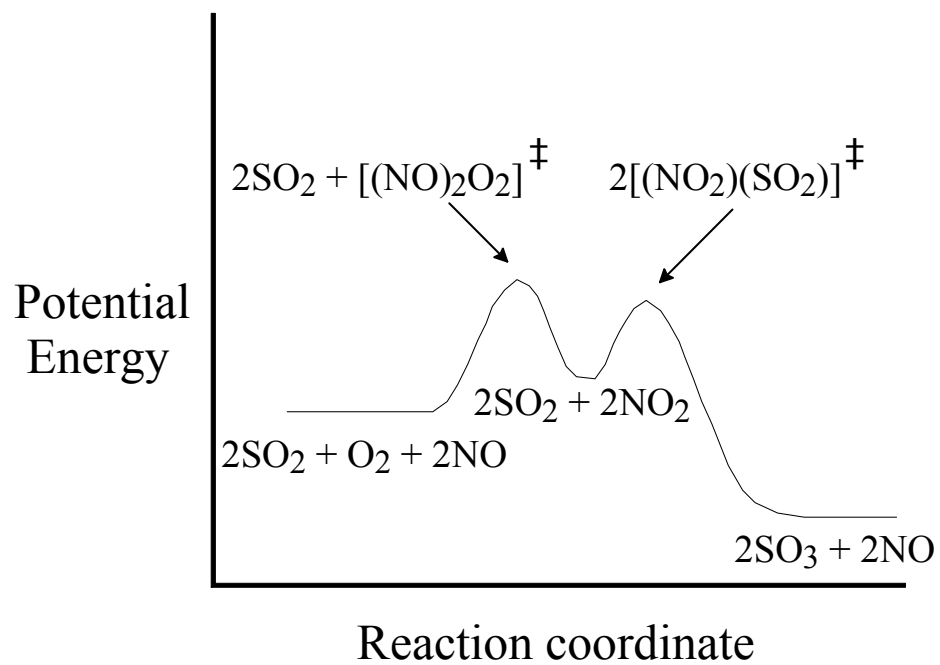
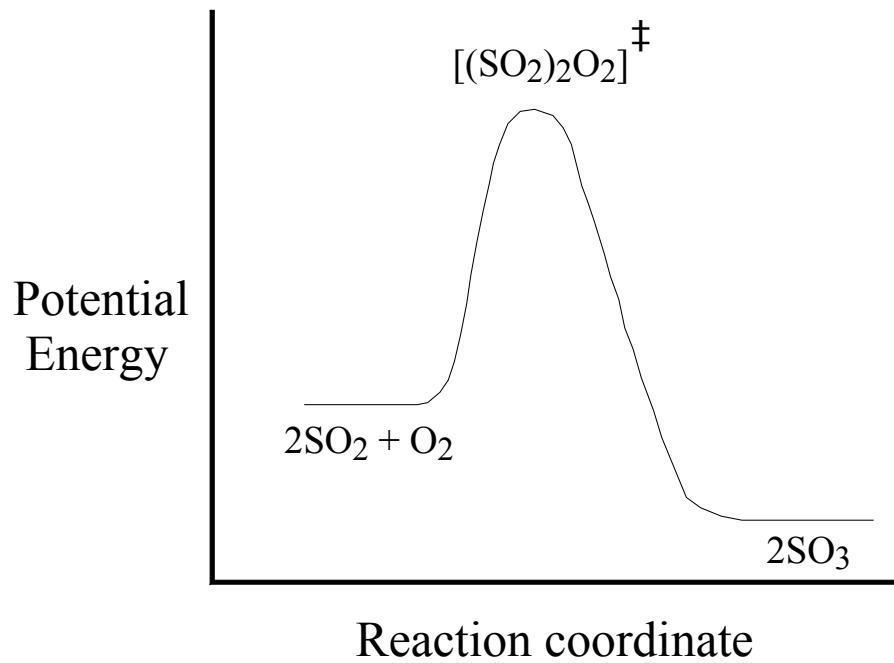
Uncatalyzed Mechanism:



Mechanism with NO Catalyst:



Arrhenius Plots  
for the Uncatalyzed and Catalyzed Reaction  
 $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$



# Heterogeneous Catalysis

$$\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$$
