

Rate Laws (3)

Reaction Mechanism

Each step in a reaction mechanism is an elementary step.

The sum of the elementary steps must give the overall balanced equation for the reaction.

The rate of the lowest elementary step is the overall rate of the reaction.

Molecularity is the number of molecules present in the elementary step. The molecularity determines the rate law of the elementary step.

If the elementary step has one molecule, then it is unimolecular, and it is first order.

If the elementary step has two molecules, then it is bimolecular, and it is second order.

If the elementary step has three molecules, then it is termolecular, and it is third order.

TABLE 12.7 Examples of Elementary Steps

Elementary Step	Molecularity	Rate Law
$A \rightarrow \text{products}$	<i>Unimolecular</i>	Rate = $k[A]$
$A + A \rightarrow \text{products}$ ($2A \rightarrow \text{products}$)	<i>Bimolecular</i>	Rate = $k[A]^2$
$A + B \rightarrow \text{products}$	<i>Bimolecular</i>	Rate = $k[A][B]$
$A + A + B \rightarrow \text{products}$ ($2A + B \rightarrow \text{products}$)	<i>Termolecular</i>	Rate = $k[A]^2[B]$
$A + B + C \rightarrow \text{products}$	<i>Termolecular</i>	Rate = $k[A][B][C]$

Rate determining step controls reaction rate;

Reaction mechanism is the way in which a chemical reaction takes place, expressed in a series of chemical equations.

Intermediate is a specie that forms during a reaction, but is then consumed. It does not appear as final product. It is considered a stepping stone between the parent substance and the final product.

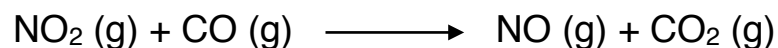
In a multistep chemical reaction, the lowest step in the rate-determining step. The reaction can not go faster than its slowest step.

The first requirement for an acceptable mechanism is that the sum of the steps should give the balanced equation

The second requirement is that the mechanism must agree with the experimentally determined rate law. Since the proposed mechanism states that the slow step is the rate determining step, the overall reaction rate must be that of the slow step.

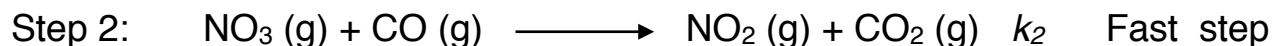
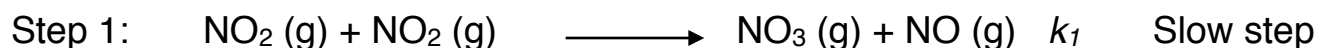
The theoretical rate has to agree with the experimental rate law.

Consider this reaction:



The experimentally derived rate law is: Experimental Rate = $K [\text{NO}_2]^2$

We propose a mechanism for the reaction:

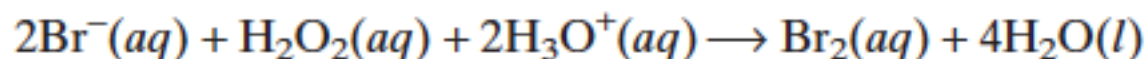


Note that NO_3 is an intermediate. It is formed in step 1 and then consumed in step 2.

$k_2 \gg k_1$, then the overall reaction will depend on the first step (the rate determining step)

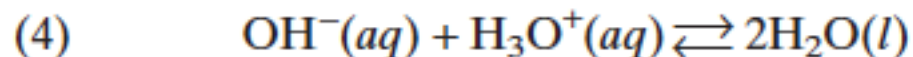
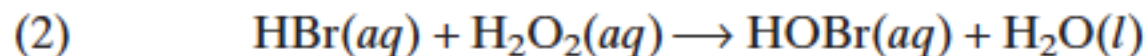
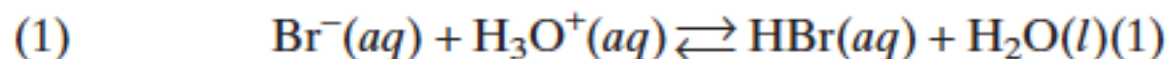
$$\text{Theoretical Rate} = k_1 [\text{NO}_2]^2$$

This theoretical rate is in agreement with the experimental rate law.



The order with respect to each of the three reactants was found to be 1.

The reaction is believed to take place in four steps, in the mechanism below:



These four steps add up to the overall reaction that was shown above.

Three of the steps are shown as equilibria. These are fast reactions.

Step 2, however is slow. It controls the overall reaction rate. It is the rate-determining step.

HOBr is an intermediate. It is formed during step 2, but then consumed in step 3.

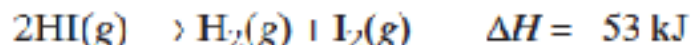
Reaction pathways and activation energy

Activation energy (E_a) is the minimum energy required to start a chemical reaction. The rate depends on the magnitude of the E_a . In general, the lower the E_a , the faster the rate.

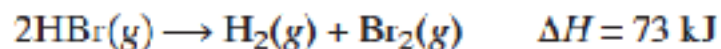
Activation energy is the minimum energy that a pair of colliding molecules (or atoms or ions) need to have before chemical change becomes a possibility. The pair then collide violently enough to overcome the mutual repulsion. The electron clouds of the two molecules merge to some extent and new bonds are created.

Activation-Energy diagram model reaction progress.

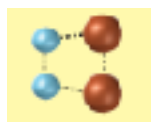
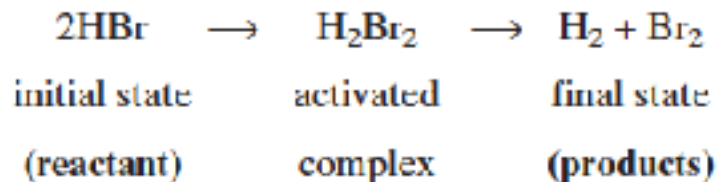
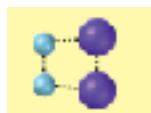
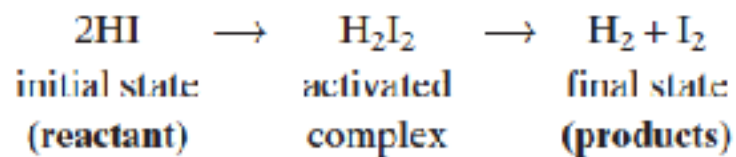
Hydrogen iodide decomposition is exothermic (releases energy). The energy of the product is lower than that of the reactants.



Hydrogen bromide decomposition is endothermic (gains energy). The energy of the product is higher than that of the reactants.



Transition state of the reaction has the activated complex. It is the most unstable state of two molecules that collide with combined kinetic energy equal to the activation energy. At the transition state, there is a 50:50 chance of either returning to the initial state without reacting, or of being rearranged and becoming product.



The activation energy (E_a) of hydrogen bromide is less than that of hydrogen iodide. Therefore, hydrogen bromide decomposed more quickly.

Activation Energies for the Decomposition of HI and HBr

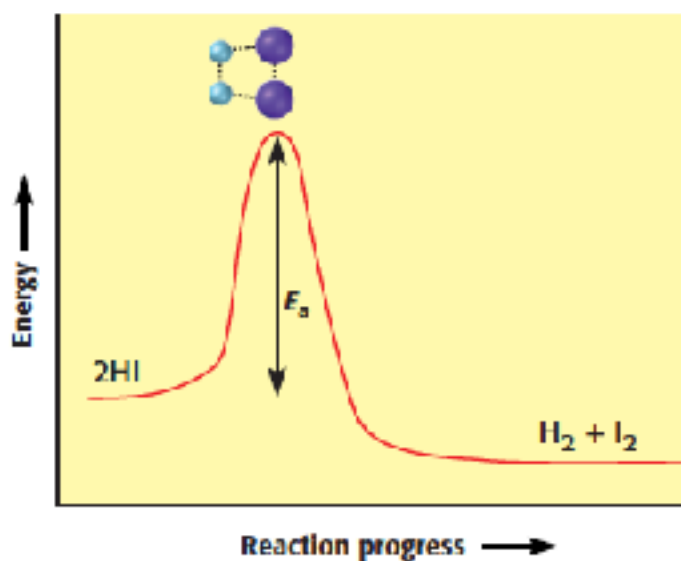
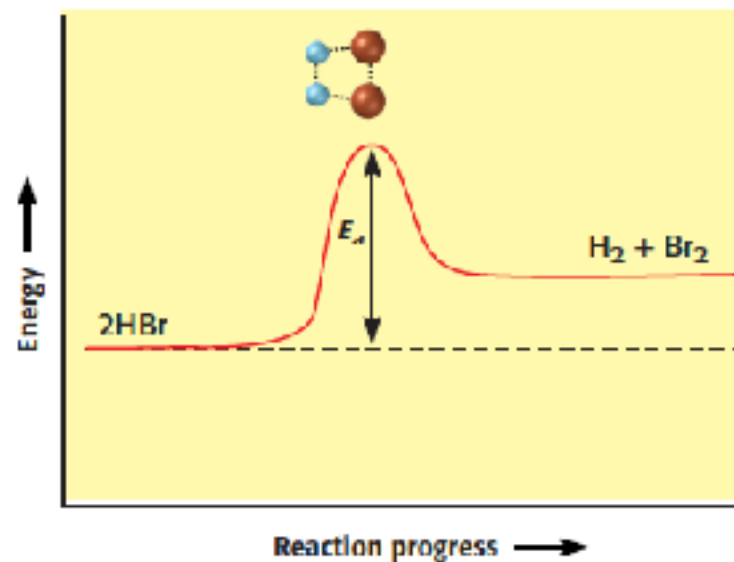


Figure 9

a The difference in energy between the bottom of this curve and the peak is the energy of activation for the decomposition of HI.



b The decomposition of HBr occurs at a faster rate than the decomposition of HI because this reaction has a lower activation energy.

Not all collision result in reaction:

Two factors are important for a reaction to happen when reacting molecules collide:

- 1- The molecules must collide with enough energy to overcome the activation energy.
- 2- The molecules must collide with the correct orientation.
- 3- The fraction of molecules with energy equal to or greater than E_a is given by:

$$f = e^{-E_a/RT}$$

As we increase the temperature, the fraction of the population that has an energy equal to or greater than E_a increases. Thus more molecules can react.

Example:

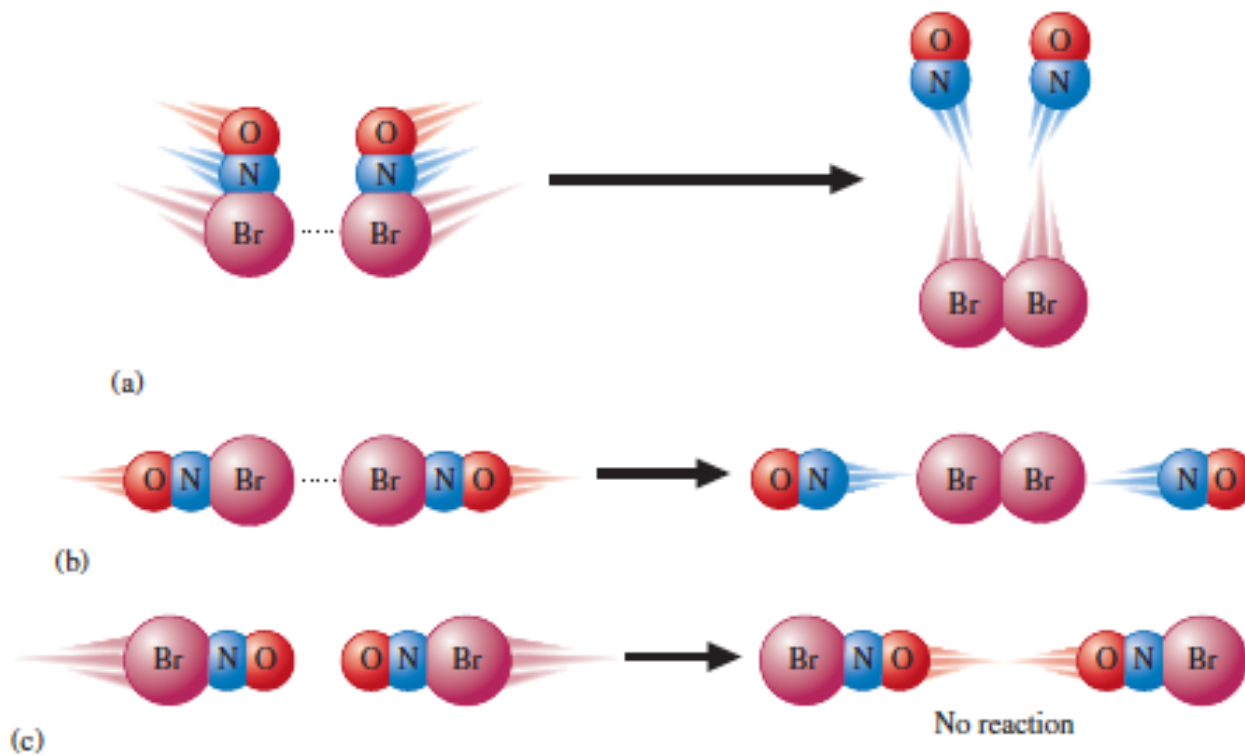


if the chlorine molecule collides with the oxygen end of the nitrogen monoxide and with kinetic energy to overcome the activation energy, the following reaction will occur.

On the other hand, this reaction will not occur if the chlorine molecule strikes the nitrogen end of the molecule, no matter how much kinetic energy they have.

Example:

Orientation is (a) and (b) lead to a reaction, but orientation (c) can not.



Catalyst Increase Reaction Rate.

Adding more reactant will usually increase the rate of a reaction. Adding extra product will sometimes cause the rate to decrease.

Adding catalyst to a reaction mixture will increase the reaction rate. Catalyst increases the rate of a chemical reaction by lowering the activation energy barrier. Catalyst saves enormous amount of energy.

Catalyst is not consumed during a chemical reaction. It is regenerated and used again and again. The catalyst will be collected unchanged at the end of the reaction.

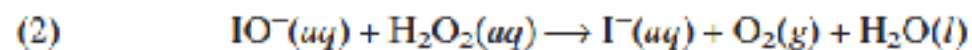
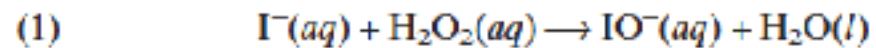
Catalyst does not change the overall reaction, the stoichiometry or the thermodynamics. The changes affect only the path the reaction takes from reactant to products. The new pathway has a different mechanism and a different rate law from that of the un-catalyzed.

Example:

Decomposition of hydrogen peroxide: Uncatalyzed

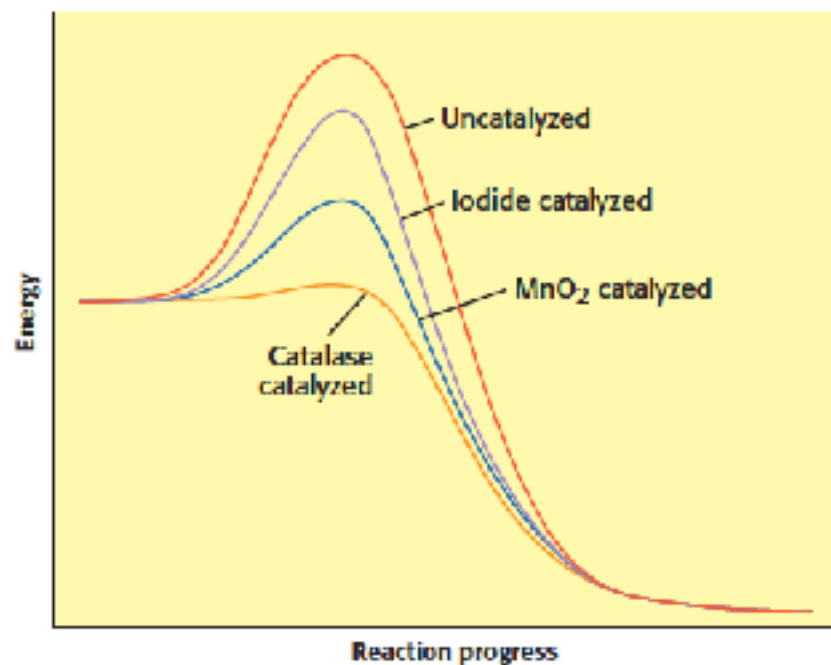


Iodide -catalyzed decomposition of hydrogen peroxide.



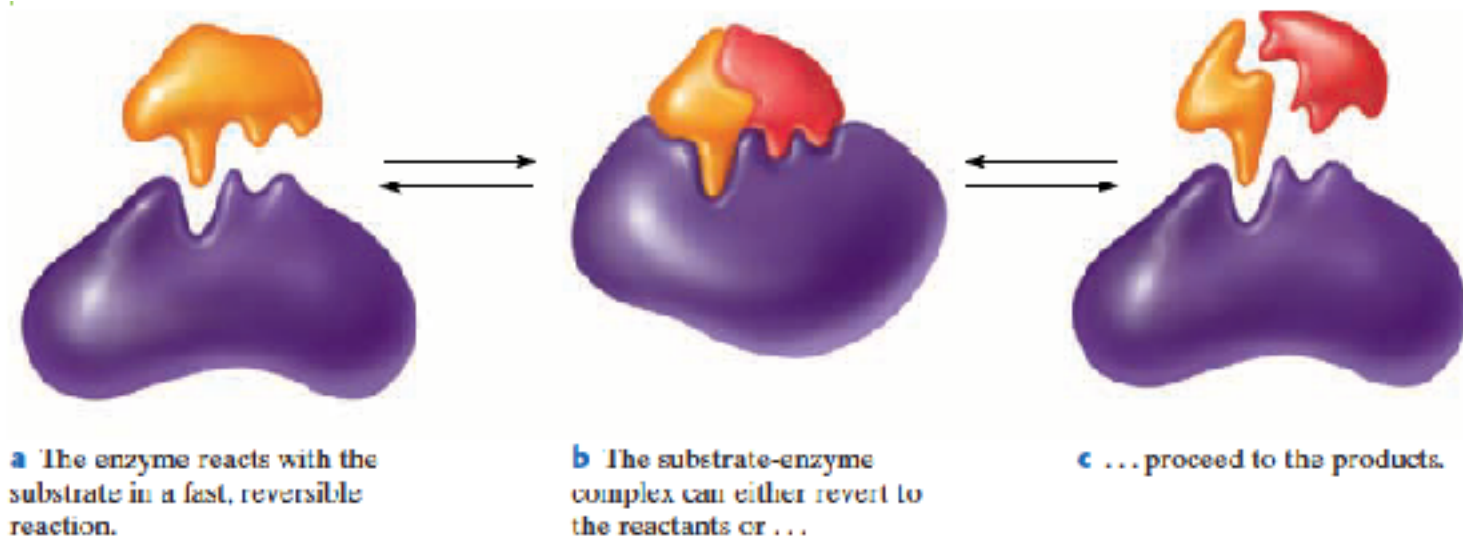
Notice that iodide is consumed in step 1, then regenerated in step 2. IO^{-} is an intermediate.

Comparison of Pathways for the Decomposition of H_2O_2



Enzymes are catalysts found in nature

Enzyme is a type of protein that speeds up metabolic reactions in plants and animals without being permanently changed or destroyed.



Factors that Affect Reaction Rates

There are several important factors, which affect rate of reactions.

- 1) **Physical state of the reactants**: reactant must come together and collide in order to react.
- 2) **Concentration of the reactants**: most chemical reactions proceed faster if the concentration of one or more reactant increased.
- 3) **Temperature of the reaction**: as T increase, the molecules move faster, they collide more frequently with high energy, leading to increased rate.
- 4) **Presence of catalyst**: catalysts are agents that increase reaction rates without being used up. They affect the kinds of collisions that lead the reaction.

The **RATE**, not the rate constant (k), depends on **CONCENTRATION**.

The **RATE CONSTANT** (k) is affected by **TEMPERATURE** and by the presence of a **CATALYST**.