

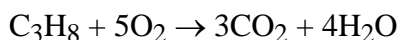
Reaction Mechanism

A **reaction mechanism** is a sequence of elementary steps which describe the process by which reactants change to products in a chemistry reaction.

An **elementary step** is a reaction which directly describes collisions on a molecular level.

Most overall reactions are not elementary.

Consider the reaction for the combustion of propane



Why is this reaction **not** an elementary reaction?

The reaction shows 1 molecule of C_3H_8 reacting with 5 molecules of O_2 . This is the correct overall stoichiometry, but could not be a description of molecular collisions. Such a description would involve 6 molecules (1 C_3H_8 and 5 O_2) colliding at once. This is highly unlikely. In a mixture of gases, the most likely number of molecules to collide at once is two. Such a collision is bimolecular. Rarely, but still possible, three molecules collide at once. This is called termolecular. It is also possible for one molecule to come apart. This is called unimolecular.

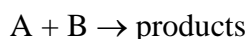
In order for a mechanism to be correct:

- (1) The steps must add up to the overall reaction
- (2) Each step must be elementary. This means that it could involve no more than three (usually no more than two) molecules colliding.
- (3) It must be consistent with the experimental rate law.

We have said before that the rate law cannot be predicted from the overall reaction.

However, we can infer the rate law for elementary reactions, since these are directly describing molecular collisions.

Consider a bimolecular elementary reaction:



In this bimolecular collision, the collision frequency, and thus the rate, is proportional to both concentrations. Doubling the A concentration doubles the collision frequency of A with B; doubling the B concentration doubles the collision frequency of A with B; doubling both A and B concentrations quadruples the collision frequency of A with B. This is mathematically expressed as:

$$\text{Rate} = k[\text{A}][\text{B}] \text{ for a bimolecular collision of A with B}$$

In a similar way, we can infer the rate law for other elementary reactions.

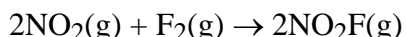
Elementary Reaction Molecularity

Rate Law

$A \rightarrow \text{product}$	Unimolecular	Rate = $k[A]$
$A + B \rightarrow \text{product}$	Bimolecular	Rate = $k[A][B]$
$A + A \rightarrow \text{product}$	Bimolecular	Rate = $k[A]^2$
$2A + B \rightarrow \text{product}$	Termolecular	Rate = $k[A]^2[B]$
$A + B + C \rightarrow \text{product}$	Termolecular	Rate = $k[A][B][C]$

The **molecularity** of a reaction is the number of molecules colliding. For elementary processes, the molecularity equals the order. A unimolecular process is first order, a bimolecular process is second order, and a termolecular process is third order.

Let's apply these principles to several examples.



Could this reaction be elementary?

Conceivably yes, since there are three molecules involved. But unlikely. What would be the rate law if this were an elementary process?

If elementary: Rate = $k[\text{NO}_2]^2[\text{F}_2]$

The experimental overall rate law is:

$$\text{Rate} = k[\text{NO}_2][\text{F}_2]$$

This experimental rate law shows that the rate is first order in both $[\text{NO}_2]$ and $[\text{F}_2]$, meaning that the rate is proportional to both these concentrations. The rate is equally dependent on both $[\text{NO}_2]$ and $[\text{F}_2]$. If the mechanism actually involved 2NO_2 colliding with an F_2 , the rate would depend more on $[\text{NO}_2]$ than $[\text{F}_2]$, since each collision would have 2NO_2 for each 1F_2 . Therefore, the overall equation is not elementary.

Proposed mechanism:

- $\text{NO}_2 + \text{F}_2 \rightarrow \text{NO}_2\text{F} + \text{F}$ slow
- $\text{NO}_2 + \text{F} \rightarrow \text{NO}_2\text{F}$ fast

Is this mechanism correct?

Each step has two molecules colliding (bimolecular). Looks reasonable.

The two steps add up to the overall reaction. The F atom formed in the first step is used up in the second step. The F atom is called an **intermediate**, something which is formed temporarily in one part of the mechanism, and then used up in a subsequent step.

Is the mechanism consistent with the experimental rate law? Assume each step has rate constants k_1 , k_2 .

Step 1: Rate = $k_1[\text{NO}_2][\text{F}_2]$ (bimolecular)

Step 2: Rate = $k_2[\text{NO}_2][\text{F}]$ (bimolecular)

In most mechanisms, one step is much slower than the others. This slow step is called the **rate-determining step**. We can assume that all other steps are rapid, almost instantaneous, compared with the slow rate-determining step, meaning that the rate of the overall reaction equals the rate of the rate-determining step. The rate-determining step is the step with the highest activation energy,

In our mechanism, we have specified step 1 as the slow step. If step 1 is the rate determining step, then step 2 is very rapid compared with step 1, and the rate of the overall reaction equals the rate of step 1. This matches our experimental data.

Step 1: Rate = $k_1[\text{NO}_2][\text{F}_2]$

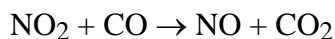
Experimental rate law: Rate = $k[\text{NO}_2][\text{F}_2]$

The mechanism is consistent with the experimental rate law.

Why would we expect step 1 to be much slower than step 2?

Step 1 involves a collision between NO_2 and F_2 . In this collision the F_2 bond must break and one F atom attaches to NO_2 . Only collisions with enough energy will be able to break the F_2 bond.

Step 2 has no bond breaking. An F atom attaches to NO_2 . This would require very little activation energy. In addition, our knowledge of chemistry tells us that F atoms would be extremely reactive, since F has the highest electronegativity of any element.



Experimental Rate Law:

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

Could the equation represent an elementary reaction?

Since the equation shows only two molecules reacting, it could easily be an elementary reaction. However, the rate law in such a case would be:

$$\text{Rate} = k[\text{NO}_2][\text{CO}] \quad (\text{collision between } \text{NO}_2 \text{ and } \text{CO})$$

Since the experimental rate law is: Rate = $k[\text{NO}_2]^2$, the mechanism is not just a simple bimolecular collision between NO_2 and CO .

Proposed mechanism

1. $\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO}$ slow
2. $\text{NO}_3 + \text{CO} \rightarrow \text{CO}_2 + \text{NO}_2$ fast

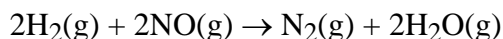
Adding up the equations, the NO_3 intermediate cancels out, and we get the overall equation:
 $\text{NO}_2 + \text{CO} \rightarrow \text{CO}_2 + \text{NO}$

Each step is bimolecular which is typical for an elementary process.

The rate law would be the rate of the slow rate-determining step. If the first step, involving the collisions of two NO_2 molecules, is the slow step then:

$$\text{Rate of first step} = k[\text{NO}_2]^2$$

This is consistent with the overall experimental rate law. Notice that the reaction is second order in NO_2 and zero order in CO . The CO concentration doesn't affect the rate, since the CO is not in the rate determining step.



$$\text{Experimental rate law: Rate} = k[\text{H}_2][\text{NO}]^2$$

Proposed Mechanism:

1. $2\text{NO} \rightleftharpoons \text{N}_2\text{O}_2$ fast equilibrium
2. $\text{N}_2\text{O}_2 + \text{H}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$ slow
3. $\text{N}_2\text{O} + \text{H}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O}$ fast

There are two intermediates: N_2O_2 and N_2O . Adding up steps 1,2,3, we see that these intermediates cancel out, and the sum equals the overall equation: $2\text{H}_2 + 2\text{NO} \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$

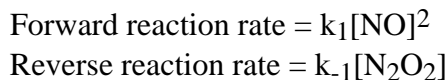
We also see that each step is bimolecular (or unimolecular for the reverse equilibrium reaction of the step 1). Thus each step is reasonable for being elementary.

To analyze whether the mechanism is consistent with the experimental rate law, we start with the slow step.

$$\text{Rate} = k_2[\text{N}_2\text{O}_2][\text{H}_2] \text{ where } k_2 \text{ is the rate constant for step 2}$$

The rate law includes N_2O_2 which is an intermediate. The rate law should always be expressed in terms of the original reacting species. To do this, we go to the prior equilibrium step (step 1) prior to the rate-determining step.

Let k_1 and k_{-1} represent the rate constants of the forward and reverse reactions of step 1. Equilibrium means that the reaction is going back and forth at equal rates, with the net overall rate equal to zero. For reaction 1:



At equilibrium, forward rate = reverse rate

$$k_1[\text{NO}]^2 = k_{-1}[\text{N}_2\text{O}_2]$$

Solving for the intermediate, $[\text{N}_2\text{O}_2]$

$$[\text{N}_2\text{O}_2] = \frac{k_1}{k_{-1}} [\text{NO}]^2$$

Substitute this into our rate-determining step expression:

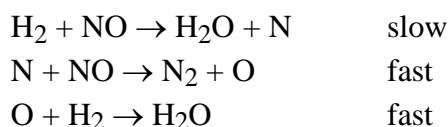
$$\text{Rate} = k_2[\text{N}_2\text{O}_2][\text{H}_2] = k_2 \frac{k_1}{k_{-1}} [\text{NO}]_2[\text{H}_2] = k[\text{NO}]_2[\text{H}_2]$$

where $k = k_2 \frac{k_1}{k_{-1}}$ (combination of constants).

This expression is consistent with our experimental rate law.

Consider two other possible mechanisms. Are these consistent with the experimental rate law?

First alternate possible mechanism:



This mechanism properly adds up to the overall equation:

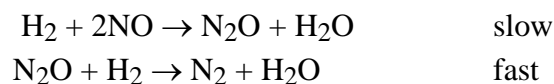


The mechanism also has acceptable bimolecular collisions in each step. However, it is not consistent with the rate law. The slow, rate-determining step, would yield a rate law:

$$\text{Rate} = k[\text{H}_2][\text{NO}]$$

which does not match the experimental: $\text{rate} = k[\text{H}_2][\text{NO}]^2$

Second alternate possible mechanism:



This also adds up to the desired equation. The rate-determining step involves three molecules (termolecular). This is possible, though unlikely. Based on this termolecular collision, the rate law would be:

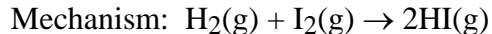
$$\text{Rate} = k[\text{H}_2][\text{NO}]^2 \quad \text{the same as the experimental rate law}$$

How could we distinguish between this mechanism, and the first proposed mechanism:

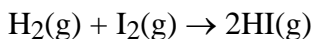
1. $2\text{NO} \rightleftharpoons \text{N}_2\text{O}_2$ fast equilibrium
2. $\text{N}_2\text{O}_2 + \text{H}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$ slow
3. $\text{N}_2\text{O} + \text{H}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O}$ fast

Both of these yield the experimental rate law. Further research is necessary. Sometimes it is possible to detect intermediates during the course of the reaction. Research indicates that the first proposed mechanism is the correct one.

For many years, this was considered to be a simple bimolecular reaction with a one-step mechanism.



As shown above, it is possible to have two different mechanisms that are consistent with the experimental rate law. An interesting example is the reaction:

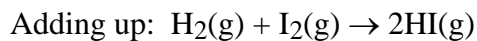


Experimental rate law: $\text{Rate} = k[\text{H}_2][\text{I}_2]$ (same as the equation itself)

The equation was considered to be elementary, and the reaction just involved a bimolecular collision between H_2 and I_2 , with the expected: $\text{rate} = k[\text{H}_2][\text{I}_2]$.

In 1967, detailed research proved that this was not a one-step mechanism. The mechanism is now described as:

- $I_2(g) \rightleftharpoons 2I(g)$ fast equilibrium
- $H_2(g) + 2I(g) \rightarrow 2HI(g)$ slow



Based on this mechanism, the rate of the slow step is:

$$\text{Rate} = k_2[H_2][I]^2 \text{ where } k_2 \text{ is the rate constant of step 2}$$

The rate constant of step 1 is k_1 . For this step:

$$\text{Forward reaction rate} = k_1[I_2]$$

$$\text{Reverse reaction rate} = k_{-1}[I]^2$$

At equilibrium, forward rate = reverse rate

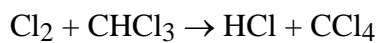
$$k_1[I_2] = k_{-1}[I]^2$$

$$\text{Solving for } [I]^2 : [I]^2 = \frac{k_1}{k_{-1}} [I_2]$$

Substitute this into our rate-determining step expression:

$$\text{Rate} = k_2[H_2][I]^2 = k_2[H_2] \frac{k_1}{k_{-1}} [I_2] = k[H_2][I_2]$$

$$\text{where } k = k_2 \frac{k_1}{k_{-1}}$$



Experimental Rate Law: $\text{Rate} = k[\text{Cl}_2]^{1/2}[\text{CHCl}_3]$

Proposed mechanism:

1. $\text{Cl}_2 \rightleftharpoons 2\text{Cl}$ fast equilibrium
2. $\text{Cl} + \text{CHCl}_3 \rightarrow \text{HCl} + \text{CCl}_3$ slow
3. $\text{CCl}_3 + \text{Cl} \rightarrow \text{CCl}_4$ fast

Adding up: $\text{Cl}_2 + \text{CHCl}_3 \rightarrow \text{HCl} + \text{CCl}_4$ with Cl and CCl_3 as intermediates

Start with the slow, rate-determining step:

$$\text{Rate} = k_2[\text{Cl}][\text{CHCl}_3]$$

Express the intermediate [Cl] in terms of initial concentrations, using the prior fast equilibrium step.

For step 1: Forward rate = $k_1[\text{Cl}_2]$
Reverse rate = $k_{-1}[\text{Cl}]^2$

At equilibrium, forward rate = reverse rate

$$k_1[\text{Cl}_2] = k_{-1}[\text{Cl}]^2$$

Solve for [Cl] $[\text{Cl}]^2 = \frac{k_1}{k_{-1}}[\text{Cl}_2]$ $[\text{Cl}] = \left(\frac{k_1}{k_{-1}}\right)^{1/2}[\text{Cl}_2]^{1/2}$

Substitute this expression into the rate-law expression for the rate-determining step.

$$\text{Rate} = k_2[\text{Cl}][\text{CHCl}_3] = k_2\left(\frac{k_1}{k_{-1}}\right)^{1/2}[\text{Cl}_2]^{1/2}[\text{CHCl}_3]$$

$$\text{Rate} = k[\text{Cl}_2]^{1/2}[\text{CHCl}_3]$$

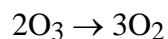
$$\text{where } k = k_2\left(\frac{k_1}{k_{-1}}\right)^{1/2}$$

The expression is consistent with the experimental rate law.

Note that in this mechanism, there is there is a fractional reaction order. The reaction is 1/2 order in Cl_2 , first-order in CHCl_3 , and 3/2 order overall.

The reaction is 1/2 order in Cl_2 . If the Cl_2 concentration is doubled, what happens to the rate?

The rate increases by a factor of $2^{1/2} = \sqrt{2}$ or 1.4 times faster



Experimental Rate Law: $\text{Rate} = k \frac{[\text{O}_3]^2}{[\text{O}_2]}$

Proposed mechanism:

1. $\text{O}_3 \rightleftharpoons \text{O}_2 + \text{O}$ fast equilibrium
2. $\text{O} + \text{O}_3 \rightarrow 2\text{O}_2$ slow

This adds up to $2\text{O}_3 \rightarrow 3\text{O}_2$, with O as an intermediate.

To analyze the rate law, start with the slow, rate-determining step.

$$\text{Rate} = k_2[\text{O}][\text{O}_3] \text{ where } k_2 \text{ is the rate constant for step 2}$$

Solve for the intermediate [O] in the prior fast equilibrium step.

At equilibrium: forward rate = reverse rate
 $k_1[\text{O}_3] = k_{-1}[\text{O}_2][\text{O}]$

where k_1, k_{-1} are the rate constants for the forward and reverse reactions of step 1.

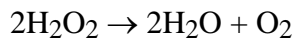
Solving for [O]: $[\text{O}] = \frac{k_1}{k_{-1}} \frac{[\text{O}_3]}{[\text{O}_2]}$

Substitute this expression for [O] into the rate law based on the rate-determining step.

$$\text{Rate} = k_2[\text{O}][\text{O}_3] = k_2 \frac{k_1}{k_{-1}} \frac{[\text{O}_3]}{[\text{O}_2]} [\text{O}_3] = k \frac{[\text{O}_3]^2}{[\text{O}_2]} \quad \text{where } k = k_2 \frac{k_1}{k_{-1}}$$

This is consistent with the experimental rate law.

Consider the equation for the decomposition of hydrogen peroxide.

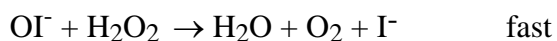
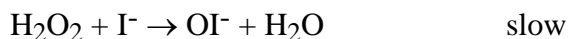


Experimental rate law: $\text{Rate} = k[\text{H}_2\text{O}_2][\text{I}^-]$

How can we have a substance like I^- in the rate law which is not in the overall equation?

I^- is a **catalyst**. It is present in the reaction system, but is not consumed. It is part of the mechanism, and it is part of the rate equation. But it is neither a reactant nor a product. It is used in one step of the mechanism, and regenerated in another step of the mechanism.

Proposed mechanism:



Adding up: $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$ I^- is the catalyst OI^- is the intermediate.

Neither I^- nor OI^- are in the overall equation—they cancel out when we add up the steps of the mechanism.

How can we tell the difference between an intermediate and a catalyst?

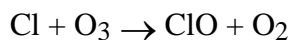
The catalyst is there in the beginning of the reaction, and also there at the end. It is altered in one step of the mechanism, and then returns in a subsequent step.

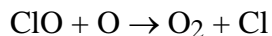
The intermediate is not there in the beginning or the end of the reaction. It is formed temporarily, during one of the middle steps, and then used up in a subsequent step.

From the slow, rate-determining step, the rate law is:

$\text{Rate} = k[\text{H}_2\text{O}_2][\text{I}^-]$ which is consistent with the experimental rate law.

Consider the following mechanism:





- (a) What is the overall equation
- (b) What is the catalyst?
- (c) What is the intermediate?

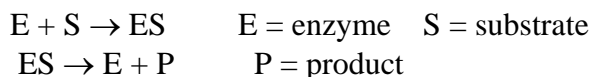
Adding up: Overall equation is: $\text{O}_3 + \text{O} \rightarrow 2\text{O}_2$

The catalyst is Cl. Cl atoms are there in the beginning and also there at the end. They are not consumed

The intermediate is ClO. ClO is formed temporarily in the first step, and then used up in the second step.

This reaction describes the catalytic decomposition of ozone, O_3 , by Cl atoms. The source of the Cl atoms are chlorofluorocarbons (CFCs) such as CCl_2F_2 , break down into Cl atoms by photons of light. The Cl atoms in the stratosphere catalyze the decomposition of ozone. CFCs are commonly used as refrigerants and formerly used as aerosols in various sprays. Their use today is curtailed due to governmental restriction designed to protect the ozone layer.

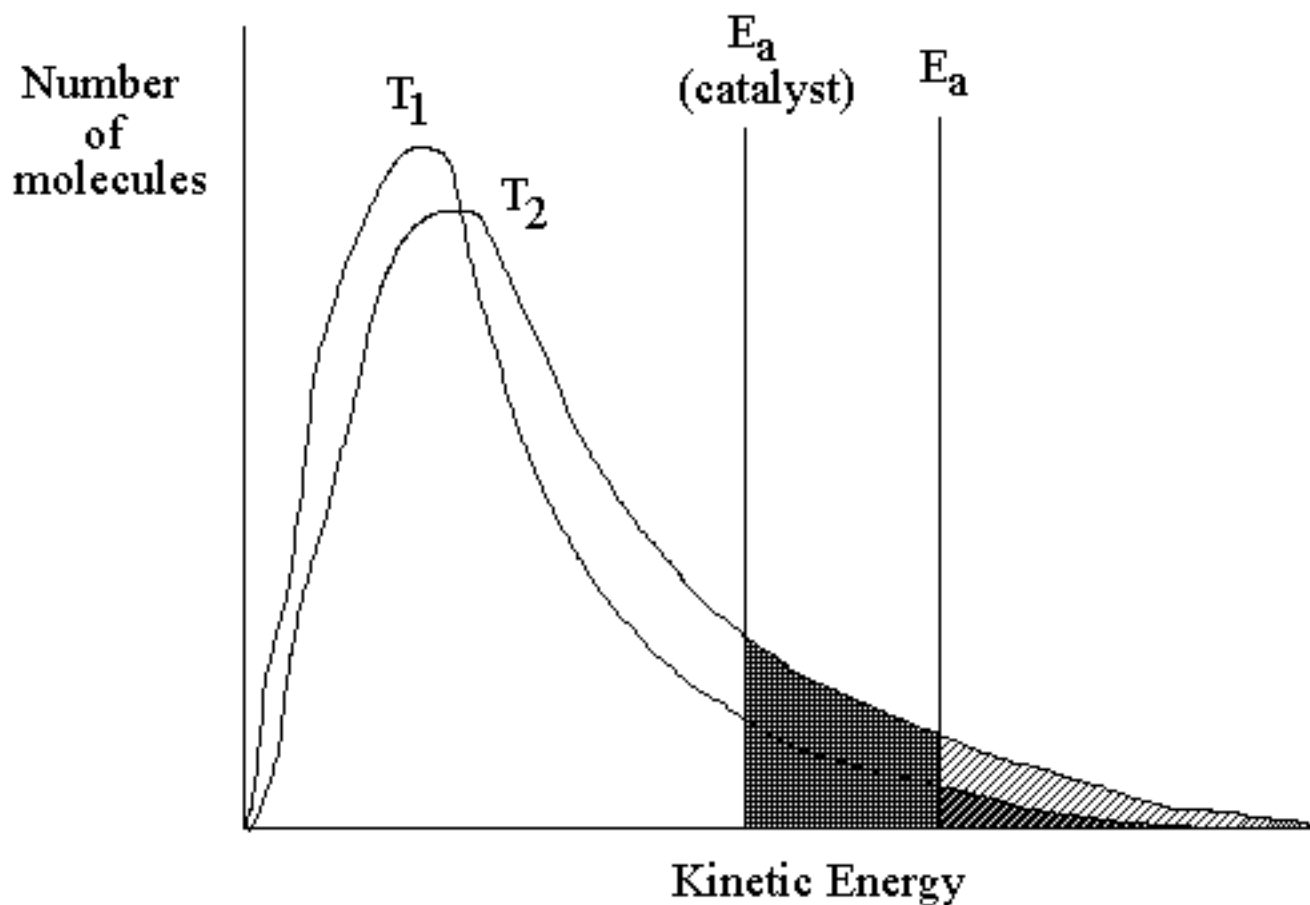
Enzymes are biological catalysts. Enzymes are large molecules, usually proteins, which attach to another specific protein called a substrate. The enzyme-substrate combination can then break down into the desired product much faster than just the substrate itself. In the process, the enzyme is regenerated. This may be represented by:



Overall: $\text{S} \rightarrow \text{P}$ The enzyme is a catalyst.

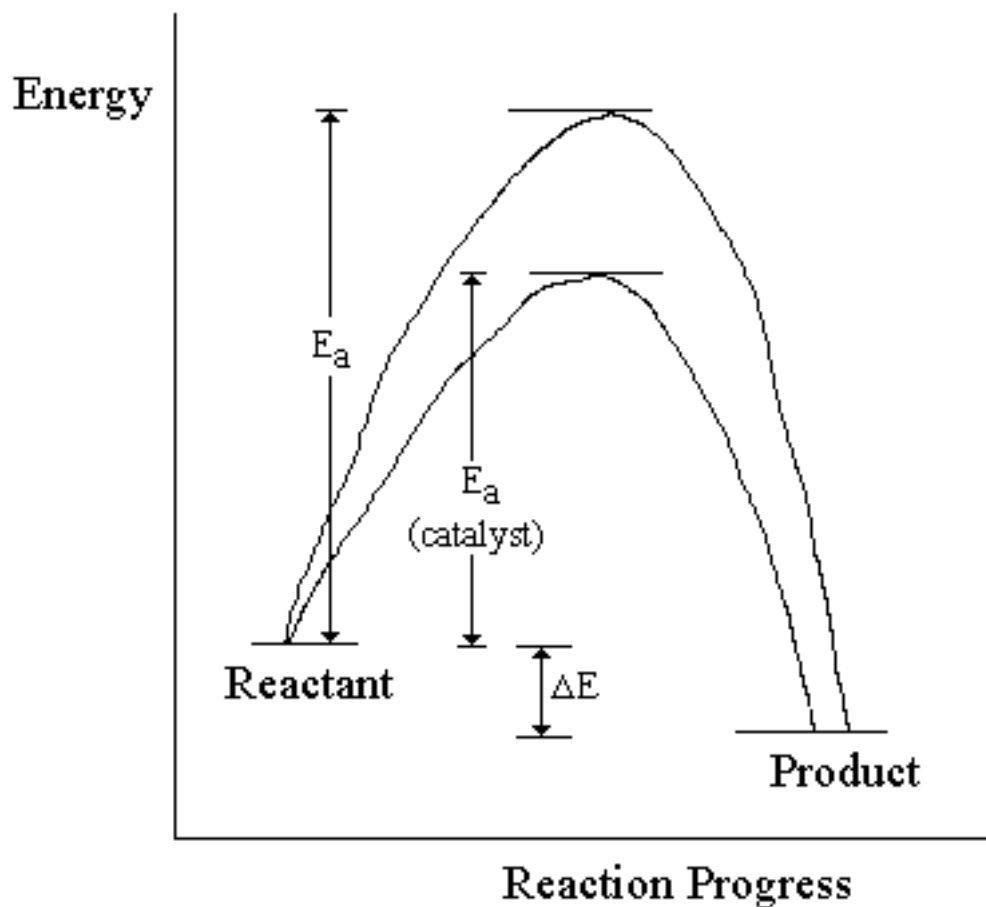
A catalyst works by providing an alternate mechanism for the reaction with a lower activation energy than the uncatalyzed reaction.

We may illustrate this with the graphs showing the distribution of molecular kinetic energies.



The catalyst lowers the activation energy. With a lower activation energy, there are more molecules (extra shaded portion in the graph) with sufficient energy to react.

This may also be illustrated using the potential energy diagram showing reaction progress.



The activation energy with the catalyst is lower than the uncatalyzed activation energy.

How does adding a catalyst change the value of ΔE or ΔH ?

ΔE and ΔH are **state functions**. Their value depends only on the initial and final states of the system—not what happens in-between. The catalyst lowers the activation energy and makes the reaction faster, but does not change the value of any thermodynamic state functions. ΔE and ΔH remain the same.