Chapter 13 Chemical Kinetics III - Section 4, 5, & 6

Chemistry by Chang and Goldsby

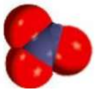
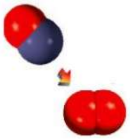
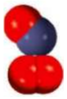
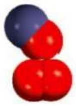
Chapter 13: Chemical Kinetics continued

13.4 Activation Energy and Temperature
13.5 Reaction Mechanisms
13.6 Catalysis

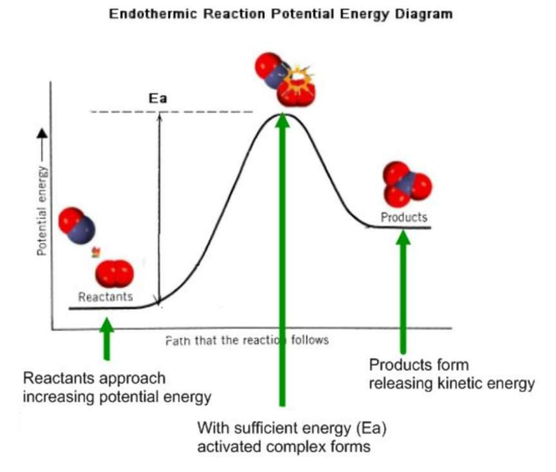
13.4 Activation Energy and Temperature Dependence of Rate Constants

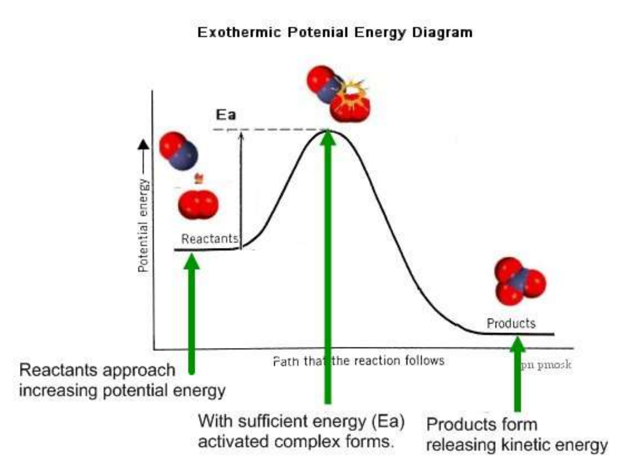
Reactions are dependent on collisions between molecules.

Only collisions between reactants with proper orientation **and** sufficient energy can produce products.

Collision theory: A reaction will only take place if three conditions are met.		
Reactants 	Product 	
1. The reactants must collide. 		
2. The collision must have the correct collision geometry to make the product. 	Correct collision geometry 	Incorrect collision geometry 
3. The collision must occur with a certain minimum energy, known as the activation energy, E_a.		

The activation energy, E_a, is the energy needed to form the transition state from the reactants shown in these reaction energy profiles.

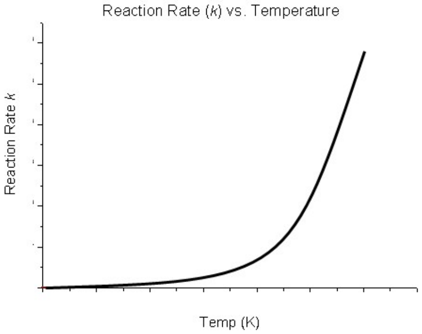




A large E_a barrier will mean that the reaction rate will be slow, creating a small value for the rate constant, k.

Important! Activation energy changes DO NOT alter the net enthalpy change, ΔH.

Reaction Rates increase with increases in temperature.



The graph to the right shows the exponential relationship of temperature and reaction rate. It plots the reaction rate constant vs. temperature which shows that the reaction rate increases exponentially with temperature.

It is not unusual for an increase in 10°C to double the rate of a reaction at a given concentration.

The explanation for why the rate constant and rate of a reaction changes with temperature involves the Maxwell-Boltzmann graph.

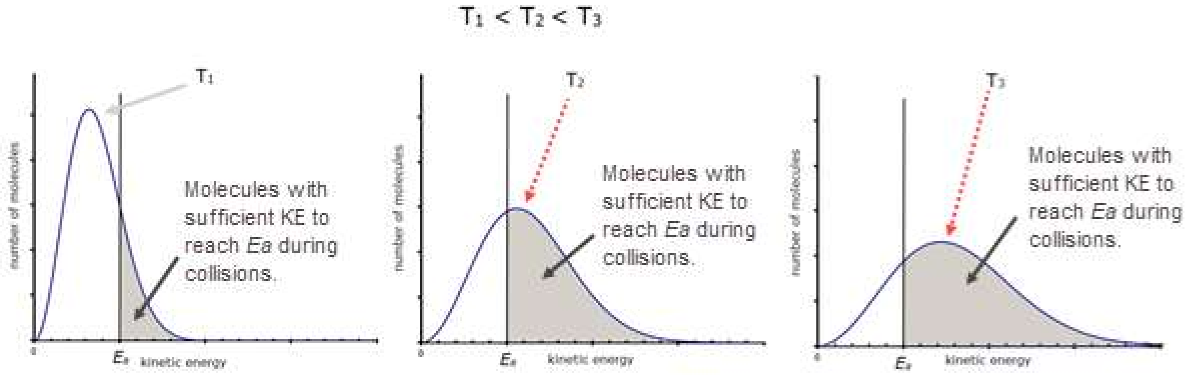
To understand the Maxwell-Boltzmann curves shown below, you must pay close attention to the axes.

> The number or fraction of molecules is the factor measured on the *y* axis ↑.
> The kinetic energy of the molecules is plotted on the x axis →.

The Maxwell-Boltzmann curve shows the % or number of molecules at various kinetic energies.
The **peak on Maxwell-Boltzmann curve** is close to the average kinetic energy (**temperature**) of the molecules.
The Maxwell-Boltzmann curve lowers and spreads out with increases in temperature.

The Maxwell-Boltzmann energy distribution curves of reactants at different temperatures shown below have a vertical line that is the E_a. The graphs show that reaction rate would increase with temperature since a greater percentage of molecular collisions have energies above the E_a that allow for the collisions to make products.

Here are the Maxwell-Boltzmann curves of a fixed sample at three temperatures. At higher temperatures more molecules have higher kinetic energies. The vertical line in the graph is the kinetic energy with sufficient energy to form the activated complex. The shaded portion of the curve represents the number of molecules with the energies needed to make the products.



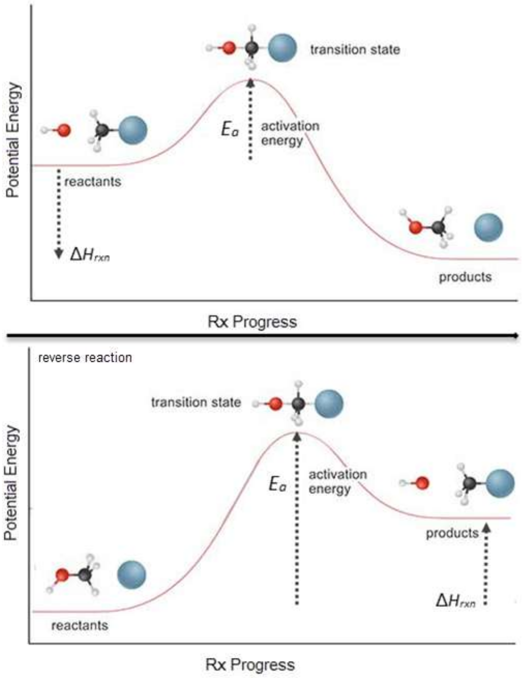
Increases in temperature result in

(1) more collisions per second
(2) **a greater percentage of collisions with sufficient E_a** to make the products.

If you are asked to explain why a reaction rate increases with temperature, **you must include both factors in your explanation.**

The Arrhenius equation is not part of AP Chemistry. You may skip the many pages of that subsection completely.

Summary:



(1) A molecular collision with **both** the proper orientation and sufficient energy, E_a, to make the activated-complex transition state is required to make products in a reaction.

(2) A high activation energy barrier for a reaction, E_a, means that the rate of the reaction and the rate constant, k, will be small.

(3) The rate constant, k, increases with temperature since there will be more frequent collations **and** a greater fraction of the molecules colliding with the proper collision orientation will have sufficient energy to form the transition state.

(4) The activation energy height is always **relative to the energy of the reactants**. Pay special attention to the E_a in the exothermic reaction and the endothermic reaction in the diagrams to the right.

(5) Changes in activation energy will only change the rate of a reaction and have no effect on ΔH of a reaction.

13.5 Reaction Mechanisms … the why behind the orders

Complex chemical reactions proceed via a series of simple unimolecular decompositions or bimolecular collisions called the reaction mechanism.

Molecularity is the term used to describe the number of particles in the collision for a step in a reaction mechanism.

Unimolecular[1] reactions involve a single particle decomposing.

$$A \rightarrow B + C$$

Bimolecular reaction collisions require two particles to collide with sufficient energy and correct orientation so that the product can be formed.

$$A + B \rightarrow C \qquad \text{or} \qquad A + A \rightarrow B$$

Termolecular reaction steps involve three particles simultaneouly colliding with sufficient energy and correct orientation so that the product can be formed.

$$A + B + C \rightarrow D$$

Termolecular reaction steps are never found in reaction mechanisms.
The chance of three particles simultaneously colliding with the right geometry and energies to form a transition state is extremely low.

The simple steps in a reaction mechanism add up to the balanced reaction.

An energy diagram that details a reaction mechanism will have an activation energy peak for each step in the mechanism.

Intermediates:

In a reaction mechanism, an intermediate chemical may be produced.
The intermediate is consumed in a subsequent step; therefore, the intermediate is not included in the net overall reaction.

The steps and intermediates in a reaction mechanism have extremely short lives (femtoseconds) and are very difficult to detect.

The rate of the reaction is dependent on the slowest step in the mechanism.
The slowest step is the rate-determining step and determines the overall rate law equation.

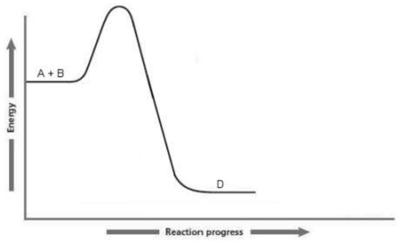
Example 1a: $A + B \rightarrow D$ as a single step reaction.

The reaction could occur in a single step as a simple bimolecular reaction.

Single step reaction: $A + B \rightarrow D$

Based on this single step, both reactant concentrations [A] and [B] have equal importance in the rate law expression. Thus, the rate law would be

$$\textbf{rate} = \boldsymbol{k}\,\textbf{[A][B]}$$



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[1] Understanding how unimolecular substances undergo change is beyond the scope of AP Chemistry.

Example 1b: **A + B → D as a two-step reaction with an intermediate.**

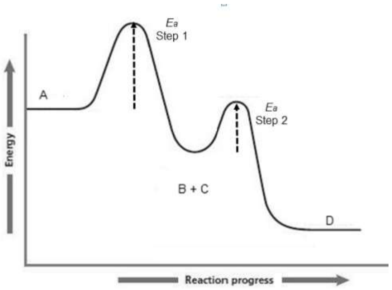
Another possible mechanism for the reaction A + B → D

Step 1: A → C (*slow*) **rate-determining step** (C intermediate)
Step 2: B + C → D (*fast*)

A + B → D net reaction

Step 1, the slow, rate determining step, with the higher E_a only has [A]. Therefore, the rate law for this mechanism is only dependent on [A].

rate = *k* [A]



Summary of Example 1b.

Each step is simple (unimolecular or bimolecular).
The two steps add up to the balanced reaction.
An intermediate C is created in Step 1 but is consumed in Step 2 and does not appear in the net reaction.
In this mechanism, Step 1 has the higher E_a and therefore is the slower step.
Increasing the concentration of A will increase the reaction rate.
Increasing the concentration of B will not have the same effect.

Example 1b analogy: If a business was selling marble sculptures, Step 1 would be carving the sculpture and Step 2 would be putting the sculpture in a box for sale. The rate determining step would be Step 1, carving the sculpture. Hiring more employees to carve the sculptures would speed up the production rate. Increasing the number of employees to box the sculptures would not speed up production.

Bottom Line: **The reactants in the slow, rate determining step will determine the order of the reaction and the instantaneous rate law expression.**

Example 2: 2 A + B → C

This reaction could not occur in a single step since it would require three body collisions (ternary molecularity). Instead, the reaction must occur in simpler (unimolecular or bimolecular) steps that add up to the net reaction.

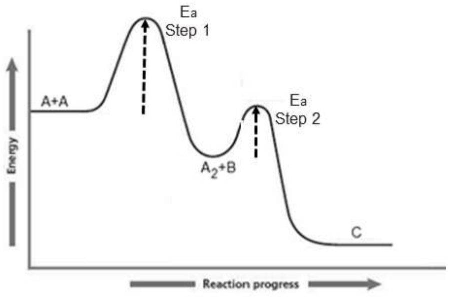
Example 2: **2 A + B → C** **with rate = *k* $[A]^2$**

The steps could have this mechanism

Step 1: A + A → A_2 (*slow*) rate-determining step
Step 2: A_2 + B → C (fast)

2 A + B → C net reaction

Each step only involves two bodies colliding.
The two steps add up to the balanced reaction.
An intermediate A_2 is created in Step 1, but A_2 is consumed in Step 2 and A_2 does not appear in the net reaction.



Increasing the concentration of A will increase the reaction rate.
Increasing the concentration of B won't have the same effect.
The reaction rate is dependent on the reactants of the slowest step in the reaction.

The slow, rate determining step depends on [A] twice and therefore, rate = *k* [A][A] rate = *k* $[A]^2$

Example 3: $2\ A + B \rightarrow C$

<u>Example 3a</u>: $2\ A + B \rightarrow C$ with rate = k [A]

The proposed mechanism is based on the reaction energy diagram at the right.

Step 1: $A + B \rightarrow X$ (*fast*)

Step 2: $A + X \rightarrow C$ (*slow*) rate determining step

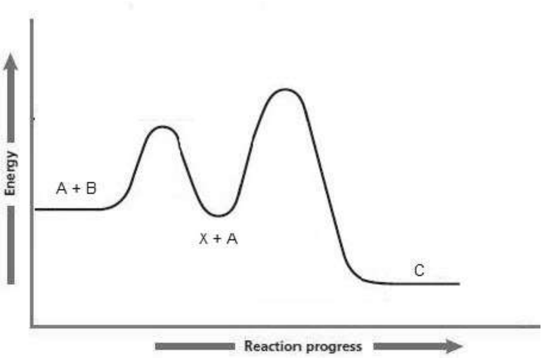
$2\ A + B \rightarrow C$ net reaction

The slow step reactants (Step 2) determine the instantaneous rate law:

rate = k [X][A]

However, **[X] can't be used in rate law since [X] is an intermediate** which isn't in the original reactant mix. There is no X used in setting up the reaction.

rate = k [A]



You cannot include the intermediate X **in the rate law** since X is not in the net, balanced reaction. You can't increase or decrease its concentration because it's not in your ingredient list.

The production of X in Step 1 is faster than its consumption in Step 2. So, the concentrations of reactants in Step 1, the fast step, would not have an impact on the overall reaction rate.

Thus, the overall reaction rate would depend only on the reactant in the net reaction in the slow step, rate = k [A]

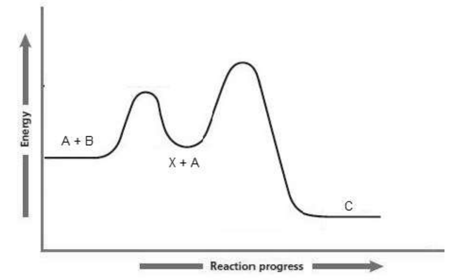
Important complication! When there is a reversible reaction, ⇄, before the slow step, there is a twist.

<u>Example 3b</u>: $2\,A + B \rightarrow C$ **rate =** $k\,[A]^2[B]$

Step 1: $A + B \rightleftarrows X$ (*fast*) **but also reversible**
Step 2: $A + X \rightarrow C$ (*slow*) rate determining step

$2\,A + B \rightarrow C$ net reaction

⇄ indicates that this is a reversible reaction and even though this step is fast, the equilibrium concentrations of A, B affect the concentration of X



Normally the reactants in the slow step would determine the rate law. But Step 1 has a reversible fast step. This complication affects the slow step, and the reactants and products of the reversible fast step will become involved in the rate law. With this complication it is possible to have a denominator in the rate law and even fractional superscripts. So, the expected answer on AP exams for a reaction with an equilibrium before the slow step will be used with reactants in the slow step.

To deal with this type of reaction (level 5) use the following technique which will work for all AP Chemistry questions.

1. Box in the full equilibrium reaction including products
2. Box in just the **reactants** of the subsequent slow reaction.

Step 1: $\boxed{A + B \rightleftarrows X}$
Step 2: $\boxed{A + X} \rightarrow C$

Step 1: $\boxed{A \rightleftarrows B + C}$
Step 2: $\boxed{B} \rightarrow D$

3. Add the boxed in substances canceling if necessary.

Step 1: $\boxed{A + B \rightleftarrows \cancel{X}}$
Step 2: $\boxed{A + \cancel{X}} \rightarrow C$
Step 3: $2A + B$

Step 1: $\boxed{A \rightleftarrows \cancel{B} + C}$
Step 2: $\boxed{\cancel{B}} \rightarrow D$
Step 3: $A \rightarrow C$

4. Remaining reactants of step 3 are used as numerators and products are used as denominators.

$$\text{rate} = k\,[A]^2[B] \qquad \text{rate} = k\frac{[A]}{[C]}$$

5. If in a FRQ justification is required in addition to showing the boxes, you must also write k_2 and k_1's forward and reverse rates are used to determine the overall k. The formula would be $k = k_1\, k_2 / \, k_{-1}$, forward rxn 1 and forward reaction 2 divided by reverse reaction 1.

If you need a more detailed explanation of equilibrium reaction rates watch this video:
https://app.screencast.com/Aszd5VfkNexXx

<u>Summary</u>
In all valid mechanisms:

(1) The sum of the individual steps of the reaction mechanism must be the same as the overall chemical equation.

(2) The **coefficients and reactants in the slow step** in the reaction mechanism will **determine the rate law**.

(a) The rate law contains only the reactants of the slow step in the reaction mechanism.
(b) If the slow step has an intermediate, the intermediate will not be included in the rate law.

Exception to (b): If the intermediate in the slow step is produced from a prior reversible equilibrium reaction, ⇄, the reactants and even products of the equilibrium step producing the intermediate may be included in the rate law.

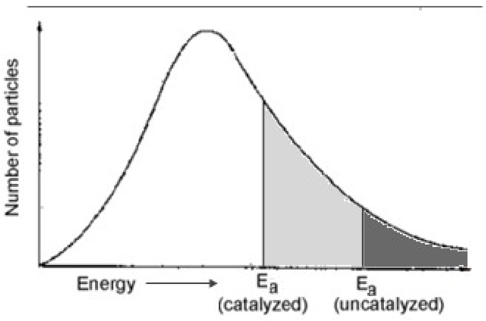
(3) An experimentally determined rate law can confirm a reaction mechanism.

13.6 Catalysis

Catalysts are substances that increase the rate of a reaction while remaining chemically unchanged.

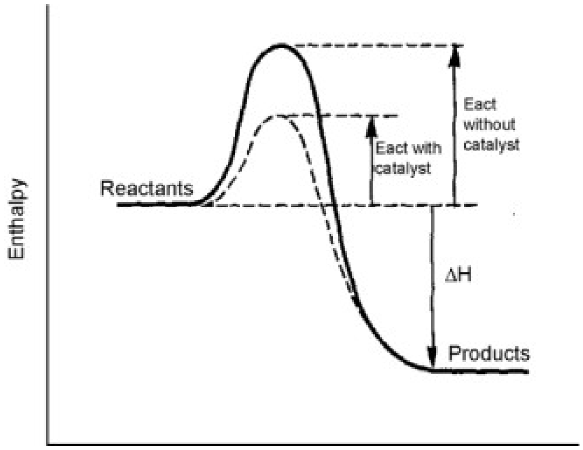
Catalysts function by providing a lower activation energy in an elementary step in a reaction mechanism.

An alternative reaction route with a lower activation energy, E_a, allows a greater number of lower energy particle collisions to produce a transition state that can form the product.



The catalyst is not consumed in the reaction because the catalyst while the catalyst may react in the rate determining step, it is regenerated later in the reaction mechanism. It is also possible that the catalyst is not altered by the reaction.

Reaction	Conditions	E_a (kJ mol^{-1})	ΔH_{rxn} (kJ mol^{-})
$A + B \rightarrow AB$	Uncatalyzed	+300	-320
	With catalyst	+200	-320



A catalyst does not change the ΔH in the reaction. The enthalpies, ΔH's, for uncatalyzed and catalyzed reactions are the same.

A catalyst just changes how quickly the energy is produced.

Note that the ΔH for this reaction diagram is unchanged by the catalyst.

Since a catalyst is present as a reactant and a product, a catalyst is often written over the arrow in a reaction:

$$A + B \xrightarrow{catalyst} C$$

A catalyst can be part of a rate law expression.

It is important to differentiate intermediates from catalysts.

An intermediate is not in the reactant mix but is a product which is later consumed as a reactant.

A catalyst is a reactant that is regenerated as a product.

Reaction with intermediate X	Reaction with intermediate X **and** catalyst Z
Step 1: $A \rightarrow X$ (*slow*) Step 2: $X + B \rightarrow C$ (*fast*) Net Reaction: $A + B \rightarrow C$ X is a product generated by A in Step 1. X is consumed in Step 2. rate = k [A]	Step 1: $A + Z \rightarrow X$ *faster but still the slower step* Step 2: $X + B \rightarrow C + Z$ *faster than Step 1* Reaction: $A + B + Z \rightarrow C + Z$ Net Reaction: $A + B \xrightarrow{z} C$ Z is a reactant in Step 1 Z is regenerated as a product in Step 2. rate = k [A][Z]
The catalyst increases the rate of the rxn with a k that is larger than without a catalyst.	

Consider the reaction mechanism: Step 1: $H_2O_2 + Br^- \rightarrow H_2O + OBr^-$ (*slow*)
Step 2: $H_2O_2 + OBr^- \rightarrow H_2O + Br^- + O_2$ (*fast*)

(a) What is the overall (net) reaction?
(b) What substance would be an intermediate in the reaction?
(c) What substance would be the catalyst for the reaction?
(d) What is the rate law for this reaction?

(a) The addition of the reactions results in:

Step 1: $H_2O_2 + \cancel{Br^-} \rightarrow H_2O + \cancel{OBr^-}$
Step 2: $\underline{H_2O_2 + \cancel{OBr^-} \rightarrow H_2O + \cancel{Br^-} + O_2}$
$2H_2O_2 \rightarrow 2H_2O + O_2$

(b) The reaction **intermediate** is OBr ⁻ since OBr ⁻ is generated as a **product** in the first reaction and OBr ⁻ is a reactant in the second. Intermediate OBr ⁻ is never seen. OBr ⁻ is a behind the scenes player.

Step 1: $H_2O_2 + Br^- \rightarrow H_2O + \mathbf{OBr^-}$ OBr^- produced in step 1
Step 2: $\underline{H_2O_2 + \mathbf{OBr^-} \rightarrow H_2O + Br^- + O_2}$ OBr^- consumed as reactant in step 2
$2H_2O_2 \rightarrow 2H_2O + O_2$

(c) The catalyst in the reaction is the bromide ion.

The bromide ion, Br ⁻, is in the reactant side in the first step (start of the reaction) and Br ⁻ is regenerated as a product in the second reaction. The bromide ion concentration will not change in this reaction.

Step 1: $H_2O_2 + \mathbf{Br^-} \rightarrow H_2O + OBr^-$ Br^- Reactant at start of reaction in step 1
Step 2: $\underline{H_2O_2 + OBr^- \rightarrow H_2O + \mathbf{Br^-} + O_2}$ Br^- Regenerated as a product in step 2
$2H_2O_2 \rightarrow 2H_2O + O_2$

$$2H_2O_2 \xrightarrow{Br^-} 2H_2O + O$$

(d) The rate = $k[H_2O_2][Br^-]$ is 1st order with respect to $[H_2O_2]$and 1st order with respect to the [Br] because they are the reactants in the slow Step 1.

Specific Classes of Catalysts in Chemical Reactions which are included in the AP Chem curriculum.

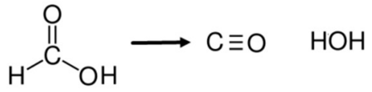
Acid-Base Catalysts

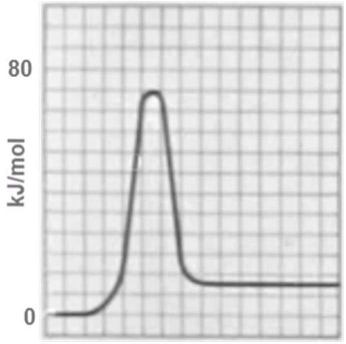
The H^+ ion (or proton) can be a catalyst in reactions especially with organic functional groups.

Methanoic acid (commonly called formic acid) decomposes slowly into carbon monoxide and water.

This is the uncatalyzed single step reaction that has a small rate constant and high activation energy and is not noticeable at room temperature:

$$HCOOH \rightarrow CO + H_2O$$





On the addition of an acid catalyst, a new mechanism with a step having a lower activation energy increases the rate of the reaction significantly so that bubbles of carbon monoxide become visible.

Catalyzed reaction:

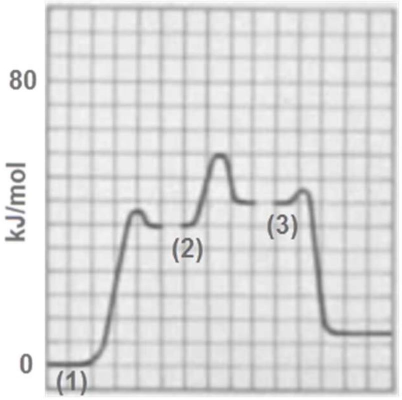
Step 1: $HCOOH + H^+ \rightarrow HCOOHH^+$
Step 2: $HCOOHH^+ \rightarrow COH^+ + H_2O$
Step 3: $COH^+ \rightarrow CO + H^+$

Net reaction:

$$HCOOH \xrightarrow{H^+} CO + H_2O$$

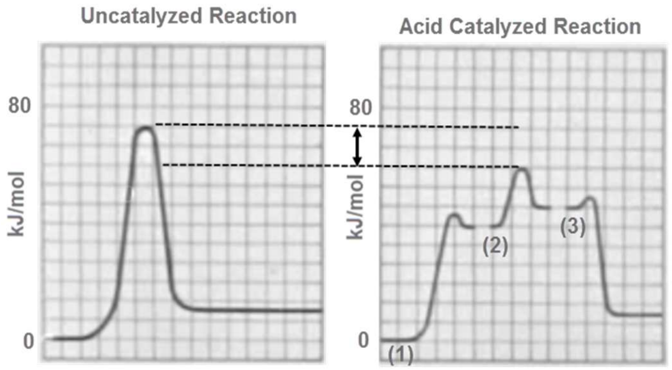
The intermediates in this reaction are $HCOOHH^+$ and COH^+.
The catalyst in the reaction is H^+.

Rate = $k[HCOOH][H^+]$



The reaction rate of the catalyzed reaction is faster than that of the uncatalyzed reaction since the overall activation energy for the catalyzed reaction is less than the uncatalyzed reaction.

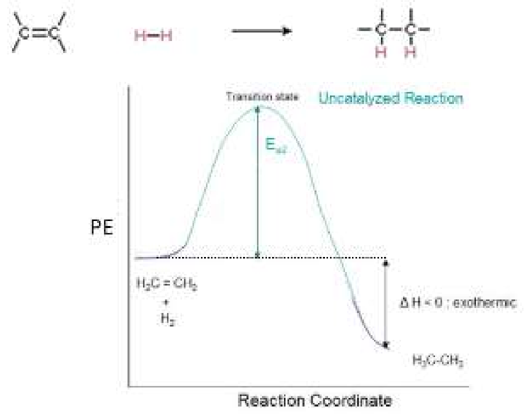
Note though that the overall ΔH for this endothermic reaction is unchanged.



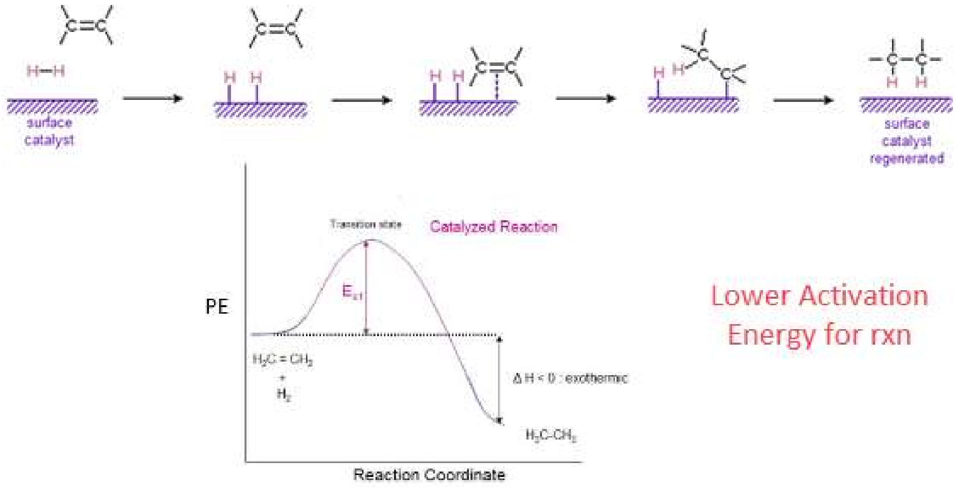
Surface Catalysts

Surface catalysts are classified as heterogeneous catalysts since they are solids while the reactants are either liquids or gases. The surface can provide a new reaction intermediate, or the surface can "hold" a reactant to increase the chance of a successful collision with a lower activation energy.

Catalysts are normally not written in the net reaction as they are regenerated and are not consumed in the reaction.



Higher Activation energy for rxn



Lower Activation Energy for rxn

Both reaction mechanisms have several steps, but only the highest E_a step is shown in the diagrams.

There are two noteworthy examples of surface catalysts:

ICE Car Catalytic Converters

In the combustion process of automobile engines, carbon monoxide, CO, and nitrogen oxides, NO and NO_2, are pollutants. These gases must be eliminated from the exhaust of the car. So, the exhaust gases are passed through a catalytic converter that has a ceramic honeycomb or beads coated with a transition metal or transition metal oxide surface catalyst.

A transition metal or transition metal oxide catalyzes the oxidation of CO to react with air to form CO_2

$$2\ CO + O_2 \xrightarrow{catalyst} CO_2$$

The catalyst will also oxidize any unburned hydrocarbon fuel into carbon dioxide and water.

The transition metal or transition metal oxide also catalyzes the reduction of the nitrogen oxides to nitrogen and oxygen.

$$2\ NO \xrightarrow{catalyst} N_2 + O_2$$

Production of Ammonia

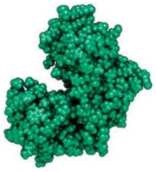
Ammonia is one of the most important inorganic compounds produced in the world. Most ammonia is used as fertilizer and there would be worldwide famine without the manufacture of ammonia. It is manufactured using nitrogen from the air and hydrogen.

$$N_2(g) + 3\ H_2(g) \xrightarrow{catalyst} 2NH_3(g)$$

This reaction cannot occur as written since it would require four body collisions which never happens. Instead, the reactions occur through a series of bimolecular collisions steps. The reaction is very slow unless a catalyst is used. The catalyst is a metal catalyst where the reactants and intermediates are absorbed onto a surface of a metal catalyst which allows for a series of simple bimolecular steps with lower activation energies.

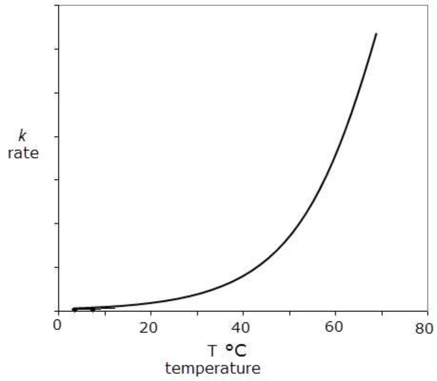
Enzymes

Enzymes[2] are biologic catalysts. Some enzymes accelerate reactions by binding to the reactants in a way that lowers the activation energy and provide a favorable orientation for reaction collisions or forming a new reaction intermediate with a lower activation energy.

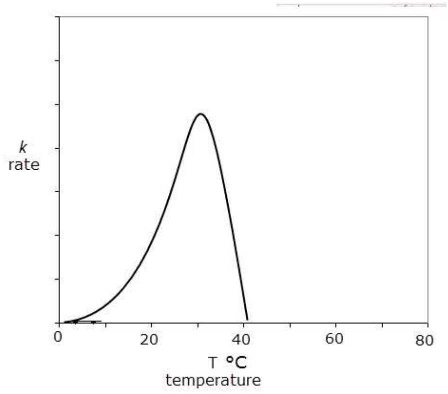
Enzymes have tertiary protein structures that are so complex that they are usually shown as spaghetti like blobs such as the enzyme hexokinase to the right, or just as a generalized shape. Enzymes are very effective catalysts. Yet they are specialized and sensitive in that they will only work within a narrow temperature range and can be deactivated if their molecular shape is altered because of the disruption of their intermolecular attractions.	

Changes in enzyme reaction rates do not continuously increase with temperature.

The ternary structure of the catalyst is dependent on intermolecular attractions which are easily disrupted at higher temperatures. Temperatures above 40°C will break the intermolecular bonds within a ternary structure "denaturing" the enzyme. As a result, enzymes will cease to operate at elevated temperatures.



Non-biological reaction rate temperature curve



Enzyme reaction rate curve

If you are given a graph that shows a sudden decrease in reaction rate with an increase in temperature, the reaction most likely uses an enzyme catalyst. You can explain the drop in reaction rate by saying that the enzyme catalyst's shape was "denatured."

Many important biological processes involve enzyme catalysts. If the temperatures of these biological systems become higher than the peak reaction rate, these critical processes will suddenly stop.

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[2] I've simplified the enzyme explanation to match what you need for the AP Chemistry exam. For a more complete explanation of enzymes, see the Chemguide UK. It is the best explanation I have seen. I recommend this especially if you plan to take AP Biology or go into a medical-biological field.

http://www.chemguide.co.uk/organicprops/aminoacids/enzymes.html

Classes of Catalysts:

Heterogeneous catalysts are catalysts having a different phase than the reactant.

The heterogeneous catalyst is usually a solid that provides a surface that allows the reactants to react. The surface area of the catalyst is important, as the larger the surface area, the greater the reactant-catalyst contact.

Homogeneous catalysts have the same phase as the reactants.

As the substances are mixed at the molecular/atomic level, surface area is not a factor. Instead, concentration will be variable.,

An extra factor controlling rate of reaction:

Solid or liquid particle size

Macroscopic particles (vs. atoms, molecules, and ions in solutions and gases) can only react on the surfaces available for reaction. The material inside the solid or liquid particle is not available for reaction. If the solid or liquid is broken into smaller pieces, its surface area increases, and more particles are available for collision; therefore, the reaction rate increases. This explains why aerosols and fine dust will often react quickly while lumps of the same material react slowly.

An important consequence of the surface area/fine power reactivity is that substances that would react slowly can react explosively in the form of a fine mist. Dust explosions are a common, serious industrial hazard. Examples of substances that are explosive in the form of dust are sawdust, powdered sugar, coal, metal powders, and even finely powdered aspirin.

A specific objective is mentioned in the AP Chemistry Curriculum that is worth your attention. In an experiment, if you are to dissolve or react a substance, using finely powdered material with a larger surface area per gram, the substance will react or dissolve much more quickly than if you used larger lumps.