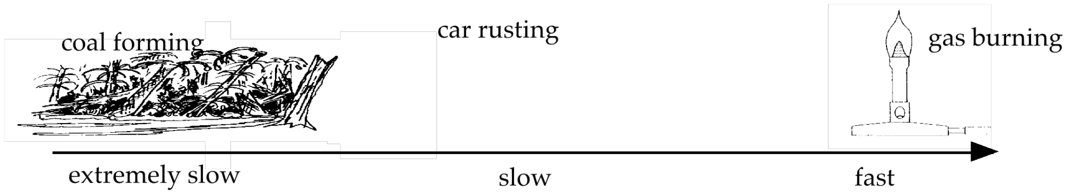
Reaction Rates

REACTIONS OCCUR AT DIFFERENT SPEEDS (rates)

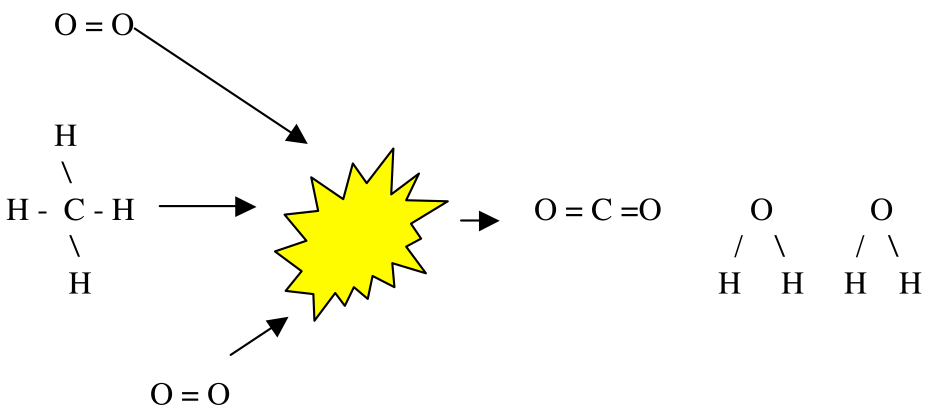
In our study of chemistry we have observed considerable variation in the rate at which different reactions occur.



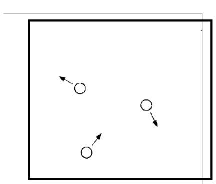
Collision Theory

This states that reactions will only occur when
1. The particles collide with each other.
2. The collisions have enough energy. This energy is called the Activation energy. E_A

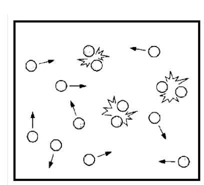
For example:- In the burning of methane, methane and oxygen molecules must collide.
At the instant of collision C-H bonds in the methane and O=O bonds in the oxygen molecules are broken and C=O bonds in carbon dioxide and O-H bonds in water molecules formed.



Concentration and collisions



low concentration



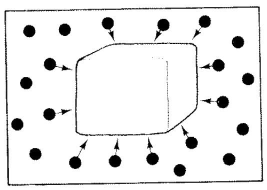
high concentration

Note Reactions only occur when
reactants collide with energy E_A
Collisions without E_A do not
cause any reaction

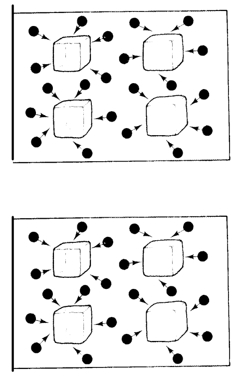
Increasing the concentration of one (or more) of the reactants will increase the rate of the reaction. Increasing the concentration of one of the reactants means that there will be more collisions between reactant molecules and so speed up the reaction.

Particle Size and Collisions

As the reaction takes place on the surface of particles the larger t he surface area the more collisions that will occur.



break large cube into 8 smaller ones



Surface Area = 6 x 1 cm^2 = 6 cm^2

Surface area = 8 x 6 x 1/2 x 1/2

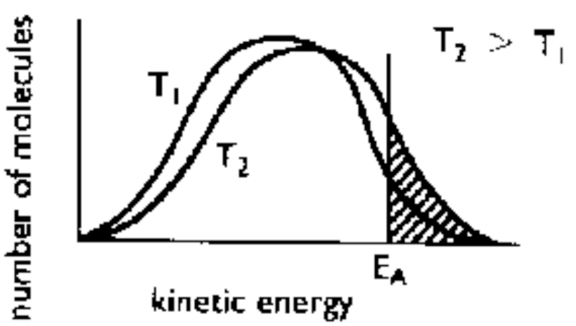
= 12 cm^3

We can see that by halving the size of the cube , we double the size of the surface area. Collisions take place on the surface. This should double the speed of reaction.

Temperature and Collisions

We have seen that for a chemical reaction to occur, collisions are necessary. If, however, we mix hydrogen and oxygen gas there is no reaction at room temperature, even though the number of collisions can be as high as 1 x 1030 per second when 1 mole of each gas is mixed.From this we can conclude that collision alone is not enough for molecules to react. Not only must particles collide they must possess a certain minimum kinetic energy before they will react on collision. This minimum energy required for reaction is called the Activation Energy (EA).

The molecules in a gas are, at any one time, in random motion and possess widely differing kinetic energies. The distribution of kinetic energy can be shown as:-



The two graphs shown show the energy of molecules with temperature T1. It also shows what will happen to the number of molecules with activation energy E_A when the temperature is raised.

Increasing the temperature raises the energy of the particles ,

1. more collisions occur.
2. a greater proportion of the collisions result in the formation of products hence the reaction speeds up.

The rate of a chemical reaction is affected by:-

a) Concentration:- The higher the concentration of reactant(s) the faster th reaction.

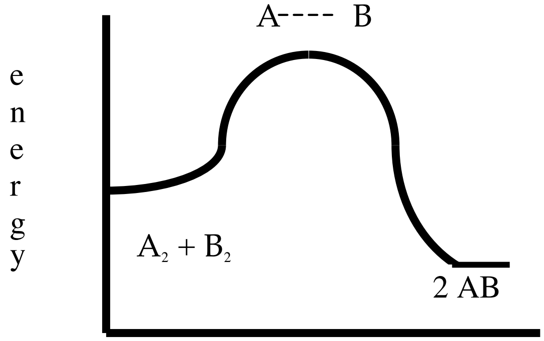
b) Surface area:- The larger the surface area the faster the reaction. A large surface area is brought about by using small particles.

c) Temperature:- The highe rthe temperature the faster the reaction. A small rise in temperature can produce a large increase in *reaction rate. A 10°C rise can double the rate*

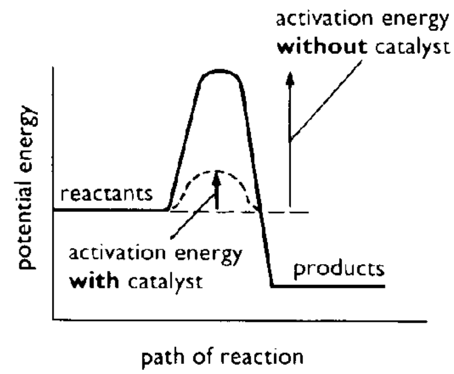
CATALYSTS.

A catalyst is a substance which speeds up a chemical reaction without being used up in the reaction. A catalyst works by providing an alternative pathway for a reaction which requires less energy on the part of the colliding molecule
i.e. a catalyst lowers the activation energy.
The catalyst has no effect on the enthalpy change (ΔH) for the reaction
On the diagram below, label the activation energy (E_A) for the reaction
a) without the use of a catalyst.
b) with the use of a catalyst.

$$A_2 + B_2 \Rightarrow \begin{matrix} A\text{---}B \\ \vdots \quad \vdots \\ A\text{---}B \end{matrix} \Rightarrow 2AB$$



Path of reaction

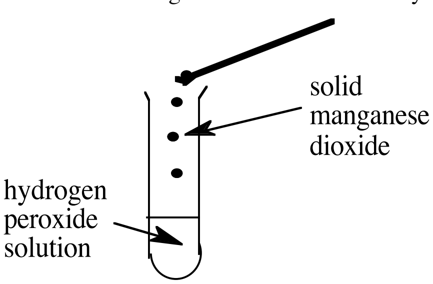


HOMOGENEOUS and HETEROGENEOUS CATALYSTS.

A homogeneous catalyst is a catalyst which is in the same physical state as the reactants.

A heterogeneous catalyst is one which is in a different physical state to the reactants.

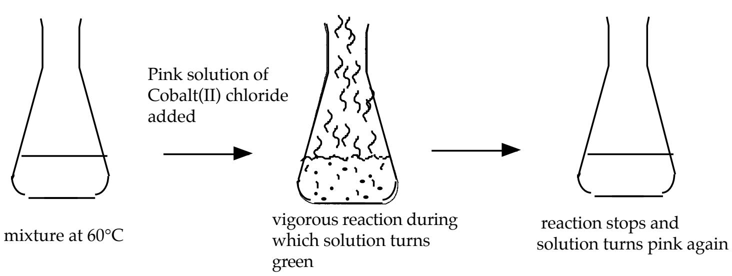
A HETEROGENEOUS CATALYST AT WORK.
Add a little manganese dioxide to some hydrogen peroxide solution in a test tube. Test the gas given off with a glowing splint.



Note When solid manganese dioxide is added to hydrogen peroxide oxygen gas is given off faster. Oxygen gas relights a glowing splint

A HOMOGENEOUS CATALYST AT WORK.

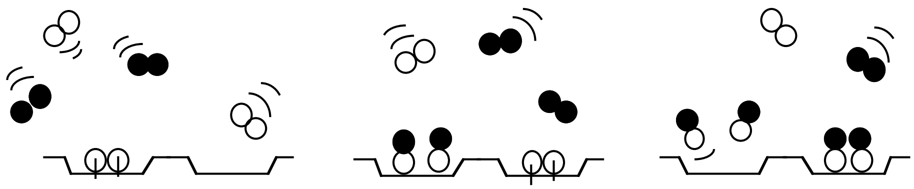
Mix together 10 ml of potassium sodium tartrate solution and 10 ml of hydrogen peroxide solution in a conical flask. Warm the mixture until it reaches a temperature of 60°C. Add a little cobalt(II) chloride solution to the mixture in the flask.



Note The catalyst must remain unchanged at end of the reaction

HOW A SURFACE CATALYST WORKS.

In a reaction that uses a heterogeneous catalyst it is usually an advantage to use as large a surface area as possible. It is thought that catalysis occurs on the surface of the catalyst at points called active sites. At these sites molecules of one of the reactants are adsorbed.



a) Adsorption
Molecules of one of the reactants form bonds with the catalyst. This weakens the bonds within the molecules.

b) Reaction
The molecules react on the surface of the catalyst. The angle of collision is likely to be favourable since

c) Desorption
The product molecules leave the catalyst site and the vacant site can be occupied by another reactant molecule.
one of the molecules is fixed.

CATALYST POISONS.

A catalyst poison is a substance which reacts with the surface of a catalyst so that it operates less effectively or not at all. Poisoning of the catalyst will occur when the catalyst poison is adsorbed more strongly onto the surface of the catalyst. By occupying the active sites the poison stops the reactant molecules occupying these sites and so the catalyst ceases to function. When this occurs the catalyst has to be regeneratedor renewed.
An example of a catalyst poison is lead in leaded petrol which will poison the catalysts in catalytic converters fitted to car exhausts . Catalytic converters use expensive rhodium, platinum and palladium rather than cheaper copper and nickel which are poisoned by trace amounts of sulphur dioxide in exhaust gases.In a catalytic converter poisonous carbon monoxide is oxidised to far less harmful carbon dioxide and acidic oxides of nitrogen are converted into harmless oxygen and nitrogen.

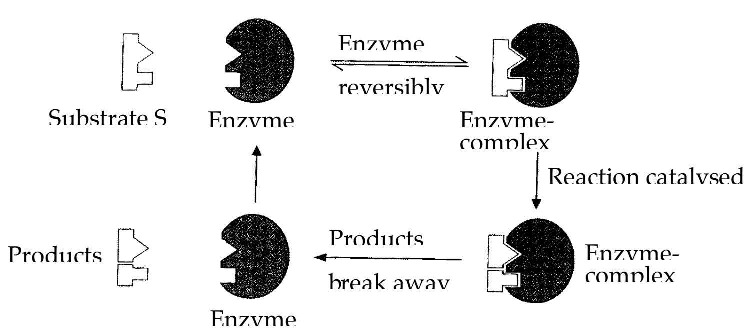
CATALYSTS IN INDUSTRY.

Catalysts are widely used in industry to reduce manufacturing costs.

Process	Catalyst used	Reaction catalysed
Making ammonia (Haber Process)	Iron	$N_2 + 3H_2 \longrightarrow 2NH_3$
Making sulphuric acid (Contact Process)	Vanadium pentoxide (V2O5)	$SO_2 + O_2 \longrightarrow SO_3$
Margarine manufacture	Nickel	hydrogenation of edible oil to give edible fat.
Making methanol from synthesis gas	Copper	$CO + 2H_2 \longrightarrow CH_3OH$

ENZYMES.

Enzymes are complex globular protein molecules which catalyse the chemical reactions which take place inside the living cells of plants and animals. Enzymes are very efficient catalysts, giving greater increases in reaction rates than inorganic catalysts. Enzymes catalyse reactions by lowering the activation energy for the reaction. The enzyme forms a complex with the substrate or substrates (reactants) and then once the products are formed they are released and the enzyme is free to form a complex with more substrate. Enzymes, are very specific to a particular reaction due to the shape of the active sites in the enzyme matching the shape of the substrate molecules in what is known as a lock and key mechanism.



ENZYMES USED IN INDUSTRY.

Enzymes are widely used in industry as unlike inorganic catalysts they work at lower temperatures, normal pressures and at pH levels that are easy to achieve. The use of an enzyme, therefore, means relatively low production costs. Enzymes are widely used in industry as unlike inorganic catalysts they work at lower temperatures, normal pressures and at pH levels that are easy to achieve. the use of an enzyme, therefore, means relatively low production costs.
Examples of industries which use enzymes include

Brewing:- Zymase is the enzyme, present in yeast, which brings about the fermentation of glucose to ethanol.

$C_6H_{12}O_6 \qquad 2C_2H_5OH + 2CO_2$

Detergents:- Enzymes such as protease are added to biological detergents in order to digest protein based stains such as blood and food stains like egg. Another advantage of biological detergents is that they have to work at relatively low temperatures (about 40°C) in order to avoid denaturing the enzyme. Using low temperatures saves energy in the washing process. A lipase may be added to break down fats.

Stone washed denim.
In order to achieve the ‘stone washed’ look of denim the denim is washed using a detergent containing cellulase enzymes.

Food industry.
Hydrolase enzymes are used in the beer and fruit juice industry to remove the haziness that forms in drinks, especially when they are chilled.

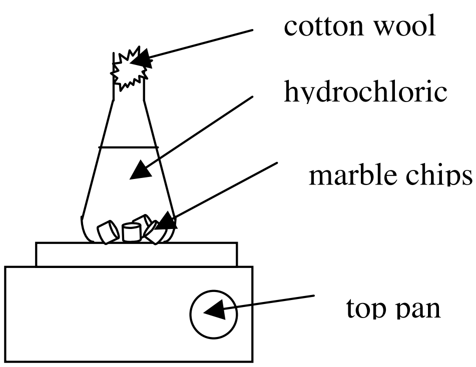
Hydrolases are also used for tenderising meat, making the soft centres of sweets (it stops the ingredients hardening).

Leather manufacture.
Hydrolases are used in the tanning industry to make hides more pliable.

Reaction Progress 3.5

Following the rate of a reaction.

Reactions can be followed by measuring changes in concentration, massor volume of reactants or products. A suitable reaction to study is that between marble chips and hydrochloric acid using the apparatus shown



Time (s)	Mass loss (g)
0	0
30	1.25
60	2.00
90	2.45
120	2.80
150	3.05
180	3.35
210	3.55
240	3.70
270	3.80
300	3.95
330	4.05
360	4.10

Equation $CaCO_3 + 2\,HCl \Rightarrow CaCl_2 + CO_2 + H_2O$

1. Draw a graph of Mass loss in grams against time in seconds.

2. Use your graph to determine the rate of reaction between 0 to 100 s.

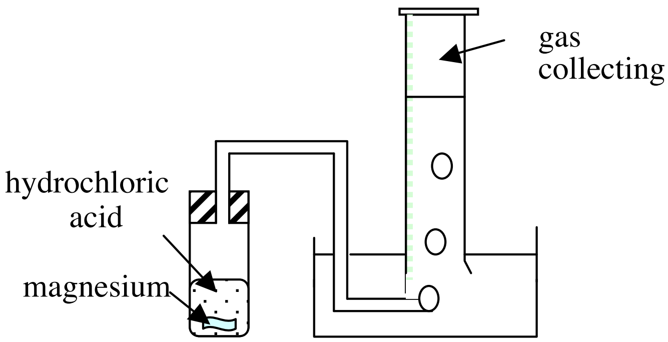
Rate of reaction = $\frac{\text{mass of } CO_2}{\text{time interval}}$

3. Use your graph to determine the rate of reaction between 100 s and 200 s.

Rate of reaction is the change in quanity of a reactant or product per unit of time.

Average rate = $\frac{\text{change in quantity}}{\text{change in time}}$

Similarly when a gas is produced we can measure the volume of gas per unit of time



Time (s)	Volume of hydrogen(cm^3)
0	0
10	22
20	40
30	51
40	62
50	70
60	76
70	80
80	84
90	87
100	89
110	90
120	90

1. Draw a graph of Volume of hydrogen ((cm^3) against time (s)
2. Calculate the average rate of reaction for time interval 0s - 20 s in $cm^3\ s^{-1}$.
3. Calculate the average rate of reaction for time interval 40s - 80 s in $cm^3\ s^{-1}$.

Activation Energy 3.6

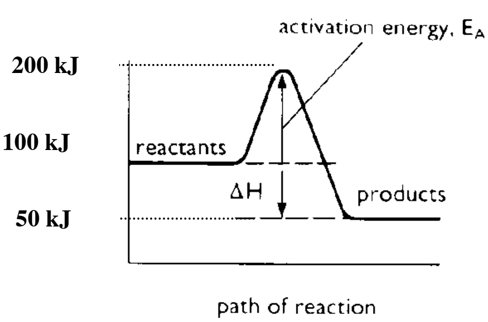
A potential energy diagram can be used to show the amount of chemical energy stored in the reactants and products of a reaction. In a reaction where energy is given out in going from reactants to products (anexothermic reaction) the energy change, which we call the enthalpy of reaction ΔH, is shown by a negative sign.

ΔH = (Potential energy of products) – (potential energy of reactants).

In a reaction where energy is taken in from the surroundings, the products will have more potential energy than the reactants and so the enthalpy change, ΔH, will be positive.

A potential energy diagram can also be used to show the value of the activation energy (EA). In most reactions not every collision between reactants results in successful reaction - in many cases the colliding particles just bounce off each other without reacting. Only pairs of reactant particles with enough energy to overcome the energy barrier, or activation energy, will go on to produce products.

Consider the potential energy diagram for the following **exothermic** reaction.



i) Calculating the enthalpy of reaction.

ΔH = Potential energy of products – Potential energy of reactants

= kJ

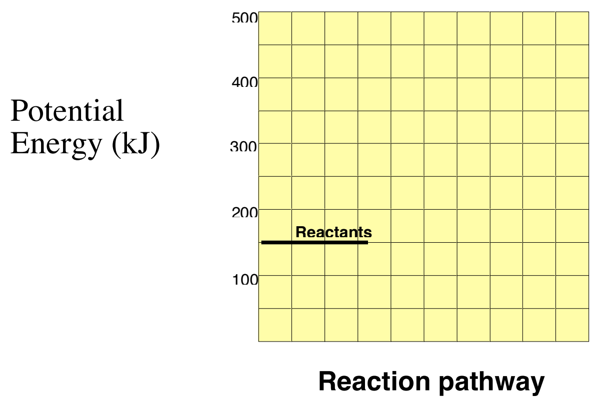
ii) Calculating the activation energy.

E_A = kJ

= kJ

An endothermic reaction.

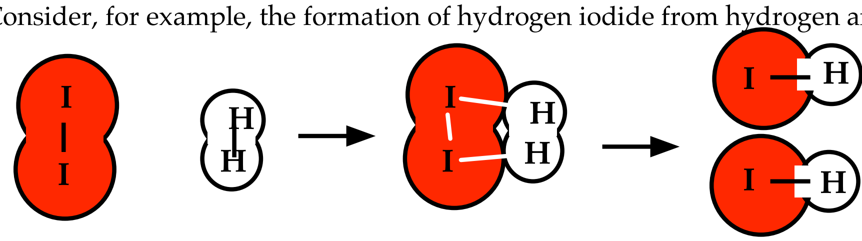
Complete the energy diagram below for an **endothermic reaction** in which the enthalpy change (ΔH) is +150 kJ and the activation energy (EA) is + 250 kJ.



THE ACTIVATED COMPLEX.

The activated complex is an unstable arrangement of atoms formed at the maximum of the potential energy barrier, during a reaction. This unstable arrangement of atoms comes about by the partial breaking of bonds holding the reactants together and the partial making of bonds in the new products.

Consider, for example, the formation of hydrogen iodide from hydrogen and iodine.



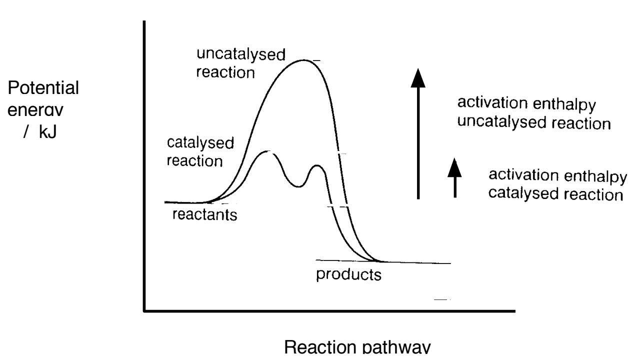
Iodine and hydrogen molecules just before collision

Activated complex with partly broken and partly made bonds As the molecules collide into each other the kinetic energy is changed into potential energy

Hydrogen iodide molecules formed after reaction

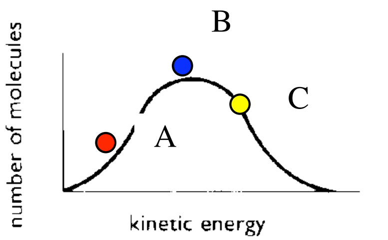
The activation energy s the additional potential energy required by colliding molecules to form the activated complex.

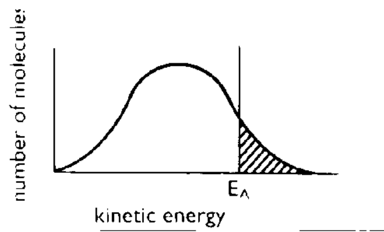
Effect of a catalyst



A catalyst is a substance which speeds up a chemical reaction without being changed at the end of the reaction. Catalysts are thought to work by providing an alternative reaction pathway with a lower activation energy. By lowering the activation energy reactant molecules in the reaction mixturewill now posses enough energy to react upon collisions and so the rate of the reaction will increase. In the potential energy diagram shown the catalysed reaction occurs as two separate steps, each of which has its own activation energy. The overall activation energy is, however, the activation energy of the first step only as it is higher than that for the second step.

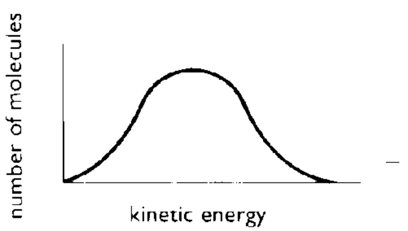
Energy Distribution 3.7

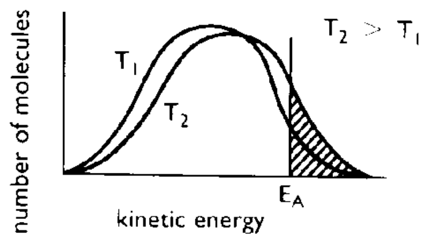




At A only a small number of molecules are represented, these molecules are low in kinetic energy.
At B a larger number of molecules have middling amount of energy.
At C a small number of molecules have a high energy
In other diagram only a small number of molecules have Ea i.e. sufficient energy to form an activatedcomplex when they collide and hence go on to form products

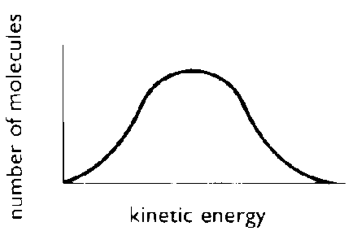
Increasing the Temperature

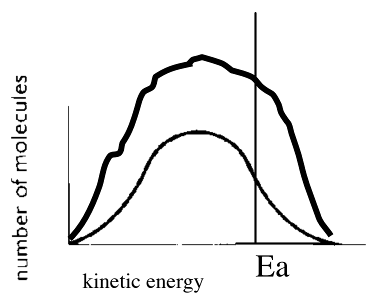




Increasing the temperature, increases the average energy of the reactant molecules, more collisions have Ea and hence the reaction rate increases

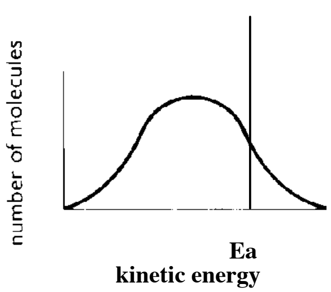
Increasing the concentration

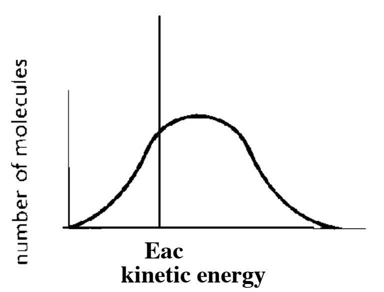




Increasing the concentration increases the number of collision with Ea. This increases the rate of reaction

Using a catalyst





Using a catalyst lowers the activation energy, more molecules when they collide will form activated complexes and go on to form products. Catalysts increase the rate of reaction.