Chapter 8a (AS-Level)

Reaction kinetics

Rates of reaction – why bother?

There are many reasons why chemists study the rate of reaction, for example to:

- Gain insight into the reaction mechanism (how the reaction proceeds).
- Understand the chemical processes taking place in our bodies and environment.
- Improve the rate of the production in chemical industries.

When a reaction proceeds through several steps, the slowest step in the mechanism determines the overall rate of the reaction, and it is called the rate-determining steps.

Chemical reactions proceed at different rates

The rate of reactions tells us how fast the reaction occurs. It is measured by amount of a reactant used up, or the amount of product produced, in a given time.

$$Reaction\ rate = \frac{Change\ in\ amount\ or\ concentration}{Time\ taken}$$

$$Rate = -\frac{\Delta[\text{Reactant}]}{\Delta\text{Time}}$$

OR:

$$Rate = +\frac{\Delta[\text{Product}]}{\Delta\text{Time}}$$

The reaction rate is a positive quantity.

Example:

$H_2O_2 + 2\ I + 2\ H \rightarrow 2\ H_2O + I_2$

If concentration of I_2 is changed from 0 to 10^{-5} mole in 10 seconds, then the reaction rate is:

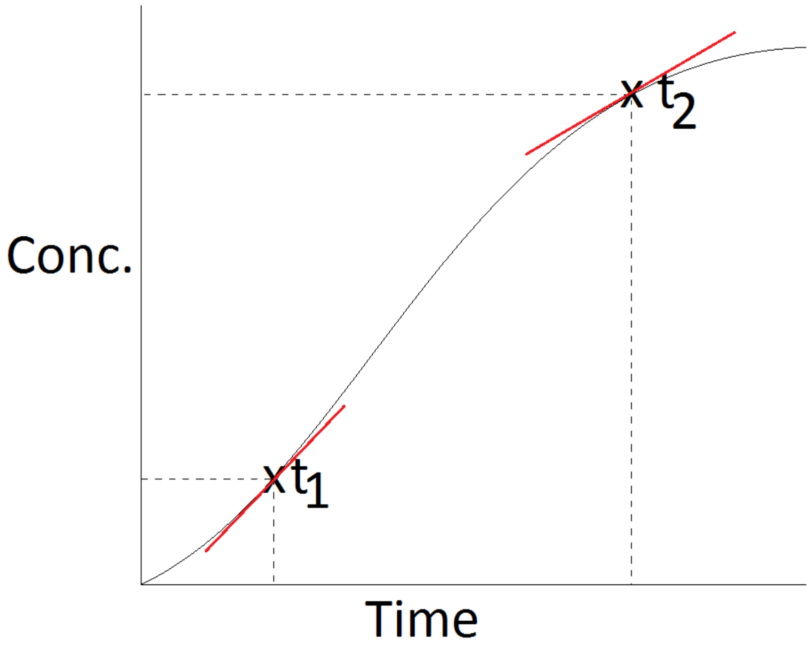
$$Rate = \frac{\Delta[I_2]}{\Delta t} = \frac{10^{-5} - 0}{10} = 10^{-6}$$

The unit is always mol.dm^{-3}.s^{-1}

When Δt approaches 0,

$Rate = \frac{\Delta[I_2]}{\Delta t} \rightarrow \frac{d[I_2]}{dt}$, which is the instantaneous reaction rate at time t.

In practice, it is the slope of the tangent at time t, to the concentration-time curve.



Rate at time t_1 > rate at time t_2

Reaction rate starts high and then decreases with time.

Factors affecting the reaction rate

1. Concentration of reactants

In general, increasing the concentration of the reactants increases the reaction rate.

Example:

$$2\ HCl + Mg \rightarrow MgCl_2 + H_2$$

Increasing HCl increases the rate, which is seen as more vigorous evolution of H_2.

In gaseous reactions, increasing the pressure increases the reaction rate e.g. as in Haber's process.

2. Temperature

In general, increasing the temperature increases the rate. Increasing the temperature by 10 degrees, increases the rate by a factor of 2 (doubles the rate).

For example, a catalytic converter only functions properly if it is hot, as the reactions on the surface of the catalyst are negligible when it is cold.

3. The surface area in heterogeneous reactions

Increasing the surface area of a solid or liquid reactant increases the rate.

Example:

$$2\ HCl + Mg \rightarrow MgCl_2 + H_2$$

Magnesium may be in ribbon or powder form. Using the powder form, the reaction is a lot faster.

4. In some reactions, the intensity of light

Increasing the light intensity of radiation (visible or UV light) increases the rate.

For example, in the free radical substation of methane by chlorine, an increase in the intensity of UV light increases the rate of the reaction.

5. Catalysts

Catalysts usually speed up the reaction by lowering the activation of the energy of the reaction.

For example, nickel is used in the hydrogenation of vegetable oils to make margarine.

Monitoring and measuring reaction rates

We can measure reaction rates in a variety of ways to study the factors which affect the chemical reaction rates. To study the effect of temperature on a reaction's rate, all the other variables must be kept constant, while the temperature may be changed. A fair test is required.

We must also know the mole ratios of the reactants and products as shown by the balanced chemical equation. No side reactions must be taking place, as these will affect the measurements.

Now the way in which the reaction progress can be monitored must be decided. There are 2 types of method accessible to us:

1. Destructive method

This based on chemical analysis, for example, using titration. Samples are taken from reaction mixture at suitable intervals, quenched (to stop the reaction, using ice for example) and analyzed (and the concentration is determined).

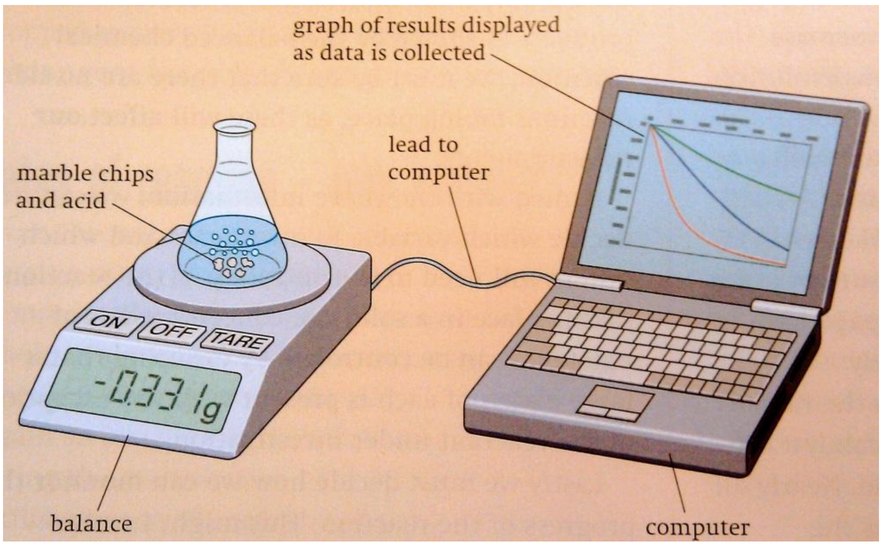
2. Non-destructive methods

This is done using physical methods to measure a property that changes as reaction proceeds. Properties like mass, volume, pressure, pH, colour, electric conductivity can be used at regular time intervals (quenching not included).

Monitoring reaction rate using mass loss

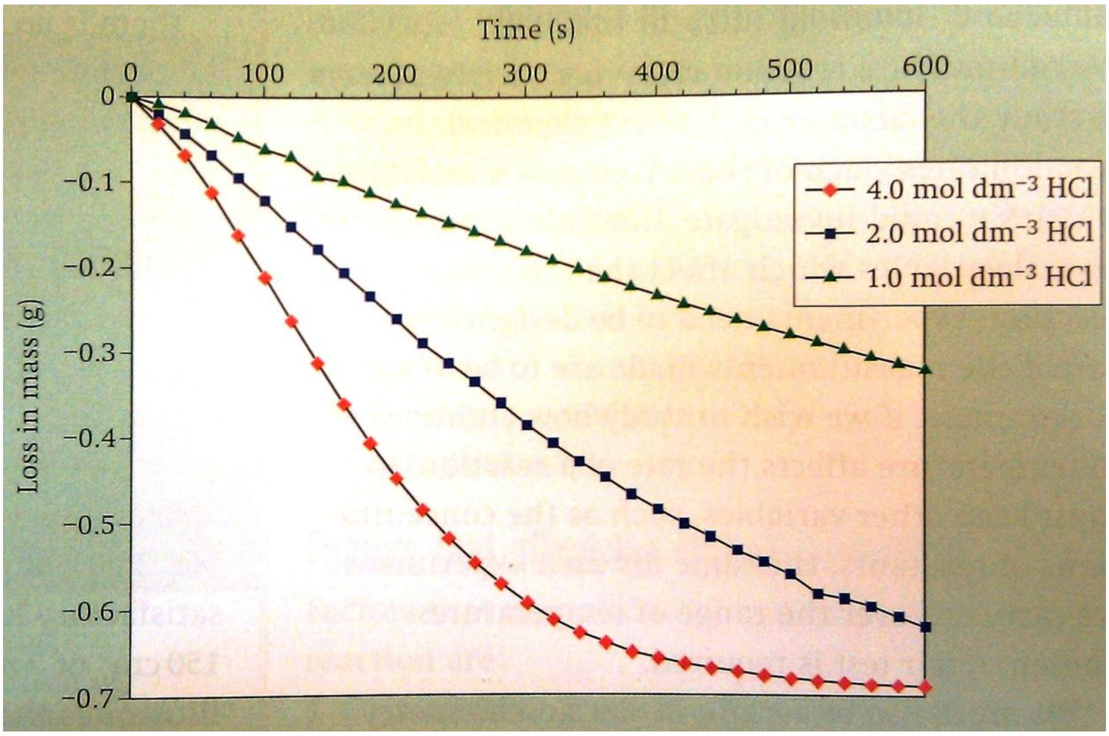
When a gas is evolved during a reaction, monitoring mass loss may provide a suitable method of measuring the reaction rate.

There needs to be sufficient loss in mass to be followed using a reasonably accurate balance. For example, 2.00 g of small marble chips will give a satisfactory loss in mass when treated with 150 cm^3 of hydrochloric acid.



Ideally, the mass loss can be monitored using a computer. The following figure shows the apparatus used to measure the mass loss during the reaction of marble chips with hydrochloric acid.

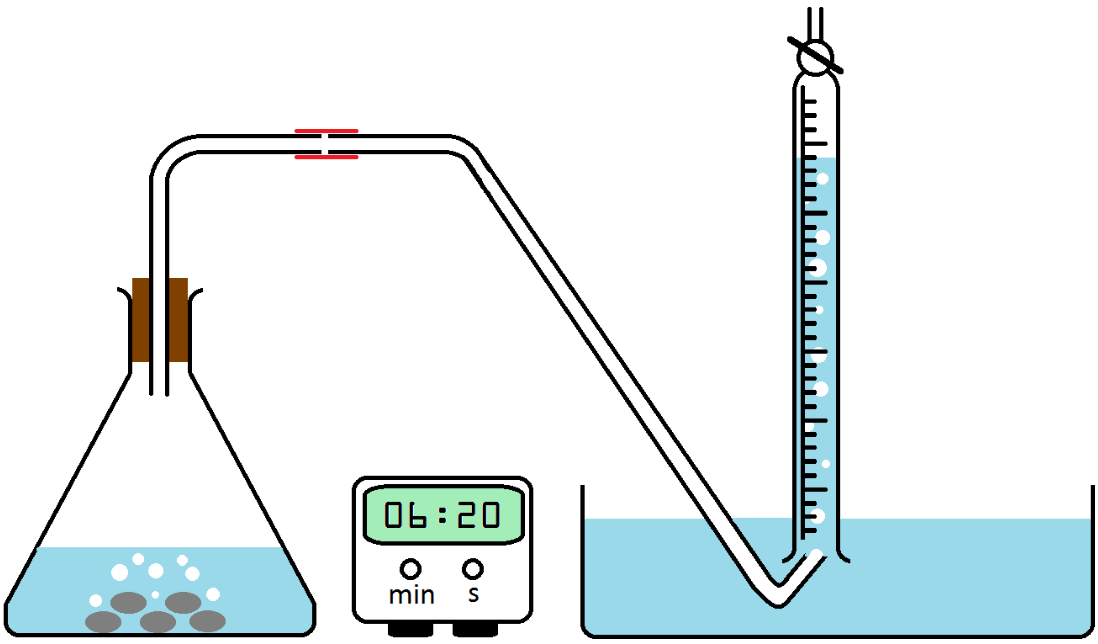
The following figure shows the computer-generated graph showing mass loss against time. The gradient shows the reaction rate at time t.



Monitoring the reaction rate using volume of gas evolved

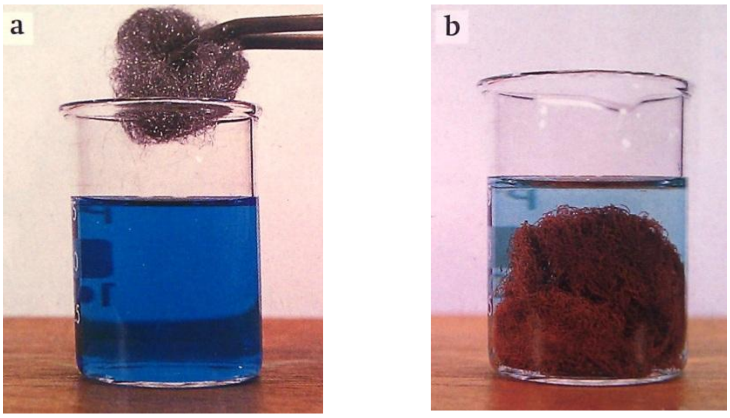
The reaction of calcium carbonate with hydrochloric acid may also be monitored by collecting the carbon dioxide evolved. The gas may be collected in a gas syringe or in an inverted water-filled burette. The volume of carbon dioxide produced over a period of time is proportional to the reaction rate.

The following figure show the apparatus used to measure the reaction rate.



Monitoring reaction rate using colour intensity

Using colour intensity, concentration of a specific substance can be measured. For example, the concentration of copper ions in the following experiment can be estimated using a spectrophotometer.



The copper ions replace the atoms of iron. After several minutes, the blue colour of (a) has become paler and a red-brown deposit has formed on the iron wool (b).

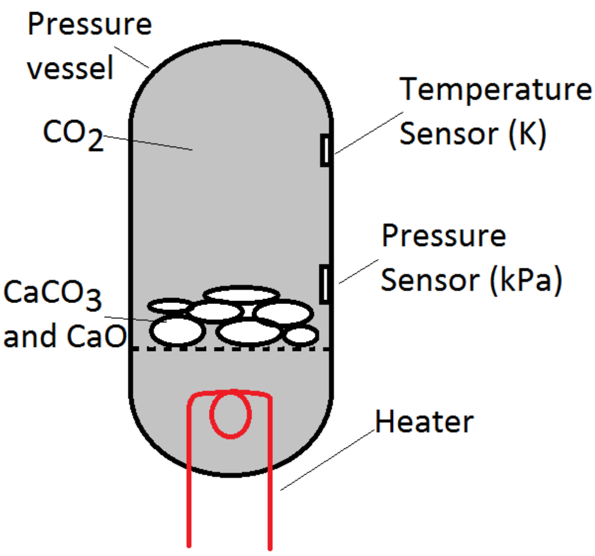
The spectrophotometer is a device that measures how much light of a particular wave-length can pass through a sample, liquid or gas.

The beaker in (a) contains 1 dm^3 of 1.00 mol dm^{-3} aqueous copper sulphate. Iron wool reacts with the copper ions in the solution, displacing them and changing the colour of the solution as a result.

$$Cu^{2+} (aq) + Fe (s) \rightarrow Fe^{2+} (aq) + Cu (s)$$

Solutions appear coloured because they absorb radiation in the visible region of the spectrum. Aqueous copper sulphate absorbs radiation in the yellow, orange and red regions, which only allows blue light to pass through and so the solution looks blue.

Measuring reaction rates of gases using pressure changes



Measurements of pressure changes at a given temperature can be used to calculate concentration change as a reaction proceeds. For example, this method can be used to monitor the production of carbon dioxide from limestone in a sealed container.

$$CaCO_3 (s) \rightleftharpoons CaO (s) + CO_2$$

The figure shows a notional system to investigate the effect of heat on the decomposition of limestone.

Monitoring reaction rates of solutions using chemical analysis

If there is a change in acidity or basicity as a reaction proceeds, suitable titrations can be made to follow the rate. The rate of formation of sulphurous acid, H_2SO_3 (a component of acid rain formed by the reaction of SO_2 with water), could be followed by measuring the increase in concentration of hydrogen ions produced.

This is monitored by titrating samples of the increasingly acidic solution against a basic solution of known concentration, for example, 0.001 mol dm^{-3} aqueous sodium hydroxide. The more sodium hydroxide that is needed to neutralize the sample, the more sulphuric acid is present.

The collision theory of reactivity

For a reaction to occur:

1. There should be collisions between the molecules of reactants
2. These collisions should be energetic enough
3. They should occur with the right orientation of molecules

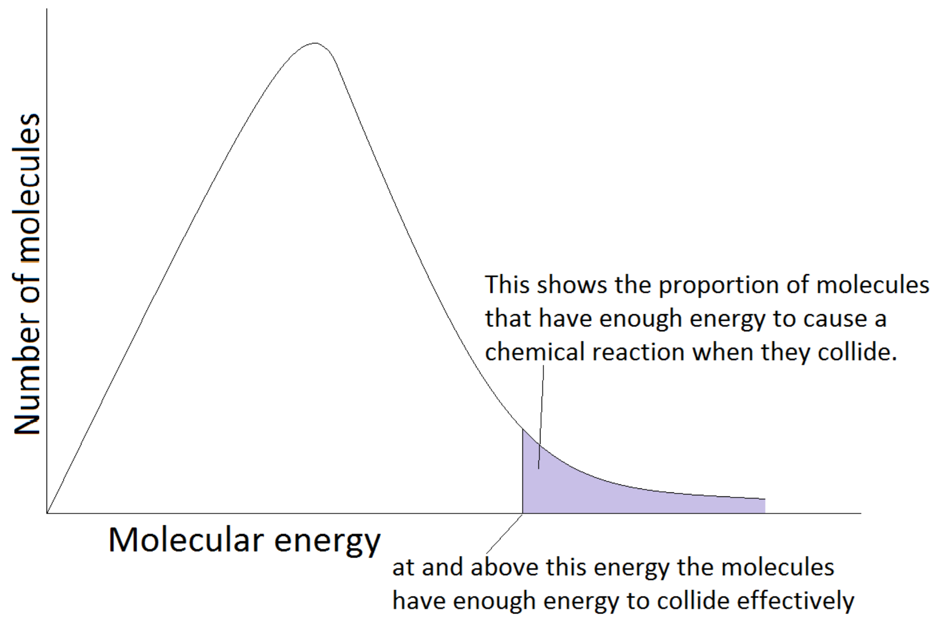
Important points:

- Molecules will react only if they collide with each other
- And if there is enough energy in the collision
- Increasing the concentration increases the probability of collision of collision, which increases the rate of the reaction
- Increasing the temperature increases the proportion of molecules with sufficient energy to react, which increases the rate of reaction

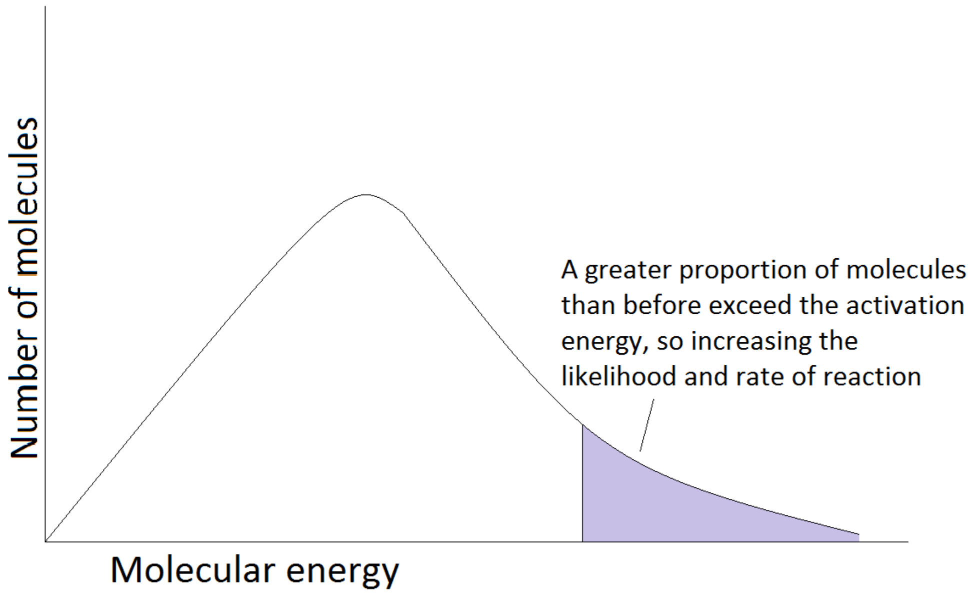
The Boltzmann distribution of molecular energies

The Boltzmann distribution represents the number of particles with particular energies.

Billions and billions of particles in a gas are in constant random motion. A few are almost motionless. A minority have momentarily speeds far above the average. The majority of particles have speeds around the average. This is shown by the graph below. The difference between the energy of the molecules is only due to speed (as they have the same mass).



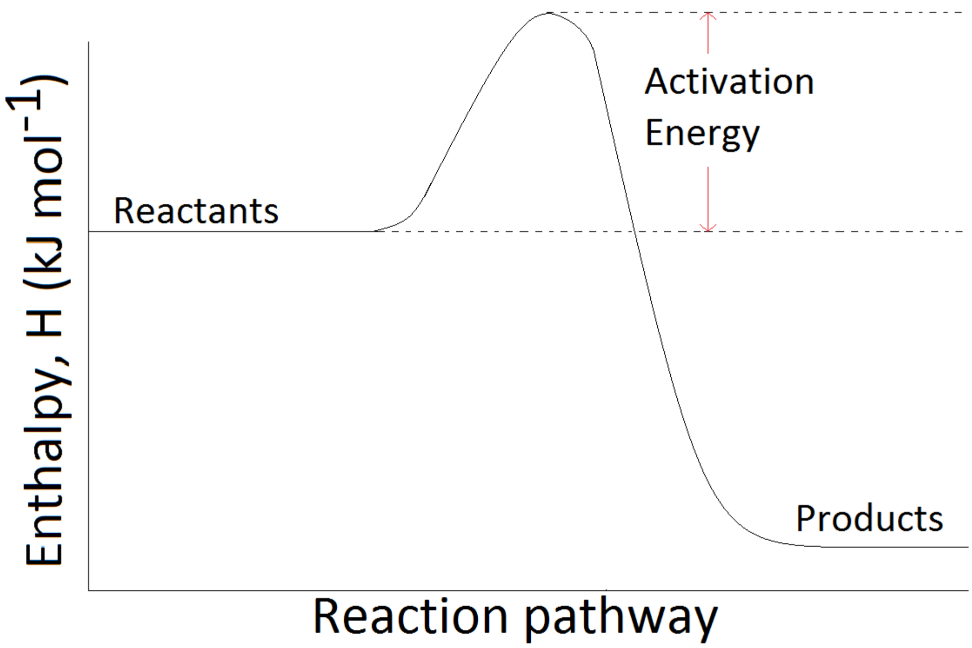
When the sample is heated, the mean energy of the molecules increases. There is a wider spread of values.



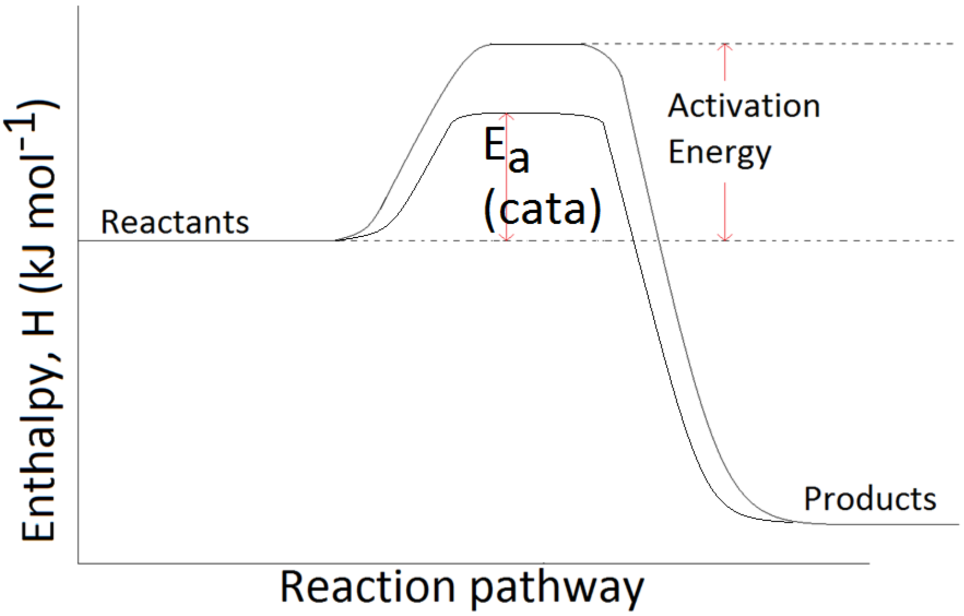
Activation energy is the minimum energy needed in a collision in a given reaction to be productive. It is shown on the above graph and the one before it as the line before the shaded area. It is shown by E_a and has a unit of kJ mol^{-1}.

For example, in the oxyacetylene torch, the molecules of oxygen and ethyne will not react together even if they collide, as the outer shell electrons of both molecules repel each other. This repulsion can only be overcome by a substantial input of energy that bonds would be broken and attractive forces can take over.

This boost of energy is given by igniting the mixture of the gases. This is shown diagrammatically in the following graph.

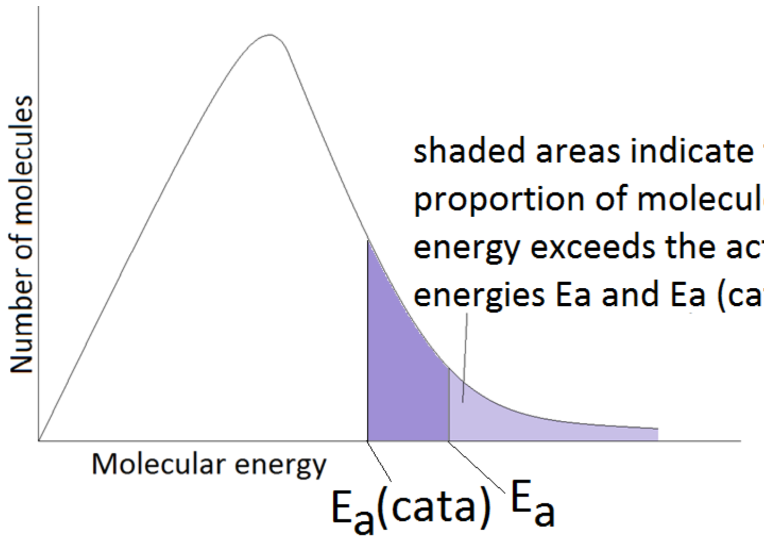


With a catalyst:



A catalyst is a substance added to reactions in the purpose of increasing the rate. It doesn't change at the end of the reaction. It lowers the energy of activation which is achieved by allowing the reaction to take place by a different mechanism or by a different pathway.

The reaction rate increases because the catalysed reaction pathway has lower activation energy than that of the uncatalysed reaction. The Boltzmann distribution below shows how the lower activation energy increases the number of molecules that will react on collision.



Enzymes

These are proteins that act as biological catalysts. Enzymes:

- Show great specificity
- Are extremely sensitive to changes in pH and temperature
- Are extremely sensitive to molecules that are inhibitors and cofactors
- Are far more efficient than the inorganic catalysts used in the chemical industry

END OF LESSON