COLLISION THEORY

Collision theory of reaction rates concentrates on the key things which decide whether a particular collision will result in a reaction - in particular, the energy of the collision, and whether or not the molecules hit each other the right way around (the orientation of the collision). We are going to look in detail at reactions which involve a collision between two species (any sort of particle - molecule, ion, or free radical). Reactions where a single species falls apart in some way are slightly simpler because orientation of collisions is no longer a factor. Reactions involving collisions between more than two species are extremely uncommon.

Reactions involving collisions between two species

Two species can only react together if they come into contact with each other. They first have to collide, and then they ***may*** react. Why "may react"? It isn't enough for the two species to collide - they have to collide the right way around, and they have to collide with enough energy for bonds to break.

The chances of all this happening if your reaction needed a collision involving more than 2 particles are remote. All three (or more) particles would have to arrive at exactly the same point in space at the same time, with everything lined up exactly right, and having enough energy to react.

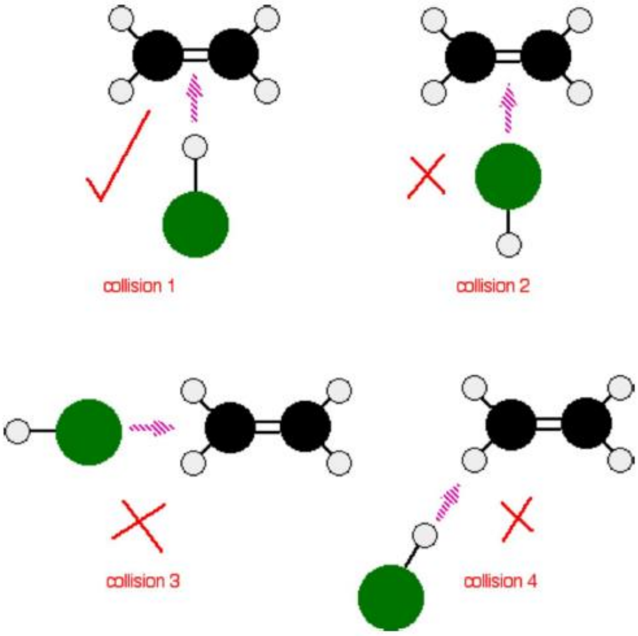
The orientation of collision

Consider a simple reaction involving a collision between two molecules - ethene, $CH_2=CH_2$, and hydrogen chloride, HCl, for example. These react to give chloroethane. As a result of the collision between the two molecules, the double bond between the two carbons is converted into a single bond. A hydrogen atom gets attached to one of the carbons and a chlorine atom to the other.

$$CH_2=CH_2 + HCl \rightarrow CH_3CH_2Cl$$

As a result of the collision between the two molecules, the double bond between the two carbons is converted into a single bond. A hydrogen atom gets attached to one of the carbons and a chlorine atom to the other.

The reaction can only happen if the hydrogen end of the H-Cl bond approaches the carbon-carbon double bond. Any other collision between the two molecules doesn't work. The two simply bounce off each other.

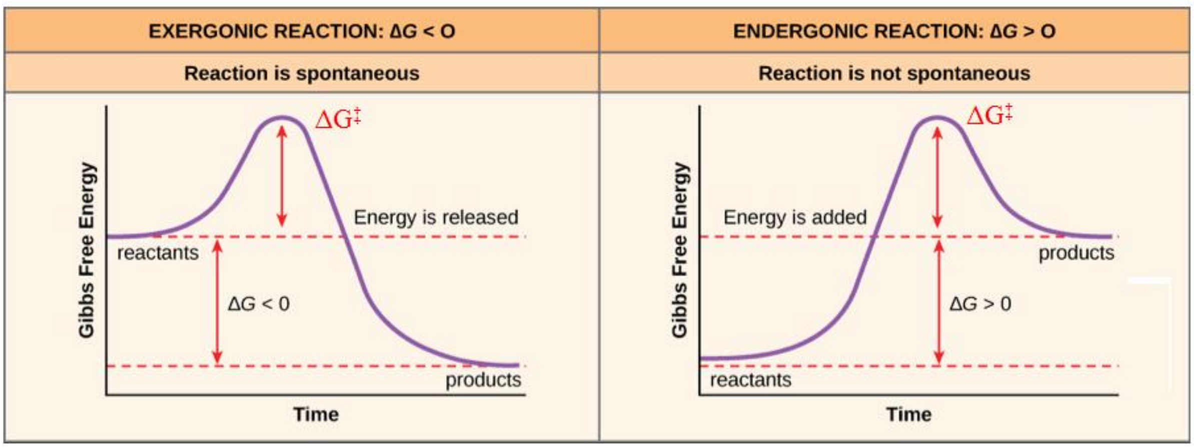


In any collision involving unsymmetrical species, you would expect that the way they hit each other will be important in deciding whether or not a reaction happens.

The energy of the collision

Activation Energy

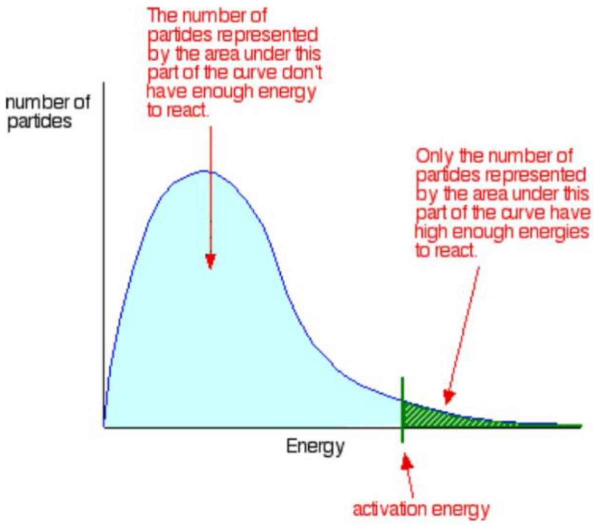
Even if the species are orientated properly, you still won't get a reaction unless the particles collide with a certain minimum energy called the activation energy of the reaction. Activation energy is the minimum energy required before a reaction can occur. You can show this on an energy profile for the reaction. For a simple over-all exothermic reaction, the energy profile looks like this:



If the particles collide with less energy than the activation energy, nothing important happens. They bounce apart. You can think of the activation energy as a barrier to the reaction. Only those collisions which have energies equal to or greater than the activation energy result in a reaction. Any chemical reaction results in the breaking of some bonds (needing energy) and the making of new ones (releasing energy). Obviously some bonds have to be broken before new ones can be made. Activation energy is involved in breaking some of the original bonds. Where collisions are relatively gentle, there isn't enough energy available to start the bond-breaking process, and so the particles don't react.

The Maxwell-Boltzmann Distribution

Because of the key role of activation energy in deciding whether a collision will result in a reaction, it would obviously be useful to know what sort of proportion of the particles present have high enough energies to react when they collide. In any system, the particles present will have a very wide range of energies. For gases, this can be shown on a graph called the Maxwell-Boltzmann Distribution which is a plot of the number of particles having each particular energy.



$$k = Ae^{-\frac{\Delta G^{\ddagger}}{RT}}$$

k = Chemical Reaction Rate
A = Pre-exponential Factor
E_a = Activation Energy
R = Gas Constant
T = Temperature in Kelvin

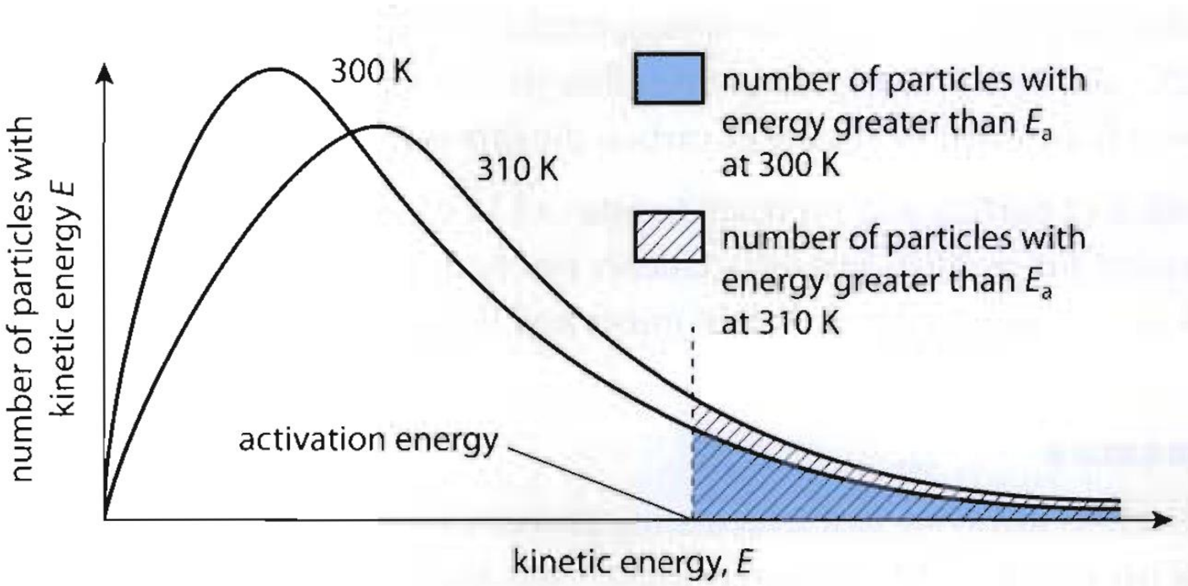
Notice that the large majority of the particles don't have enough energy to react when they collide. To enable them to react we either have to change the shape of the curve, or move the activation energy further to the left.

You can change the shape of the curve by changing the temperature of the reaction and you can change the position of the activation energy by adding a catalyst to the reaction.

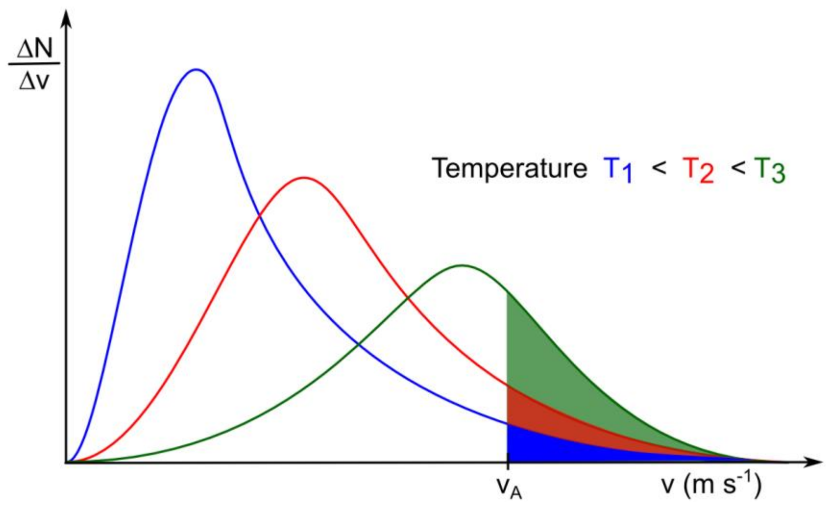
THE EFFECT OF TEMPERATURE

As you increase the temperature the rate of reaction increases. As a rough approximation, for many reactions happening at around room temperature, the rate of reaction doubles for every 10°C rise in temperature. You have to be careful not to take this too literally. It doesn't apply to all reactions. Even where it is approximately true, it may be that the rate doubles every 9°C or 11°C or whatever. The number of degrees needed to double the rate will also change gradually as the temperature increases.

Particles can only react when they collide. If you heat a substance, the particles move faster and so collide more frequently. That will speed up the rate of reaction. Also, Collisions only result in a reaction if the particles collide with enough energy to get the reaction started (activation energy). Increasing the temperature changes the shape of the graph.



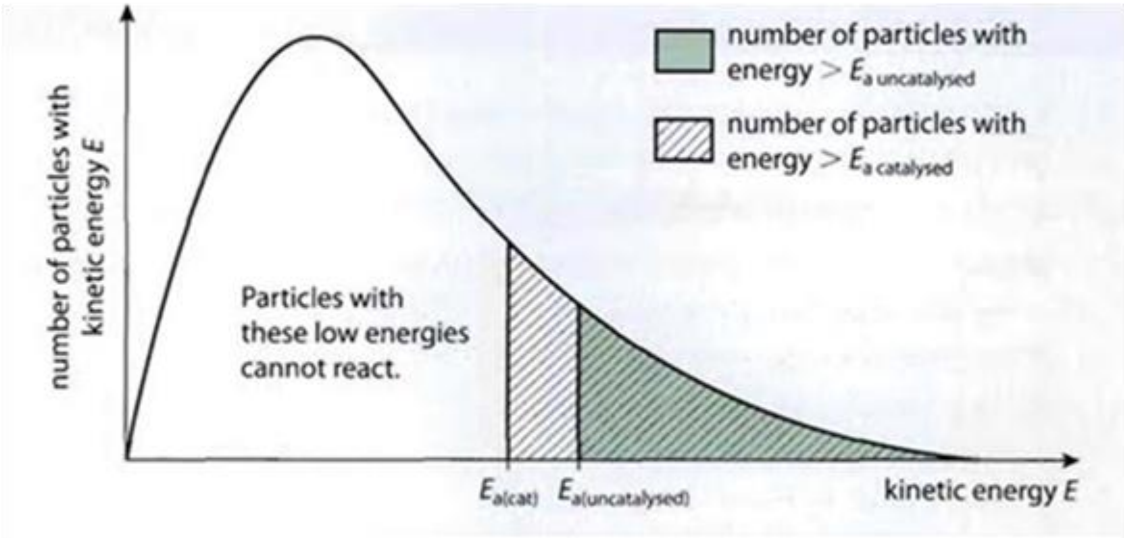
Increasing the temperature increases reaction rates because of the disproportionately large increase in the number of high energy collisions..



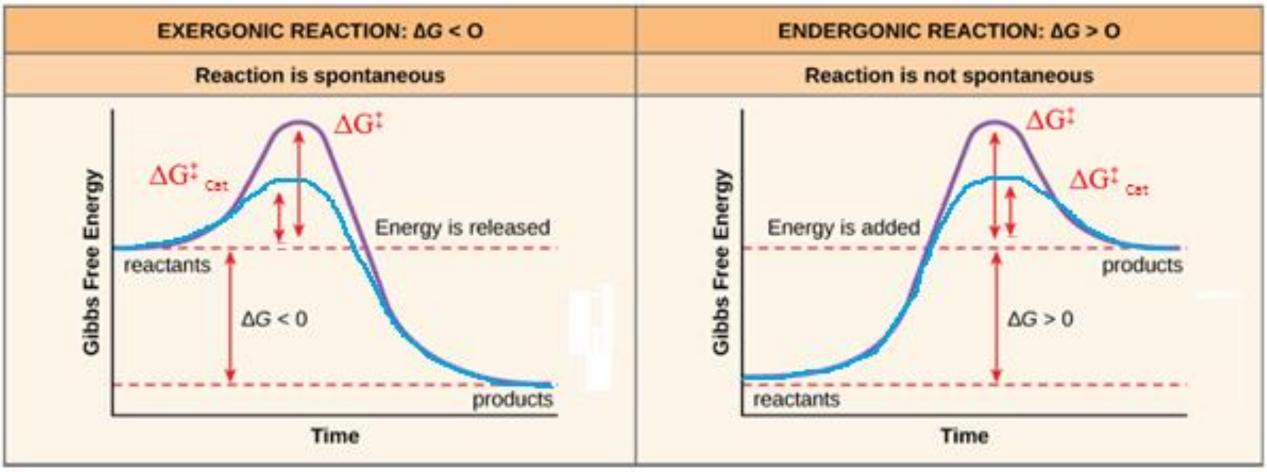
THE EFFECT OF CATALYSTS

A catalyst is a substance which speeds up a reaction, but is chemically unchanged at the end of the reaction.

To increase the rate of a reaction you need to increase the number of successful collisions. One possible way of doing this is to provide an alternative way for the reaction to happen which has a lower activation energy.



Adding a catalyst has exactly this effect on activation energy. A catalyst provides an alternative route for the reaction. That alternative route has a lower activation energy.



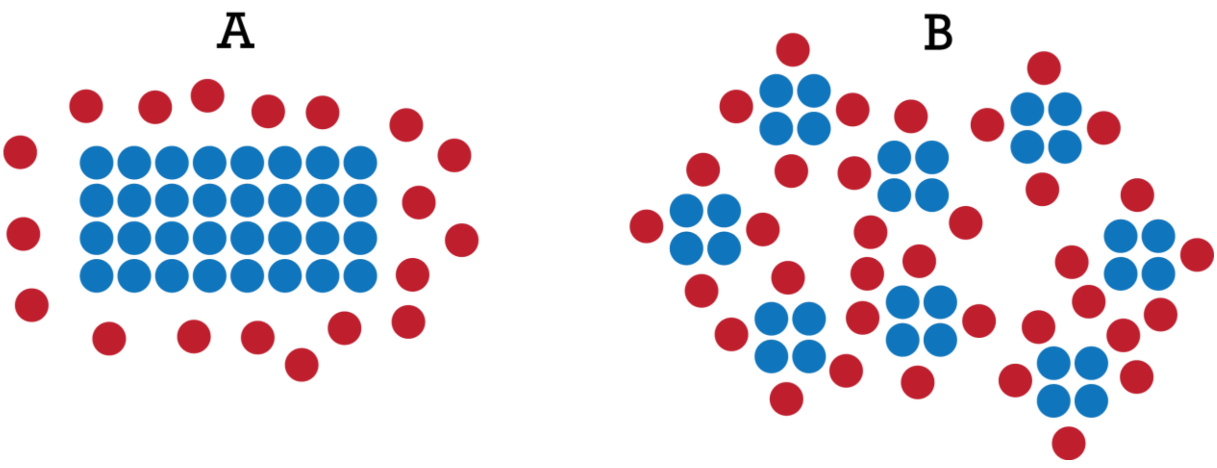
Be very careful if you are asked about this in an exam. The correct form of words is "A catalyst provides an alternative route for the reaction with a lower activation energy." It does not "lower the activation energy of the reaction". There is a subtle difference between the two statements that is easily illustrated with a simple analogy. Suppose you have a mountain between two valleys so that the only way for people to get from one valley to the other is over the mountain. Only the most active people will manage to get from one valley to the other. Now suppose a tunnel is cut through the mountain. Many more people will now manage to get from one valley to the other by this easier route. You could say that the tunnel route has a lower activation energy than going over the mountain. But you haven't lowered the mountain! The tunnel has provided an alternative route but hasn't lowered the original one. The original mountain is still there, and some people will still choose to climb it.

In the chemistry case, if particles collide with enough energy they can still react in exactly the same way as if the catalyst wasn't there. It is simply that the majority of particles will react via the easier catalysed route.

THE EFFECT OF SURFACE AREA

This applies to reactions involving a solid and a gas, or a solid and a liquid and it also includes cases where the solid is acting as a catalyst.

The more finely divided the solid is, the faster the reaction happens. A powdered and distributed solid will produce a faster reaction than if the same mass is present as a single lump. The powdered solid has a greater surface area than the single lump.



You are only going to get a reaction if the particles in the gas or liquid collide with the particles in the solid. Increasing the surface area of the solid increases the chances of collision taking place.

SOLVENT EFFECT

The nature of the solvent can also affect the reaction rates of solute particles. For example, a sodium acetate solution reacts with methyl iodide in an exchange reaction to give methyl acetate and sodium iodide.

$$CH_3CO_2Na(aq) + CH_3I(l) \rightarrow CH_3CO_2CH_3(aq) + NaI(aq)$$

This reaction occurs 10 million times more rapidly in the organic solvent dimethylformamide [DMF; $(CH_3)_2NCHO$] than it does in methanol (CH_3OH). Although both are organic solvents with similar dielectric constants (36.7 for DMF versus 32.6 for methanol), methanol is able to hydrogen bond with acetate ions, whereas DMF cannot. Hydrogen bonding reduces the reactivity of the oxygen atoms in the acetate ion.

Solvent viscosity is also important in determining reaction rates. In highly viscous solvents, dissolved particles diffuse much more slowly than in less viscous solvents and can collide less frequently per unit time. Thus the reaction rates of most reactions decrease rapidly with increasing solvent viscosity.

PHASE EFFECT

When two reactants are in the same fluid phase, their particles collide more frequently than when one or both reactants are solids (or when they are in different fluids that do not mix). If the reactants are uniformly dispersed in a single homogeneous solution, then the number of collisions per unit time depends on concentration and temperature, as we have just seen. If the reaction is heterogeneous, however, the reactants are in two different phases, and collisions between the reactants can occur only at interfaces between phases. The number of collisions between reactants per unit time is substantially reduced relative to the homogeneous case, and, hence, so is the reaction rate. The reaction rate of a heterogeneous reaction depends on the surface area of the more condensed phase.

NATURE OF REACTANTS

Individual properties of substances also affect reaction rates. The scope of these properties is broad and there are few generalizations that you can apply consistently. Some of the properties in this category are state of matter, molecular size, bond type and bond strength.

State of Matter

Gases tend to react faster than solids or liquids: It takes energy to separate particles from each other. In order to burn candle wax, the solid wax has to be melted and then vaporized before it reacts with oxygen. Methane gas is already in the gas state so it burns faster than wax.

Aqueous ions tend to react faster than species in other states of matter: Solid lead(II) nitrate will react with solid potassium iodide, but the reaction is really, really slow. That's because the ionic bonding in each reactant is strong and the ions in each compound are hard to separate from each other. When aqueous solutions of these compounds are mixed, the formation of lead(II) iodide is rapid. In aqueous solutions, the ions of each compound are dissociated. When the two the solutions are mixed together, all that is required for a reaction to occur is contact between the lead(II) ions and the iodide ions.

Bond Type

Reactions involving ionic species tend to proceed faster than reactions involving molecular compounds.

Bond Strength

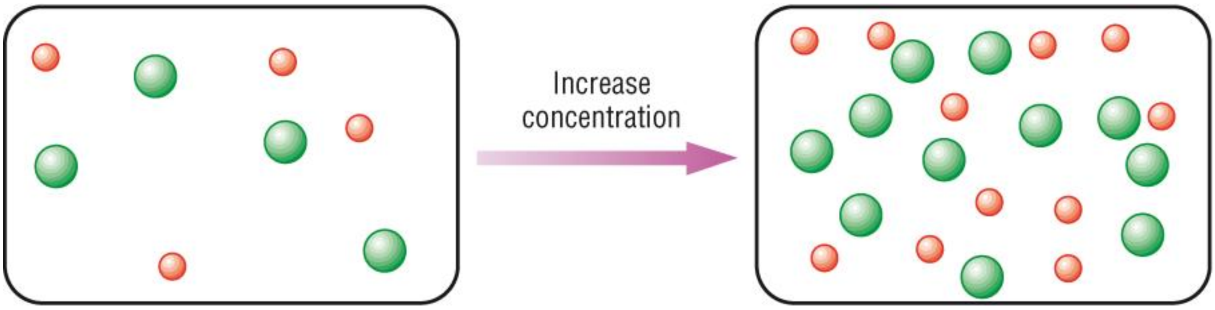
Reactions involving the breaking of weaker bonds proceed faster than reactions involving the breaking of stronger bonds. For example, double carbon to carbon bonds are stronger than single C-C bonds.

Number of Bonds/Molecular Size

Reactions involving the breaking of fewer bonds per reactant proceed faster than those involving the breaking of a larger number of bonds per reactant.

THE EFFECT OF CONCENTRATION

For many reactions involving liquids or gases, increasing the concentration of the reactants increases the rate of reaction. In a few cases, increasing the concentration of one of the reactants may have little noticeable effect of the rate.
In order for any reaction to happen, those particles must first collide. This is true whether both particles are in solution, or whether one is in solution and the other a solid. If the concentration is higher, the chances of collision are greater.



If a reaction only involves a single particle splitting up in some way, then the number of collisions is irrelevant. What matters now is how many of the particles have enough energy to react at any one time. Suppose that at any one time 1 in a million particles have enough energy to equal or exceed the activation energy. If you had 100 million particles, 100 of them would react. If you had 200 million particles in the same volume, 200 of them would now react. The rate of reaction has doubled by doubling the concentration.

THE EFFECT OF PRESSURE

Increasing the pressure on a reaction involving reacting gases increases the rate of reaction. Changing the pressure on a reaction which involves only solids or liquids has no effect on the
rate.
Increasing the pressure of a gas is exactly the same as increasing its concentration. If you have a given mass of gas, the way you increase its pressure is to squeeze it into a smaller volume. If you have the same mass in a smaller volume, then its concentration is higher.