Characteristics of the Boltzmann distribution

- Most gas molecules have energies within a comparatively narrow range.
- The curve will only meet the energy axis at infinity energy. No molecules have zero energy.
- The area under the distribution curve gives the total number of gas molecules.
- Only those molecules with more energy than the activation energy of the reaction are able to react.

The effect of a concentration change on reaction rate

If the concentration of a reactant in solution or in a gas mixture is increased,

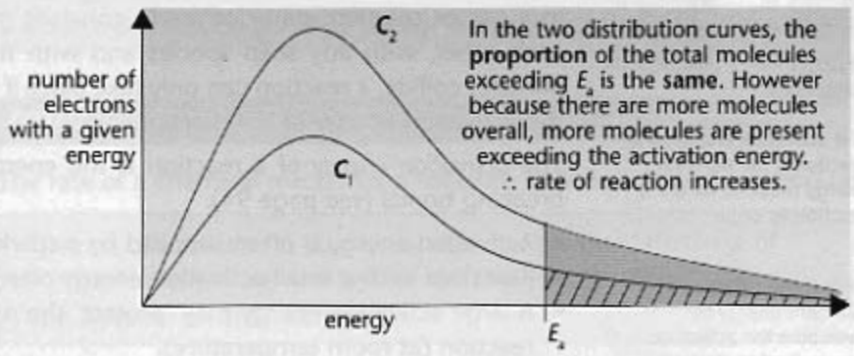
A reaction can only take place if the activation energy is exceeded.

- there are more particles present per volume
- more collisions take place each second
- more collisions exceed the activation energy every second
- therefore the rate of reaction increases.

The diagram below shows distribution curves for two concentrations, C_1 and C_2 where concentration, C_2 > concentration, C_1.

Note that the proportion of the total number of molecules exceeding the activation energy is the same. The rate increases because there are more molecules per volume and more molecules must now exceed the activation energy.

- Providing the temperature is the same, distribution curves for different concentrations have the same shape.



For reactions involving gases, increasing the pressure also increases the concentration of any gas. This results in an increased reaction rate.

The effect of a change in surface area on reaction rate

For a reaction involving a solid, the reaction takes place at a faster rate when the solid is in a powdered form rather than as lumps.
Calcium carbonate reacts with hydrochloric acid producing carbon dioxide gas:

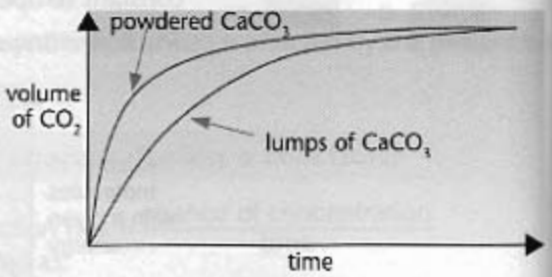
$$CaCO_3(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

By measuring the volume of carbon dioxide gas evolved with time, the rate of this reaction can be monitored. The graph below compares the reaction rates when using an excess of calcium carbonate as powder and as lumps. The same volume of the same concentration of hydrochloric acid has been reacted in both experiments.

The gradient provides an indication of reaction rate.

The steeper the curve, the faster the reaction.

The final volume is the same in both experiments since the same amount (in mol) of hydrochloric acid has been reacted with an excess of calcium carbonate.



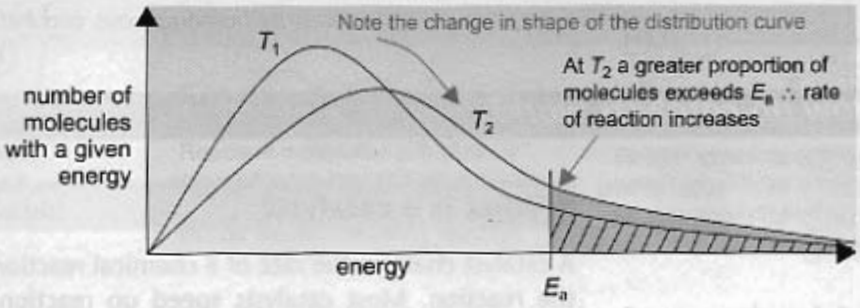
The gradient of the graph is much steeper with powdered carbonate because the surface area available for the reaction with hydrochloric acid is much greater than with lumps allowing more collisions per second.

The effect of a temperature change on reaction rate

The average kinetic energy of the particles is proportional to temperature. As temperature increases, so does the kinetic energy of gas molecules.

The diagram below shows distribution curves for a sample of gas at two temperatures, T_1 and T_2, where temperature, T_2 > temperature, T_1.

Increasing the temperature **moves** the distribution curve to the right.



Increasing the temperature **does not change** the activation energy or the total number of molecules – the **shape of the curve changes.**

A **greater proportion** of molecules **exceeds the activation energy at higher temperature.**

The Boltzmann distribution curve is displaced to the right with the peak lower. The average energy is now increased.

The total area under each curve is a measure of the total number of molecules present, and this is the same for each curve.

An increase in temperature increases the rate of a reaction because:

- the molecules move faster and have more kinetic energy
- there are more collisions each second
- the increased kinetic energy produces more energetic collisions
- a greater proportion of molecules exceed the activation energy.

The feasibility of a chemical reaction

EDEXCEL M2
NICCEA M2
WJEC CH2

The value of the enthalpy change for a reaction provides an indication of the *relative stability* of reactants and products and the *feasibility* of a reaction.

For example, sucrose is oxidised by oxygen in a highly exothermic reaction:

$$C_{12}H_{22}O_{11}(s) + 12O_2(g) \longrightarrow 12CO_2(l) + 11H_2O(g) \quad \Delta H = -5644 \text{ kJmol}^{-1}$$

- The reaction is *very likely* to take place because of the great amount of energy released in this reaction – the products are *thermodynamically* far more stable.
- However, the reaction does not take place spontaneously at room temperature because the reaction has a large activation energy which acts as an energy barrier – the reactants are *kinetically* stable.

Activation energy is the energy barrier of a reaction.

Progress check

1 Explain the following, in terms of collision theory and distribution graphs.
(a) Reactions take place quicker when the reactants are more concentrated.
(b) Reactions take place quicker at higher temperatures.

1 (a) Because there are more molecules per volume, more collisions take place each second. More collisions exceed the activation energy every second, increasing the reaction rate.
(b) The molecules move faster and have more kinetic energy. There are more collisions each second and the increased kinetic energy produces more energetic collisions. A greater proportion of molecules exceeds the activation energy.