8 Reaction kinetics

As with equilibria, reaction kinetics are introduced in this chapter for AS Level but are revisited in Chapter 26 for A Level.

Simple rate equations

You know from practical work that the rates of chemical reactions are affected by three main conditions:

- temperature
- concentration
- presence of a catalyst

For AS Level you need to be able to explain the effects of changes in these conditions using the collision theory. It is important that you learn the correct terms to use when describing how reactions are influenced.

NOW TEST YOURSELF

1 Outline on a molecular scale how each of the factors above affects the rate of a reaction.

A reaction cannot take place unless the reacting particles collide with sufficient energy.

- Not all collisions result in changes and the minimum energy required is called the activation energy, E_a.
- Increasing the temperature increases the proportion of successful collisions.
- Increasing the concentration increases the chance of collisions taking place.
- In the presence of a catalyst, a reaction has a different mechanism – one of lower activation energy, giving more successful collisions.

- For AS Level you need to be able to link these observations to the distribution of molecular energies and also to explain the effects.

Boltzmann distribution of energies

The energy of molecules is directly proportional to their absolute temperature. The graph in Figure 8.1 shows a typical distribution of energies at constant temperature. This is known as the Boltzmann distribution.

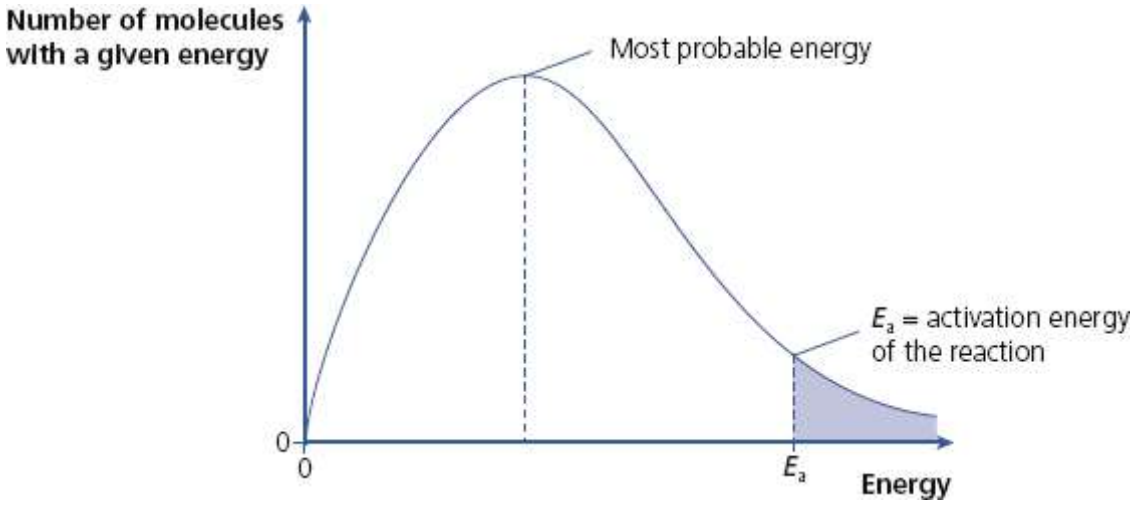

Figure 8.1 Boltzmann distribution

There are a number of points to remember about this graph:

- The distribution always goes through the origin.
- The curve approaches the x-axis but does not touch it.
- The peak represents the most probable energy.
- The area under the curve represents the total number of particles.
- E_a represents the activation energy (the minimum energy needed for reaction). The shaded portion represents the number of particles with energy higher than or equal to the activation energy ($E \geq E_a$).

The effect of temperature

An increase in temperature changes the shape of the Boltzmann distribution curve as shown in Figure 8.2.

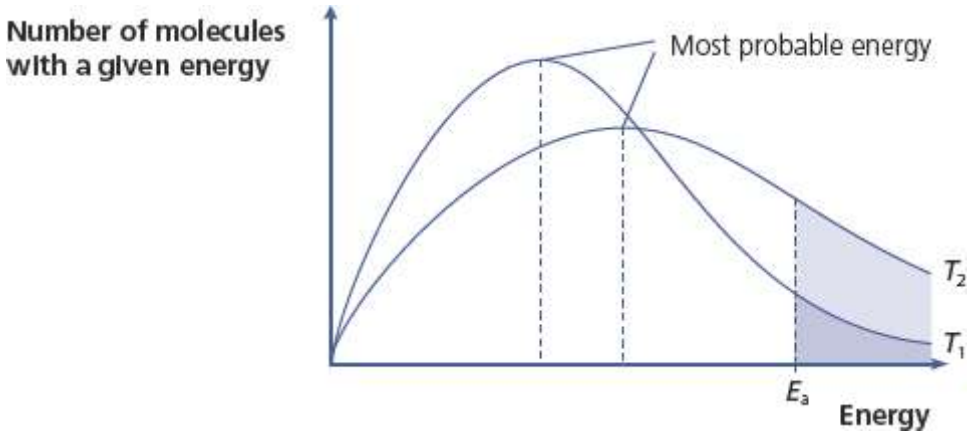

Figure 8.2 Boltzmann distribution at different temperatures

Notice that only the temperature has changed, so the areas under the two curves are the same. The graph shows that at a higher temperature, T_2:

- There are fewer particles with lower energy (the curve is flatter).
- The most probable energy is higher.
- More particles have $E \geq E_a$.

At higher temperature, a greater proportion of particles have sufficient energy to react, and hence the rate of reaction increases. The reverse is true at lower temperatures.

The effect of concentration

The Boltzmann distribution is not relevant here. The explanation given at the beginning of the chapter in terms of increasing the chance of collisions is adequate. It is worth remembering that increasing the pressure of a gas phase reaction has the same effect as increasing concentration in the liquid phase.

The effect of a catalyst

Remember that catalysts speed up chemical reactions without being permanently changed themselves. In the presence of a catalyst, a reaction has a different mechanism with a different activation energy, E_{cat}. This is shown in Figure 8.3.

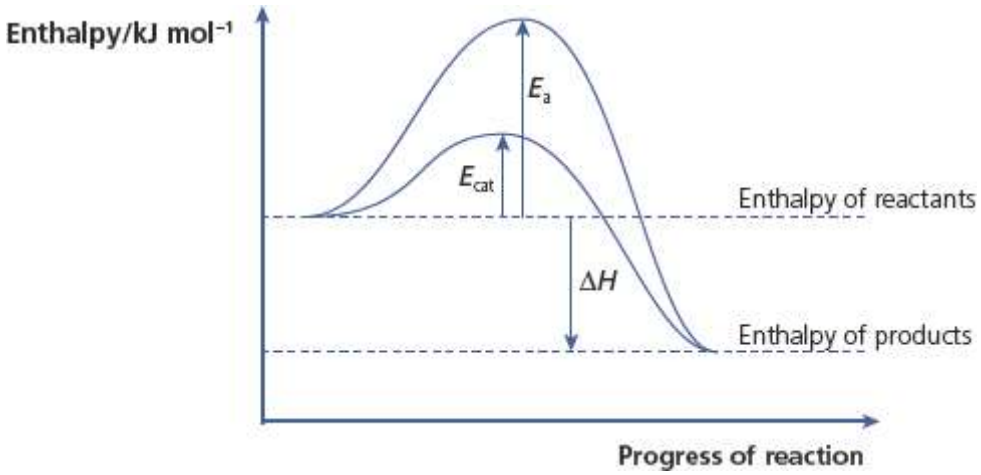

Figure 8.3 Activation energy in the presence and absence of a catalyst

KEY TERM

Catalysis is the process whereby the activation energy of a reaction is lowered by the presence of another element or compound.

It is important to remember that catalysts do not change the Boltzmann distribution for the temperature concerned. In a reaction that is speeded up, the position of E_a simply moves to the left, increasing the proportion of particles with $E \geq E_a$, as shown in Figure 8.4.

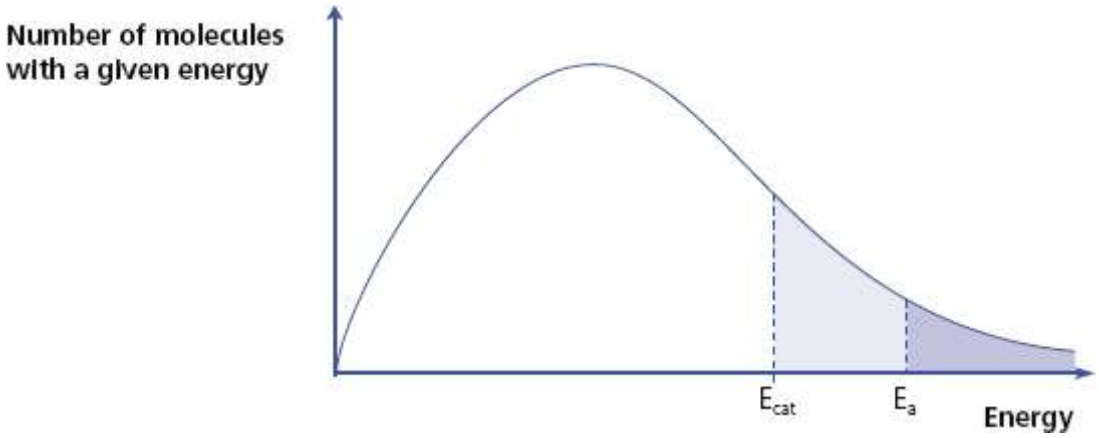

Figure 8.4 Position of E_a in the presence and absence of a catalyst

NOW TEST YOURSELF

2 a Look at Figure 8.2. Explain what the two shaded portions to the right of the graph tell you.

b Now look at Figure 8.4. Again, explain what the two shaded portions to the right of the graph tell you.

REVISION ACTIVITY

a Sketch the energy profile for an endothermic reaction:

$A + B \rightarrow C + D$; $\Delta H^{\ominus}$ is +ve

On your profile, label the activation energy for the reaction E_a and $\Delta H^{\ominus}$.

b Sketch the Boltzmann distribution curves for a reaction at two different temperatures where $T_2 > T_1$.

Use your curves to explain why the reaction is faster at T_2 than at T_1.

END OF CHAPTER CHECK

By now you should be able to:

- explain the terms rate of reaction, frequency of collisions and effective collisions
- define activation energy, E_a, and sketch and use the Boltzmann distribution to explain its significance and the effect of temperature on reaction rates
- construct and interpret a reaction pathway diagram showing the effect of the presence of a catalyst