Edexcel IAL Chemistry A-level

Topic 9: Introduction to Kinetics and Equilibria

Detailed notes

9A: Kinetics

Collision Theory

Chemical reactions occur when reactant particles **collide**. For a reaction to occur successfully, these collisions must have energy greater than or equal to the **activation energy** of the reaction, and the **particle orientation** must be correct. The activation energy is the minimum amount of energy required for two particles to react.

Maxwell-Boltzmann Distribution

Not all molecules in a substance have the same amount of energy. Their energies are **distributed** in a pattern called the **Maxwell-Boltzmann distribution**:
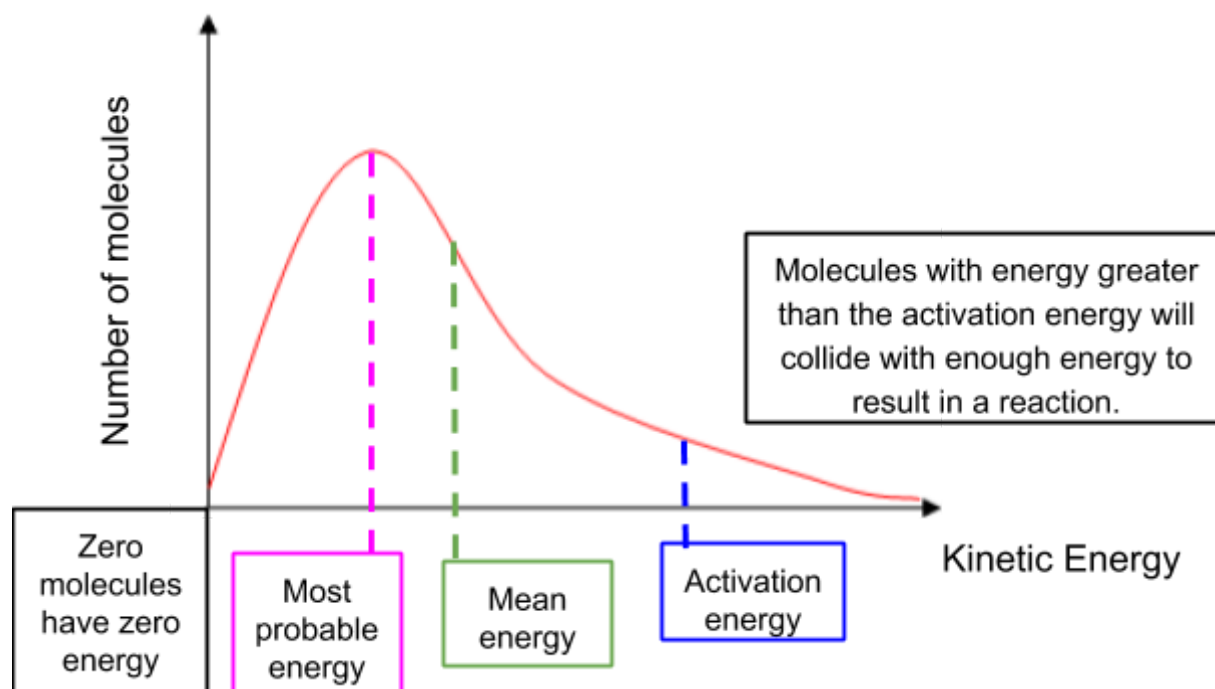
Changing the reaction conditions will **alter the shape of the curve,** so that the number of particles with energy greater than the activation energy is different. The total **area under the curve** represents the **total number of molecules** in the sample, and so it **must remain constant**.

Reaction Conditions

The conditions of a reaction impact the collisions of the particles and can be altered to provide the particles with **more energy**. Therefore, the conditions can be changed to increase the likelihood of a collision occurring with sufficient energy to react. This will lead to a greater rate of reaction.
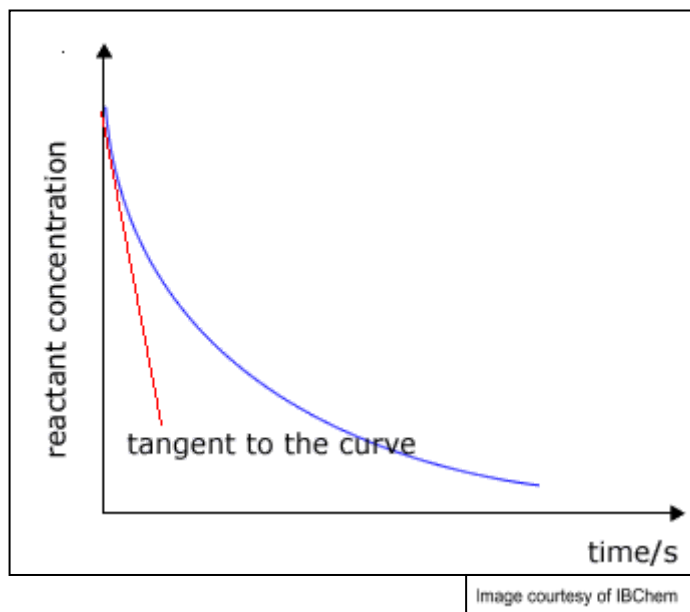
Rate of Reaction

Rate of reaction can be calculated from empirical data that has been plotted on graphs.

On a **concentration-time graph**, the rate of reaction is equal to the gradient of the curve at a given point. Therefore, the graph can be used to find the rate at a certain time by drawing a tangent to the curve at this given time. Drawing a **tangent** to the curve when **time = 0** finds the **initial rate** of reaction. The tangent at any other position finds the rate of reaction at that moment in time.

Example:

Image courtesy of IBChem

The overall rate of reaction can also be calculated using the following equation:

$$\text{Rate (s}^{-1}) = \frac{1}{\text{Time taken (s)}}$$

Effect of Temperature

When a substance is heated, **thermal energy** is transferred to it. This energy is converted to **kinetic energy** and the molecules of the substance move **faster and further**. Increased movement of the molecules means **collisions occur more often** and with **greater energy**. As a result, more collisions have energy greater than the activation energy and result in a reaction.

Therefore, **increasing the reaction temperature will increase the rate of reaction** as more collisions of greater energy occur in a given time.

The Maxwell-Boltzmann distribution at an increased temperature **shifts to the right** because a **greater proportion** of molecules have energy greater than or equal to the activation energy.

Example:

Image courtesy of johelpschemistry.blogspot.com
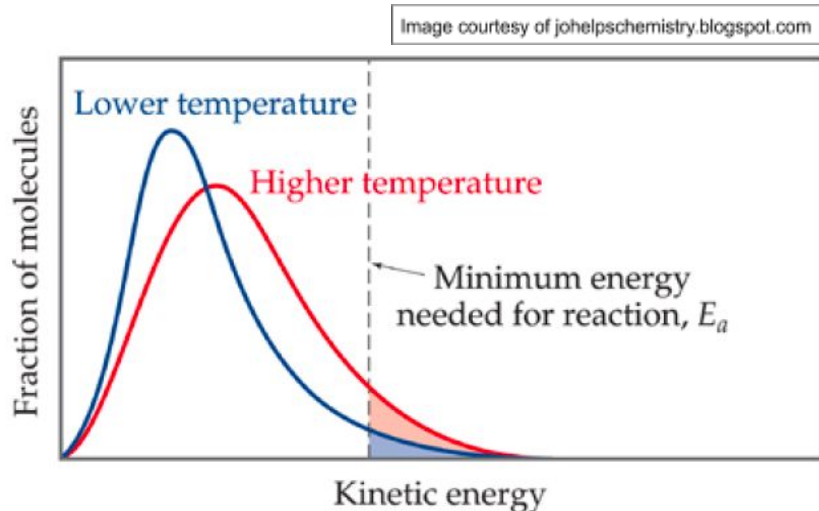
Effect of Concentration and Pressure

When the concentration of a sample is increased, there are more molecules of substance in the same volume, meaning they are **packed closer together**. Therefore, collisions between molecules become **more likely** and the probability of a collision occurring with energy greater than or equal to the activation energy increases. As a result, the rate of reaction increases.

Increasing the **pressure** of a gas has a similar effect as molecules are **packed closer together** into a smaller volume.

These changes make successful collisions occur more frequently, however, they don't change the **energy** of the **individual particles**. Therefore, the shape of the Maxwell-Boltzmann distribution **does not shift** towards the right as it does with a temperature increase.

Effect of Surface Area

Increasing the surface area of a reactant, for example by crushing it into a powder, increases the **number of exposed reactant particles**. This means there are more frequent, successful collisions, so the rate of reaction **increases**.

As with concentration and pressure changes, it does not change the energy of the individual particles, so the **shape** of the Maxwell-Boltzmann distribution **does not change**.

Effect of Catalysts

A catalyst is a substance that **increases the rate of reaction without being used up** in the reaction. It works by providing an **alternative reaction path** that requires a **lower activation energy** for the reaction to occur.

The Maxwell-Boltzmann distribution curve is **unchanged in shape** but the **position of the activation energy is shifted to the left** so that a greater proportion of molecules have sufficient energy to react.

Example:

Image courtesy of slideshare.net
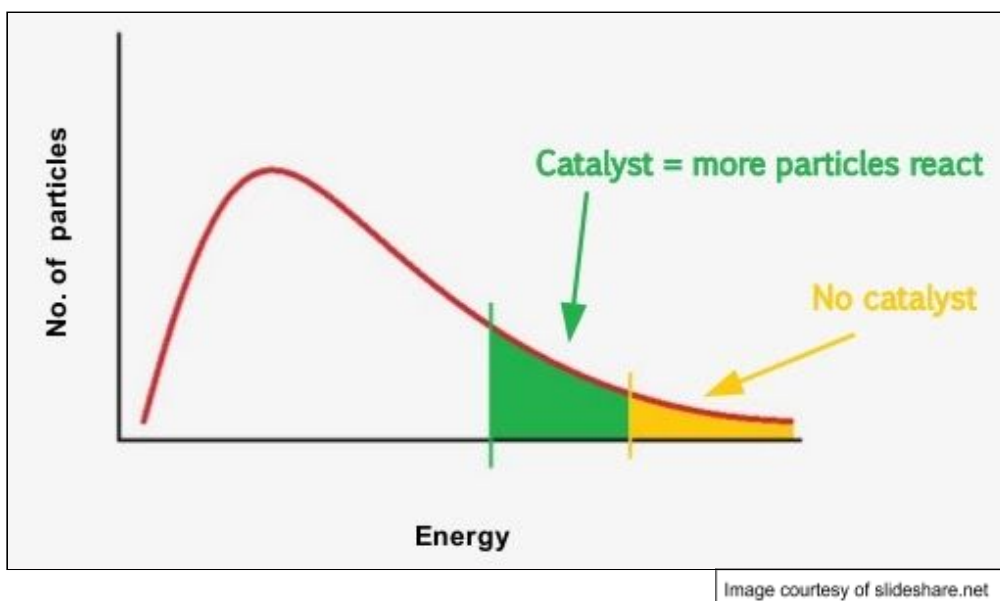
Catalysts are used in industry because they **lower the energy costs** of the reaction process. They allow lower temperatures and pressures to be used, whilst still achieving the same rate of reaction. They can also give a **higher atom economy**.

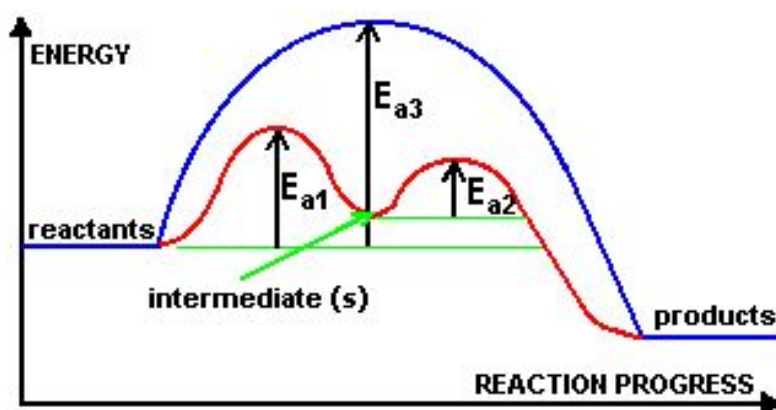## The Reaction Profile of a Catalysed Reaction
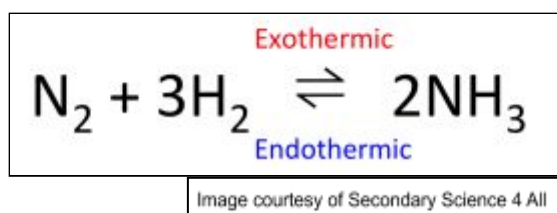

Image courtesy of docbrown.info

There is a **dip** in the **energy profile** for the catalysed reaction. This represents the **intermediate** formed during the reaction. The intermediate is **less stable** (and therefore higher in energy) than the reactants and products.

9B: Equilibria

Dynamic Equilibrium

Reversible reactions are reactions in which the products of a reaction can react together to reform the original reactants. They are represented using a **double arrow**.

Example:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

Exothermic (forward)
Endothermic (backward)

Image courtesy of Secondary Science 4 All

In each reversible reaction system, one reaction will be **endothermic** and the opposite reaction will be **exothermic**.

These reversible reactions can eventually reach a state of **dynamic equilibrium**. This occurs when the **rate** of the forward reaction is **equal** to the rate of the backward. At this point, the **concentrations** of the reactants and products remain **constant.**

Dynamic equilibrium can only occur in **closed systems** where no substances can get in or out.

Le Chatelier's Principle

Le Chatelier's principle is used to predict how an equilibrium mixture will change if the **reaction conditions are altered**. It states:

> **When a system is subject to change, the system will alter to lessen the effect of that change.**

It is a useful principle to consider in industry, since the reaction conditions can be altered to **maximise the yield** of a desired product.

An example of a system that may reach equilibrium is a **homogeneous system**. A homogeneous system is one in which the reactants and products are all in the **same state.**

Changing Temperature
Increasing temperature favours the **endothermic reaction** (+ve ΔH) as the excess heat needs to be removed from the system to lessen the effect of the initial increase. It will increase the yield of the endothermic products.
Likewise, **decreasing** temperature favours the **exothermic reaction** (-ve ΔH) as the loss of heat needs to be gained. The yield of the exothermic products will be increased.

In exam questions, the **ΔH of the forward reaction will be given** so it is clear which direction is endothermic and which is exothermic.

Changing Pressure
Increasing pressure favours the reaction direction which produces **fewer moles of gas,** as this will help to release the built up pressure. It will increase the yield of the products of fewest moles.
Likewise, **decreasing** pressure favours the reaction direction which produces the most moles, since this will help to increase the pressure. The yield of the products with the most moles will be increased.

Changing Concentration
Increasing the concentration of the reactants will favour the reaction direction that **produces the products** as more molecules are available to react. The reactant particles will react to increase the yield of the products, thereby decreasing the concentration of the reactants.
Likewise, **increasing** the concentration of products will favour the reaction that **reforms the reactants**.
A similar argument can be used to explain the effect of **decreasing** the concentration of reactants and products.

Catalysts
Catalysts appear not to affect the equilibrium position as they **affect the forward and backward reaction equally**. However, they do allow equilibrium to be reached **faster**.

Compromise between Rate of Reaction and Product Yield

Changing the conditions of reaction can shift the position of the equilibrium to favour the production of either the products or the reactants, as described above. However, a condition change which produces a **higher proportion of the product** may also **reduce the rate of the reaction**. The rate of reaction is increased by increases in temperature, pressure or concentration.

For example, **decreasing the temperature** of reaction with a **forward endothermic reaction** would **increase** the product **yield**, but **decrease** the **rate** of reaction.

In the industry, when a factor increases the product yield but decreases the rate of a reaction, a **compromise** must be made. If the product yield was the only thing taken into account, the rate of

reaction would occur **so slowly** that the product is not actually made at a useful rate. Therefore, reaction conditions are selected to give both a **relatively good product yield** and a **relatively fast rate of reaction**.