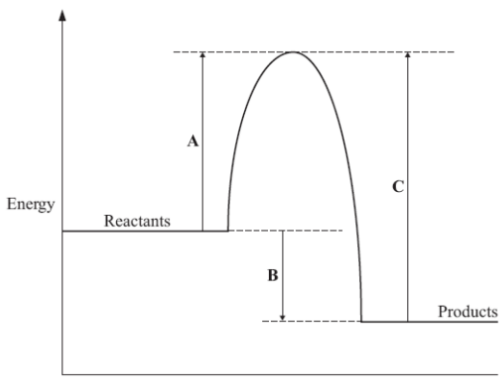
Topic 13a – Rates
Revision Notes

1) Collision theory

- Rate of reaction = amount of substance produced per second (g/s or cm^3/s)
- 5 ways of increasing rate are to increase surface area, increase concentration, increase temperature, use a catalyst, increase pressure (if gases involved)
- The effect of changing these factors is explained using Collision Theory. For a reaction to occur particles must collide with a minimum amount of energy (called the Activation Energy). To increase the rate we need to increase the number of successful collisions per second.
- Increased surface area = more particles exposed = greater collision frequency
- **Increased concentration = particles closer together = greater collision frequency**
- Increased temperature = particles have more energy and move faster = greater collision frequency <u>and</u> more collisions are successful = double effect on rate
- Adding a catalyst = lower activation energy = more collisions are successful
- **Increasing the pressure in a reaction involving gases has the same effect as increasing the concentration of a solution i.e. particles closer together = greater collision frequency (more collisions per second)**

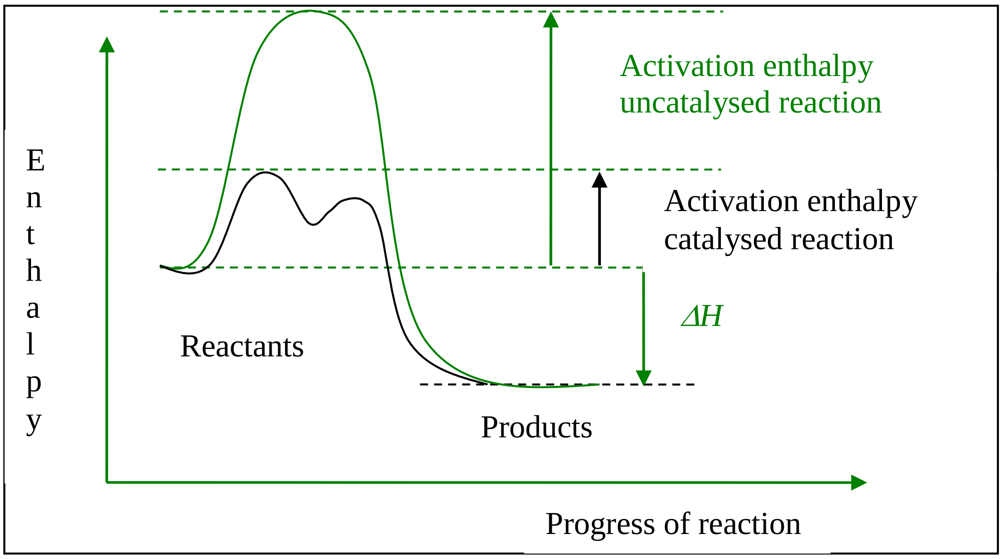
2) Activation energy

- The activation energy is the minimum energy needed for a reaction to occur
- It corresponds to the energy needed to break the bonds in the reactants and can be shown on an enthalpy profile diagram (A on the diagram below)
- If the reaction in the diagram was reversible then C would be the activation energy for the backward reaction
- B represents the enthalpy change for the forward reaction (ΔH –ve). The enthalpy change for the backward reaction would be – B (ΔH +ve)



3) Catalysts

- A catalyst speeds up a reaction without being used up on the reaction
- The catalyst provides an alternative route for the reaction with a lower activation energy than the uncatalysed reaction
- Catalysts do not appear in the equation for a reaction. They are written on top of the arrow



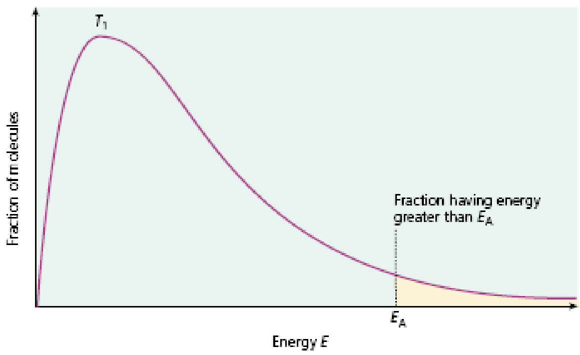
Source:http://www.york.ac.uk/org/seg/salters/chemistry

a) Production costs

- Catalysts enable production costs to be lowered in the following ways
- Catalysts may allow reactions to be carried out at lower temperatures. This reduces energy demands and emissions of CO_2 from burning fossil fuels
- Catalysts may allow a product to be made by a different reaction with better atom economy and less waste
- Enzymes are biological catalysts which generate very specific products under conditions close to room temperature and pressure
- Catalysts are important in industrial processes e.g. Fe in Haber process, Ziegler-Natta for poly(ethene) production and Pt/Pd/Rh in catalytic converters

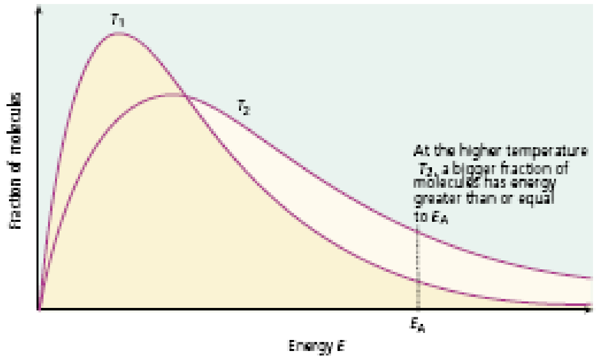
4) <u>The Boltzmann Distribution</u>

- The Boltzmann distribution is a graph showing the distribution of molecular energies in a gas
- The x-axis is labelled “energy” and the y-axis is labelled “number of molecules”
- The area under the curve gives the total number of particles in the sample



a) Effect of temperature

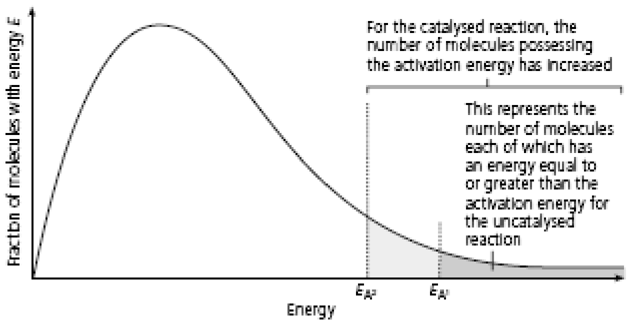
- Increasing the temperature lowers the peak and shifts the distribution to the right. The area under the curve does not change



- Increasing the temperature means more molecules have the activation energy so more collisions are successful
- Lowering the temperature raises the peak and shifts the distribution to the left. The area under the curve does not change
- Decreasing the temperature means fewer molecules have the activation energy so fewer collisions are successful

b) Effect of a catalyst

- As stated above, catalysts lower the activation energy for a reaction by providing an alternative route for the reaction



- In terms of the Boltzmann distribution, lowering the activation energy means more molecules have the activation energy (so more collisions will be successful and the rate will increase)

Topic 13b – Equilibrium
Revision Notes

1) Dynamic Equilibrium

In a closed system, a reversible reaction will reach a state of dynamic equilibrium. A dynamic equilibrium has the following characteristics

- Rate of forward reaction = rate of backward reaction
- Concentrations are constant

2) Le Chatelier's Principle

- Le Chatelier's Principle predicts how a system in dynamic equilibrium will respond to a change. The Principle states that: "When the conditions on a system in equilibrium are changed, the equilibrium moves to oppose the change"
- The position of equilibrium (composition of the mixture of reactants and products) will shift to the left or right if a change is made to concentration, temperature or pressure.
- The following reaction, which is used to produce hydrogen for the Haber Process, will be used as an example.

$CH_4(g) + H_2O(g)$ $CO(g) + 3H_2(g)$ ℕH +205 kJ mol^{-1}

a) Effect of changing concentration

- If methane or steam is added, the equilibrium will shift to the right to oppose the change (remove the added methane or steam).
- If carbon monoxide or hydrogen is removed, the equilibrium will shift to the right to oppose the change (replace the carbon monoxide or hydrogen that has been removed).

b) Effect of changing temperature

- If the temperature is increased, the equilibrium will shift to the right to oppose the change (it will move in the endothermic direction as this removes added heat).
- If the temperature is decreased, the equilibrium will shift to the left to oppose the change (it will move in the exothermic direction as this replaces the heat that has been removed).

c) Effect of changing pressure

- In the above reaction there are 2 moles of gas on the left and 4 moles of gas on the right. The products have a bigger volume than the reactants.
- If the pressure is increased, the equilibrium will shift to the left to oppose the change (it will move to the side with the smaller volume or fewer gaseous moles).
- If the pressure is decreased, the equilibrium will shift to the right to oppose the change (it will move to the side with the larger volume or more gaseous moles).

d) Effect of adding a catalyst

- Adding a catalyst has no effect on the position of equilibrium.
- A catalyst speeds up the rates of the forward and backward reactions equally so its effect is to reduce the time taken to reach equilibrium

3) <u>The Haber Process</u>

The Haber Process produces ammonia, NH_3, which is used to make the following.

- Fertilisers including ammonium sulphate
- Polyamides such as nylon
- Explosives e.g. TNT

The equation for the Haber Process is:

$$\mathbf{N_2(g) + 3H_2(g) \quad 2NH_3(g) \quad \Delta H = -92\ kJ\ mol^{-1}}$$

Applying Le Chatelier's Principle, the highest yield of ammonia is obtained with the following conditions.

- **Low temperature** – the forward reaction is exothermic. If temperature is lowered the equilibrium will shift in the exothermic direction to replace the heat that has been removed.
- **High pressure** – there are fewer gaseous moles on the right. If the pressure is increased the equilibrium will shift to the side with the smaller volume.
- **Compromise conditions** - in practice a low temperature is not used as the reaction rate would be too low. A temperature of 450 C gives a reasonable yield at a reasonable rate. In addition, a very high pressure is not used as it is expensive to produce and requires expensive equipment. A pressure of 200 atm gives a reasonable yield at a reasonable cost.
- **Concentration** – ammonia is removed as it is formed and unreacted nitrogen and hydrogen are recycled to the reaction vessel.
- **Catalyst** - an iron catalyst is used. This speeds up the rates of the forward and backward reactions equally and reduces the time taken to reach equilibrium.