Rates and equilibrium

Rates of reaction - collision theory

Introduction:

- The term rate is used to describe the speed of a reaction.
- Different reaction will have different rates

Rate of reaction:

The rate of a reaction is defined as the change in concentration of a reactant or product in a given time

Rate = $\frac{\text{Change in concentration}}{\text{Time}}$ Units: $\frac{\text{mole dm}^{-3}}{\text{s}}$ = mol dm^{-3} s^{-1}

- When a reaction starts the concentrations of the reactants are at their highest, the rate is at its fastest.
- As the reactants are used up the concentration decreases, so does the rate.
- When one of the reactants is used up the reaction stops. The rate is 0/

Factors affecting the rate of a chemical reaction:

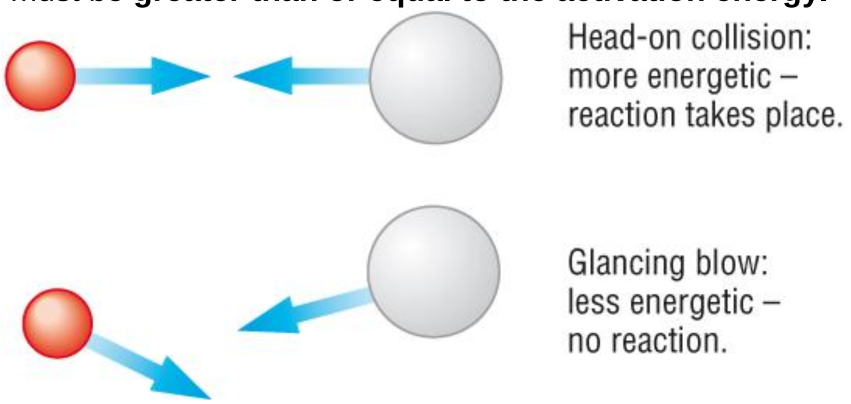
1. **Temperature** – An increase in temperature will increase the rate of reaction.
2. **Pressure** - Higher pressure increases the rate of a reaction
3. **Concentration** – An increase in concentration (or pressure) will increase the rate of reaction.
4. **Surface area** – An increase in surface are (which is a decrease in particle size) will increase the rate of reaction.
5. **Catalyst** – A suitable catalyst will increase the rate of a reaction.

Collision theory:

- This is used to explain how reacting molecules collide leading to a reaction
- When 2 molecules collide a reaction only occurs if the conditions are right.

1) Activation energy.

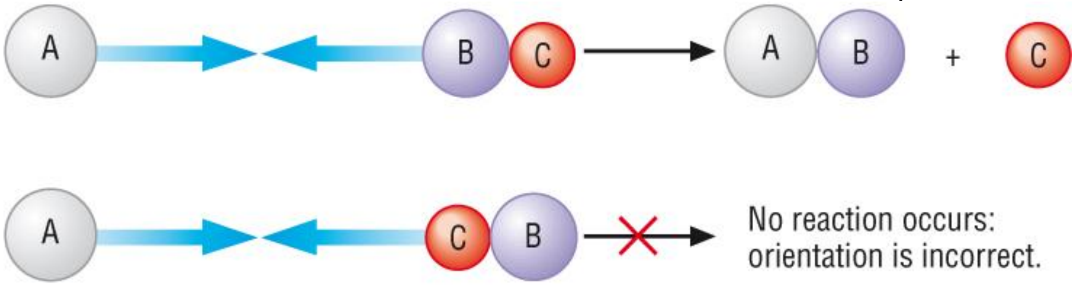
- Reacting molecules have to collide with enough energy to break the initial bonds, **the activation energy**.
- The collision must be **greater than or equal to the activation energy.**



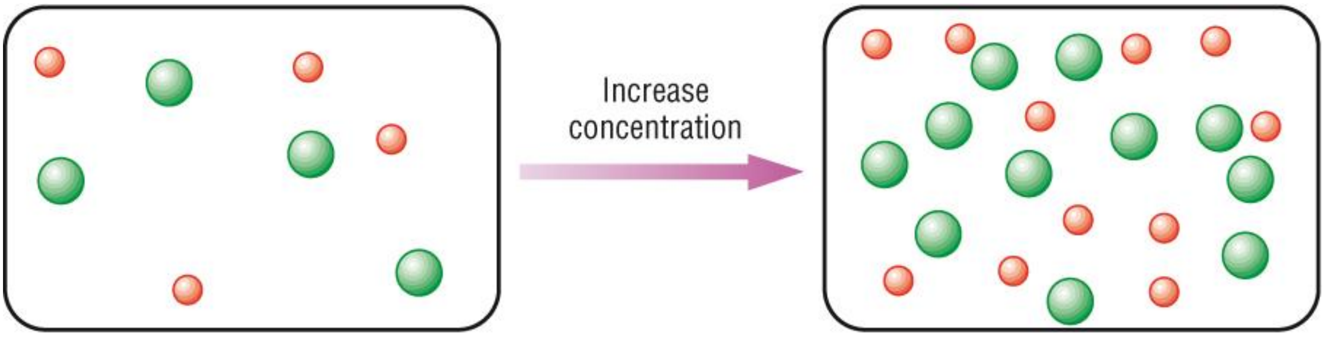
- If the collision is less than the activation energy, they just bounce apart.

2) Orientation:

- The molecules must collide in the correct orientation in order for the products to be made:



The effect of concentration on reaction rate:



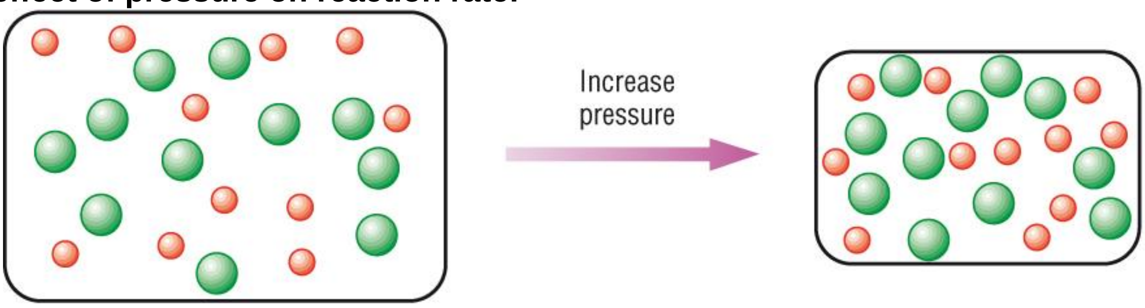
Here we have a few molecules.
There are few collisions.
The rate of reaction is low.

Here we have many molecules.
There are more collisions.
The rate of reaction is greater.

Increase in concentration
Increase in No particle per volume
Increase in the collision frequency
Increases the rate of the reaction

- This means that in a certain amount of time, more collision will take place.
- This means there will be more collisions with energy greater than or equal to the activation energy.
- Which means the rate increases.

The effect of pressure on reaction rate:



Here we have a number of gaseous molecules.
The molecules have space to move around
and there is little chance of a collision.

Increasing the pressure decreases the
volume and increases the concentration.
The molecules have less space to move in
and are more likely to collide.

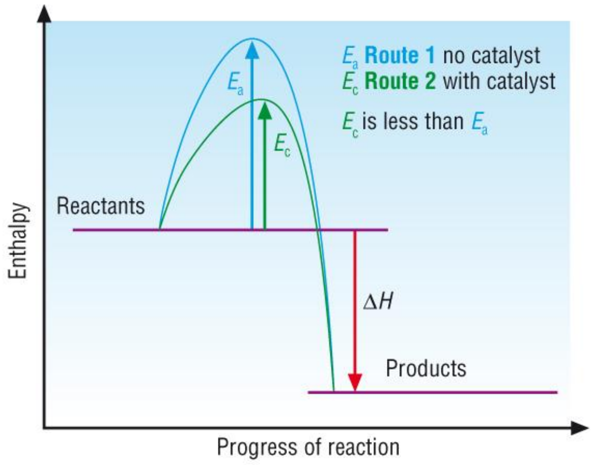
Increase in pressure
Decrease in the volume
Increase in the No particle per volume
Increase in the collision frequency
Increases the rate of the reaction

- This means that in a certain amount of time, more collision will take place.
- This means there will be more collisions with energy greater than or equal to the activation energy.
- Which means the rate increases.

Questions 1-2 P 203

Catalysts

What is a catalyst?



- A catalyst increases the rate of a reaction without being used up in the process.
- A catalyst must then form an intermediate with a lower activation energy.
- This means that an alternative route for the reaction is provided by the catalyst.
- The catalyst comes out unchanged at the end of the reaction.

Reducing energy consumption and helping environment:

- Catalysts offer a route to products with a lower activation energy.
- This means that the energy costs in industry would be lower with the use of a catalyst.
- As the energy cost are usually in the form of electricity, gas or oil, it saves energy costs as well as contributions to climate change.
- About 80% of the chemical industrial processes involve the use of a catalyst to save costs.
- About half the elements on the Periodic table are used as or in catalysts. Especially the Transition metals.
- Catalysts can also improve the % yield making it more effective.

Economic importance of catalysts

- Is a very profitable branch of chemistry as it can save businesses lots of money on their energy bills by lowering activation energies.

The Haber process:

- Makes ammonia from hydrogen and nitrogen:

$$N_{2(g)} \quad + \quad 3H_{2(g)} \quad \leftrightarrows \quad 2NH_{3(g)}$$

- The ammonia made is mainly used in the manufacture of fertilisers.
- Fertilisers are important in a world with a population boom.
- The triple bond in nitrogen requires a lot of energy to break. This means that the activation energy for this reaction will be high.
- The 'Zeigler-Natta' catalyst weakens the triple bond in nitrogen and therefore lowers the activation energy.

Catalytic converters:

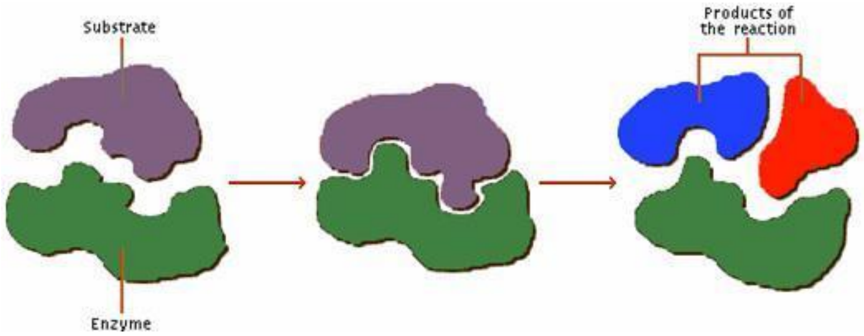
- Used in exhaust systems in cars are used to improve air quality and reduce photochemical smog.

Enzymes as biological catalysts:

- Most common is in the fermentation of fruits to alcohol.
- Loius Pastuer researched enzyme catalysis in the production of **one product**.
- This is called **specificity**.

Emil Fischer

- Explained that enzymes work on a '**lock and key**' mechanism.
- The molecule being catalysed is called the substrate. Its shape must fit exactly the shape of the enzyme.
- It is thought that as the enzyme holds the substrate in place, other bonds in the molecule are weakened and therefore easier to break.



- Enzymes are large protein molecules, they are able to operate in mild conditions - lowering the activation energy.

Enzymes in industry:

- The benefits of using enzymes as an industrial catalyst:

1. Lower temperature and pressures reduce running costs
2. Enzymes are usually specific making only one product, no side reactions so reducing the costs of separation and purification.
3. Chemical catalysts are often poisonous which means they are difficult to dispose of. Enzymes are biodegradable.

- Biological washing powders use enzymes which is why they should be used at around 30 - 40 ^{o}C as above that temperature they become denatured.

Protease	**Breaks down protein stains**
Amylase	**Breaks down starches**
Lipases	**Breaks down fats and greases**

- Ibuprofen is separated from its reaction mixture using enzymes.

Types of catalyst:

1) Homogeneous catalyst

- The catalyst and reactants are in the same phase (ie all in the same solvent, aq)

Examples
Acid catalysis of the esterification of ethanol

$$CH_3CH_2OH \;+\; CH_3{-}C(=O)OH \;\rightleftharpoons\; CH_3{-}C(=O)OCH_2H_5 \;+\; H_2O$$

The hydrogen ions from the acid is in the same phase as the reactants.
The hydrogen ion becomes involved in the reaction mechanism but the concentration of the acid will be the same at the end.

2) Heterogeneous catalyst

- The catalyst and reactants are in different phases (ie gas reactants, solid catalyst)

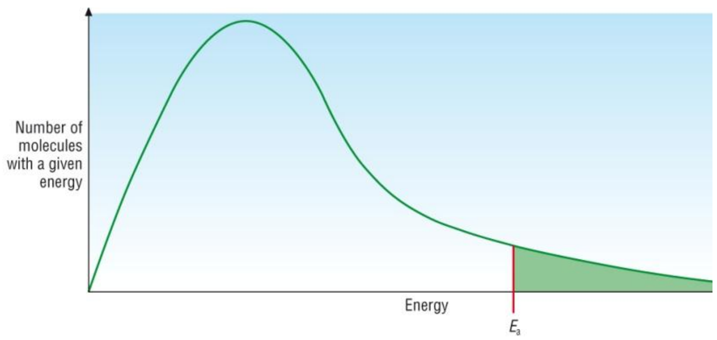
Examples
Cracking, isomerisation and reforming reactions in the oil industry.

Haber process – Production of ammonia

- Ammonia used to be produced by using an electrical discharge tube with nitrogen.
- Ammonia is used in the production of fertillisers
- Fritz Haber used a gas phase reaction between nitrogen and hydrogen:
  $N_{2(g)} + H_{2(g)} \rightarrow NH_{3(g)}$
- The process uses a finely divided **iron** catalyst.
- The iron catalyst weakly absorbs the nitrogen molecules weakening the very strong triple bonds.

Questions 1 - 4 P 205 / Questions 1 - 4 P 207

<u>The Boltzmann distribution</u>



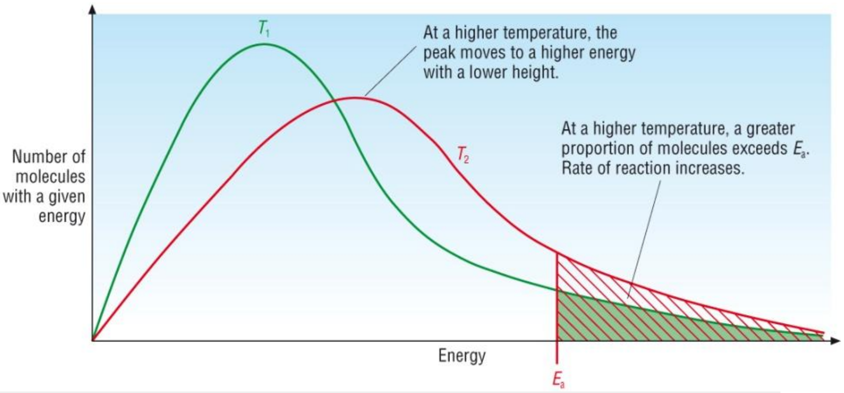
- In a gas or liquid it is assumed that the molecules collide with elastic collisions.
- This means that no energy is lost during a collision with the container or other molecules.
- As the molecules are moving, they have kinetic energy.
- In any sample of gas or liquid there will be a distribution of energies:

Some will have high energy:	**This means they will move very fast**
Some will have low energy	**This means they will move very slow**
Most will have average energy	**Most will move with the average speed**

Important features of the Boltzmann distribution:

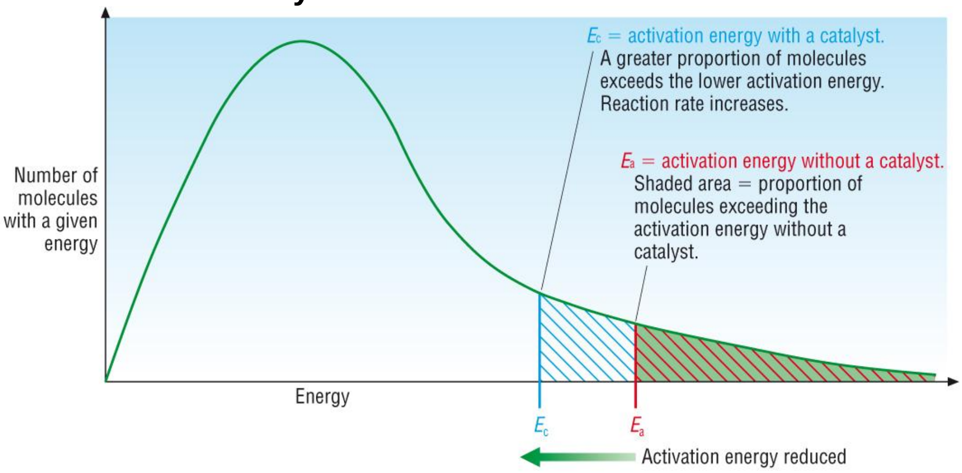
The area under the curve is equal to the total number of molecules in the sample:	**The area does not change**
No molecules have zero energy:	**The curve starts at 0,0**
There is no maximum energy for a molecule:	**The curve never touches the axis**
Only molecules with energy greater than the activation energy are able to react	**The activation energy is the minimum energy required to react**

The effect of temperature on reaction rate:



	Increase in temperature
	Increase in kinetic energy of molecules
	Increase in the speed of the molecules
	- Increases the collision frequency
	- Increases the No of collisions with energy > activation energy
	More successful collisions
	Increase in the rate

The effect of a catalyst on reaction rate:



	Catalysts offer a route with a lower activation energy
	As more molecules will overcome the lower activation energy
	An increases in the number of successful collisions
	Increases the rate of the reaction

Questions 1-3 P209

Chemical equilibrium

Reversible reactions:

- Consider the reaction:

$$Mg_{(s)} \quad + \quad H_2SO_{4(aq)} \quad \rightarrow \quad MgSO_{4(aq)} \quad + \quad H_{2(g)}$$

- The reaction stops when all of the limiting reagent has been used up.
- The reaction is said to go to completion and this is indicated by $\rightarrow$
- Some reactions are reversible though:

$$2SO_{2(g)} \quad + \quad O_{2(g)} \quad \leftrightarrows \quad 2SO_{3(g)}$$

- This reaction is reversible and can take place in the forward direction (above) or the reverse direction (below):

$$2SO_{3(g)} \quad \leftrightarrows \quad 2SO_{2(g)} \quad + \quad O_{2(g)}$$

- The reaction is described as reversible. Equilibrium is indicated by $\leftrightarrows$

Dynamic equilibrium:

- When a reversible reaction has appeared to have stopped we say it has reached an equilibrium.
- At equilibrium the rate of the forward and reverse reaction occurs at the same rate.
- This means that the concentrations of the reactants and products are the same.
- There is **no observable change**.
- This is described as **DYNAMIC**.
- The extent of how far the reaction has gone towards the products is called **'the position of the equilibrium'**
- **Equilibrium is stable under fixed conditions and in an isolated system:**

Fixed conditions: Temperature and pressure remains the same.

Isolated system: No material is added or removed from the system

Factors affecting the position of equilibrium:

- The position of an equilibrium can be altered by altering the conditions or adding / removing material from the system.

1) Changing the concentration of reactants or products

2) Changing the pressure (if gases involved)

3) Changing temperature

- The effects of these changes can be predicted using:

Le Chatelier's Principle

When a system in equilibrium is subject to a change, the equilibrium will shift so as to counteract the change.

- The position of the equilibrium shifts so as to oppose the change imposed upon it.
- It is possible to use these to make an equilibrium system shift in the direction we want.

1) Changing the concentration of reactants or products

- This reaction shows how a reversible reaction can be manipulated by changing the concentration of the reactants then products:

$$Co(H_2O)_6^{2+} + 4Cl^-_{(aq)} \leftrightarrows CoCl_4^{2-}{}_{(aq)} + 6H_2O_{(aq)}$$

Pink   Blue

- Adding HCl to the reaction mixture increases the concentration of Cl^- ions.
- The equilibrium shifts towards the products in order to reduce the concentration of the Cl^- ions.
- The resulting colour change is from pink to blue.
- At this point if you add H_2O molecules to the reaction mixture, the Cl^- concentration decreases
- The reaction moves towards the reactants in order to increase the Cl^- ion concentration..
- The resulting colour change is from blue to pink.

A change in concentration affects the position of the equilibrium
The equilibrium moves to oppose the change imposed upon it

Concentration Summary:

- **An increase in the concentration of the reactants moves the equilibrium towards the products. The equilibrium removes the extra reactants by shifting the equilibrium in the forward direction.**
- **An increase in the concentration of the products moves the equilibrium towards the reactants. The equilibrium removes the extra products by shifting the equilibrium in the reverse direction.**

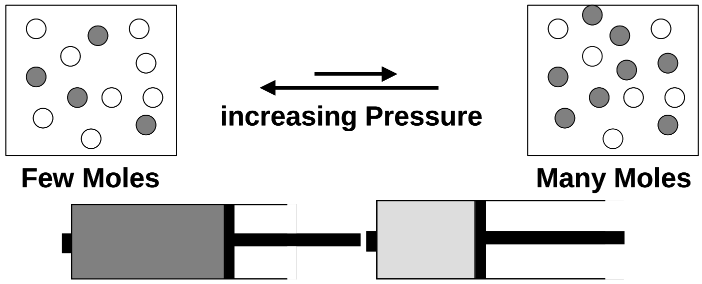
2) Changing the pressure (if gases involved)

- The syringe contains 2 gases in equilibria:

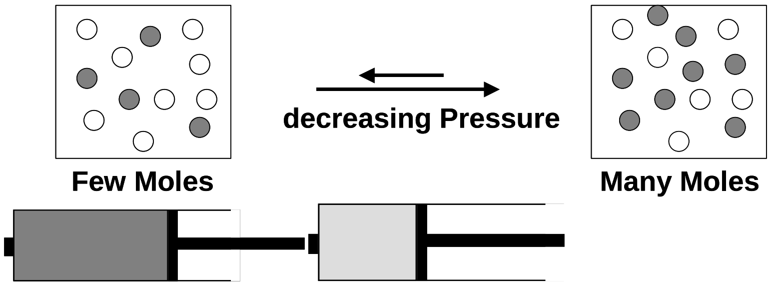
N_2O_4	$\leftrightarrows$	$2NO_2$
Colourless		**Brown**
1 Mole		**2 Moles**

Low pressure High pressure

- You should have noticed that when you increase the pressure of the system you get an initial darkening (due to concentration of gases), followed by a lightening of the brown NO_2 colour.
- This suggests that an increase in pressure moves the equilibrium in the reverse direction. Towards the side with the least number of moles.



- If you reduce pressure you would see an initial lightening (due to dilution of gases), followed by a darkening of the brown NO_2 colour.
- This suggests that a decrease in pressure moves the equilibrium in the forward direction. Towards the side with the most number of moles.



- If you increase the pressure, the equilibrium will move to the side that will reduce pressure. The side with the least number of moles.
- If you decrease the pressure, the equilibrium will move to the side that will increase pressure. The side with the most number of moles.
- If there is an **equal number of moles of reactants and products**, a change in pressure will have **no effect on the equilibrium**.

A change in concentration affects the position of the equilibrium
The equilibrium moves to oppose the change imposed upon it

Pressure Summary:

- **If you increase the pressure, the equilibrium will move to the side that will reduce pressure – the side with the least number of moles of GAS.**
- **If you decrease the pressure, the equilibrium will move to the side that will increase pressure – the side with the most number of moles of GAS.**

3) Changing temperature:

a) Ammonium chloride

- The white solid vaporises on heating into $NH_{3(g)}$ and $HCl_{(g)}$.
- Further up the tube when the vapour has cooled $NH_4Cl_{(s)}$ reforms.
- This is an example of a reversible reaction:

$$NH_4Cl_{(s)} \rightarrow NH_{3(g)} + HCl_{(g)} \quad \text{On heating}$$

$$NH_{3(g)} + HCl_{(g)} \rightarrow NH_4Cl_{(s)} \quad \text{On cooling}$$

A change in temperature affects the position of the equilibrium

$$NH_4Cl_{(s)} \rightleftarrows NH_{3(g)} + HCl_{(g)} \quad \mathbf{\Delta H = endothermic}$$

- Heating the reaction moves it to the products. The cold side – endothermic.
- Cooling moves the reaction to the reactants. The hot side – exothermic.

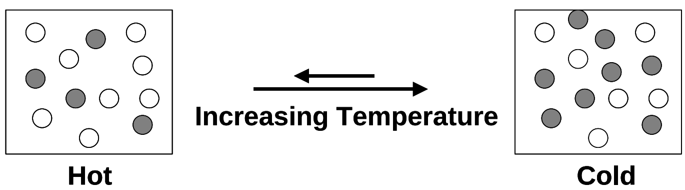
The equilibrium moves to oppose the change imposed upon it

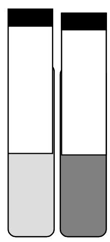
b) Nitrogen oxides:

- The syringe contains 2 gases in equilibria:

N_2O_4	$\rightleftarrows$	**$2NO_2$**	**$\Delta H^\theta = +58KJ\ Mol^{-1}$**
Colourless		**Brown**	**Endothermic**
Hot		**Cold**	

- The hot syringe had a very dark brown colour.
- Heat moves the reaction moves towards the products.
- An increase in temperature increases the amount of NO_2. The equilibrium moved in the forward direction (towards the cold side).





- The cool syringe had a very pale brown colour.
- Cooling moves the reaction moves towards the reactants.
- A decrease in temperature increases the amount of N_2O_4. The equilibrium moved in the reverse direction (towards the hot side).

A change in temperature affects the position of the equilibrium
The equilibrium moves to oppose the change imposed upon it

Temperature Summary:

- **If you increase the temperature, the equilibrium will move to the side that will reduce temperature.**
- **If you decrease the temperature, the equilibrium will move to the side that will increase temperature.**

A change in concentration affects the position of the equilibrium
The equilibrium moves to oppose the change imposed upon it

The effect of a catalyst on an equilibrium system

- A catalyst has **no effect** on the position of the equilibrium.
- A catalyst speeds up the rate of a reaction so it will only increase the rate at which equilibrium is achieved.
- This is true for the forward and reverse reaction.

<u>**Equilibrium and industry: The Haber process**</u>

- Ammonia is used as it is soluble and is readily oxidised into nitric acid by the **'Ostwald process'**.
- The reaction:

$$N_{2(g)} + 3H_{2(g)} \rightleftarrows 2NH_{3(g)} \qquad \Delta H = -92 KjMol^{-1}$$

Endothermic	**Exothermic**
4 Moles	**2 Moles**
high pressure	**Low pressure**

The problem:

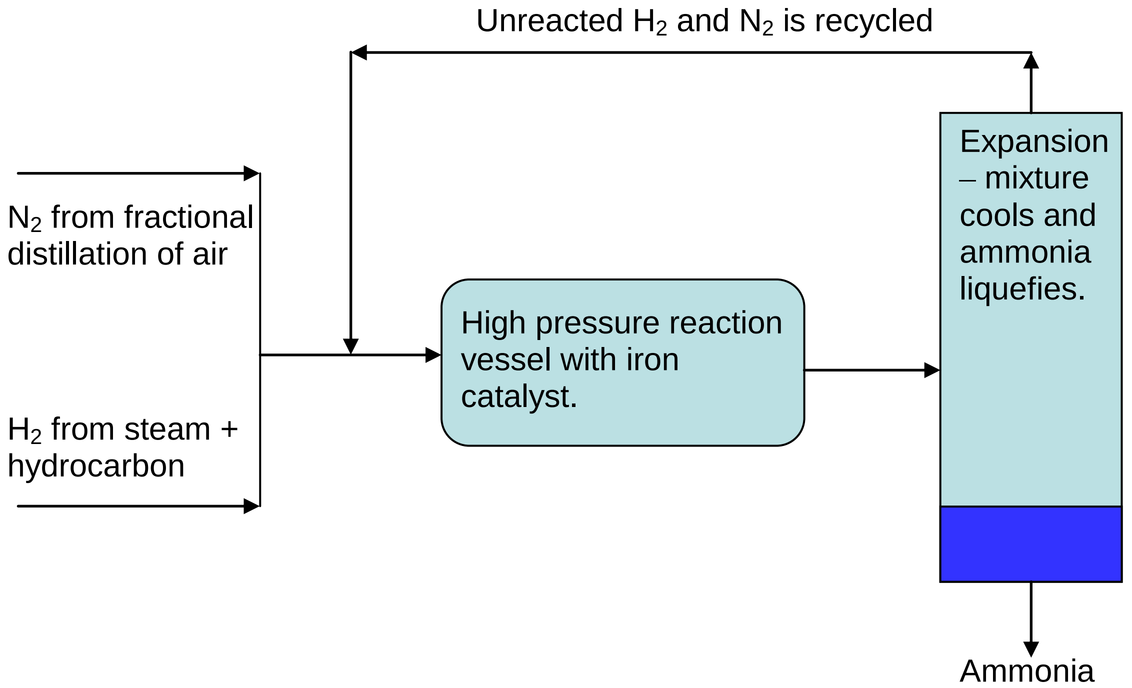
1. **The equilibrium lies over to the reactants.**
2. **Nitrogen has a triple bond which makes it very hard to break. This gives the reaction a high activation energy**

The solutions:

Process	**Equilibria**	**Rate**	**Compromise**
Temperature	**Decrease temperature** – will move equilibria to the exothermic side – the products	**Increase temperature** – will increase the rate of reaction as activation energy is more likely to be overcome.	Moderate temperature of 400 - 500 ^{o}C used.
Pressure	**Increase pressure** – Moves equilibrium to products with fewest moles of gas.	**Increase pressure** – will increase the rate of reaction as more particles per volume.	Cost of pumps and reaction vessel becomes very expensive – 200 atm
Catalyst	No effect	Increases the rate	Finely divided iron with metal oxide promoters
Remove ammonia as it is formed	Equilibrium is never reached so the rate doesn't slow down.		
Recycle unreacted H_2 and N_2			

- The plants run continuously with a lower energy and less expensive to build than conventional plants.
- 80% goes to making fertillisers such as ammonium sulphate.
- A proportion makes nitric acid which goes on to make explosives.

The process:



- Other industrial processes include the contact process - converting sulphur dioxide to sulphur trioxide.

Questions 1-2 P211 / 1-2 P213 / 8-13 P215 / 2 P217