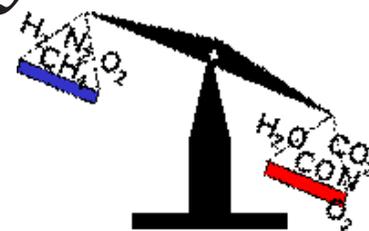
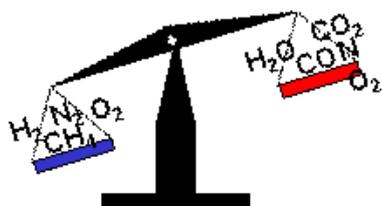


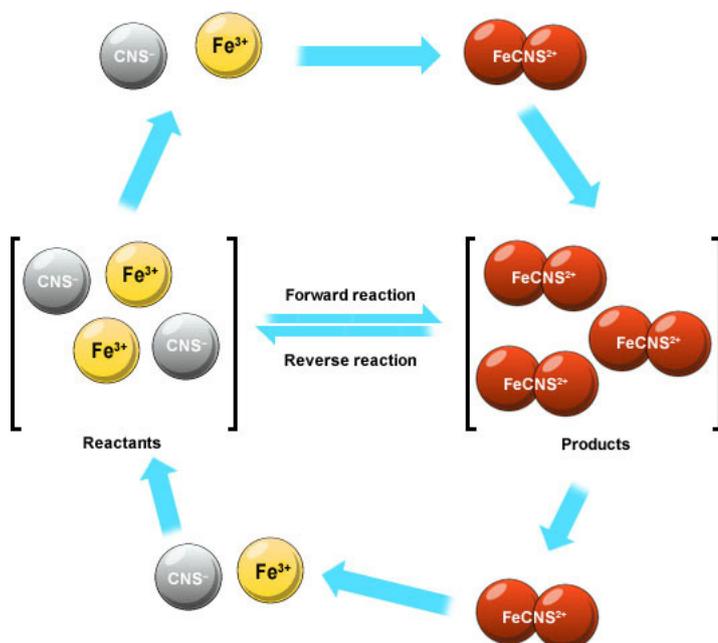
Higher Chemistry



Unit 3:

Principles to Production - Part 3

Student:



Lesson	Activities	Done	Checked
3.16 <i>Reversibility & Equilibrium</i>	1. Reversible Reactions		
	2. Concept of Equilibrium		
	<i>Check Test</i>	Score: / 8	
	<i>Home Practice</i>	Score: / 10	
3.17 <i>Changing Conditions</i>	1. Changing the Concentration		
	2. Changing the Temperature or Pressure		
	3. Adding a Catalyst		
	<i>Check Test</i>	Score: / 8	
<i>Consolidation Work</i>	<i>Consolidation A</i>	Score: / 10	
	<i>Consolidation B</i>	Score: / 10	
	<i>Consolidation C</i>	Score: / 10	
	<i>Consolidation D</i>	Score: / 10	
<i>End-of-Section Assessment</i>	Score: _____ %	Grade: _____	

3.16 Reversibility & Equilibrium

This first lesson looks at three examples of reversible reactions and introduces the concept of chemical equilibrium

Reversible Reactions

This activity investigates a reversible reaction between cobalt chloride and water

A **reversible** reaction is a reaction that can go both **forwards** acid + alcohol \rightarrow ester (**condensation**) and **backwards** ester \rightarrow acid + alcohol (**hydrolysis**)

Equations for such reactions should use *two-way arrows* to show the reaction can go in either direction.



There are many examples of **reversible** reactions, especially in Organic Chemistry.

Suitable examples for study often involve a **colour change**.



Taken straight from the oven, or having been dried in front of a bunsen burner, the paper is **blue** in colour.

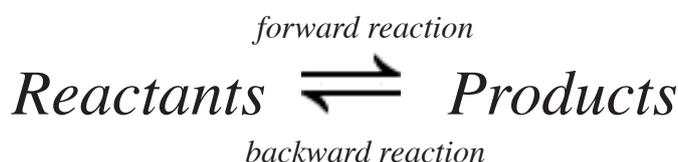


Pressed against a damp paper towel and the paper is **pink**. dry it and it turns **blue**, dampen it and it goes **pink** and so on.

Semantics

The words 'reactants' and 'products' have to be used slightly differently for **reversible** reactions. Strictly speaking $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ is the *product* of the *forward reaction* but is the *reactant* in the *backward reaction*. Similarly CoCl_2 and H_2O are the *reactants* for the *forward reaction* and the *products* of the *backward reaction*.

To make life easier; once the **equation** is written, we continue to call the chemicals on the left the **reactants** and the chemicals on the right the **products**.



Concept Of Equilibrium

This activity explains what is meant by chemical equilibrium

Scenario 1

A piece of **cobalt chloride** paper is removed from a *hot oven*.

It is very **blue**, and we can assume that it is all (100%) **anhydrous** CoCl_2 .



Quite quickly **water** molecules from the air begin to react with the CoCl_2 to *convert it* into the **hydrated** form $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. The **blue** colour will *start to fade*.



However, this is a **reversible** reaction. So some of the **hydrated** $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ formed will *lose water*. At this stage there is so little $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ that the **backward** reaction will be very slow.



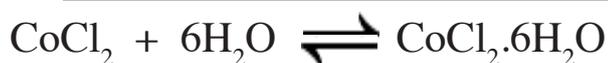
As time passes, there will be less water in the air round the paper so *the rate at which the CoCl_2 hydrates will drop*. At the same time, the **increasing concentration** of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ means that the **rate of the backward** reaction must increase.



At this stage the paper will *still* be getting **less blue**, **more pink**.

Eventually, however,

$$\text{rate of forward} = \text{rate of backward}$$



From now on *the paper will not seem to change* - **EQUILIBRIUM** reached.

Scenario 2

In the same room a piece of **cobalt chloride** paper is taken off a *wet towel*.

It is very **pink**, and we can assume that it is all (100%) **hydrated** $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$



Quite quickly **water** molecules will leave the paper and some of the $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ will be *converted into* the **anhydrous** form CoCl_2 . The **pink** colour will *start to darken*.



However, this is a **reversible** reaction. So some of the **anhydrous** CoCl_2 formed will *react with water* in the air. At this stage there is so little CoCl_2 that the **backward** reaction will be very slow.



As time passes, there will be less $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in the paper so *the rate at which the $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ dehydrates will drop*. At the same time, the **increasing concentration** of CoCl_2 means that the **rate of the backward** reaction must increase.



At this stage the paper will *still* be getting **less pink**, **more blue**.

Eventually, however,

$$\text{rate of forward} = \text{rate of backward}$$



From now on *the paper will not seem to change* - **EQUILIBRIUM** reached.

A close look at both pieces of paper should show that they are the *same colour*. The relative amounts of CoCl_2 (*blue*) and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (*pink*) will depend on factors such as *temperature of the room, humidity of the air* etc.

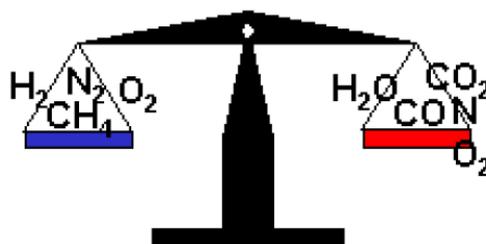
The pieces of paper will still be *losing* and *gaining* water molecules:- *the reactions are still taking place*. The situation is still *dynamic*, not *static*. However, the *number of water molecules leaving the paper every second* is exactly the *same* as the *number entering the paper each second*.

Key Statements About Equilibrium

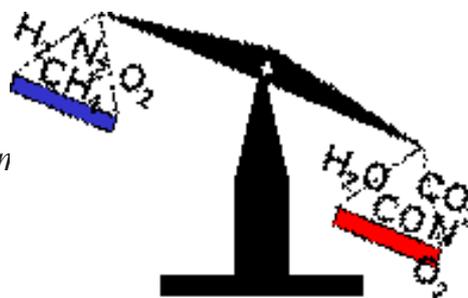
① Chemical equilibrium always involves a *reversible* reaction: \rightleftharpoons

② At equilibrium, the *forward* and *backward* reactions do not stop, but continue at an *equal rate*. This is called a *dynamic equilibrium*.

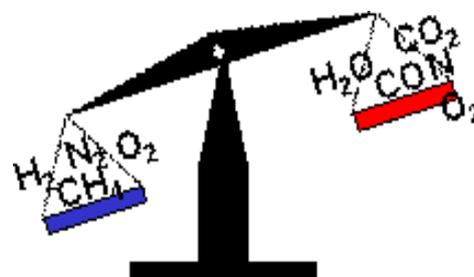
③ At equilibrium the *concentrations* of *reactants* and *products* remain constant, although they are *rarely equal*



④ If the *equilibrium mixture* contains a greater proportion of *products* than *reactants*, then we say that the *equilibrium* “*lies over to the right*”.



⑤ If the *equilibrium mixture* contains a greater proportion of *reactants* than *products*, then we say that the *equilibrium* “*lies over to the left*”.



⑥ The *equilibrium position* is the same whether the reaction starts off with *100% reactants* or with *100% products*.

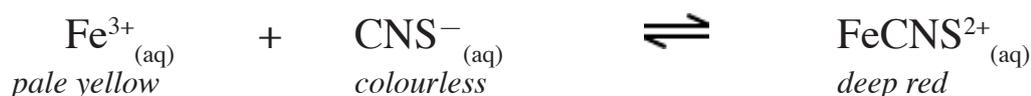
3.17 Changing Conditions

This lesson considers what happens in an equilibrium mixture if the conditions are altered.

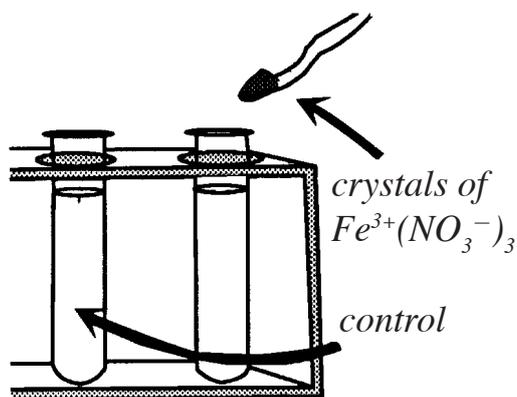
Changing The Concentration

This activity considers what happens if the concentration of just one of the substances is changed

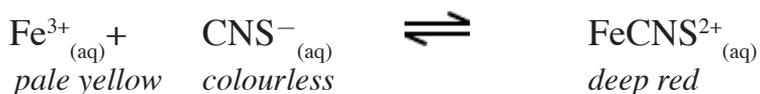
A suitable **equilibrium mixture** to study is formed when $\text{Fe}^{3+}_{(\text{aq})}$ ions react with *thiocyanate* ions, $\text{CNS}^{-}_{(\text{aq})}$ to form $\text{FeCNS}^{2+}_{(\text{aq})}$. **Colour** differences between the **reactants** and the **product** allow us to monitor changes in the **mixture**.



The **equilibrium mixture** is usually **reddy-orange** in colour, a **mixture** of **red** and **yellow**.



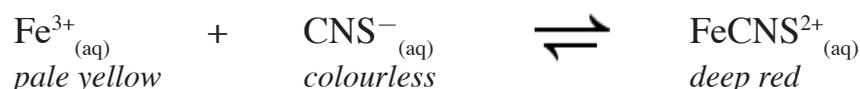
Result When crystals of $\text{Fe}^{3+}(\text{NO}_3^-)_3$ are added to the **equilibrium mixture**



the **colour darkens** showing that the **equilibrium** has shifted to the **right** :- more $\text{FeCNS}^{2+}_{(\text{aq})}$ produced

Explanation Adding $\text{Fe}^{3+}(\text{NO}_3^-)_3$ **increases** the **concentration** of Fe^{3+} ions.

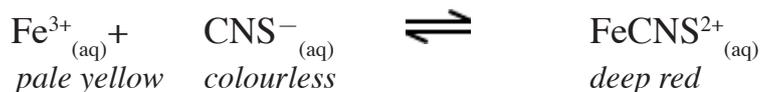
This **increases** the **rate** of the **forward** reaction



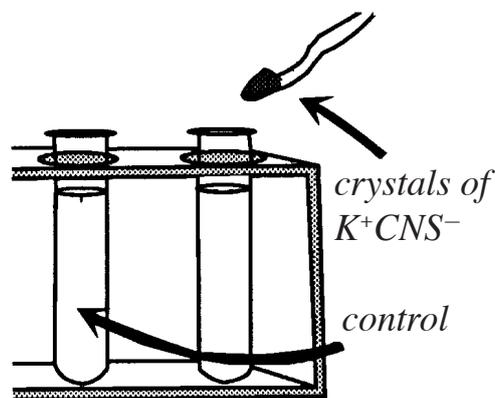
$\text{FeCNS}^{2+}_{(\text{aq})}$ is being **produced faster** than it **breaks up**. Soon there will be more $\text{FeCNS}^{2+}_{(\text{aq})}$ and less $\text{CNS}^{-}_{(\text{aq})}$ i.e. **equilibrium has moved to right**.

Conclusion Increasing concentration of a reactant shifts equilibrium to the right.

Result When crystals of K^+CNS^- are added to the *equilibrium mixture*

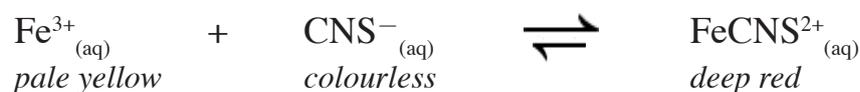


the *colour darkens* showing that the *equilibrium* has shifted to the *right* :- more $\text{FeCNS}^{2+}_{(aq)}$ produced



Explanation Adding K^+CNS^- *increases* the *concentration* of CNS^- ions.

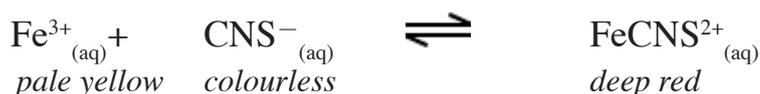
This *increases* the *rate* of the *forward* reaction



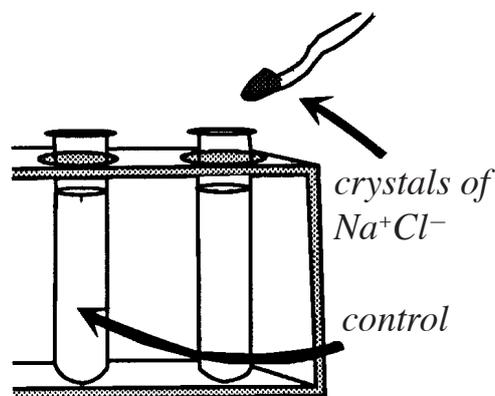
$\text{FeCNS}^{2+}_{(aq)}$ is being *produced faster* than it *breaks up*. Soon there will be more $\text{FeCNS}^{2+}_{(aq)}$ and less $\text{Fe}^{3+}_{(aq)}$ i.e. *equilibrium has moved to right*.

Conclusion *Increasing concentration of a reactant shifts equilibrium to the right.*

Result When crystals of Na^+Cl^- are added to the *equilibrium mixture*

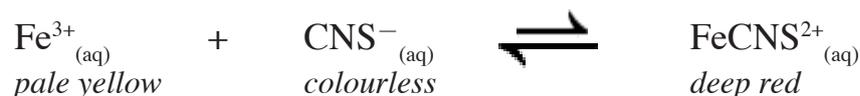


the *colour lightens* showing that the *equilibrium* has shifted to the *left* :- more $\text{Fe}^{3+}_{(aq)}$ and $\text{CNS}^-_{(aq)}$ produced



Explanation Adding Na^+Cl^- *decreases* the *concentration* of Fe^{3+} ions.

This *decreases* the *rate* of the *forward* reaction



$\text{FeCNS}^{2+}_{(aq)}$ is now *breaking up faster* than it is *being made*. Soon there will be more $\text{CNS}^-_{(aq)}$, 'more' $\text{Fe}^{3+}_{(aq)}$ and less $\text{FeCNS}^{2+}_{(aq)}$ i.e. *equilibrium has moved to left*.

Conclusion *Decreasing concentration of a reactant shifts equilibrium to the left.*

A French Chemist called Le Chatelier observed many equilibria and made the following observation:

“ *an equilibrium system always changes to reduce the effect of any outside change made on it* ”

This is known as Le Chatelier's Principle

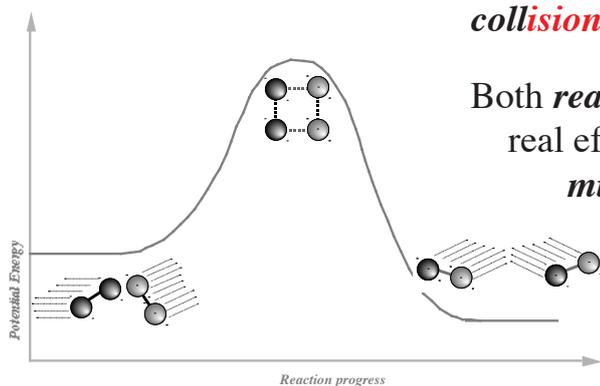
For example, if you add Fe^{3+} ions to $Fe^{3+}_{(aq)} + CNS^{-}_{(aq)} \rightleftharpoons FeCNS^{2+}_{(aq)}$, then the equilibrium will adjust to try and remove those extra Fe^{3+} ions.

This can only be done by converting Fe^{3+} ions into more $FeCNS^{2-}$ ions i.e. by shifting the equilibrium to the right.

Changing The Temperature

This activity considers what happens in an equilibrium mixture if the temperature is changed

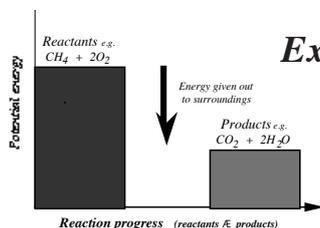
Primary Effect: Back in Unit 1, you learnt that **increasing** the **temperature increases** the number of **collisions** and also **increases** the proportion of **collisions** that have E_a (**successful collisions**).



Both **reactants** and **products** will benefit equally - so no real effect on **equilibrium position**, but the **equilibrium mixture** will be formed **more quickly** than normal.

What does make a difference is the fact that one reaction will always be **exothermic** while the reverse reaction will be **endothermic**.

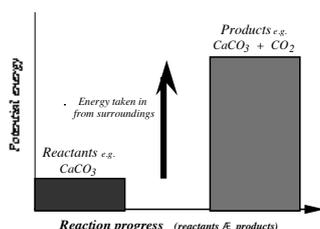
Secondary Effect:



Exothermic reactions release energy to the **surroundings**.

It is easier to **lose energy** if the **surroundings** are **cold**

Decreasing temperature favours the exothermic reaction

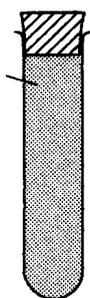


Endothermic reactions take in energy from the **surroundings**.

It is easier to **gain energy** if the **surroundings** are **hot**.

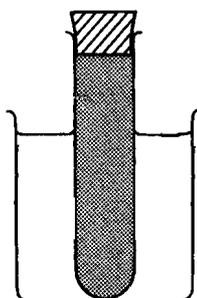
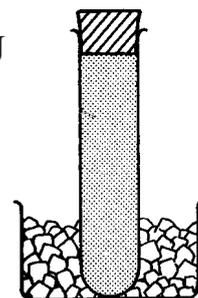
Increasing temperature favours the endothermic reaction.

Example: Whenever the **brown** gas NO_2 , *nitrogen dioxide*, is produced it goes on to form N_2O_4 , *dinitrogen tetroxide*, a **pale yellow** gas. This reaction is **reversible** so a **mixture** of both gases exist.



The **formation** of N_2O_4 (**forward** reaction) is **exothermic**

Surrounding the tube in ice favours the **forward** reaction, the equilibrium shifts to **right**, mixture gets **paler**



The **formation** of NO_2 (**backward** reaction) is **endothermic**.

Surrounding the tube with hot water favours the **backward** reaction, the equilibrium shifts to **left**, mixture gets **darker**.

Using Le Chateliers Principle:



If the temperature of the surroundings rises, then the equilibrium will adjust to try and reduce this effect, i.e. will try and cool down the surroundings.

The endothermic reaction (backward) will have to increase to take in more energy, so equilibrium will shift to the left and the mixture will become darker.

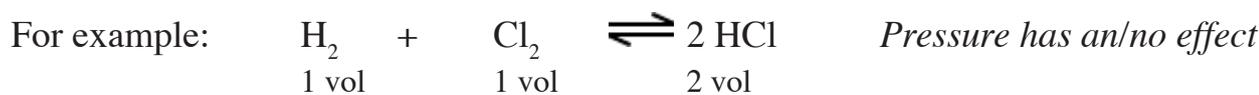
If the temperature of the surroundings drops, then the equilibrium will adjust to try and reduce this effect, i.e. will try and warm up the surroundings.

The exothermic reaction (forward) will have to increase to release more energy, so equilibrium will shift to the right and the mixture will become paler.

Changing The Pressure

This activity considers what happens in an equilibrium mixture if the pressure is changed

Pressure only affects **equilibria** where *at least one* of the chemicals is a gas, and there are **unequal volumes** of gas on each side of the equation.

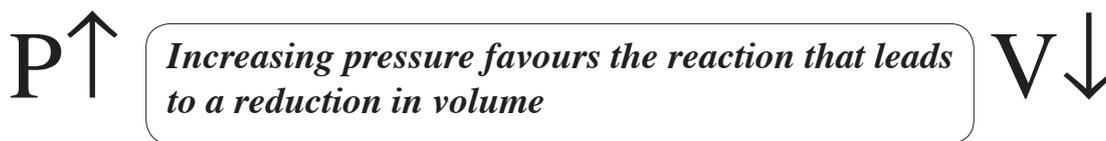


Primary Effect: **Increasing pressure** pushes gas molecules **closer together**. This **increases** the number of **collisions** and **speeds** up the reaction.

However, if *both reactions* involve gases they will be **speeded up equally**.

Secondary Effect: One of the reactions will lead to a **reduction in volume**.

It is easier to **reduce volume** if the **pressure** is **high**

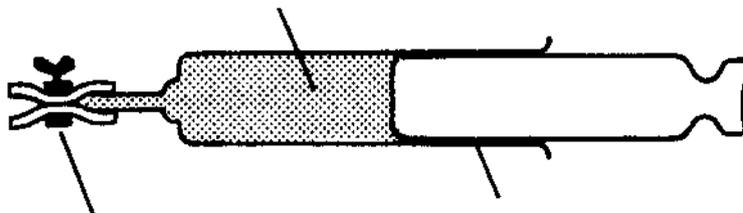
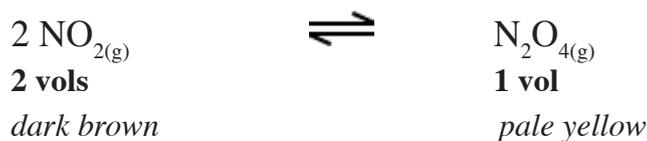


The other reaction will lead to an **expansion in volume**.

It is easier to **expand volume** if the **pressure** is **low**



Example: The same mixture of the **brown** gas NO_2 , *nitrogen dioxide*, and N_2O_4 , *dinitrogen tetroxide*, a **pale yellow** gas is used to show the effect of pressure



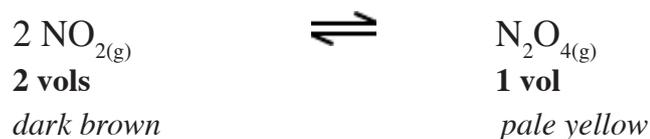
The **formation** of N_2O_4 (**forward** reaction) will reduce the volume of gas

Increasing the pressure *favours the forward reaction*,
the *equilibrium shifts to right*, mixture gets **paler**

The **formation** of NO_2 (**backward** reaction) will expand the volume of gas

Decreasing the pressure *favours the backward reaction*,
the *equilibrium shifts to left*, mixture gets **darker**.

Using Le Chateliers Principle:



If the pressure rises, then the equilibrium will adjust to try and reduce this effect, i.e. will try and remove gas molecules from the mixture.

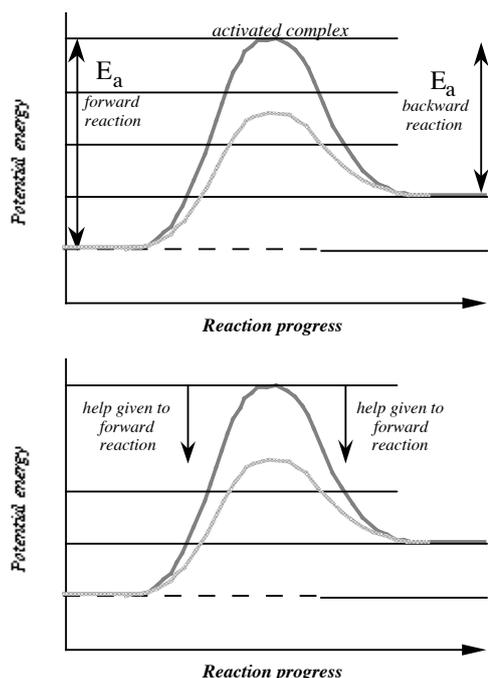
The forward reaction will have to increase to get rid of gas molecules, so equilibrium will shift to the right and the mixture will become paler.

If the pressure drops, then the equilibrium will adjust to try and reduce this effect, i.e. will try and add gas molecules to the mixture.

The backward reaction will have to increase to add more gas molecules, so equilibrium will shift to the left and the mixture will become darker.

Using a Catalyst

This activity considers what happens in an equilibrium mixture if a catalyst is used



Again, in Unit 1, you were asked to learn that when **reactants collide** with enough **energy** (E_a) then an **activated complex** will form before breaking up to make **products**.

This is equally true for **reversible** reactions. The **backward** reaction products \rightarrow reactants will involve the formation of the same **activated complex**.

The **activation energies** for the **forward** and **backward** reactions are **different**. (This is **one** of the factors that will eventually determine the **position of equilibrium**).

A **catalyst** works by providing an **alternative reaction pathway** with a **lower activation energy**.

From the diagram above, it can be seen that the **catalyst** provides an **equal** amount of help to **both** reactions, i.e. **catalysts do not favour one reaction more than the other**.

As a result,

Using a catalyst has no effect on the equilibrium position

This does not mean that **catalysts** are not used in **reversible** reactions. All the other **advantages** still apply, in particular, with **both reactions speeded up** the time taken to reach **equilibrium can be much shorter**.

SUMMARY OF CHANGING POSITION OF EQUILIBRIUM

<i>Change applied</i>	<i>Effect on position of equilibrium</i>
Concentration	
adding a reactant	equilibrium shifts to right \rightarrow
removing a reactant	equilibrium shifts to left \leftarrow
adding a product	equilibrium shifts to left \leftarrow
removing a product	equilibrium shifts to right \rightarrow

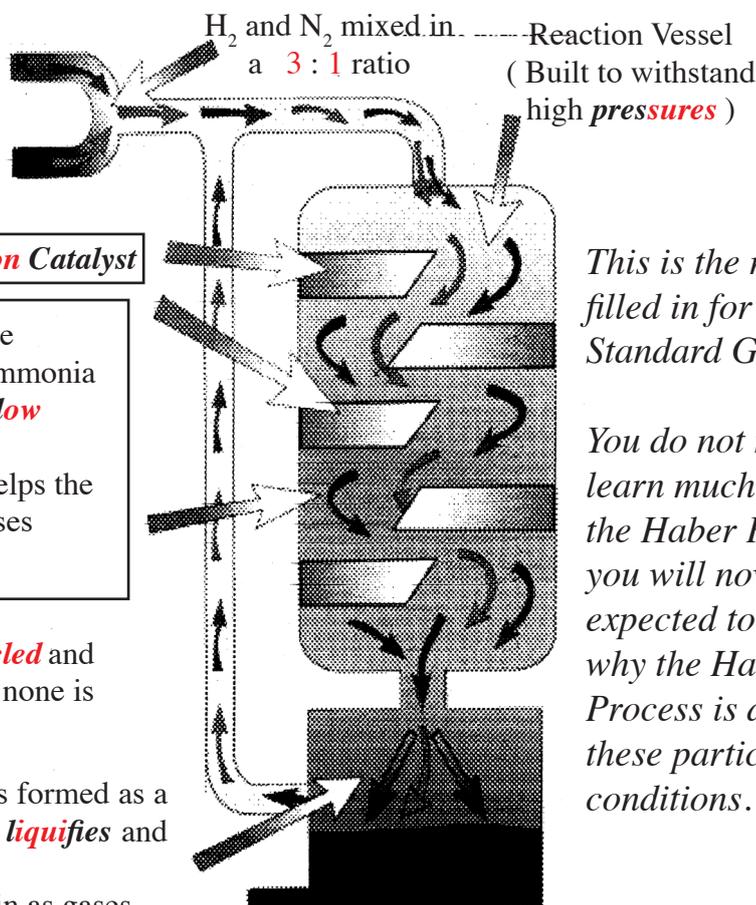
<i>Change applied</i>	<i>Effect on position of equilibrium</i>
<p>Temperature</p> <p>increasing temperature</p> <p>decreasing temperature</p>	<p>equilibrium shifts in direction of endothermic reaction</p> <p>equilibrium shifts in direction of exothermic reaction</p>
<p>Pressure</p> <p>increasing pressure</p> <p>decreasing pressure</p>	<p>equilibrium shifts in direction which reduces vols of gas</p> <p>equilibrium shifts in direction which increases vols of gas</p>
<p>Catalyst</p>	<p>no effect on equilibrium position; equilibrium achieved quicker</p>

CASE study - The Haber Process



Hydrogen gas, made from **methane** or **oil**.

Nitrogen gas, from the air (**fractional distillation** of liquid air)



Trays of **Iron Catalyst**

500 °C a **lower** temperature would yield more ammonia but would be too **slow**

350 atm A **high** pressure helps the H₂ and the N₂ gases react

Unreacted N₂ and H₂ is **recycled** and passed through again so that none is wasted

Condenser. The ammonia is formed as a **gas** but as it cools down, it **liquifies** and is removed.

The N₂ and H₂ remain as gases.

This is the note you filled in for your Standard Grade notes.

You do not need to learn much more about the Haber Process, but you will now be expected to explain why the Haber Process is done under these particular conditions.

UNIT 3 - Part 3 Equilibrium

Equilibrium

- | | |
|---|---|
| <p>1. Reversible reactions attain a state of dynamic equilibrium when the rates of the forward and reverse reactions are equal.</p> | <p>reactants \rightleftharpoons products</p> |
| <p>2. At equilibrium, the concentrations of reactants and products remain constant although not necessarily equal</p> | <p>position of equilibrium - relative amounts of reactants and products</p> <p>“over to the right” - more product</p> <p>“over to the left” - more reactant</p> |
| <p>3. Changes in concentration, temperature and pressure can alter the position of equilibrium</p> | <p>Concentration reactant \uparrow, helps reactant \rightarrow product</p> <p>Concentration product \uparrow, helps product \rightarrow reactant</p> <p>Temperature \uparrow, helps endothermic reaction</p> <p>Temperature \downarrow, helps exothermic reaction</p> <p>Pressure \uparrow, helps reaction reducing moles of gases</p> <p>Pressure \downarrow, helps reaction increasing moles of gases</p> |
| <p>4. A catalyst speeds up the attainment of equilibrium but does not affect the position of equilibrium</p> | <p>Catalyst lowers the activation energies of both reactions by the same amount - it helps both reactions equally.</p> |
| <p>5. The effects of temperature, pressure, the use of a catalyst, recycling of unreacted gases and the removal of product can be considered in relation to the Haber Process.</p> | <p>Temperature - production of ammonia is exothermic, but moderately high temperature (400°C) used to keep speed of reactions up.</p> <p>Pressure - % of ammonia produced increases as pressure \uparrow. 200 atmospheres used, increased yield not enough to justify expense of higher pressure.</p> <p>Catalyst - $N_2 + H_2$ pass over trays of finely divided iron (large surface area)</p> <p>Product- under pressure, the NH_3 forms as a liquid and can be drained off (reducing rate of reverse reaction)</p> <p>Recycling - unreacted $N_2 + H_2$ can be sent through reaction chamber again (low % that react first time not such a problem - no real waste)</p> |