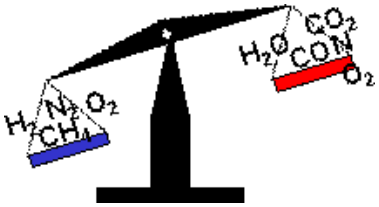
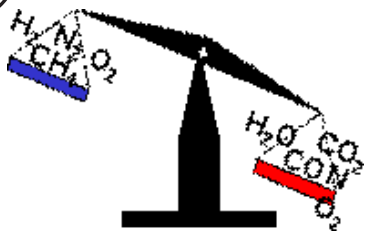
# Higher Chemistry




## *Topic 3:*

# *Industrial Processes & Equilibrium*

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# 3.1 Reversibility & Equilibrium

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

## Reversible Reactions

*This activity linvestigates a reversible reaction between cobalt chloride and water*

A ***reversible*** reaction is a reaction that can go both ***forwards*** acid + alcohol → ester (***condensation***)

and ***backwards*** ester → acid + alcohol (***hydrolysis***)

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

acid + alcohol ⇌ ester

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

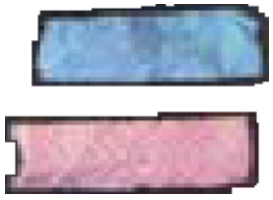
Suitable examples for study often involve a ***colour change***.

$$CoCl_2 + 6H_2O \rightleftharpoons CoCl_2.6H_2O$$

*anhydrous* *Blue*

*hydrated* *Pink*

One such 'reaction' involves the conversion of ***anhydrous*** $CoCl_2$ into ***hydrated*** $CoCl_2.6H_2O$



*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 $CoCl_2.6H_2O$ 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***.

*forward reaction*

*Reactants* ⇌ *Products*

*backward reaction*

# 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 $CoCl_2.6H_2O$. The ***blue*** colour will *start to fade*.

$$CoCl_2 + 6H_2O \longrightarrow CoCl_2.6H_2O$$

However, this is a ***reversible*** *reaction*. So some of the ***hydrated*** $CoCl_2.6H_2O$ formed will *lose water*. At this stage there is so little $CoCl_2.6H_2O$ that the ***backward*** *reaction* will be very slow.

$$CoCl_2 + 6H_2O \rightleftharpoons CoCl_2.6H_2O$$

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 $CoCl_2.6H_2O$ means that the ***rate*** *of the* ***backward*** *reaction must increase*.

$$CoCl_2 + 6H_2O \rightleftharpoons CoCl_2.6H_2O$$

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

Eventually, however,

***rate of forward = rate of backward***

$$CoCl_2 + 6H_2O \rightleftharpoons CoCl_2.6H_2O$$

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*** $CoCl_2.6H_2O$

*Quite quickly* ***water*** molecules will leave the paper and some of the $CoCl_2.6H_2O$ will be *converted into* the ***anhydrous*** form $CoCl_2$ . The ***pink*** colour will *start to darken*.

$$CoCl_2.6H_2O \longrightarrow CoCl_2 + 6H_2O$$

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.

$$CoCl_2.6H_2O \rightleftharpoons CoCl_2 + 6H_2O$$

As time passes, there will be less $CoCl_2.6H_2O$ in the paper so *the* ***rate*** *at which the* $CoCl_2.6H_2O$ ***dehydrates*** *will drop*. At the same time, the *increasing* ***concentration*** of $CoCl_2$means that the ***rate*** *of the* ***backward*** *reaction must increase*.

$$CoCl_2.6H_2O \rightleftharpoons CoCl_2 + 6H_2O$$

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

Eventually, however,

***rate of forward = rate of backward***

$$CoCl_2.6H_2O \rightleftharpoons CoCl_2 + 6H_2O$$

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 $CoCl_2.6H_2O$ (***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:- t*he 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

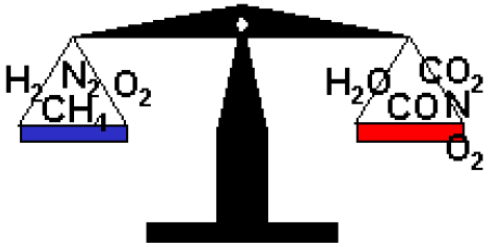
*This activity summarises the main characteristics of an Equilibrium system.*

### *Key Statements About Equilibrium*

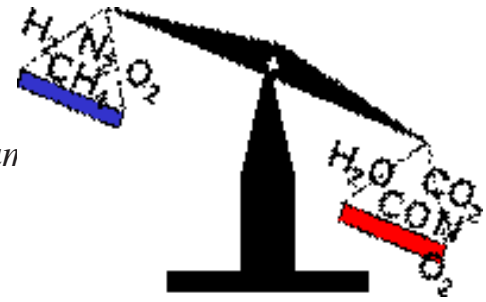
① *Chemical equilibrium* always involves a ***reversible*** reaction: ⇌

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

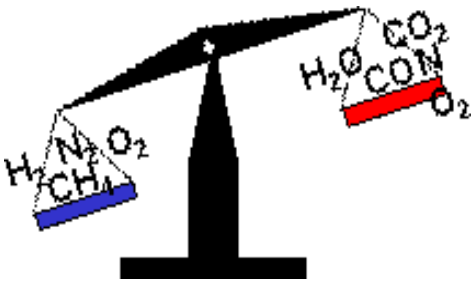
③ At *equilibrium* the ***concentrations*** of ***reactants*** and ***products*** remain *constant,* although they are *rarely equal*




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***.

# 3.2 Changing Conditions

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

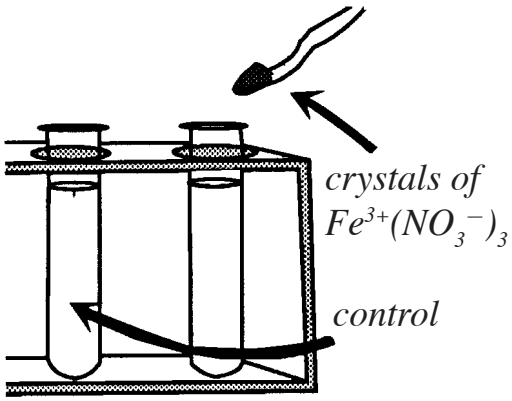
## Changing The Concentration

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

$$\underset{\text{pale yellow}}{Fe^{3+}_{(aq)}} + \underset{\text{colourless}}{CNS^-_{(aq)}} \rightleftharpoons \underset{\text{deep red}}{FeCNS^{2+}_{(aq)}}$$

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




***Result*** When crystals of $Fe^{3+}(NO_3^-)_3$ are added to the ***equilibrium mixture***

$$\underset{\text{pale yellow}}{Fe^{3+}_{(aq)}} + \underset{\text{colourless}}{CNS^-_{(aq)}} \rightleftharpoons \underset{\text{deep red}}{FeCNS^{2+}_{(aq)}}$$

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

***Explanation*** Adding $Fe^{3+}(NO_3^-)_3$ ***increases*** the ***concentration*** of $Fe^{3+}$ ions.

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

$$\underset{\text{pale yellow}}{Fe^{3+}_{(aq)}} + \underset{\text{colourless}}{CNS^-_{(aq)}} \rightleftharpoons \underset{\text{deep red}}{FeCNS^{2+}_{(aq)}}$$

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

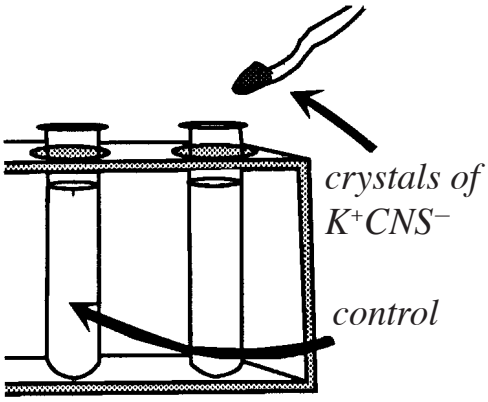
***Conclusion*** *Increasing concentration of a reactant shifts equilibrium to the right.*

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

$Fe^{3+}_{(aq)}$ + $CNS^-_{(aq)}$ ⇌ $FeCNS^{2+}_{(aq)}$

*pale yellow* *colourless* *deep red*

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




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

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

$Fe^{3+}_{(aq)}$ + $CNS^-_{(aq)}$ ⇌ $FeCNS^{2+}_{(aq)}$

*pale yellow* *colourless* *deep red*

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

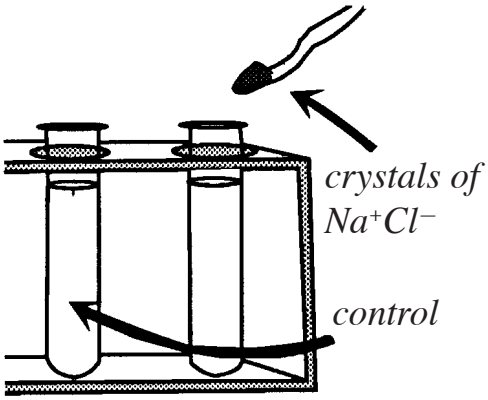
***Conclusion*** *Increasing concentration of a reactant shifts equilibrium to the right.*

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

$Fe^{3+}_{(aq)}$ + $CNS^-_{(aq)}$ ⇌ $FeCNS^{2+}_{(aq)}$

*pale yellow* *colourless* *deep red*

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




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

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

$Fe^{3+}_{(aq)}$ + $CNS^-_{(aq)}$ ⇌ $FeCNS^{2+}_{(aq)}$

*pale yellow* *colourless* *deep red*

$FeCNS^{2+}_{(aq)}$ is now *breaking up* ***faster*** than it is *being made*. Soon there will be more $CNS^-_{(aq)}$ , 'more' $Fe^{3+}_{(aq)}$ and less $FeCNS^{2+}_{(aq)}$ 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

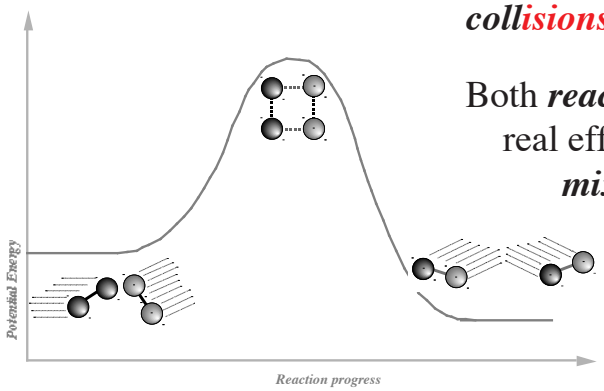
For example, *if you add $Fe^{3+}$ ions to then the equilibrium will adjust to try and remove those extra $Fe^{3+}$ ions.* $Fe^{3+}_{(aq)} + CNS^{-}_{(aq)} \rightleftharpoons FeCNS^{2+}_{(aq)}$,

*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*

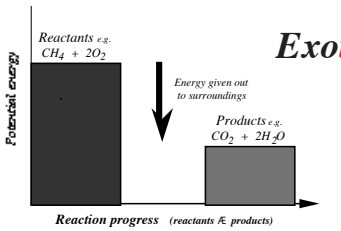
***Primary Effect:*** Back in Unit 1, you learnt that ***increasing*** the ***temperature increases*** the *number* of ***collisions*** and also ***increases*** the *proportion* of ***collisions*** that have $\mathbf{E_a}$ (*successful* ***collisions***).




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***.

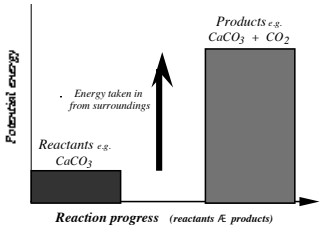
***Secondary Effect:***




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

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

***Decreasing temperature favours the exothermic reaction***

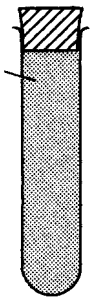



***Endothermic*** reactions *take in energy* from the ***surroundings***.

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

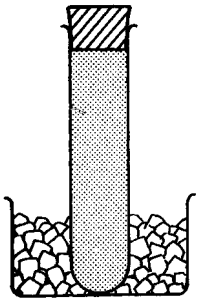
***Increasing temperature favours the endothermic reaction.***

***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.



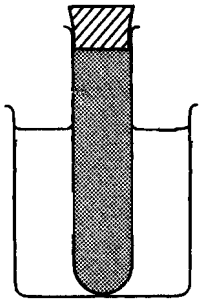
$$2\,NO_{2(g)} \rightleftharpoons N_2O_{4(g)} \qquad \Delta H = -58\ kJ$$

*dark brown* — *pale yellow*



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*:

$$2\,NO_{2(g)} \rightleftharpoons N_2O_{4(g)} \qquad \Delta H = -58\ kJ$$

*dark brown* — *pale yellow*

*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 numbers of moles*** of gas on each side of the equation.

For example:

$$\underset{1\text{ mol}}{H_2} + \underset{1\text{ mol}}{Cl_2} \rightleftharpoons \underset{2\text{ mol}}{2\,HCl}$$ *Pressure has an/no effect*

$$\underset{1\text{ mol}}{N_2} + \underset{3\text{ mol}}{3H_2} \rightleftharpoons \underset{2\text{ mol}}{2\,NH_3}$$ *Pressure has an/no effect*

***Explanation ① :*** ***Increasing pressure*** pushes gas molecules ***closer together***. This ***increases*** the *number* of ***collisions*** and ***speeds*** up the reaction.

If *both reactions* involve equal moles of gases they will be ***speeded up equally***.

If *one reaction* has more moles of gases they will be ***speeded up more*** and this reaction will be favored.

***Explanation ② :*** Later in the course you will learn that because *gases are mainly empty space*, the size of the individual molecules has no effect on the volume occupied by a gas - the volume depends ***only*** on the ***number*** of gas molecules - the ***number*** of ***moles*** of gas.

Therefore, any differences in ***number of moles*** will lead to an *identical* change in ***volumes*** of gases.

$$\underset{\substack{1\text{ mol}\\1\text{ vol}}}{N_2} + \underset{\substack{3\text{ mol}\\3\text{ vols}}}{3H_2} \rightleftharpoons \underset{\substack{2\text{ mol}\\2\text{ vols}}}{2\,NH_3}$$

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

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

P↑ ***Increasing pressure favours the reaction that leads to a reduction in volume*** V↓

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

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

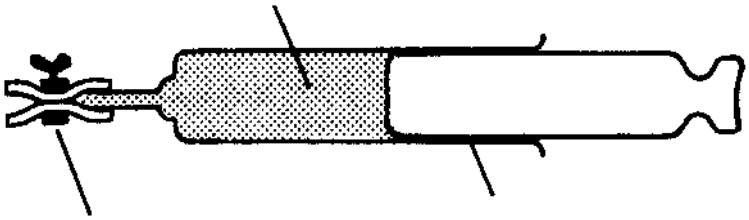
P↓ ***Decreasing pressure favours the reaction that leads to an expansion in volume*** V↑

***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

$2\ NO_{2(g)}$ ⇌ $N_2O_{4(g)}$

**2 vols** **1 vol**

*dark brown* *pale yellow*



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*:

$2\ NO_{2(g)}$ ⇌ $N_2O_{4(g)}$

**2 vols** **1 vol**

*dark brown* *pale yellow*

*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.*

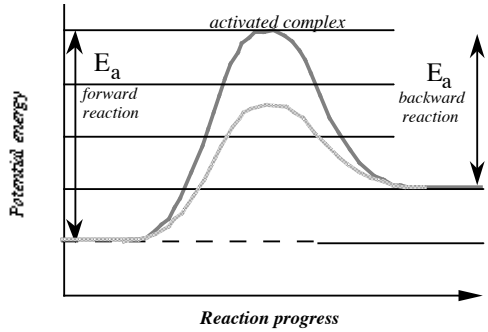
*The forward reaction will have to increase to get rid of gas molecules, so equilibrium will shift to the right and the mixture will become paler.*

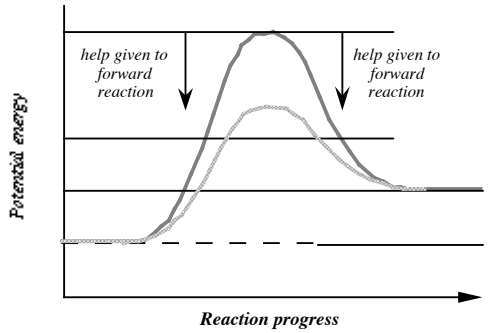
*If the pressuredrops, then the equilibrium will adjust to try and reduce this effect, i.e. will try and add gas molecules to the mixture.*

*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* → *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 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*

| *Change applied* | *Effect on position of equilibrium* |
|---|---|
| ***Concentration*** | |
| *adding a reactant* | equilibrium *shifts to right* → |
| *removing a reactant* | equilibrium *shifts to left* ← |
| *adding a product* | equilibrium *shifts to left* ← |
| *removing a product* | equilibrium *shifts to right* → |

| *Change applied* | *Effect on position of equilibrium* |
|---|---|
| ***Temperature*** | |
| *increasing temperature* | equilibrium *shifts in direction of* ***endothermic reaction*** |
| *decreasing temperature* | equilibrium *shifts in direction of* ***exothermic reaction*** |
| ***Pressure*** | |
| *increasing pressure* | equilibrium *shifts in direction which* ***reduces vols of gas*** |
| *decreasing pressure* | equilibrium *shifts in direction which* ***increases vols of gas*** |
| ***Catalyst*** | |
| | no effect on equilibrium position; equilibrium achieved quicker |

# 3.3 Equilibrium - Chromatograpy

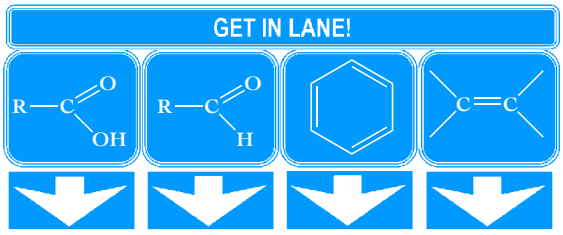
*This lesson topic explores the technique of chromatography.*

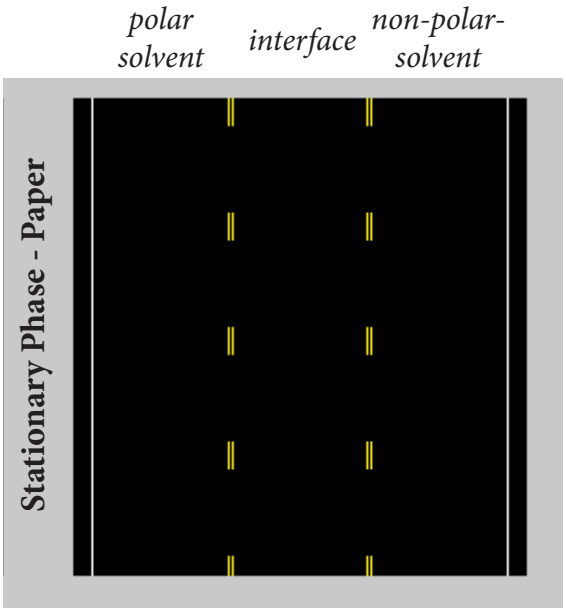
## Background Theory

*This activity looks at the principles behind chromatography.*

Chromatography is the general name for a wide range of techniques that are used to ***separate*** and ***identify*** molecules based on their properties. In general, ***chromatography*** involves two phases:

- *A **Stationary Phase**. This is typically a solid*
  *e.g. paper, silica gel or powder filled tube.*
- A ***Mobile Phase***. This is typically a ***liquid*** or mixture of ***liquids***. It can be a ***gas***.




***Polar solvents*** (e.g. *water)* tend to 'stick' to the paper (***hydrogen bonding***) and travel ***slowly*** up the paper - the *slow lane*.

***Non-polar solvents*** (e.g. *hexane*) do not form strong attractions with the paper or the polar solvents (*immiscible*) and tend to move ***quickly*** - the *fast lane*.

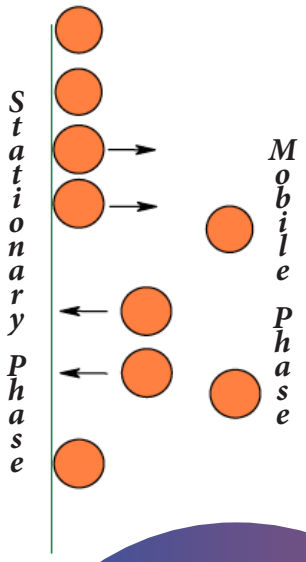
***Polar molecules*** will spend most of their time dissolved in the *polar solvent* (*slow lane*) but may have some solubility in the *non-polar solvent* so may also spend time in the *middle lane* or even the *fast lane*.

Similarly ***non-polar molecules*** will spend most of their time dissolved in the ***non-polar solvent*** (*fast lane*) but may have some solubility in the ***polar solvent*** so may also spend time in the *middle lane* or even the *slow lane*. The ***proportion*** of time spent in each '*lane*' will determine how ***fast*** the molecules move.

Solute molecules will be constantly ***moving backwards*** and ***forwards*** between the ***different*** solvents and this is a special type of reversible reaction called *Partition*.

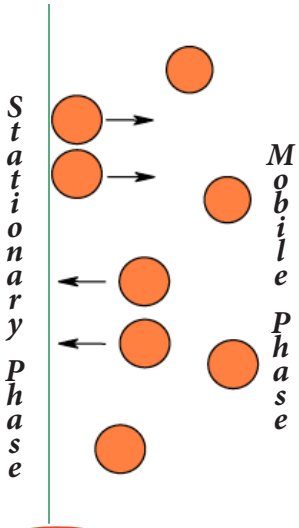
Like most ***reversible*** reaction, one direction will be '*favoured*' but eventually ***the concentrations will become constant*** and ***the rates*** at which solute molecules move ***will become equal***.

$$\textbf{Solute}_{(\text{polar solvent})} \rightleftharpoons \textbf{Solute}_{(\text{non-polar solvent})}$$

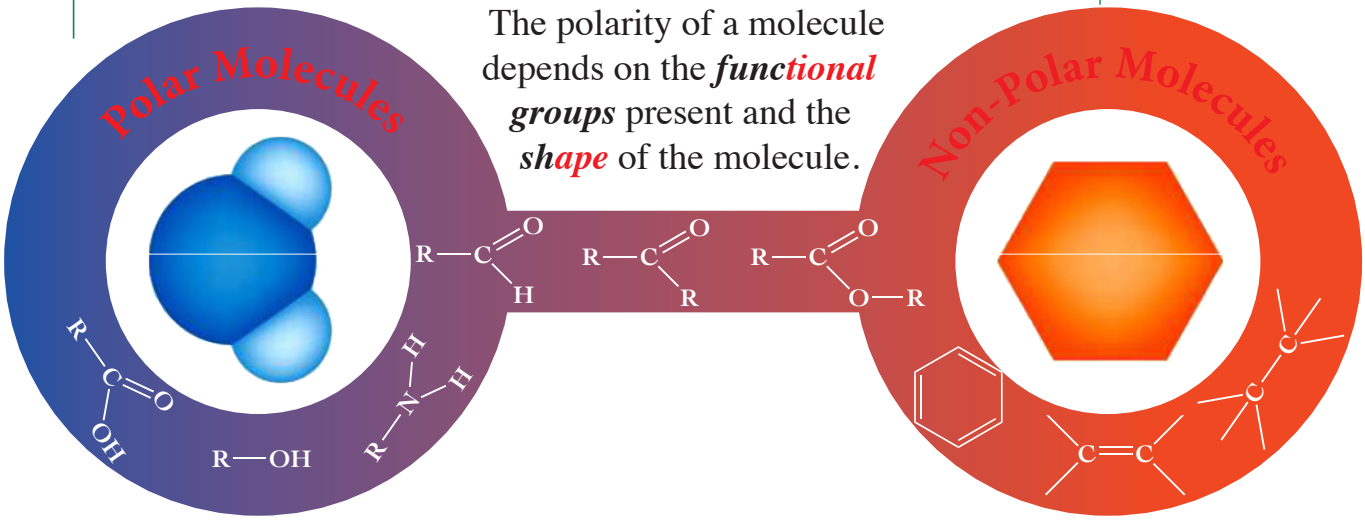



The more ***polar*** the solute molecule, the ***further to the left*** will lie the ***position*** of ***equilibrium***, meaning the molecules will spend ***more*** of their ***time*** attached to the ***stationary phase*** and they will *move more* ***slowly*** up the paper.

The more ***non-polar*** the solute molecule, the ***equilibrium position*** will lie *over to the* ***right***, meaning they will spend more of their time in the ***mobile*** *phase* and they will *move more* ***quickly*** up the paper.




The polarity of a molecule depends on the ***functional groups*** present and the ***shape*** of the molecule.




***Acids Alcohols Amines Aldehydes Ketones Esters Aromatics Alkenes Alkanes***

***hydrogen bonding*** → ***polar-polar attractions*** → ***london dispersion***

## Running a Chromatogram

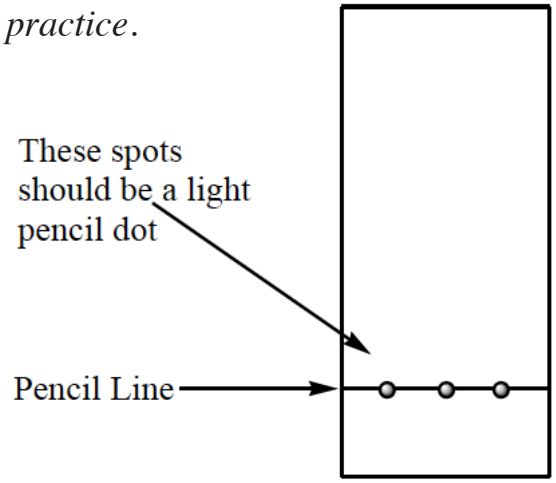
*This activity looks at how Chromatography is done in practice.*

A *light* ***pencil*** *line* about *1.5–2 cm* from the ***bottom*** of the sheet is drawn.

Samples are ***spotted*** onto this line.

The sheet is placed in a tank containing about 1 cm of ***solvent***.

The chromatogram runs until the ***solvent*** is near, but not too near, to the top of the sheet.




The ***position*** reached by the ***solvent*** - the ***solvent front*** - is marked in ***pencil***.

Either using a ***chemical spray*** or ***UV*** light, the ***positions*** reached by the samples are marked.

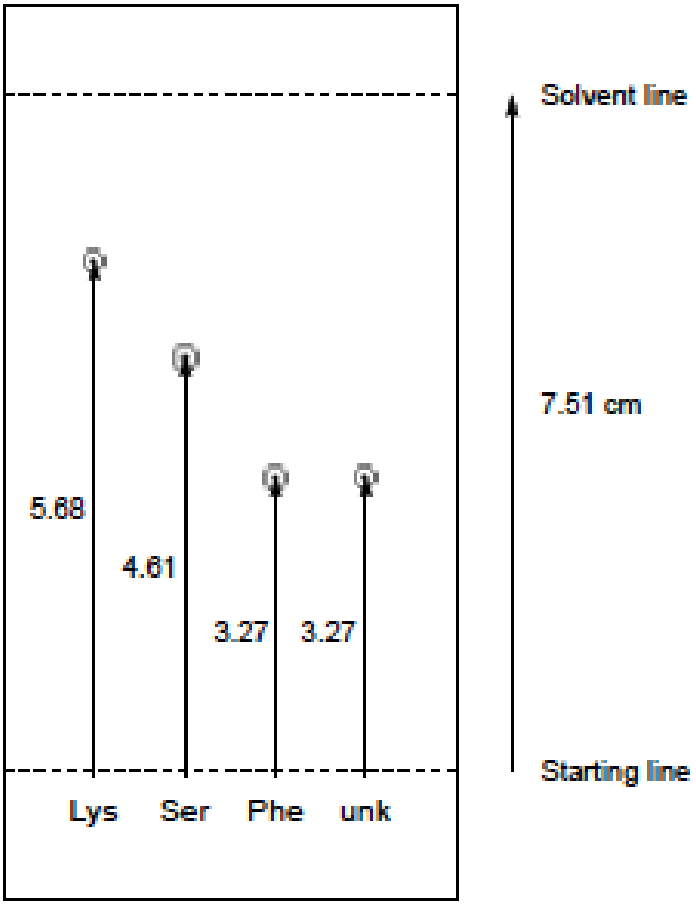
## Retention Ratio - $R_f$ values

*This activity looks at how Rf values are measured and used.*

Generally speaking, it is better to run unknowns and known samples under exactly the same conditions at the same time.

However, where similar chromatograms are routinely ran repeatedly, there is the option of using $R_f$ values.

$$R_f = \frac{\text{distance traveled by compound (cm)}}{\text{distance traveled by solvent (cm)}}$$




$R_f$ calculations:

Lys $\frac{5.68}{7.51} = 0.756$

Ser $\frac{4.61}{7.51} = 0.614$

Phe $\frac{3.27}{7.51} = 0.435$

unk $\frac{3.27}{7.51} = 0.435$

# 3.4 Analysis - Chromatography

*This lesson topic explores the technique of chromatography.*

This practical should have helped you:

1. *learn how chemists use chromatography to separate and analyze organic compounds*
2. *learn the technique of thin layer chromatography (TLC)*
3. *identify the components in various over-the-counter analgesics (Hedex, Anadin, etc.)*
4. *examine the polarity of molecules and their interaction silica gel and organic solvents.*

## Introduction

## Aim

## Method

## Results

## Conclusion

# 3.5 Fertiliser Industry

*This lesson topic considers some important aspects of the chemical industry by examining the manufacture of ammonia and some of the economic considerations of its production on a large scale.*

## Chemical Industry

***Importance:***

- ➢ the Chemical Industry is one of the largest British industries.
- ➢ it is the only manufacturing industry to export more than it imports and so earns a trade balance surplus from these exports for Britain
- ➢ also invisible trade balance surplus from selling licences to use British processes abroad
- ➢ the chemical industry involves the investment of large sums of money but employs relatively few people making it a capital intensive and not a labour intensive industry.

***Products:*** The 4 main categories of products that the industry makes are

- ❖ basic inorganics & fertilisers
- ❖ dyestuffs, paints & pigments
- ❖ petrochemicals & polymers
- ❖ pharmaceuticals & other speciality chemicals

## Raw Materials & Feedstocks

*This activity considers the production of the starting materials for Industrial processes such as the Haber process.*

*A **feedstock** is a substance from which another substance can be made by extraction or by chemical change.*

*A **raw material** is a substance which is available naturally in the Earth's crust (i.e. in the ground, sea, atmosphere, or living material). They are:*

- ✢ ***fossil fuels*** – *coal*, *oil* and *natural gas*
- ✢ ***metallic ores*** – eg ***aluminium*** extracted from *bauxite* ($Al_2O_3$)
- ✢ ***minerals*** – ***chlorine*** from *sodium chloride*
- ✢ ***water & air*** – water in ***hydration*** of *ethene* to *ethanol* and ***nitrogen*** in the ***Haber Process***, *oxygen* in the catalytic oxidation of *ammonia*, the ***Ostwald Process***
- ✢ ***organic materials*** – of plant and animal origin eg ***vegetable oils*** and ***starch***

***Crude oil*** is a ***raw material*** from which *naphtha* is obtained by ***fractional distillation***. *Naphtha* is a ***feedstock*** that can be ***cracked*** to produce ***ethene***. *Ethene* is then the ***feedstock*** for making many ***polymers***.

***Stage 1:*** Steam converts methane to carbon monoxide and hydrogen.

① $CH_{4(g)} + H_2O_{(g)} \longrightarrow CO_{(g)} + 3\,H_{2(g)}$ $\Delta H = +210$ kJ

*natural gas* *steam*

***Stage 2:*** Hydrogen removes oxygen from air to produce more steam and leave nitrogen.

② $4\,N_{2(g)} + O_{2(g)} + 2\,H_{2(g)} \longrightarrow 4\,N_{2(g)} + 2\,H_2O_{(g)}$ $\Delta H = -484$ kJ

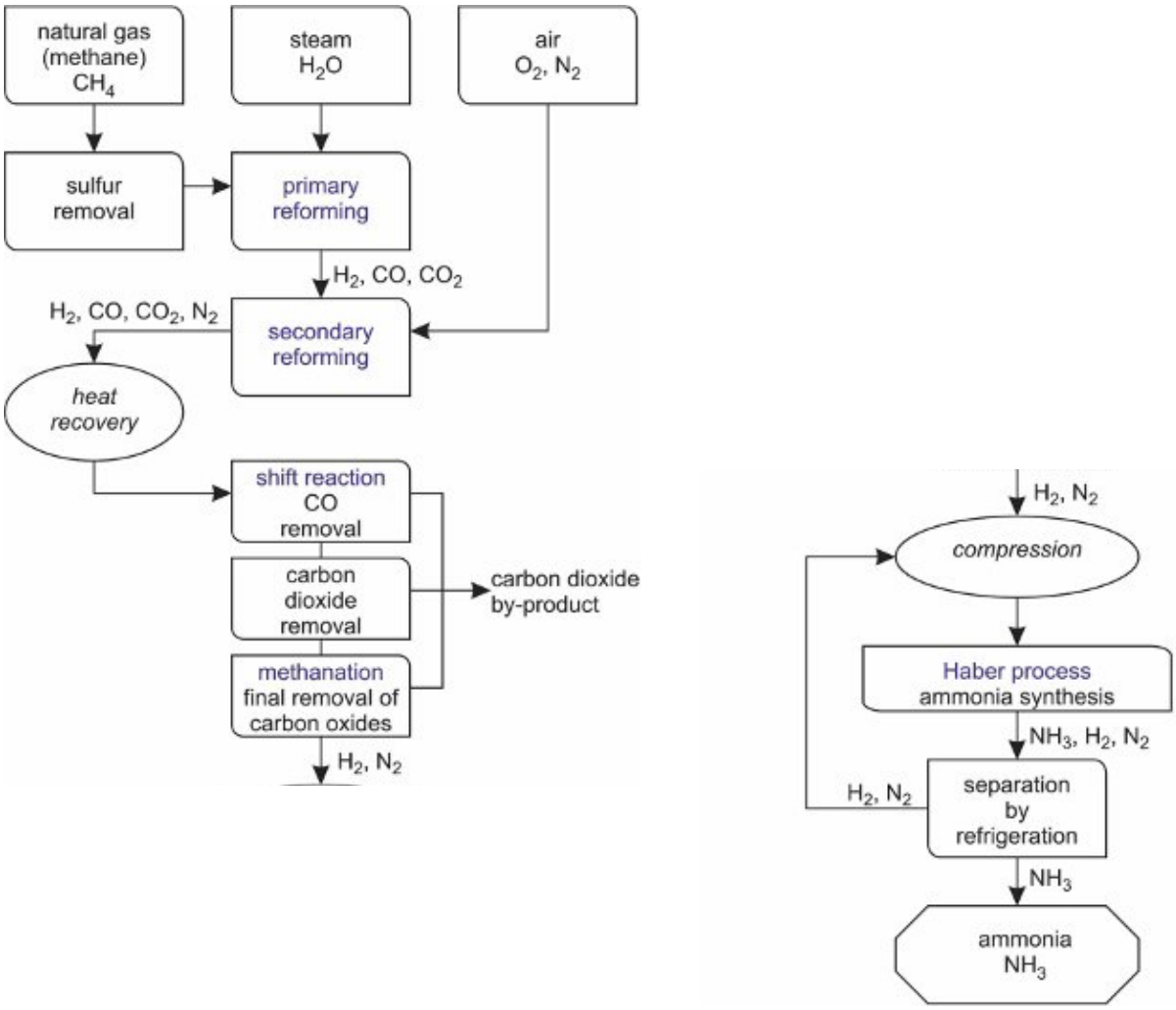
*air*

***Stage 3:*** Steam converts carbon monoxide to carbon dioxide and more hydrogen.

③ $CO_{(g)} + H_2O_{(g)} \longrightarrow CO_{2(g)} + H_{2(g)}$ $\Delta H = -41$ kJ

***Overall Equation:***

***Overall ΔH:***



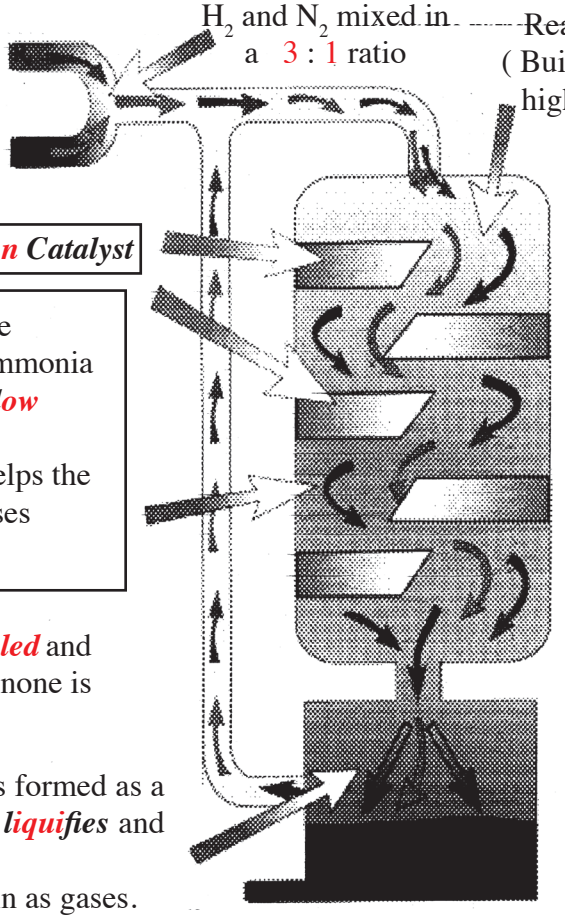
# Reaction Conditions

*This activity considers the optimum conditions for the reaction by which ammonia is produced in the Haber process.*

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

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

***Nitrogen*** gas, from the air




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

***350 atm*** A ***high*** pressure helps the $H_2$ and the $N_2$ gases react

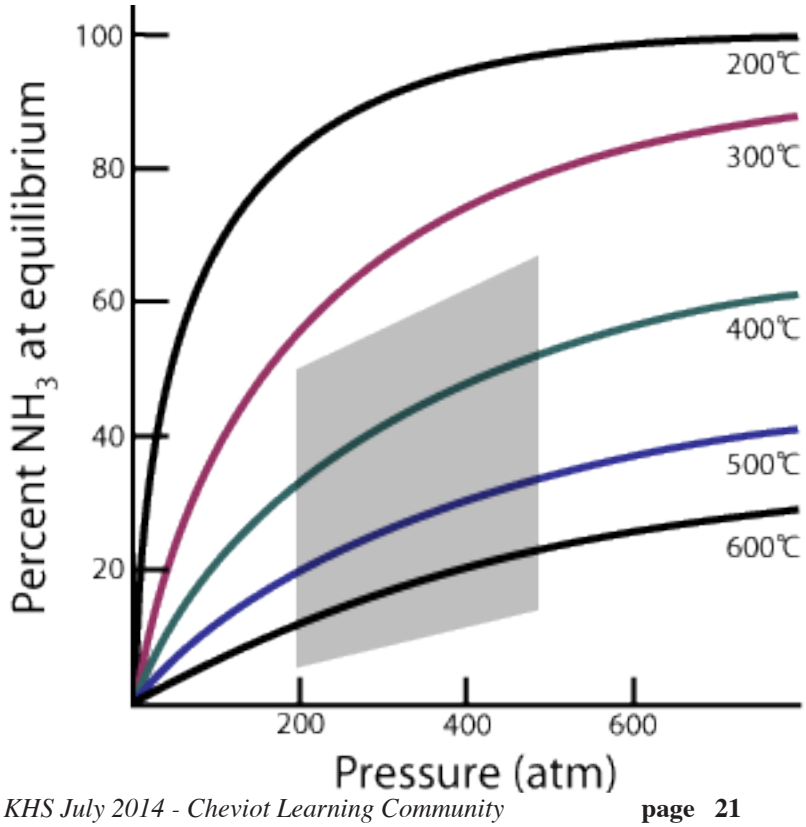
***Unreacted*** $N_2$ and $H_2$ is ***recycled*** and passed through again so that none is wasted

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

The $N_2$ and $H_2$ remain as gases.

*This is the note you probably filled in during a previous Chemisry course.*

*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.*




*The Haber Process is an industrial process and the conditions chosen will often involve compromises between the desire for high yield and other factors such as construction and maintenance costs, running costs, labour costs, catalyst life etc.*

The graph opposite shows the % yield of ***ammonia*** under different conditions of ***temperature*** and ***pressure***.

Because of ***recycling***, it is possible to achieve an overall yield of 98 % ***ammonia***.

| ***Theoretical conditions with explanations*** | ***Actual conditions with reasons*** |
|---|---|
| ***Temperature***<br>$N_2 + 3H_2 \rightleftharpoons 2\,NH_3 \quad \Delta H = -92$ kJ<br>The ***forward*** reaction is ***exothermic*** so we would *predict* a ***low temperature***. The graph confirms that a *temperature of 100 °C* would be best. | ***Temperature***<br>*Actual Temperature* = 350 - 450°C<br>At the ***lower temperature*** the reaction is too ***slow*** |
| ***Pressure***<br>$N_2 + 3H_2 \rightleftharpoons 2\,NH_3$<br>**4 vols** **2 vols**<br>The ***forward reaction*** leads to a ***reduction in volume*** so we would *predict* a ***high pressure***. The graph confirms that a ***pressure*** in excess of 400 atm is best. | ***Pressure***<br>*Actual Pressure* = 200 atmospheres<br>A ***higher pressure*** would be ***better*** but the reaction chamber would be much more ***expensive*** to build, and maintenance costs would be higher too. |
| ***Concentration***<br>$N_2 + 3H_2 \rightleftharpoons 2\,NH_3$<br>Ideally we would want to:<br>***increase*** the ***concentration*** of *reactant(s)*<br>***decrease*** the ***concentration*** of *product* | ***Concentration***<br>At this ***pressure*** $NH_3$ *liquifies* easily and can be drained away - ***decreasing concentration***.<br>The $N_2$ and $H_2$ can be *recycled* - ***increasing concentration.*** |
| ***Catalyst***<br>should be used to ***speed*** up ***equilibrium*** reactions | ***Catalyst***<br>*finely divided* ***iron*** is used as a catalyst |

### *Factors Influencing the Choice of Synthetic Route / Reaction Conditions*

- cost, availability of feedstocks
- the yield of the reaction
- can unreacted starting materials be recycled?
- can by-products be sold?
- difficulty and cost of waste disposal
- energy consumption
- emissions to the atmosphere

The conditions under which a chemical process operates are chosen to maximise economic efficiency. For example:

- raising the temperature may increase the rate of a reaction but it will increase energy costs so may not be economic
- increasing the pressure may shift an equilibrium in favour of the product but will mean using stronger reaction vessels and more powerful compressors and may not be economic.

# 3.6 Sulphuric Acid Industry

The sulfuric acid industry is of major global importance. Over a hundred thousand million litres of sulfuric acid are manufactured in the world every year. Only petrochemicals, such as petrol and plastics, are manufactured in larger quantities.

*This lesson topic considers the manufacture of sulfuric acid in terms of raw materials, reaction conditions, and economic considerations.*

## Sources of Sulphur

*This activity considers the different sources of sulphur that are readily available.*

There are four main sources of sulphur used by the chemical industry.

① ***Sulphur dioxide from smelting metal ores***

Many metal ores are obtained from the ground as metal sulphides. The first step in extracting the metal is to convert the metal sulphide to an oxide by roasting it in air.

e.g. $2\ ZnS + 3\ O_2 \longrightarrow 2\ ZnO + 2\ SO_2$

This produces the oxide of the metal and also sulphur dioxide as a by-product.

*A **by-product** is any other substance produced in the course of making the main product.*

Rather than releasing the sulphur dioxide into the air (where it would produce acid rain and pollute the environment) it can be converted into sulphuric acid and sold. This not only solves the pollution problem but also makes the metal extraction process more profitable. Sulphuric acid plants are therefore often located beside metal ore smelters.

② ***Mineral deposits of anhydrite***

Anhydrite (calcium sulphate) is roasted with coke (carbon) and sand (silicon dioxide) to produce sulphur dioxide and calcium silicate.

$$2\ CaSO_4 + C + 2\ SiO_2 \longrightarrow 2\ CaSiO_3 + 2\ SO_2 + CO_2$$

The sulphur dioxide is then used to manufacture sulphuric acid while the calcium silicate can be sold for use in cement and is therefore a commercial by-product.

③ ***Sulphur deposits in the ground***

$$S + O_2 \longrightarrow SO_2$$

In this case, there is no by-product to consider. On the other hand, there is the cost of importing and transporting the sulphur. The UK has no natural sulphur deposits.

④ ***Sulphur extracted from crude oil and natural gas***

Crude oil and natural gas often have some sulphur compounds present. To meet modern standards for fuels (e.g. low-sulphur diesel) most of the sulphur in the compounds is converted to the element and then sold on to the sulphuric acid industry.

## Manufacturing Process

Nearly all sulphuric acid is manufactured today by a process known as the 'contact process', so called because the main step involves gases reacting when in contact with a catalyst.

*This activity considers the stages involved in manufacturing sulphuric acid and the reaction conditions to give the best economic yield.*

***Stage 1:*** The first stage is the manufacture of sulphur dioxide.

① $S_{(l)} + O_{2(g)} \longrightarrow SO_{2(g)}$ $\Delta H = -299$ kJ

***Stage 2:*** Sulphur dioxide along with excess air is passed through a catalytic converter containing four beds of vanadium(V) oxide.

② $2\,SO_{2(g)} + O_{2(g)} \longrightarrow 2\,SO_{3(g)}$ $\Delta H = -98$ kJ

The position of equilibrium lies to the right, with a total conversion of 99 % being possible under 'normal' conditions (room temperature and pressure).

However, the reaction is carried out at around 450 °C as the catalyst does not function below 400 °C.

Increasing the temperature will decrease the yield of sulphur trioxide as higher temperatures favour the endothermic reaction (reverse reaction, in this case). Also, since the reaction is exothermic it has to be cooled using heat exchangers to prevent further increase in temperature.

In terms of pressure, increasing the pressure would increase the yield of sulphur trioxide as there are more moles of gas on the left than on the right. However, since the conversion is already close to 99 %, the cost of using a high-pressure plant is not worth it.

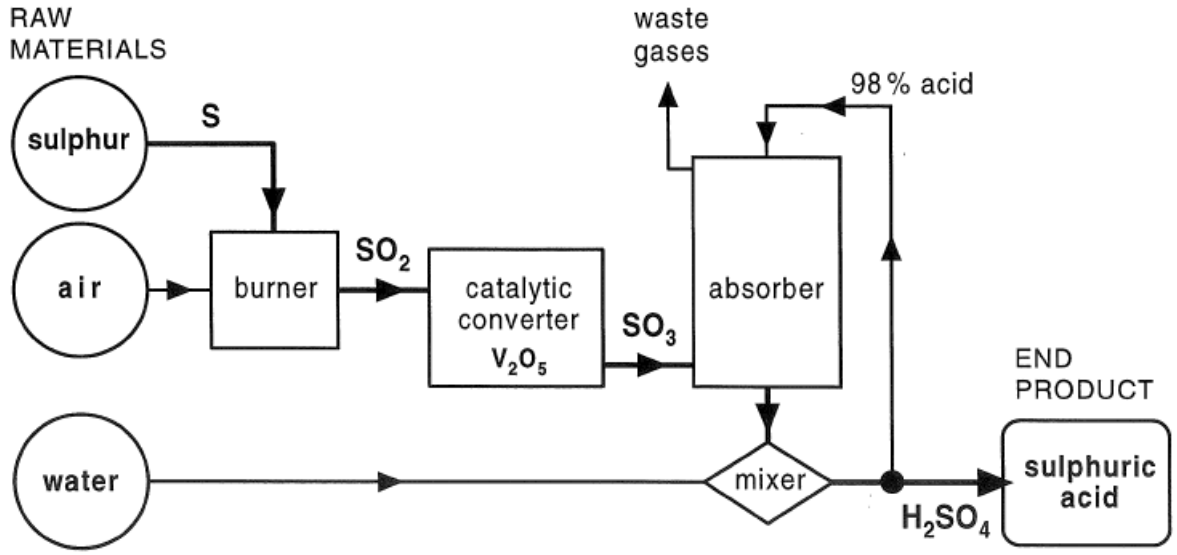
***Stage 3:*** The sulphur trioxide produced reacts with water to form sulphuric acid.

③ $SO_{3(g)} + H_2O_{(l)} \longrightarrow H_2SO_{4(l)}$ $\Delta H = -130$ kJ

In reality, $SO_3$ is not that soluble in water so the sulphur trioxide is first absorbed in a mixture of 98 % sulphuric acid and 2 % water. The concentration of this mixture is maintained at 98 % by constant addition of water.

***Overall Equation:***

***Overall ΔH:***




## Cost Considerations

Costs come under 3 main categories – capital, fixed and variable costs.

The amount of money paid by the chemical industry for raw materials, energy, labour, research and development, plant design and construction, waste disposal, warehousing, packaging, distribution, marketing and sales must all be covered by the selling price of the product. Sales must also produce a profit to invest in new research and to pay off loans.

***Capital Costs*** *are the costs associated with setting up a production process, especially the building of the plant and all the support facilities required.*

These are incurred when building the plant. The life of a plant is assumed to be only about 10 years after which it is written off. The cost of this depreciation is recovered under fixed costs.

***Fixed Costs*** *are costs that tend to remain much the same throughout the year and do not depend on the quantity of product being manufactured*

These are costs that are the same whether 1 ton or 1000 tons of product are made. The effect of the fixed cost decreases as the amount of product increases. They include:

- depreciation of the plant
- labour
- land purchase

***Variable Costs*** *are costs that change throughout the year depending on how much or how little product is being manufactured.*

These are directly related to output and include

- raw materials and energy
- packaging
- waste disposal and effluent treatment

# Supplementary - Molar Relationships 1

*This lesson looks again at the work covered in earlier courses which concentrated on Moles as Masses.*

## Solids, Liquids & Gases

*This activity looks at how the **masses** of substances can be used to calculate the **number of moles**.*

If you know the ***formula*** of a substance you can calculate its ***formula mass*** in amu (atomic mass units; mass of 1 proton = 1amu).

e.g. $CaCO_3$ = 1 x Ca = 1 x 40 = 40
1 x C = 1 x 12 = 12
3 x 0 = 3 x 16 = 48 =100 amu

By definition,

***1 mole*** = ***formula mass*** in ***grammes*** or gramme formula mass ***gfm***

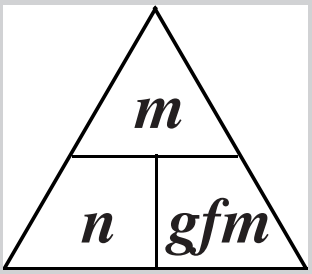
e.g. 1 mole of $CaCO_3$ = 100 g

Remember that ***1 mole*** of any substance contains the ***same amount*** of substance as ***1 mole*** of any other substance.

| 1 mole of $CaCO_3$ | = | 1 mole of $C_6H_{12}O_6$ | = | 1 mole of $(NH_4)_2SO_4$ |
|---|---|---|---|---|
| g | = | g | = | g |

***moles*** *of a substance* = ***mass*** *of substance* ÷ ***gfm***

$$n = m \div gfm$$




***mass*** *of substance* = ***moles*** *of a substance* ***x*** ***gfm***

$$m = n \times gfm$$

e.g. 25g of $CaCO_3$

$n = m \div gfm$
$= 24 \div 100$
$= 0.25$ moles

## Solutions

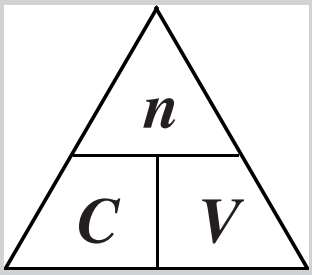
*This activity looks at how the **concentration** and **volume** of a solution can be used to calculate the **number of moles** of solute present.*

The ***concentration*** of a solution (***C***) is measured in ***moles per litre***, abbreviated to ***mol $l^{-1}$***.
The ***volume*** of a solution (***V***) is measured in cubic centimetres ($cm^3$) or in ***litres*** (*l*).

1000 $cm^3$ = 1 litre = 1000 m*l*

***moles*** *in a solution* = ***concentration*** ***x*** ***volume***

$$n = C \times V$$




***concentration*** = ***moles*** *dissolved* ÷ ***volume***

$$C = n \div V$$

e.g. 250 $cm^3$ of a 2 mol $l^{-1}$ solution of hydrochloric acid.

$n = C \times V$
$= 2 \times 0.25$ (volumes must be in litres)
$= 0.5$ moles of HCl ( = 0.5 moles of $H^+$ ions)
$= 18.25$g of HCl (*gfm* = 36.5g)

250 $cm^3$ of a 1 mol $l^{-1}$ solution of sulphuric acid acid.

$n = C \times V$
$= 1 \times 0.25$ (volumes must be in litres)
$= 0.25$ moles of $H_2SO_4$ ( = 0.5 moles of $H^+$ ions)
$= 24.5$g of $H_2SO_4$ (*gfm* = 98g)

e.g. 11g ofcarbon dioxide dissolved in 500 $cm^3$

*gfm* of $CO_2$ = 44g = 1mole
11g = 0.25 mole

$C = n \div V$
$= 0.25 \div 0.5$ (volumes must be in litres)
$= 0.5$ moles per litre
$= 0.5$ mole $l^{-1}$ or 0.5 M

## Equations

*This activity looks at how the **equation** for a reaction can be used to calculate reacting masses.*

A ***balanced chemical equation*** tells you the ***reactants*** and the ***products*** in a reaction, and the relative ***amounts*** involved.

e.g *methane* + *oxygen* → +

\+ → +

The ***number*** written in ***front*** of each ***formula*** tells you the ***number*** of each molecule involved in the **reaction**. This equation tells you that ***one*** *molecule of methane* reacts with ***two*** *molecules of oxygen* to form ***one*** *molecule of* ***carbon dioxide*** and ***two*** *molecules of* ***water***.

The ***molar relationships*** are exactly the same:

| | |
|---|---|
| $CH_4$ ; *gfm* = 16 g | |
| $O_2$ ; *gfm* = g | |
| $CO_2$ ; *gfm* = g | |
| $H_2O$ ; *gfm* = g | |

| $CH_4$ + | $O_2$ | → | $CO_2$ + | $H_2O$ |
|---|---|---|---|---|
| ***1****mole* | *moles* | | *moles* | *moles* |
| *16g* | *g* | | *g* | *g* |

*(mass must be conserved during chemical reactions)*

Most of the time we only need to concentrate on ***two*** of the substances in the reaction.

e.g. What mass of *carbon dioxide* is produced when 64g of *methane* is burned in a plentiful supply of air ?

| | $CH_4$ + | $O_2$ | → | $CO_2$ + | $H_2O$ |
|---|---|---|---|---|---|
| *Step 1* | | | | | |
| *Step 2* | ***1****mole* | | | *moles* | |
| *Step 3* | *16g* | | | *g* | |
| *Step 4* | *64g* | | | *(64 / 16 ) x* | *g* |
| | | | | = | *g* |

Step 4 involves the use of ***proportion***; which is an essential mathematical ability for anyone wishing to study Chemistry.

# 3.7 % Yields & The Atom Economy

*This lesson looks at some of the tools Industrial Chemists use to evaluate synthetic routes and their associated economic and environmental costs.*

## Percentage Yield

*This activity is about calculating the percentage yield of a product in a chemical reaction.*

During ***industrial*** *reactions*, many reactions are ***reversible*** and ***side-reactions*** producing various ***by-products*** are also possible. For both these reasons *actual mass* of ***products*** are often ***much lower*** than the expected *theoretical mass*.

Historically, Percentage Yield has been the main means of evaluating reaction efficiency.

***Balanced equations*** provide us with ***molar relationships*** between *reactants* and *products* which allow the *calculation* of the ***theoretical product mass.***

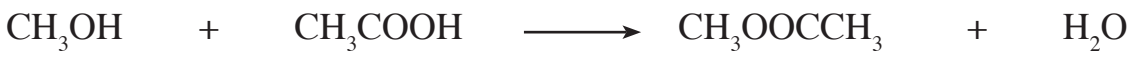
***Percentage Yields*** are calculated as follows:

$$Yield = \frac{actual\ product\ mass}{theoretical\ product\ mass} \times 100\ \%$$

For example,

When 5g of methanol reacts with excess ethanoic acid 9.6g of methyl ethanoate is produced. What is the percentage yield in this reaction?

***Tip:*** *Ignore the mass of product given (actual product mass) and concentrate on calculating the product mass that would be expected (theoretical product mass).*




1 mole 1 mole

32g 74g

5g 5 / 32 x 74 g

= 11.56g

*Theoretical product mass* = 11.56g

*Actual product mass* = 9.6g

***Percentage yield*** = 9.6 / 11.56 × 100

= 83%

## Atom Economy

*This activity is about calculating the atom economy for a particular reaction.*

The concept of '***Atom Economy***' derives from the principles of '***Green Chemistry***'and the need to ***reduce*** the production of ***hazardous waste***. At first, the ***Chemical Industry*** responded to ***Environmental Legislation*** by increasing the ***treatment*** of waste, which was very ***expensive.***

***Atom Economy*** is a measure of the ***proportion*** of ***reactant*** atoms which make it into the desired ***product*** of a chemical reaction. It can also, therefore, give an indication of the ***proportion*** of ***reactant*** atoms forming ***waste*** products.

The target is now to choose reactions that get as close as possible to an ***Atom Economy*** of 100%, representing 0% waste.

***Atom Economy*** is calculated as follows:

$$\text{Atom Economy} = \frac{\text{mass of desired product(s)}}{\text{total mass of reactants}} \times 100$$

***For example,***

*Hydrazine ($N_2H_4$) is used for rocket fuel. Calculate the atom economy for hydrazine production.*

$$2\,NH_3 + NaOCl \longrightarrow N_2H_4 + NaCl + H_2O$$

2 mole 1 mole 1 mole

34 g 74.5 g 32 g

108.5 g 32 g

*Total mass of reactants* = 108.5 g

*Actual product mass* = 32 g

***Atom Economy*** = 32 / 108.5 × 100

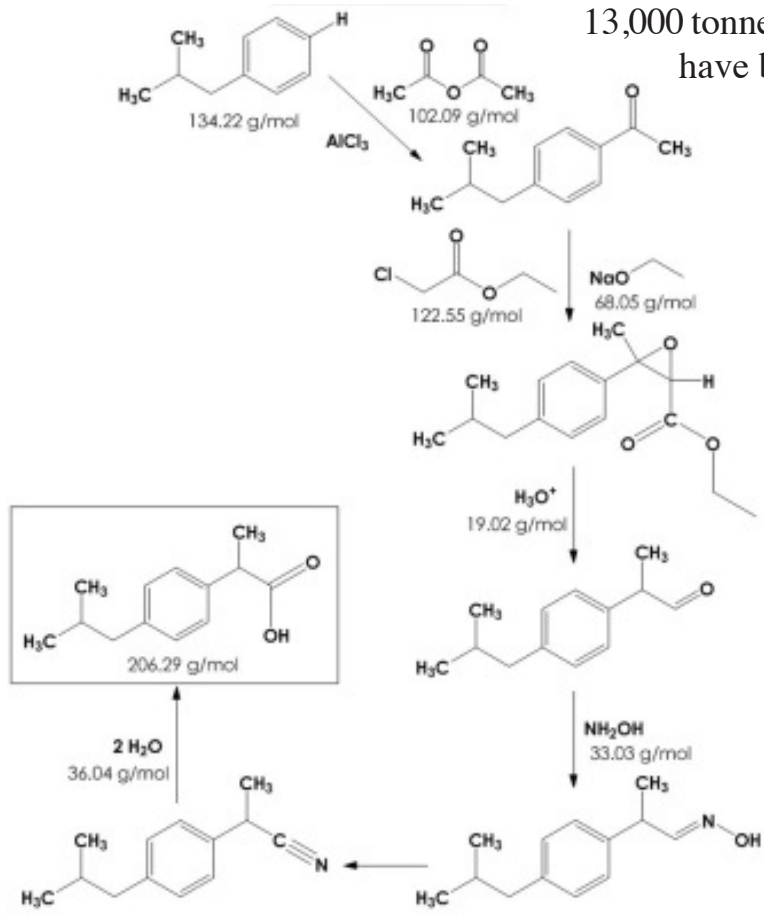
= 30 %

This reaction has a very poor Atom Economy with 70% of the reactant atoms ending up in waste products (NaCl and $H_2O$).

This may be mitigated if the waste products can be successfully utilised. However, salt water may have little commercial value but expensive disposal costs.

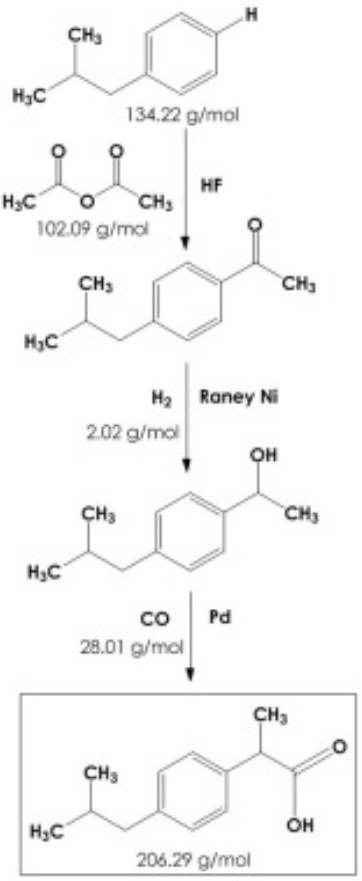
# Ibuprofen Production

*This activity looks at why Industrial Chemists redesigned the synthesis route for the production of Ibuprofen.*




13,000 tonnes per annum of the painkiller Ibuprofen have been produced since its introduction in the 1980s.

Initially, Boots used a six-step production process. They then developed a new, improved three-stage process to producing Ibuprofen with a much better atom economy.




$$\text{Atom Economy} = \frac{\text{mass of desired product(s)}}{\text{total mass of reactants}} \times 100$$

$$= \frac{206.9 \text{ g/mol}}{(134.22 + 102.09 + 122.55 + 68.05 + 19.02 + 33.03 + 36.04)} \times 100$$

$$= \frac{206.9 \text{ g/mol}}{515.00 \text{ g/mol}} \times 100$$

***% Atom Economy = 40 %***

This improvement in atom economy resulted in a reduction in the quantity of unwanted by-products, and therefore in significant environmental and economic cost savings.

$$\text{Atom Economy} = \frac{\text{mass of desired product(s)}}{\text{total mass of reactants}} \times 100$$

$$= \frac{206.9 \text{ g/mol}}{(134.22 + 102.09 + 2.02 + 28.01)} \times 100$$

$$= \frac{206.9 \text{ g/mol}}{266.34 \text{ g/mol}} \times 100$$

***% Atom Economy = 77 %***

# *UNIT 3 - Topic 3 Industrial Processes & Equilibrium*

## *Equilibrium*

1. ***Reversible reactions** attain a state of **dynamic** equilibrium when the **rates** of the forward and reverse reactions are **equal**.*

   reactants ⇔ products

2. *At equilibrium, the concentrations of reactants and products remain **constant** although **not** necessarily equal*

   position of equilibrium - relative amounts of reactants and products
   "over to the right" - more product
   "over to the left" - more reactant

3. *Changes in concentration, temperature and pressure can alter the position of equilibrium*

   Concentration reactant ↑ , helps reactant→product
   Concentration product ↑ , helps product→reactant

   Temperature ↑ , helps endothermic reaction
   Temperature ↓ , helps exothermic reaction

   Pressure ↑ , helps reaction reducing moles of ***gases***
   Pressure ↓ , helps reaction increasing moles of ***gases***

4. *A **catalyst** speeds up the attainment of equilibrium but does not affect the position of equilibrium*

   Catalyst lowers the activation energies of both reactions by the same amount - it helps both reactions equally.

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**.*

   ***Temperature*** - production of ammonia is exothermic, but moderately high temperature (400°C) used to keep speed of reactions up.

   ***Pressure*** - % of ammonia prduced increses as pressure ↑ . 200 atmospheres used, increased yield not enough to justify expense of higher pressure.

   ***Catalyst*** - $N_2 + H_2$ pass over trays of finely divided ***iron*** (large surface area)

   ***Product***- under pressure, the $NH_3$ forms as a liquid and can be drained off (reducing rate of reverse reaction)

   ***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)

6. *Molecules will partition themselves between two solvents depending on relative solubilities.*

7. *This is an example of a dynamic equilibrium.*

8. *In chromatography, one solvent is a stationary phase while the other is the mobile phase.*

9. *Polar molecules are in the stationary phase and move more slowly, while non-polar molecules occupy the mobile phase.*

$$R_f = \frac{\text{distance traveled by compound (cm)}}{\text{distance traveled by solvent (cm)}}$$

## *Chemical Industry*

10. *The UK chemical industry is a major contributor to both the quality of our life and our national economy*

11. *Stages in the manufacture of a new product can include **research**, **pilot study**, **scaling-up**, **production** and **review***

12. *A chemical manufacturing process usually involves a sequence of steps*

13. *A **feedstock** is a reactant from which other chemicals can be **extracted** or **synthesised***

14. *The major **raw materials** in the chemical industry are fossil fuels, air, metallic ores & minerals, and water*

15. *Process **conditions** are chosen to maximise economic efficiency*

16. *Manufacturing costs include **capital** costs, **fixed** costs and **variable** costs*

17. *The UK chemical industry is, by and large, capital rather than labour intensive*

18. *Safety and environmental issues are of major importance to the chemical industry*

19. *Both historical and practical factors affect the location of chemical industries*

20. *The efficient use of energy is significant in most chemical processes*

21. *Factors influencing the choice of a particular route include cost, availability and suitability of feedstock(s), yield of product(s), opportunities for the recycling of reactants and marketability of by-products*

22. *Percentage yields can be calculated from mass of reactant(s) and product(s) using balanced equations*

$$\text{Yield} = \frac{\text{actual product mass}}{\text{theoretical product mass}} \times 100 \%$$

23. *Atom economy is derived from the principles of green chemistry*

24. *Atom economy is a measure of the proportion of reactants that become useful products*

$$\text{Atom Economy} = \frac{\text{mass of desired product(s)}}{\text{total mass of reactants}} \times 100$$