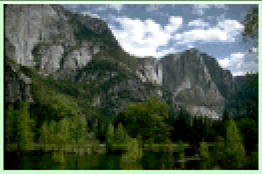
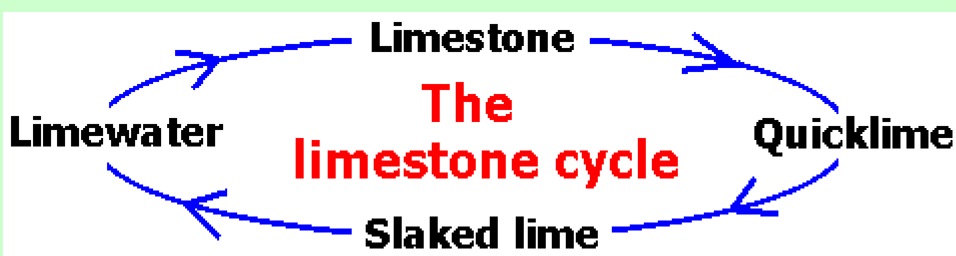
Industrial Chemistry



Limestone - a very useful material

- **Limestone**, is a **sedimentary rock** formed by the mineral and 'shelly' remains of marine organisms, including coral, in warm shallow fertile seas. It is chemically mainly calcium carbonate and is a useful material that is **quarried and used directly as a building material**. It reacts with acids - 'fizzing' due to carbon dioxide formation - test with 'limewater' - milky white precipitate.
- It is a valuable natural mineral resource and is quarried in large quantities in many countries (**see environmental impact**).
- Other uses of limestone rock are outlined below and it is an **important raw material in the manufacture of cement and glass and iron**.
- **Powdered limestone can be used to neutralise acidity in lakes and soils**
- **When limestone is heated in a kiln at over 900°C, it breaks down into quicklime** (calcium oxide) and carbon dioxide. Both are useful products. This type of reaction is **endothermic** and an example of **thermal decomposition** (and **other carbonates** behave in a similar way).
  - calcium carbonate (limestone) ==> calcium oxide (quicklime) + carbon dioxide
  - $\mathbf{CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}}$
  - This is a **reversible endothermic reaction**. To ensure the change is to favour the right hand side, a high temperature of over 900°C is needed as well as the continual removal of the carbon dioxide.
- **Note on other carbonates** These also show a similar **thermal decomposition** to $CaCO_3$ above ...
  - copper(II) carbonate$_{\mathbf{(green)}}$ ==> copper(II) oxide$_{\mathbf{(black)}}$ + carbon dioxide
  - $\mathbf{CuCO_{3(s)} ==> CuO_{(s)} + CO_{2(g)}}$
  - zinc carbonate$_{\mathbf{(white)}}$ ==> zinc oxide$_{\mathbf{(yellow\ hot,\ white\ cold)}}$ + carbon dioxide
  - $\mathbf{ZnCO_{3(s)} ==> ZnO_{(s)} + CO_{2(g)}}$
  - **$FeCO_3$ and $MnCO_3$ behave in a similar way**
- **Quicklime reacts very exothermically with water to produce slaked lime** (calcium hydroxide).
  - calcium oxide (quicklime) + water ==> calcium hydroxide (slaked lime)
    - this is a very exothermic reaction, the quicklime 'puffs' up and steam is produced!
    - $\mathbf{CaO_{(s)} + H_2O_{(l)} ==> Ca(OH)_{2(s)}}$

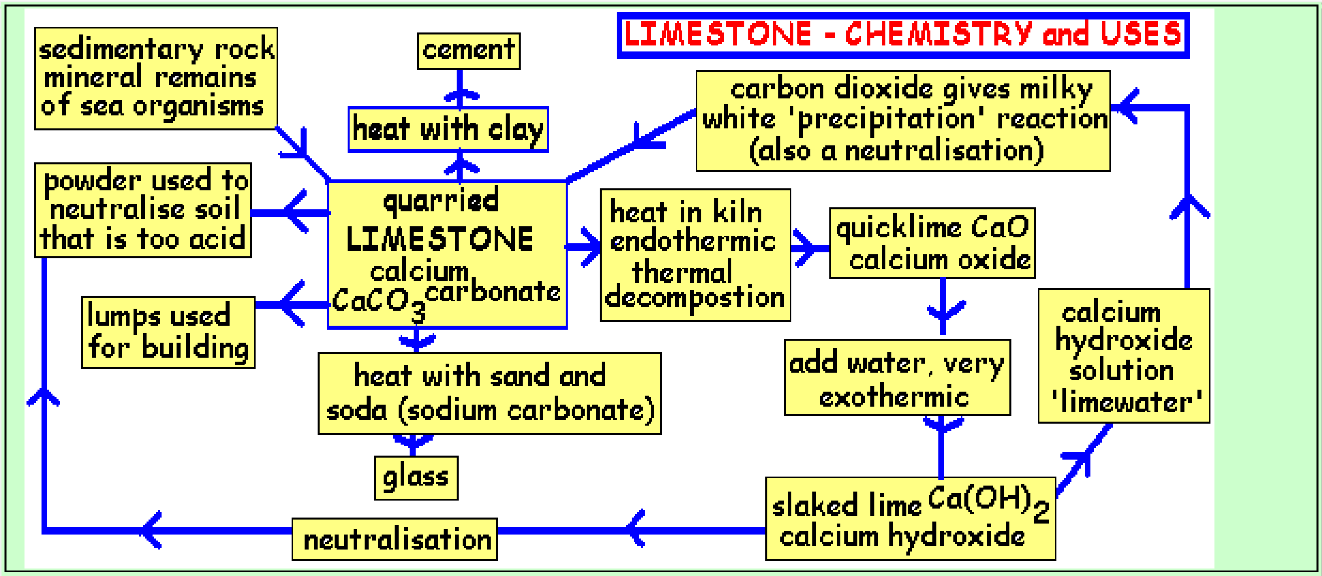


- **Lime (calcium oxide) and slaked lime (calcium hydroxide) are both used to reduce the acidity of soil** on land, they are both faster and stronger acting than limestone powder. They are also **used to reduce acidity in lakes and rivers due to acid rain**. They are also used to neutralise potentially **harmful industrial acid waste** including sulphur dioxide in the flue gases of power stations.
- In the **test for carbon dioxide**, calcium hydroxide solution (**limewater**) forms a white milky **precipitate** of calcium carbonate (back to where you started!).
  - calcium hydroxide + carbon dioxide ==> calcium carbonate + water
  - $\mathbf{Ca(OH)_{2(aq)} + CO_{2(g)} ==> CaCO_{3(s)} + H_2O_{(l)}}$

- **The oxides and hydroxides readily react with acids.**
  - general word equation**: oxide or hydroxide + acid ==> salt + water**
    - **examples ...**
    - calcium oxide + hydrochloric acid ==> calcium chloride + water
    - calcium hydroxide + nitric acid ==> magnesium nitrate + water
    - calcium hydroxide + sulphuric acid ==> calcium sulphate + water
    - $CaO_{(s)} + 2HCl_{(aq)} ==> CaCl_{2(aq)} + H_2O_{(l)}$
    - $Ca(OH)_{2(s)} + 2HNO_{3(aq)} ==> Ca(NO_3)_{2(aq)} + H_2O_{(l)}$
    - $Ca(OH)_{2(s)} + H_2SO_{4(aq)} ==> CaSO_{4(aq,s*)} +2 H_2O_{(l)}$
    - ***** the sulphates of eg calcium and barium are not very soluble, this slows the reaction down!

- **Solubility of calcium compounds** (and the chemically similar magnesium)**:**
  - **Magnesium and calcium oxides or hydroxides are slightly soluble in water forming alkaline solutions**. They readily react and dissolve in most acids
  - **Magnesium and calcium carbonate are insoluble in water** but readily **dissolve in most dilute acids** like hydrochloric, nitric and sulphuric. Calcium carbonate reacts slowly in dilute sulphuric acid because calcium sulphate is not very soluble and coats the limestone
  - Equation examples for calcium carbonate (similar for magnesium carbonate) **...**
  - calcium carbonate + hydrochloric acid ==> calcium chloride + water + carbon dioxide
    - $CaCO_{3(s)} + 2HCl_{(aq)} ==> CaCl_{2(aq)} + H_2O_{(l)} + CO_{2(g)}$
  - calcium carbonate + nitric acid ==> calcium nitrate + water + carbon dioxide
    - $CaCO_{3(s)} + 2HNO_{3(aq)} ==> Ca(NO_3)_{2(aq)} + H_2O_{(l)} + CO_{2(g)}$
  - calcium carbonate + sulphuric acid ==> calcium sulphate + water + carbon dioxide
    - $CaCO_{3(s)} + H_2SO_{4(aq)} ==> CaSO_{4(aq,s)} + H_2O_{(l)} + CO_{2(g)}$
- **Magnesium and calcium hydrogencarbonate are soluble in water** and cause 'hardness' ie scum with 'traditional' non-detergent soaps. **Formulae are $Mg(HCO_3)_2$ and $Ca(HCO_3)_2$**
- **Cement** is produced by **roasting a mixture of powdered limestone with powdered clay* in a rotary kiln.** When cement is mixed with water, sand and crushed rock, a slow chemical reaction produces a hard, stone-like building material called concrete.
  - *** Clay is used directly to make pottery and other ceramics**
- **Glass** is made by heating a **mixture of limestone** ($CaCO_3$), **sand** (mainly silica = silicon dioxide = SiO_2) and **'soda'** (sodium carbonate, Na_2CO_3).
- **Limestone** is used to remove acidic oxide impurities in the extraction of iron and in making steel.

Calcium oxide and calcium hydroxide also react with acids to form salt.



Why is sulphuric acid a useful material? How is it made? – Contact Process

Because sulphuric acid has so many uses the industrial development of a country is sometimes measured by the amount of sulphuric acid that is used each year. Sulphuric acid is made starting from the element sulphur which is found in the Earth's crust.

- **Sulphuric acid is used as car battery acid and is used to make fertilisers, dyes and detergents.**
  - eg ammonia + sulphuric acid ==> ammonium sulphate (a fertiliser salt)
  - $\mathbf{2NH_{3(aq)} + H_2SO_{4(aq)} ==> (NH_4)_2SO_{4(aq)}}$ => evaporation to get crystals
  - Its acid action make it good for **cleaning metal surfaces** in industry.
- Sulphuric acid is manufactured from the **raw materials sulphur, air and water**.
- **(1)** Sulphur is burned in air to form sulphur dioxide (exothermic).
  - In the reaction the sulphur is oxidised (O gain) $\mathbf{S_{(s)} + O_{2(g)} ==> SO_{2(g)}}$
- Note: **Sulphur dioxide itself is a useful chemical in its own right:**
  - **It** is **used as a bleach** in the manufacture of wood pulp for paper manufacture
  - and its toxic nature makes it useful as a **food preservative** by killing bacteria.
- **(2)** In the reactor the sulphur dioxide is mixed with air and the mixture passed over a catalyst of vanadium oxide V_2O_5 at a high temperature (about 450°C) and at a pressure of between one and two atmospheres. It is a 2nd exothermic oxidation and is known as the **Contact Process**.
- In the reactor the **sulphur dioxide is oxidised** in the reversible exothermic reaction ...
  - $\mathbf{2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}}$
- The reaction forms sulphur trioxide and the equilibrium is very much to the right hand side ...
  - despite the reaction being exothermic and a high temperature used (favours reverse reaction R to L, energy change equilibrium rule)
  - the reaction is favoured by high pressure (pressure equilibrium rule, 3 => 2 gas molecules), but only a small increase in pressure is used to give high yields of sulphur trioxide, because the right hand side is energetically very favourable (quite exothermic)
  - the use of a catalyst ensures a fast reaction without having to use too a higher temperature which would favour the left hand side (energy change equilibrium

rule)

- **(3)** The sulphur trioxide is dissolved in concentrated sulphuric acid to form fuming sulphuric acid (oleum).
    - $SO_{3(g)} + H_2SO_{4(l)} ==> H_2S_2O_{7(l)}$
- **(4)** Water is then carefully added to the oleum to produce concentrated sulphuric acid (98%).
    - $H_2S_2O_{7(l)} + H_2O_{(l)} ==> 2H_2SO_{4(l)}$
    - If the sulphur trioxide is added directly to water an acid mist forms which is difficult to contain because the reaction to form sulphuric acid solution is very exothermic!
- Good **anti-pollution measures** need to be in place since the sulphur oxides are harmful and would cause local acid rain! To help this situation AND help the economics of the process, any unreacted sulphur dioxide is recycled through the reactor.
- **Concentrated sulphuric acid** can be used in the laboratory as a dehydrating agent. Dehydration is the removal of water or the elements of water from a compound.
    - When added to some organic compounds containing hydrogen and oxygen, e.g. sugar, concentrated sulphuric acid removes the elements of water from the compound leaving carbon.
    - When added to copper sulphate crystals concentrated sulphuric acid removes the water of crystallisation leaving anhydrous copper sulphate

What is titanium and how is it produced?

Titanium is a very important metal for various specialised uses. It is more difficult to extract from its ore than other, more common metals.

- Titanium is a transition metal and is strong and resistant to corrosion.
    - Titanium alloys are amongst the strongest of metal alloys.
- It is used in aeroplanes, in nuclear reactor alloys and for replacement hip joints.
- Titanium is extracted from the raw material is the ore rutile which contains titanium dioxide.
- The **rutile** titanium oxide **ore** is heated with carbon and chlorine to make titanium chloride
    - $TiO_2 + 2Cl_2 + C ==> TiCl_4 + CO_2$
- After the oxide is converted into titanium chloride $TiCl_4$ it is then reacted with sodium or magnesium to form titanium metal and sodium chloride or magnesium Chloride.
    - This reaction is **carried out in an atmosphere of inert argon gas** so non of the metals involved becomes oxidised by atmospheric oxygen.
    - $TiCl_4 + 2Mg ==> Ti + 2MgCl_2$ or $TiCl_4 + 4Na ==> Ti + 4NaCl$
    - These are examples of **metal displacement reactions** eg the less reactive titanium is displaced by the more reactive sodium or magnesium.
    - Overall the **titanium oxide ore is reduced** to titanium metal (overall O loss, oxide => metal)

The Synthesis of ammonia - The Haber Process

- **Ammonia gas is synthesised** in the chemical industry by **reacting nitrogen gas with hydrogen gas**.
- The **nitrogen is obtained from air** (80% N_2).
- The **hydrogen is made by reacting methane (natural gas) and water** or from cracking hydrocarbons (both reactions are done at high temperature with a catalyst).
  - **$CH_4 + H_2O$ ==> $3H_2 + CO$**
  - eg C_8H_{18} ==> $C_8H_{16} + H_2$
- The synthesis equation for this **reversible reaction** is ...

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

- .. which means a **dynamic equilibrium** will form, so no chance of 100% yield!
- In forming ammonia 92kJ of heat energy is given out (ie **exothermic**, 46kJ of heat released per mole of ammonia formed).
- Four moles of 'reactant' gas form two moles of 'product' gas, so there is net decrease in gas molecules on forming ammonia.
- So applying the equilibrium rules from section 2 the **formation of ammonia** is favoured by
  - using **high pressure** because you are going from 4 to 2 gas molecules (the high pressure also speeds up the reaction because it effectively increases the concentration of the gas molecules).
  - and **low temperature** because is an exothermic reaction,
  - to try to get the **optimum conditions to get the biggest yield of ammonia**,
  - these arguments make the point that **the yield* of an equilibrium reaction depends on the conditions used**.
    - ** * The word 'yield' means how much product you get compared to the theoretical maximum possible if the reaction goes 100%.**
- In industry pressures of **200 - 300 times normal atmospheric pressure are used** in line with the theory.
- Theoretically **a low temperature would give a high yield of ammonia BUT** ...
  - **Nitrogen** is very **stable molecule** and not very reactive ie **chemically inert**.
  - **To speed up the reaction** an **iron catalyst** is used as well as a **higher temperature** (eg 400-450^{o}C).
  - The higher temperature is an economic compromise, ie it is more economic to get a low yield fast, than a high yield slowly!
  - **Note: a catalyst does NOT affect the yield of a reaction**, ie the equilibrium position BUT you do get there faster!
- On **cooling the reacted mixture the ammonia liquefies** and is removed and stored in cylinders.
- Any **unreacted nitrogen or hydrogen is recycled** back through the reactor chamber, nothing is wasted!

The Uses of Ammonia

(a) Ammonia is used to manufacture nitric acid.

- **Ammonia** is oxidised with oxygen from air using a **hot platinum catalyst** to form **nitrogen monoxide** and water.
- $4NH_{3(g)} + 5O_{2(g)} \longrightarrow 4NO_{(g)} + 6H_2O_{(g)}$

- The gas is cooled and reacted with more oxygen to form **nitrogen dioxide**.
- **$2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)}$**
- This is reacted with more oxygen and water to form **nitric acid**.
- **$4NO_{2(g)} + O_{2(g)} + 2H_2O_{(l)} \longrightarrow 4HNO_{3(aq)}$**
- **Nitric acid is used in dye making processes and artificial nitrogenous fertilisers** (see below).

(b) Ammonia is used to manufacture 'artificial' nitrogenous fertilisers.

- **Ammonia is a pungent smelling alkaline gas** that is **very soluble in water.**
- **The gas or solution turns litmus or universal indicator blue** because it is a soluble weak base or weak alkali (more on theory on the **Acids, Bases Salts** page or on the **Extra Aqueous Chemistry** page).
- The fertiliser salts are made by **neutralising** ammonia solution with the appropriate acid (more method details on **Acids, Bases and Salts**, but the equations are given below).
- The resulting solution is heated, **evaporating the water to crystallise** the salt eg

ammonia + sulphuric acid $\longrightarrow$ ammonium sulphate

$$2NH_{3(aq)} + H_2SO_{4(aq)} \longrightarrow (NH_4)_2SO_{4(aq)}$$

AND

ammonia + nitric acid $\longrightarrow$ ammonium nitrate

$$NH_{3(aq)} + HNO_{3(aq)} \longrightarrow NH_4NO_{3(aq)}$$

- These equations are sometimes written in terms of the ficticious 'ammonium hydroxide' which is, as shown above, quite simply an aqueous solution of ammonia, but this is how it looks in some textbooks! About 1% of the dissolved ammonia forms ammonium and hydroxide
  - ammonium hydroxide + sulphuric acid $\longrightarrow$ ammonium sulphate + water
  - $2NH_4OH_{(aq)} + H_2SO_{4(aq)} \longrightarrow (NH_4)_2SO_{4(aq)} + 2H_2O_{(l)}$
  - ammonium hydroxide + nitric acid $\longrightarrow$ ammonium nitrate + water
  - $NH_4OH_{(aq)} + HNO_{3(aq)} \longrightarrow NH_4NO_{3(aq)} + H_2O_{(l)}$
- **If ammonium salts are mixed with sodium hydroxide solution, free ammonia is formed** (detected by smell and damp red litmus turning blue)**.**
  - eg ammonium chloride + sodium hydroxide ==> sodium chloride + water + ammonia
  - $NH_4Cl + NaOH \Rightarrow NaCl + H_2O + NH_3$
- **Artificial fertilisers are important to agriculture and used on fields to increase crop yields but they should be applied in a balanced manner** (see below).
  - **Fertilisers** usually contain compounds of **three essential elements** for healthy and productive plant growth **to increase crop yield**. They replace nutrient minerals used by a previous crop or enriches poor soil and more nitrogen gets converted into plant protein.
    - **nitrogen** eg from ammonium or nitrate salts like ammonium sulphate, ammonium sulphate or ammonium phosphate or urea
    - **phosphorus** eg from potassium phosphate or ammonium phosphate
    - **potassium** eg from potassium phosphate, potassium sulphate.
  - **Fertilisers must be soluble in water to be taken in by plant roots.**

Problems with using 'artificial' fertilisers

- **Overuse** of ammonia fertilisers on fields can **cause major environmental problems** as well as being **uneconomic**.
- **Ammonium salts are water soluble** and get washed into the groundwater, rivers and streams by rain contaminating them with ammonium ions and nitrate ions.
- **This contamination causes several problems**.
- **Excess fertilisers in streams and rivers cause eutrophication**.
  - Overuse of fertilisers results in appreciable amounts of them dissolving in rain water.
  - This **increases levels of nitrate or phosphate** in rivers and lakes.
  - This causes '**algal bloom**' ie too much rapid growth of water plants on the surface where the sunlight is the strongest.
  - This **prevents light** from reaching plants lower in the water.
  - These **lower plants decay** and the active aerobic bacteria **use up any dissolved oxygen**.
  - This means any microorganisms or higher **life forms relying on oxygen cannot respire**.
  - All the **eco-cycles are affected** and fish and other respiring aquatic animals die.
  - The **river or stream becomes 'dead' below the surface** as all the food webs are disrupted.
- **Nitrates are potentially carcinogenic** (cancer or tumor forming).
  - The presence in drinking water is a health hazard.
  - Rivers and lakes can be used as initial sources for domestic water supply.
  - You cannot easily remove the nitrate from the water, it costs too much!
  - So levels of nitrate are carefully monitored in our water supply.

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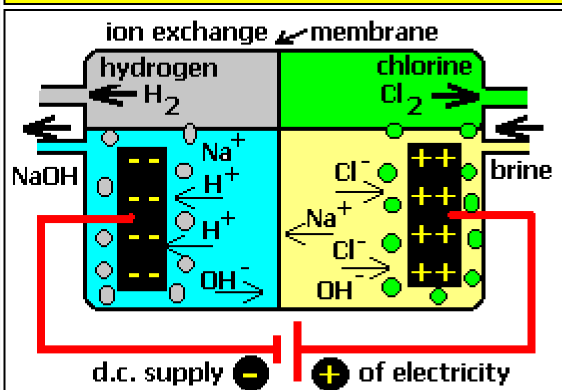
The Industrial Electrolysis of Sodium Chloride Solution or brine - made from concentrated 'rock salt' solution



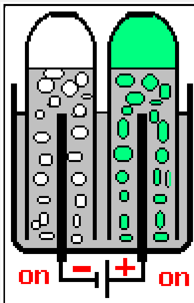
Summary equation: $\mathbf{2NaCl_{(aq)} + 2H_2O_{(l)} \Longrightarrow 2NaOH_{(aq)} + H_{2(g)} + Cl_{2(g)}}$

Summary of the ions involved and what happens to them at the two electrodes

negative electrode product	ions from water	ions from salt	positive electrode product
$H_{2(g)}$ <=	<= $H^+_{(aq)}$	$Cl^-_{(aq)}$ =>	=> $Cl_{2(g)}$
ion left =>	OH^-	Na^+	<= ion left

When electricity is passed through the sodium chloride solution (brine) there are **three products**, **(1) hydrogen** is formed at the **negative electrode** (-ve cathode), **(2) chlorine at the positive electrode** (+ve anode) and **(3) sodium hydroxide** is left in solution.

summary equation: **sodium chloride + water ==>sodium hydroxide + hydrogen + chlorine**



The industrial electrodes must be made of an inert material like titanium which is not attacked by chlorine or alkali. However a simple cell using carbon electrodes can be used to demonstrate the industrial process in the laboratory. The **cathode gas gives a squeaky pop with a lit splint - hydrogen**. The **anode gas turns damp blue litmus red and then bleaches it white - chlorine**.

The electrode equation theory and details

- The **(-) cathode** attracts the Na^+ and $\mathbf{H^+}$ ions. The hydrogen ions are reduced by electron ($\mathbf{e^-}$) gain to form hydrogen molecules:
- $\mathbf{2H^+_{(aq)} + 2e^- ==> H_{2(g)}}$
- The **(+) anode** attracts the OH^- and $\mathbf{Cl^-}$ ions. The chloride ions are oxidised by electron loss to give chlorine molecules:
- $\mathbf{2Cl^-_{(aq)} ==> Cl_{2(g)} + 2e^-}$

SODIUM HYDROXIDE NaOH	**Sodium hydroxide** is used in the manufacture of soaps, detergents, paper, ceramics and to make soluble salts of organic acids with low solubility in water (eg soluble Aspirin). It isn't a halogen compound, but it is made from the electrolysis of salt solution.

Chemical Economics

- The greater the amount of starting materials (reactants) the greater amount of new substances (products) formed.
- However in the real world **chemical processes are not 100% perfectly efficient!**
  - The amount that you actually make is called the **yield**.
  - The **percentage % yield = actual yield x 100 / predicted yield**
  - The predicted yield assumes there is no loss of product, ie no waste, and the reaction goes 100% in the desired direction.
  - If no product is obtained then the yield is 0%!
  - In reality, yields can typically range from 5% to 95% for a variety of chemical processes.

- **Why aren't processes 100% efficient?** Typical reasons are:
  - **Loss in filtration** of a solid product, ie some may get through as very fine particles or more likely dissolved in the liquid residue.
  - **Loss in evaporation** if the product is a volatile liquid.
  - **Loss in transferring liquids**, ie traces left on the sides of containers.
  - **The reaction may be an equilibrium**, so its impossible to get 100% yield anyway and this means that **the yield of an equilibrium reaction depends on the conditions used.**
- The **costs of making new substances depends on**:
  - **Price of energy** (eg gas, electricity).
  - **Starting materials** (reactants).
  - **Labour** (wages).
  - **Equipment** (chemical plant eg machines, reactors, heat transfer systems).
  - **Speed of manufacture** (time efficiency).
- These **cost factors can be analysed in more detail** eg
  - **The higher the operating pressure of the reactor, the higher the cost**. The engineering is more costly due to eg thicker steel reaction vessel, higher health and safety standards require.
  - **The higher the temperature the higher the energy cost.** Fortunately this cost is reduced if the reaction is exothermic and the reaction does go faster at higher temperature.

- **Time is money! so catalysts save time and money** by speeding up the reaction.
- **The rate of reaction must be high enough to give a reasonable yield in reasonable time** eg at least within 24 hours for a continuously working plant.
- **Often with equilibrium reactions, it is possible to recycle unreacted starting materials back through the reactor**. The % yield must be high enough at least per day, but an initial low yield is quite acceptable if the unreacted starting materials can be recycled many times on a continuous basis through the reactor.
- **Optimum reaction conditions are geared to the lowest cost situation**. This often means 'balancing' the rate of reaction versus the highest % yield. It is often best to get a low yield fast and recycle!
- **Automating the chemical plants** with sensors, controls, computer software etc. significantly reduces the wages bill.

DONE