# Section 12 Industrial Chemistry

## 12.1 HESS'S LAW.

At the end of 12.1 you should be able to

1. Carry out an experiment to confirm Hess's Law

Hess's law states that the enthalpy change in a reaction is independent of the path followed and depends only on the initial and final states in the system.

Consider the following example: -

An aqueous solution of potassium chloride can be prepared from potassium hydroxide by two different methods.

Method 1.

Solid potassium hydroxide is dissolved in water to form an aqueous solution of potassium hydroxide. The enthalpy change for this reaction can be determined.

$KOH_{(s)} + H_2O_{(l)} \Rightarrow KOH_{(aq)} \quad \Delta H_1$

The aqueous solution of potassium hydroxide is then reacted with hydrochloric acid solution to form a solution of potassium chloride. The enthalpy change for this reaction can also be determined.

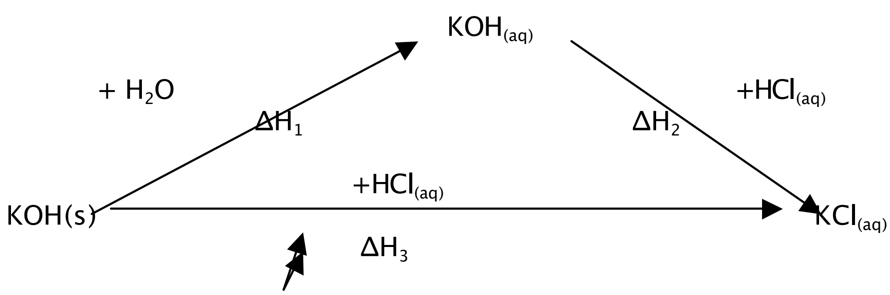
$KOH_{(aq)} + HCl_{(aq)} \Rightarrow NaCl_{(aq)} \quad \Delta H_2$

Method 2.

Solid potassium hydroxide is reacted with hydrochloric acid solution to prepare potassium chloride solution in a single step.

$KOH_{(s)} + HCl_{(aq)} \Rightarrow KCl_{(aq)} \quad \Delta H_3$

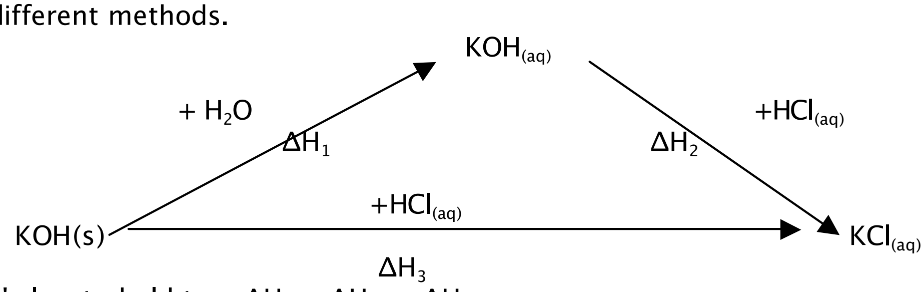
These two methods of preparing potassium chloride solution starting from solid potassium hydroxide can be shown in the following diagram.




Using Hess's law we can easily see that $\Delta H_3 = \Delta H_1 + \Delta H_2$

Verification of Hess's Law

We can experimentally confirm Hess's law, which states that the overall enthalpy change for a reaction is independent of the pathway taken, by determining the heat of formation of potassium chloride solution by two different methods.




For Hess's law to hold true $\Delta H_3 = \Delta H_1 + \Delta H_2$

METHOD 1:-

1. Place $50cm^3$ of 1M hydrochloric acid solution in a plastic beaker
2. Measure the temperature of the hydrochloric acid solution.
3. Weigh out 2.5g of potassium hydroxide pellets.
4. Add the 2.5g of potassium hydroxide to the hydrochloric acid and stir using the thermometer until the pellets have dissolved. Measure the highest temperature

reached and so calculate the temperature rise ($\Delta T_3$)

5. Calculate the amount of heat liberated using ($\Delta H_3 = -c\ m\ \Delta T_3$)

where c = specific heat capacity of the solution = 4.18 kJ $kg^{-1}$ $^oC^{-1}$.
m = mass of solution in kilograms = 0.05kg
$\Delta T_3$ = temperature rise in $^oC$.

$\Delta H_3$ = x x = kJ

METHOD 2:-

In this experiment the same potassium chloride solution will be made but two steps taken $\Delta H_1 + \Delta H_2$
By adding together the enthalpy changes for the two separate steps we should find that they equal the enthalpy change for the single step process.

$\Delta H_1$

1. Place 50$cm^3$ of water in a plastic beaker
2. Measure the temperature of the water.
3. Weigh out 2.5g of potassium hydroxide pellets.
4. Add the 2.5g of potassium hydroxide to the water and stir using the thermometer until the pellets have dissolved. Measure the highest temperature reached and so calculate the temperature rise ($\Delta$T1). [Keep this solution]
5. Calculate the amount of heat liberated using ($\Delta H_1 = -c\ m\ \Delta T_1$)

where c = specific heat capacity of the solution = 4.18 kJ $kg^{-1}$ $^oC^{-1}$.
m = mass of solution in kilograms = 0.05kg
$\Delta T_1$ = temperature rise in $^oC$.

$\Delta H_1$ = x x = kJ

$\Delta H_2$

1. Place 50$cm^3$ of 1 M hydrochloric acid in a plastic beaker
2. Measure the temperature of the hydrochloric acid solution
3. Measure the temperature of the potassium hydroxide solution from part A.
4. Calculate the average temperature of the two solutions and use the average temperature as the initial temperature for the reaction.
5. Add the hydrochloric acid and the potassium hydroxide solutions together in one plastic beaker. Stir quickly to mix the solutions and measure the highest temperature reached. Calculate the temperature increase $\Delta H_2$
6. Calculate the amount of heat liberated using ($\Delta H_2 = -c\ m\ \Delta T_2$)

where c = specific heat capacity of the solution = 4.18 kJ $kg^{-1}$ $^oC^{-1}$.
m = mass of solution in kilograms = 0.10kg (total mass of two solutions)
$\Delta T_2$ = temperature rise in $^oC$.

$\Delta H_2$ = x x = kJ

Add the enthalpy changes for both steps together and compare then with the enthalpy change for the single step reaction.

$\Delta H_1 + \Delta H_2$ = kJ

$\Delta H_3$ = kJ

## 12.2 Applying Hess's Law

At the end of 12.2 you should be able to

1. Calculate energy changes for different reactions by applying Hess's Law

The value of Hess's law is that it can be used to calculate the enthalpy change for a reaction that is otherwise difficult (or impossible) to carry out in the laboratory.

e.g. $C_{(s)} + 1/2\ O_{2(g)} \Rightarrow CO_{(g)}$

It is, however, an easy matter to determine the enthalpy changes for the combustion of carbon ($\Delta H_a$ below) and carbon monoxide ($\Delta H_b$ below)

(a) $C_{(s)} + O_{2(g)} \Rightarrow CO_{2(g)}$ $\Delta H_a = -394$ kJ

(b) $CO_{(g)}$ + 1/2 $O_{2(g)}$ => $CO_{2(g)}$ $\Delta H_b$ = -284 kJ

These two equations, (a) and (b), can be rearranged in such a way that, when they are added together they will form the equation for the formation of carbon monoxide.

This equation is: - $C_{(s)}$ + 1/2 $O_{2(g)}$ => $CO_{(g)}$

By considering the two equations whose enthalpies are known we can see that equation (a) has 1 mole of C(s) on the left hand side of the equation and that the equation we are trying to form also has 1 mole of carbon on the left hand side of the equation. We, therefore, leave equation (a) unaltered as: -

(a) $C_{(s)}$ + $O_{2(g)}$ => $CO_{2(g)}$ $\Delta H_1$ = -394 kJ

The equation we are trying to form has 1 mole of $CO_{(g)}$ on the right hand side of the equation. Looking at equation (b) we can see that it too has 1 mole of $CO_{(g)}$ but on the left hand side. By reversing equation (b) we can obtain a new equation (c) which has 1 mole of $CO_{(g)}$ on the right hand side.

(c) $CO_{2(g)}$ => $CO_{(g)}$ + 1/2 $O_{2(g)}$ $\Delta H_c$ = + 284 kJ

Note: - when equation (2) is reversed the sign of the enthalpy change is reversed as well.

Adding equations a + c gives

$C_{(s)}$ + 1/2 $O_{2(g)}$ => $CO_{(g)}$ $\Delta H$ = -394 kJ + 284 kJ

= -110 kJ

HEAT OF FORMATION.

Hess's law can also be used to determine other enthalpy changes, such as the heat of formation of a compound.
The heat of formation of a compound is defined as the amount of heat energy taken in or given out when 1 mole of a substance is formed from its elements in their normal state.

e.g. methane C + $2H_2$ => $CH_4$

The heat of combustion of carbon, hydrogen and methane are

(a) C + $O_2$ => $CO_2$ $\Delta H_a$ = -394 kJ

(b) $H_2$ + 1/2 $O_2$ => $H_2O$ $\Delta H_b$ = -286 kJ

(c) $CH_4$ + $2O_2$ => $CO_2$ + 2 $H_2O$ $\Delta H_c$ = -891 kJ

2b $2H_2$ + ***$O_2$*** => ***2 $H_2O$*** $\Delta H$ = -572 kJ

reverse c ***$CO_2$*** + ***2 $H_2O$*** => $CH_4$ + ***$2O_2$*** $\Delta H$ = 891 kJ } add a $C + O_2 \Rightarrow CO_2$ $\Delta H = -394$ kJ

$C + 2H_2 \Rightarrow CH_4$ $\Delta H = -75$ kJ

e.g. 2 ethane $2C + 3H_2 \Rightarrow C_2H_6$

The heat of combustion of carbon, hydrogen and methane are

(a) $C + O_2 \Rightarrow CO_2$ $\Delta H_a = -394$ kJ

(b) $H_2 + 1/2\ O_2 \Rightarrow H_2O$ $\Delta H_b = -286$ kJ

(c) $C_2H_6 + 7/2O_2 \Rightarrow CO_2 + 3H_2O$ $\Delta H_c = -1560$ kJ

3b $3H_2 + 3/2\ O_2 \Rightarrow 3H_2O$ $\Delta H = -858$ kJ

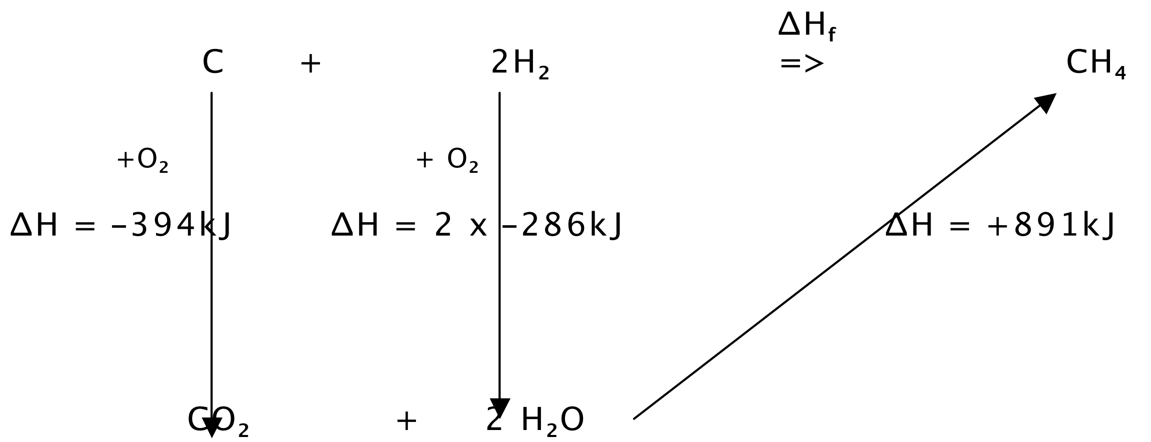
reverse c $2CO_2 + 3H_2O \Rightarrow C_2H_6 + 7/2\ O_2$ $\Delta H = 1560$ kJ

2a $2C + 2O_2 \Rightarrow 2CO_2$ $\Delta H = -788$ kJ

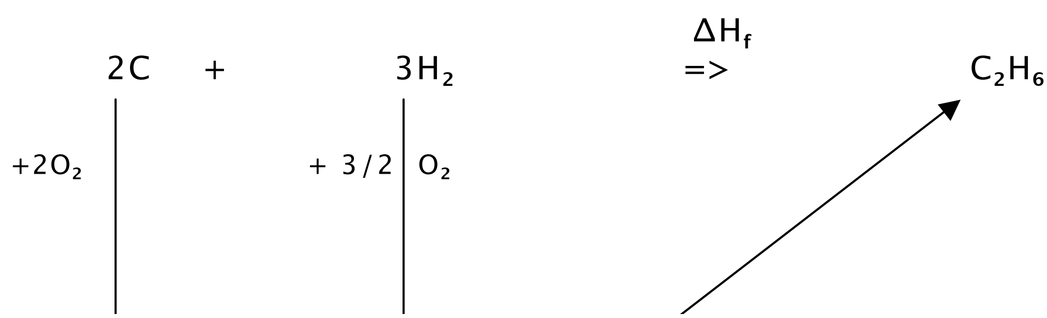
(add)

$2C + 3H_2 \Rightarrow C_2H_6$ $\Delta H = -86$ kJ

Another way of doing these is




$\Delta H_f = -394 - 572 + 891 = -75$ kJ



$\Delta H = 2 \times -394 kJ$ $\Delta H = 3 \times -286 kJ$ $\Delta H = +1560 kJ$

$2CO_2$ + $3\ H_2O$

$\Delta H_f = -788 - 858 + 1560 = -86\ kJ$

EXAMPLES FOR PRACTICE

Answer the following questions in your jotter.

1. a) Define the heat of formation of propane.
   b) Write a balanced equation for the heat of formation of propane.
   c) Given the following information, calculate the heat of formation of propane.

   Heat of combustion of propane = –2220 kJ $mol^{-1}$
   Heat of combustion of carbon = –394 kJ $mol^{-1}$
   Heat of combustion of hydrogen = – 286 kJ $mol^{-1}$ (–106 kJ)

2. The heat of combustion of pentane is –3510 kJ.
   The heat of combustion of carbon is –394 kJ
   The heat of combustion of hydrogen = – 286 kJ mol–1
   Calculate the heat of Formation of pentane. (–176 kJ)

3. Ethyne ($C_2H_2$) is used as a fuel in oxyacetylene burners.
   Use the heats of combustion of ethyne, carbon, and hydrogen in the data book to calculate the heat of formation of ethyne. (+226 kJ)

4. Use the heats of combustion of carbon, hydrogen and ethanol in the data book to calculate the heat of formation of ethanol.

   $C\ + 3\ H_2\ + 1/2\ O_2 \Rightarrow C_2H_5OH$ (–279 kJ)

5. Calculate the enthalpy of formation of carbon disulphide ($CS_2$) given:–

(1) $C + O_2 \Rightarrow CO_2$  $\Delta H_1 = -394$ kJ
(2) $S + O_2 \Rightarrow SO_2$  $\Delta H_2 = -294$ kJ
(3) $CS_2 + 3\,O_2 \Rightarrow CO_2 + 2\,SO_2$  $\Delta H_3 = -1072$ kJ (+90 kJ)

6. Calculate the heat of formation of benzene using the heats of combustion of carbon, hydrogen and benzene given in the data book. (+46 kJ)

## 12.2 Fertiliser Industry

At the end of this unit you should be able to

1. Describe the effects pressure, temperature and the use of a catalyst in relation to the Haber Process.
2. Describe how recycling gases and the removal of product help to make the Haber Process economically viable.

The most important chemical in the fertiliser industry is ammonia.

### Feedstocks and raw materials

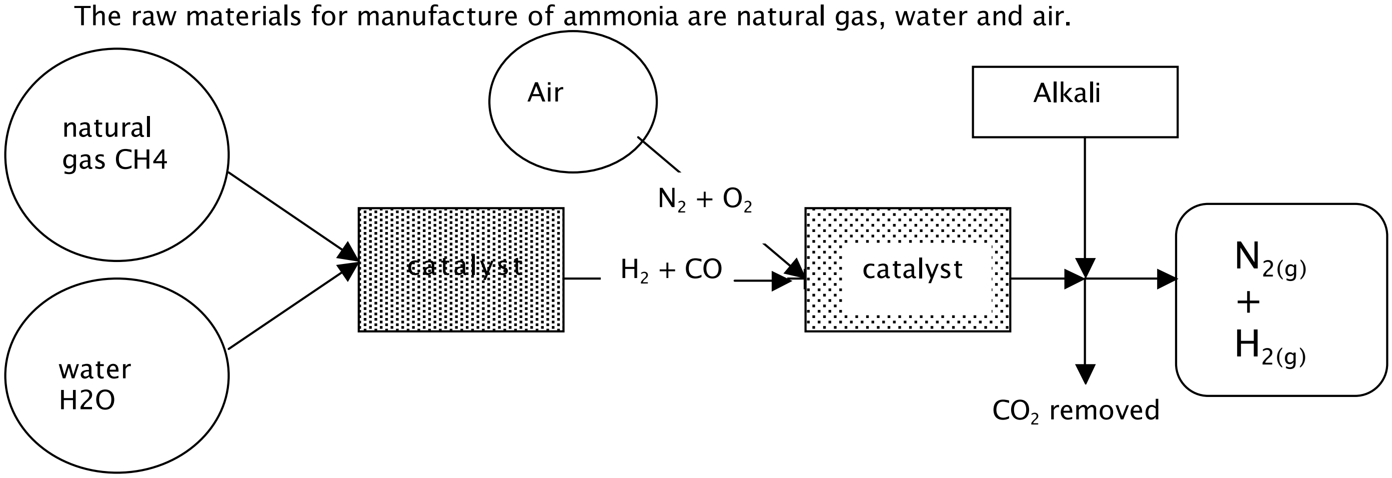
A feedstock is a substance from which another substance can be made by extraction or by chemical change.
A raw material is a substance, which is available naturally in the Earth's crust (ground, sea atmosphere)

Ammonia is manufactured from nitrogen and hydrogen using the Haber Process.

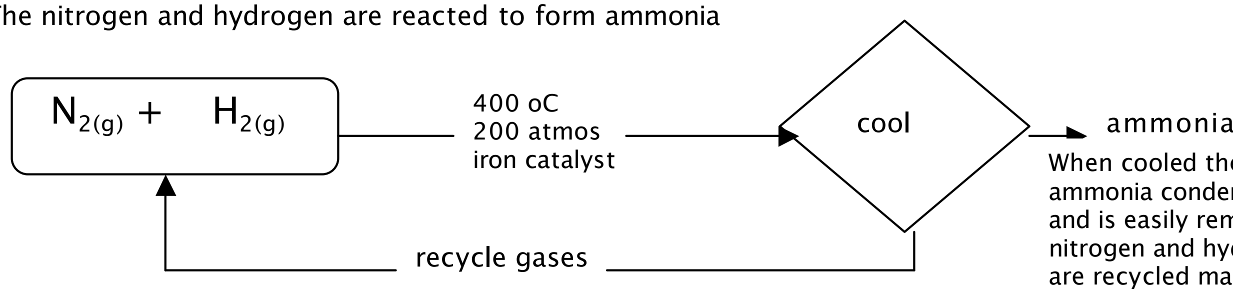
$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad \Delta H = -92\text{kJ mol}^{-1}$$

A high yield of ammonia would be attained at .............. temperature, and a ................. pressure.
In practice a low temperature makes the reaction too slow. A moderate temperature of 400ºC is used to achieve a faster reaction at a lower yield. A high pressure is used but note that the higher the pressure the greater the cost. The optimum pressure balancing both is 200Atmos.

Nitrogen and hydrogen are the feedstocks in the above process but neither are raw materials. The raw materials for manufacture of ammonia are natural gas, water and air.



The nitrogen and hydrogen are reacted to form ammonia




When cooled the ammonia condenses and is easily removed, nitrogen and hydrogen are recycled making process economically viable.

## 12.4 Sulphuric acid

At the end of this unit you should be able to describe the manufacture of sulphuric acid in terms of
1. Raw materials used
2. Reaction conditions
3. Economic considerations

The sulphuric acid industry is of major global importance. Over 100,000,000,000, litres of sulphuric acid are manufactured each year.

### Sources of sulphur

There are 4 main sources of sulphur used by the chemical industry

1. Sulphur dioxide from smelting metal ores
   $2\ ZnS + 3\ O_2 => 2\ ZnO + 2\ SO_2$
2. Mineral deposits of anhydrite, a form of calcium sulphite
   $2\ CaSO_4 + C + SiO_2 => 2\ CaSiO_3 + 2\ SO_2 + CO_2$
3. Sulphur deposits in the ground. Easily converted to sulphur dioxide by burning it. No natural deposits in Britain.
4. Sulphur extracted from crude oil and natural gas.

**A by-product is any substance produced in the course of making the main product.**
**By-products often turn processes from ideas into economically viable factories.**
**Sulphuric acid plants are often located near metal ore smelters or or oil refineries**

### Manufacture of sulphuric acid

Nearly all sulphuric acid is made using the CONTACT PROCESS

**Stage 1** Manufacture of sulphur dioxide

$S(l) + O2(g) => SO2(g)$ $\Delta H = -299$ kJ mol-1

Molten sulphur is sprayed into and burned in a stream of dry air to produce sulphur dioxide. The emerging gas mixture needs to be cooled from 1000°C to about 400°C for the second stage. Heat exchangers are used; the hot air/water produced being used to heat factory.

**Stage 2** Sulphur dioxide conversion

$SO_{2(g)} + 1/2O_{2(g)} \rightleftharpoons SO3(g)$ $\Delta H = -94$ kJ mol-1

In the converter sulphur dioxide combines with oxygen at about 450oC in the presence of a vanadium(V) oxide catalyst. Modern converters contain about 4 layers of catalyst to maintain about 99.5% conversion. The gases being cooled between each layer to make such a high conversion possible.

**Stage 3** Sulphur trioxide absorption

$SO3(g) + H2O(l) => H2SO4(l)$ $\Delta H = -130$ kJ mol-1

Sulphur trioxide is absorbed not into water but into 98% sulphuric acid at 150oC and diluted back to 98% sulphuric acid by addition of water. This prevents the formation of mist of sulphuric acid caused by rapid reaction between sulphur trioxide and water.

Costs

| Capital costs | Fixed costs | Variable costs |
|---|---|---|
| Research an development<br>Plant construction<br>Buildings | Depreciation of plant<br>Labour<br>Land purchase or | Raw materials<br>Energy<br>Overheads<br>Effluent treatment |

| | |
|---|---|
| Infrastructures | rental |
| | Sales expenses |

Companies will only manufacture chemicals such as sulphuric acid if they can do so profitably.

Capital costs

These are the costs associated with setting up the production process, especially the building of the plant and support facilities required.
e.g. offices, staff canteens, security entrances, roads and parking.

Variable costs

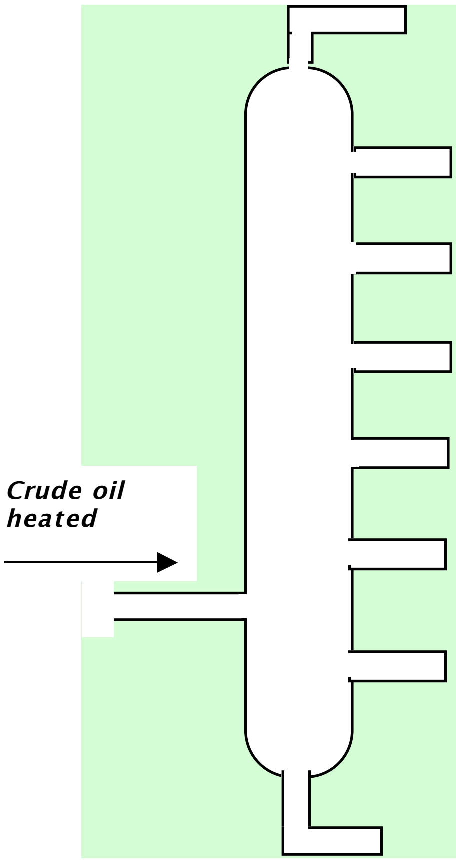
These are the costs that change throughout the year depending on how much product is being manufactured.
e.g. buying raw materials, despatching the product, treatment of waste to make it safe.

Fixed costs

These are costs, which tend to stay fixed throughout the year and do not depend upon the quantity of product
e.g. depreciation of buildings and machines, catalyst licences, rates, sales advertising, heating and lighting

## 12.5 OIL REFINING

Crude oil as it is found in the ground consists of a series of compounds which can be split up into fractions(groups of compounds with similar B.Pts.) by fractionally distilling it. Each fraction consists of groups of hydrocarbons.




| | |
|---|---|
| ***Petroleum gas*** | ***used as a fuel. 20°C $C_1$ -> $C_4$*** |
| ***gasoline*** | ***Petrol used for cars etc. 70°C $C_5$ -> $C_{11}$*** |
| ***Naptha*** | ***used to make chemicals 120°C $C_8$ – $C_{10}$ branched chains*** |
| ***Paraffin(kerosine)*** | ***used as jet fuel, heating and lighting 170°C $C_9$ -> $C_{14}$*** |
| ***Diesel oil*** | ***used in cars, lorries and trains 270°C $C_{12}$ -> $C_{20}$*** |
| ***Fuel oil*** | ***used for ships factories and central heating 300°C $C_{16}$ -> $C_{30}$*** |
| ***Lubricating oil waxes*** | ***Lubricant for machines 325°C $C_{30}$ -> $C_{40}$*** |
| ***Bitumen*** | ***roads and roofs >350°C >C40*** |

Oil refining is a typical example of a continuous process. A continuous process has feedstock input continuously and products removed without stopping the process. (See advantages and disadvantages compared to batch process)

Cracking

To match market demand for the most widely used fractions i.e. petrol and diesel the larger less useful fractions are cracked. Cracking also provides alkenes which are essential for plastic industry.

Removing sulphur

Sulphur will poison many catalysts used in modern engines and is removed by forming hydrogen sulphide, a volatile product which can be reduced to sulphur and sold to sulphuric acid plants.

An oil refinery is costly to construct (high capital costs) but requires only a small workforce to operate it(low running costs) Hence is capital intensive rather than labour intensive. Grangemouth oil refinery is located on the Firth of Forth having been built on a chemical site had access to road, rail and sea links and although not large enough to take huge tankers has pipelines to Finnart in the west and Hound Point in the east.

Processing Natural Gas

Natural gas from the North Sea fields comes ashore by pipeline at St. Fergus in Aberdeenshire from where it is piped to Mossmorran in Fife for processing.

Polythene Industry

Poly(ethene) is the most widely used of all plastics. Originally poly(ethene)was made by compressing ethene with a little oxygen in a sealed container. This was kept closed for 24 hours. The poly(ethene) was removed at the end of this time.

This type of approach is known as a batch process.

In a batch process, a reaction vessel is filled with the feedstocks and left for the reaction to take place. On completion the products are separated from the reactant mixture.

With the development of catalysts in the 1950's it became possible to change to a continuous process.

**Batch**

Advantages

More cost effective for small quantities being made.
Capital outlay on plant is less.
Slow reactions can be carried out.
A variety of different products can be made in the same reaction vessel.
A higher yield is normally possible.

Disadvantages

Filling and emptying the reaction vessel can be time consuming with no production during this 'down time'.
Larger workforce needed.
Thorough cleaning of reaction vessel is needed between making one product and another or contamination is possible.
It can be difficult to control fast exothermic reactions.

**Continuous**

Advantages

More cost effective where large quantities are required.
No expensive 'down time' when the plant is not operating.
Process is easier to automate so reducing labour costs.
Contamination risk is low if only one product is made.
Easier to achieve a consistent quality of product.

Disadvantages

High capital cost in setting up the plant.
Costs rise if plant is not operated at full potential.
Contamination risk is high if plant is used to make more than one product.

## 12. 6 Pharmaceutical Industry

A t the end of this unit you should be able to

1. Describe what happens between discovery of a new drug and its emergence on the market.

Pharmaceuticals are substances used as medicines. In terms of tonnage of chemicals made in Britain they are only a very small part, however in financial terms their contribution is enormous. Drugs are however extremely expensive to design, make and test before they can be sold. The stages before a new product can be manufactured on a commercial scale are shown below.

Research & Development — To find the best manufacturing route

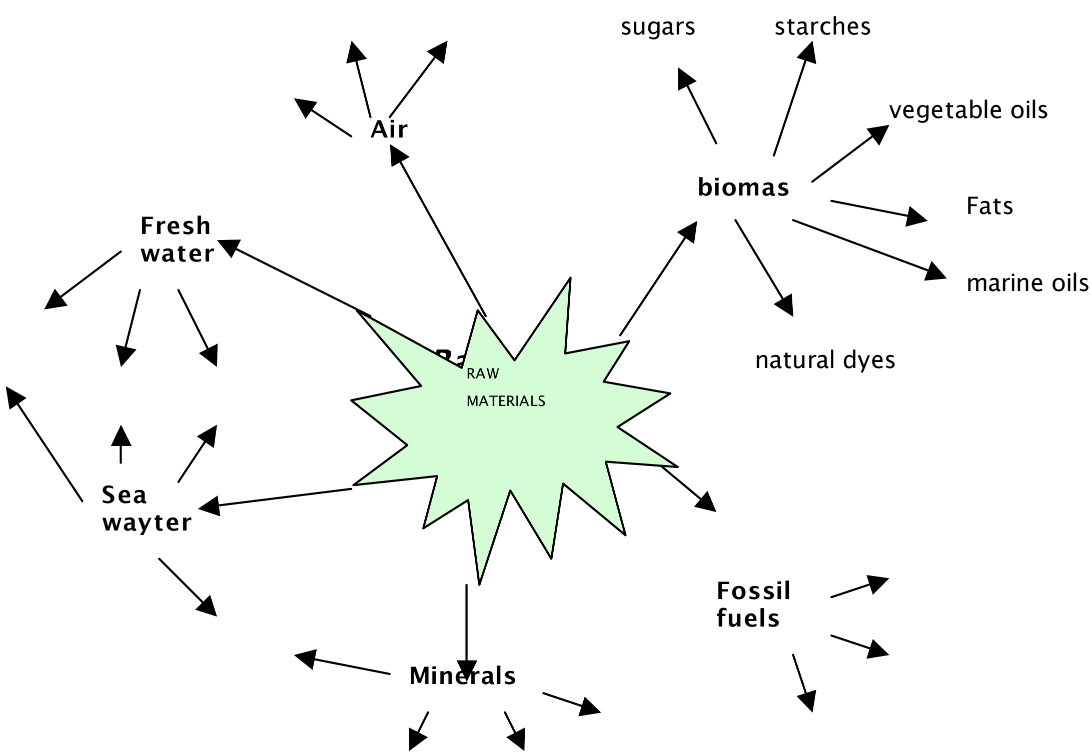
Laboratory Process — To modify process

Pilot Plant — To assess product quality, hazards and costs

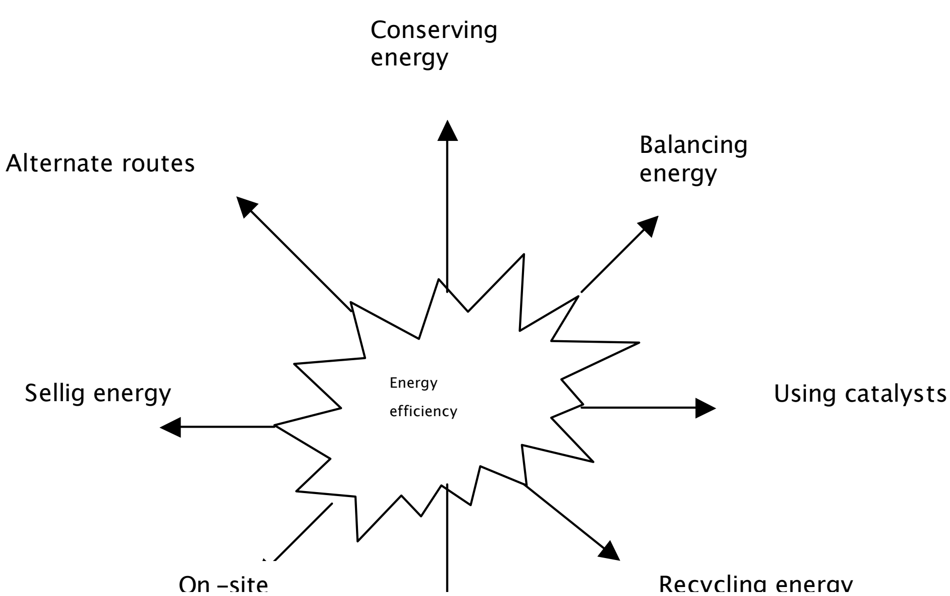
Scaling up

Once a new drug has been discovered the company may patent it. This prevents rival companies from making the same product for 20 years.
A patent is a document that prevents anyone from manufacturing and selling a product except under licence.

## 12.7 Chemical Industry




## Energy Efficiency



Consumer products