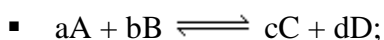


## 9.5 – Industrial Chemistry (Option):

### Δ. Construct word and balanced formulae equations of all chemical reactions as they are encountered in this module:

- *The EQUILIBRIUM Constant:*

– For the basic **reversible** reaction, depicted as:



$$K = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

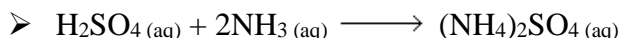
Where [A], [B], [C] and [D] are the equilibrium concentrations of the quantities A, B, C and D

- *Uses of SULFURIC ACID:*

– **Fertiliser Production:**

- Creating *ammonium sulfate*:

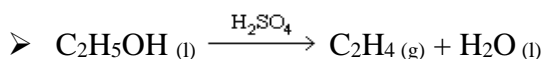
➤ sulfuric acid + ammonia  $\longrightarrow$  ammonium sulfate



– **Dehydrating Agent:**

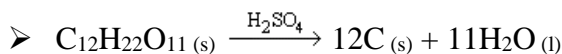
- Dehydration of *ethanol*:

➤ ethanol  $\xrightarrow{\text{H}_2\text{SO}_4}$  ethylene + water



- Dehydration of *sucrose*:

➤ sucrose  $\xrightarrow{\text{H}_2\text{SO}_4}$  carbon + water



– **Oxidising Agent:**

- The oxidation of *copper* into *copper ions*:

➤ FULL:  $\text{Cu}(\text{s}) + 2\text{H}_2\text{SO}_4(\text{aq}) \longrightarrow \text{CuSO}_4(\text{aq}) + \text{SO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$

➤ Oxidation:  $\text{Cu}(\text{s}) \longrightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{e}^-$

➤ Reduction:  $\text{H}_2\text{SO}_4(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{SO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$

- *Sulfuric Acid IONISATION:*

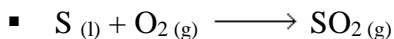
– **Step ONE:**  $\text{H}_2\text{SO}_4(\text{l}) + \text{H}_2\text{O}(\text{l}) \longrightarrow \text{HSO}_4^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \quad \Delta H = -90 \text{ kJ/mol}$

– **Step TWO:**  $\text{HSO}_4^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{SO}_4^{2-}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$

- *Production of Sulfuric Acid (CONTACT Process):*

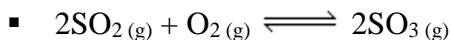
- **Sulfur Dioxide Production:**

- sulfur + oxygen  $\longrightarrow$  sulfur dioxide



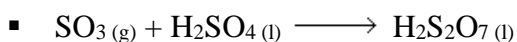
- **Sulfur Trioxide Conversion:**

- sulfur dioxide + oxygen  $\rightleftharpoons$  sulfur trioxide



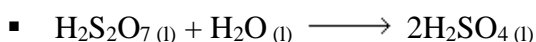
- **Oleum Absorption:**

- sulfur trioxide + sulfuric acid  $\longrightarrow$  oleum



- **Oleum Dilution:**

- oleum + water  $\longrightarrow$  sulfuric acid



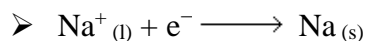
- *ELECTROLYSIS of Sodium Chloride:*

- **Molten NaCl:**

- *Overall reaction:*

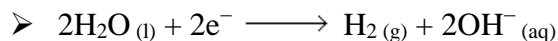
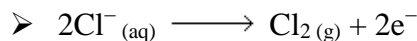


- *Half-equations:*



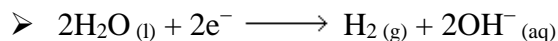
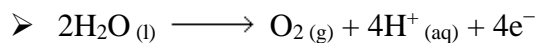
- **Concentrated NaCl:**

- *Half-equations:*

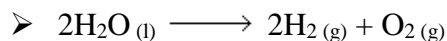


- **Dilute NaCl:**

- *Half-equations:*



- *Overall reaction:*



- **Production of SODIUM HYDROXIDE:**
  - **Mercury Cell:**
    - *Electrolytic half-equations:*
      - ANODE (*titanium*):  $2\text{Cl}^-_{(\text{aq})} \longrightarrow \text{Cl}_{2(\text{g})} + 2\text{e}^-$
      - CATHODE (*mercury*):  $\text{Na}^+_{(\text{aq})} + \text{e}^- \longrightarrow \text{Na}_{(\text{Hg})}$
    - *Hydrolysis of sodium:*
      - sodium + water  $\longrightarrow$  sodium hydroxide + hydrogen
      - $2\text{Na}_{(\text{s})} + 2\text{H}_2\text{O}_{(\text{l})} \longrightarrow 2\text{NaOH}_{(\text{aq})} + \text{H}_{2(\text{g})}$
  - **Diaphragm Cell:**
    - *Electrolytic half-equations:*
      - ANODE (*carbon*):  $2\text{Cl}^-_{(\text{aq})} \longrightarrow \text{Cl}_{2(\text{g})} + 2\text{e}^-$
      - CATHODE (*steel*):  $2\text{H}_2\text{O}_{(\text{aq})} + 2\text{e}^- \longrightarrow 2\text{OH}^-_{(\text{aq})} + \text{H}_{2(\text{g})}$
  - **Membrane Cell:**
    - *Electrolytic half-equations:*
      - ANODE (*titanium*):  $2\text{Cl}^-_{(\text{aq})} \longrightarrow \text{Cl}_{2(\text{g})} + 2\text{e}^-$
      - CATHODE (*nickel*):  $2\text{H}_2\text{O}_{(\text{aq})} + 2\text{e}^- \longrightarrow 2\text{OH}^-_{(\text{aq})} + \text{H}_{2(\text{g})}$
- **SOLVAY Process:**
  - **Brine Purification:**
    - $\text{Ca}^{2+}_{(\text{aq})} + \text{CO}_3^{2-}_{(\text{aq})} \longrightarrow \text{CaCO}_3_{(\text{s})}$
    - $\text{Mg}^{2+}_{(\text{aq})} + \text{OH}^-_{(\text{aq})} \longrightarrow \text{Mg}(\text{OH})_{2(\text{s})}$
  - **Carbon Dioxide Formation:**
    - $\text{CaCO}_3_{(\text{s})} \xrightarrow{\Delta} \text{CO}_{2(\text{g})} + \text{CaO}_{(\text{s})}$
  - **Hydrogen Carbonate Formation:**
    - *Carbonic acid formation:*
      - $\text{CO}_{2(\text{g})} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons \text{H}_2\text{CO}_{3(\text{aq})}$
    - *Ammonia saturation:*
      - $\text{H}_2\text{CO}_{3(\text{aq})} + \text{NH}_3_{(\text{aq})} \rightleftharpoons \text{HCO}_3^-_{(\text{aq})} + \text{NH}_4^+_{(\text{aq})}$
    - *Overall:*
      - $\text{CO}_{2(\text{g})} + \text{NH}_3_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \longrightarrow \text{HCO}_3^-_{(\text{aq})} + \text{NH}_4^+_{(\text{aq})}$
      - $\text{NaCl}_{(\text{aq})} + \text{CO}_{2(\text{g})} + \text{NH}_3_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \longrightarrow \text{NaHCO}_3_{(\text{s})} + \text{NH}_4\text{Cl}_{(\text{aq})}$

- **Sodium Carbonate Formation:**
  - *Thermal decomposition:*
    - $\text{NaHCO}_3(\text{s}) \xrightarrow{\Delta} \text{NaCO}_3(\text{s}) + \text{CO}_2(\text{g})$
- **Ammonia Recovery:**
  - *Lime-slaking*
    - $\text{CaO}(\text{s}) + \text{H}_2\text{O}(\text{l}) \longrightarrow \text{Ca(OH)}_2(\text{aq})$
  - *Ammonia recovery:*
    - $\text{NH}_4\text{Cl}(\text{aq}) + \text{Ca(OH)}_2(\text{aq}) \longrightarrow \text{CaCl}_2(\text{aq}) + \text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$
- **Overall Solvay Process:**
  - $2\text{NaCl}(\text{aq}) + \text{CaCO}_3(\text{s}) \longrightarrow \text{Na}_2\text{CO}_3(\text{s}) + \text{CaCl}_2(\text{aq})$
- **PRACTICALS:**
  - **Quantitative Analysis of Equilibrium:**
    - Cobalt complex-ion equilibrium:
      - $\text{Co(H}_2\text{O)}_6^{2+}(\text{aq}) + 4\text{Cl}^-(\text{aq}) \rightleftharpoons \text{CoCl}_4^{2-}(\text{aq}) + 6\text{H}_2\text{O}(\text{l}) \quad \Delta H < 0$ 

(PINK) (BLUE)

## 1. Industrial chemistry processes have enabled scientists to develop replacements for natural products:

- *Discuss the issues associated with shrinking world resources with regard to one identified natural product that is not a fossil fuel, identifying the replacement materials used and/or current research in place to find a replacement for the named material:*

– RUBBER:

- **Natural Rubber:**

- Up until the 1940's, all rubber was sourced from plantations of rubber trees in tropical areas such as Malaya and Burma.
- These trees would be 'tapped', that is, an incision made into the bark of the tree and the latex sap collected and refined into a useable rubber.
- Demand for natural rubber increased greatly during WWII (mainly for military vehicles), and supply routes were interrupted by the conflict.
- As the natural sources could not cope with the large demand, a synthetic rubber was developed.

- **Synthetic Rubber:**

- For the war effort, scientists in Germany and USA developed synthetic rubbers, the most common of which is SBR (styrene-butadiene).
- Even after the war, natural rubber could not keep up with demand, and hence today 80% of rubber production is synthetic.
- Other synthetic rubbers include poly(isoprene) and poly(isobutylene).

- *Identify data, gather and process information to identify and discuss the issues associated with the increased need for a natural resource that is not a fossil fuel and evaluate the progress currently being made to solve the problems identified:*

– From ABOVE; Continued use of natural rubber would present many issues:

- Deforestation of tropical rainforests to make way for rubber plantations.
- Exploitation of cheap labour in developing tropical nations.
- Inconsistent supply of rubber due to variable weather conditions, etc.

- Because of these issues, and others, the development of synthetic rubber occurred.
- In *general*, the replacement of a natural product with a synthetic one stems from one or more of the following issues:
  - Increased demand for natural product; even if only temporarily.
  - Inability of natural sources to keep up with demand; even if temporary.
  - Depletion of limited natural resources.
  - Competition of natural resource for other uses.
  - Escalating prices of natural resource.
  - Cheaper, and more available, synthetic product.
  - Greater reliability (consistency) of supply of synthetic product.

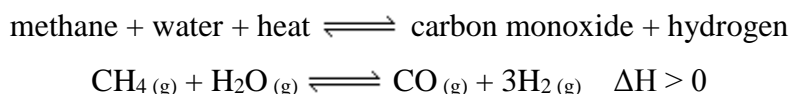
## 2. Many industrial processes involve manipulation of equilibrium reactions:

- **RECALL:**

- *Reversible* reactions do not go to completion, but reach a point of equilibrium.
- *Le Chatelier's Principle* states that if a chemical system at equilibrium is subjected to a change in conditions, the system will readjust itself to counteract that change.

- *Discuss explain the effect of changing the following factors on identified equilibrium reactions: pressure, volume, concentration and temperature:*

- To demonstrate the effect of changing reaction conditions (i.e. changing *pressure, volume, concentration and temperature*) on a reversible reaction, take as an example the reversible hydrolysis of methane:



- **Change in Pressure:**

- For a closed-system composed completely (or in some cases *predominantly*) of gases, if the *total* pressure on the system is:
  - INCREASED, the equilibrium will favour the side that reduces pressure, that is, has less moles of gas; thus opposing the change:
    - ◆ For this reaction, an increase in pressure will encourage the reverse reaction, as there are 2 moles of gas on the left, and 4 on the right.
  - DECREASED, the equilibrium will favour the side that increases pressure, that is, produces more moles of gas; thus opposing the change:
    - ◆ For this reaction, decreasing pressure will encourage the forward reaction, producing more gas to increase the pressure.

- **Change in Volume:**

- For a closed-system (no species allowed to escape), a change in volume is very similar to a change in pressure. If *volume* is:
  - INCREASED, then the pressure decreases, and as stated above, the reaction will favour the side with more moles; so if the reaction flask was suddenly increased in double in volume, more products would form.

- DECREASED, then the pressure increases, and also stated about, the reverse reaction will proceed to produce less moles.
- **Change in Concentration:**
- When the *concentration* of a particular substance (species) is:
    - INCREASED, the equilibrium point will shift towards the **opposite** side of the equation; this opposes the change, as it reduces the concentration of the species by producing more products on the opposite side.
      - ◆ EG: If more water is added (concentration increased) to the reaction, the concentration of reactants on the opposite side will increase, that is, an increase in the forward reaction.
    - DECREASED, the equilibrium point will shift towards the **same** side of the equation the species is on; this opposes the change, as it increases the concentration of the species by the opposite reaction.
      - ◆ EG: If more carbon monoxide is removed (concentration reduced), the concentration of reactants on the same side will increase, through an increase in the forward reaction.
- **Change in Temperature:**
- It must be determined whether a reaction is endothermic or exothermic before making equilibrium predictions about changes in temperature.
  - If a reaction is endothermic (which this example is), then if temperature:
    - INCREASES, the forward reaction will proceed, to cool the mixture being heated to return to equilibrium; so, if methane and water were heated, the forward reaction would occur rapidly.
    - DECREASES, the reverse reaction will proceed, to heat the mixture being cooled. Hence, if the mixture was cooled, CO and H<sub>2</sub> would more readily combine to form the reactants.
  - If a reaction is exothermic then if temperature:
    - INCREASES, the reverse reaction will proceed, to cool the mixture being heated to return to equilibrium.
    - DECREASES, the forward reaction will proceed, to heat the mixture being cooled.



- *Interpret the equilibrium constant expression (no units required) from the chemical equation of equilibrium reactions:*
  - For any reversible reaction, at its point of equilibrium, we can calculate a constant.
  - This constant is called the **equilibrium constant** (K).
  - A simple reversible reaction can be represented generally as:
    - $aA + bB \rightleftharpoons cC + dD$
  - When this reaction reaches equilibrium, the equilibrium constant is defined as:

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Where [A], [B], [C] and [D] are the equilibrium concentrations of the quantities A, B, C and D

- **Tip:** Put *products* over *reactants*; coefficients change into exponents.
- *Process and present information from secondary sources to calculate K from equilibrium conditions:*

- **EG:** Calculate the equilibrium constant for the following reversible reaction, if at equilibrium at 450°C, in a 1.0 L container, there is 2.3 mol of H<sub>2</sub>, 2.8 mol of I<sub>2</sub> and 17.1 mol of HI:
  - $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
- For this reaction, the equation for the equilibrium constant is:

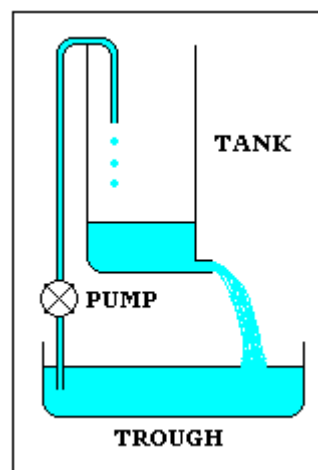
$$K = \frac{[HI]^2}{[H_2][I_2]}$$

- Firstly, find the *concentrations* of reactants and products:
  - $[H_2] = n/v = 2.3/1 = 2.3$
  - $[I_2] = n/v = 2.8/1 = 2.8$
  - $[HI] = n/v = 17.1/1 = 17.1$
- However, note that we need  $[HI]^2$ . This is because the species HI has a coefficient of 2 in front of it, and this changes to an exponent of 2 in the equation:
  - $[HI]^2 = (17.1)^2 = 292.41$
- Hence, at 450 °C, the equilibrium constant is:
  - $K = 292.41 / (2.3 \times 2.8)$   
= 45.4

- **A Few Notes:**
- The equilibrium constant is given as a number only (*dimensionless*).
  - Only the concentrations of *gaseous*, *aqueous* or *liquid* species are taken into account; any solid reactants/products are ignored.
  - The equilibrium constant (K) is only measured at equilibrium at constant temperature.
- Most of the time, questions asked will not be as simple as punching in given numbers to find the value of K:
- **EG:** HSC 2003; Q30 d. (iii):
    - A 1 L reaction vessel initially contained 0.25 mol NO and 0.12 mol O<sub>2</sub>. After equilibrium was established, there was only 0.05 mol NO. Calculate the equilibrium constant for this reaction:
      - ◆  $2\text{NO}_{(g)} + \text{O}_{2(g)} \rightleftharpoons 2\text{NO}_{2(g)}$
    - **Answer:**
      - ◆ **Reaction:**  $2\text{NO}_{(g)} + \text{O}_{2(g)} \rightleftharpoons 2\text{NO}_{2(g)}$
      - ◆ **Moles initially:** 0.25      0.12      0.0
      - ◆ **Moles at equilibrium:** 0.25 – 2x    0.12 – x      2x
        - But at equilibrium NO = 0.05
        - So: 0.25 – 2x = 0.05, x = 0.1
      - ◆ **HENCE at equilibrium:**
        - [NO] = 0.05
        - [O<sub>2</sub>] = 0.12 – 0.1 = 0.02
        - [NO<sub>2</sub>] = 2 × 0.1 = 0.2
      - ◆ Thus, the equilibrium constant is:
        - $K = \frac{[\text{NO}_2]^2}{[\text{NO}]^2[\text{O}_2]} = 800$ .
    - **NOTE:** In order to form the expressions ‘0.25 – 2x’ etc., we note that at equilibrium, there *will* be an amount of NO<sub>2</sub>. But the reaction ratio is 2:1:2 so we say that there will be ‘2x’ amount of NO<sub>2</sub>. But in order to get ‘2x’ NO<sub>2</sub>, ‘2x’ of NO would have had to react, and ‘x’ of O<sub>2</sub> would have had to react as well, according to the reaction ratios. Hence the amounts left are ‘0.25 – 2x’ of NO and ‘0.12 – x’ of O<sub>2</sub>.

- *Identify that temperature is the only factor that changes the value of the equilibrium constant ( $K$ ) for a given equation:*
  - Depending on reaction conditions for a particular reversible reaction, the position of equilibrium may change, the concentration of species may change, the reaction quotient may change, BUT the value of **K** is constant.
    - *The only factor that can change K is TEMPERATURE.*
  - For **exothermic** reactions, if temperature:
    - *Increases*, then more reactants form (which are the denominator of the equation) so hence the equilibrium constant will DECREASE.
    - *Decreases*, then more products form (which are the numerator of the equation) so hence the equilibrium constant will INCREASE.
  - For **endothermic** reactions, if temperature:
    - *Increases*, more products form (which are the numerator of the equation) so hence the equilibrium constant will INCREASE.
    - *Decreases*, then more reactants form (which are the denominator of the equation) so hence the equilibrium constant will DECREASE.
- **PRACTICAL** – *Identify data, plan and perform a first-hand investigation to model an equilibrium reaction:*

- The apparatus shown was set up in the laboratory.
- A *trough* was filled with water, and an *open tank* placed over it. A hose connected to a pump was placed into the trough, and lead into the tank. As the water entered the tank, it leaked back into the trough.
- The water being pumped to the tank modelled a **forward** reaction, and the leakage back to the trough modelled the **reverse** reaction.
- The experiment began with all the water in the trough, but at a point in time, both water levels were equal. This represented *equilibrium*.
- Adding more water to the trough modelled the increase in concentration of a reactant; at first the trough level was higher, but eventually it levelled out.
- Increasing the pump-rate modelled the action of a catalyst.

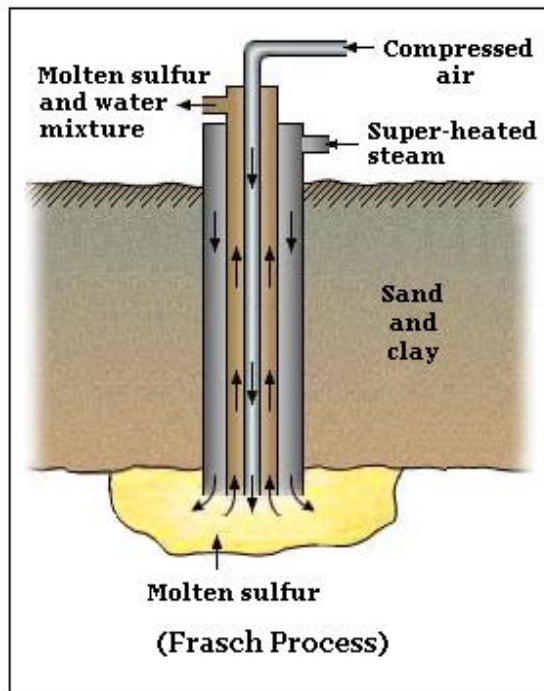


- **PRACTICAL** – Choose equipment and perform a first-hand investigation to gather information and qualitatively analyse an equilibrium reaction:
  - For this practical, the equilibrium of **cobalt complex-ions** was used:
    - **EG:**  $\text{Co}(\text{H}_2\text{O})_6^{2+}(\text{aq}) + 4\text{Cl}^-(\text{aq}) \rightleftharpoons \text{CoCl}_4^{2-}(\text{aq}) + 6\text{H}_2\text{O}(\text{l}) \quad \Delta\text{H} < 0$   
(PINK) (BLUE)
  - 10 mL solution of this reaction at equilibrium was placed into test-tubes.
  - A variety of different ‘changes’ of reaction conditions were imposed onto different test-tubes, and the changes qualitatively analysed:
    - The concentration of **Cl<sup>-</sup>** ions was increased through the addition of hydrochloric acid (HCl). This shifted the equilibrium to the RIGHT, and the solution turned a darker blue, as more  $\text{CoCl}_4^{2-}$  was formed.
    - More **water** was added and this shifted the equilibrium to the LEFT. The solution turned pinker, as more  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  ions were formed.
    - The concentration of water was decreased through the addition of **ethanol**; this ties up some water molecules, and caused the forward reaction to increase.
    - The test-tube was **heated**, and this caused it to increase in *blueness*. This is because the forward reaction is endothermic, and proceeded to oppose the heat.

### 3. Sulfuric acid is one of the most important industrial chemicals:

- *Outline three uses of sulfuric acid in industry:*
  - **Fertilisers:**
    - Most of the sulfuric acid industrially produced is used to make fertilisers. *Superphosphate* fertiliser (which contains calcium sulfates and calcium dihydrogen phosphates) and ammonium sulfate are both commercial fertilisers produced using sulfuric acid.
    - Production of *ammonium sulfate*:
      - sulfuric acid + ammonia  $\longrightarrow$  ammonium sulfate
      - $\text{H}_2\text{SO}_4 (\text{aq}) + 2\text{NH}_3 (\text{aq}) \longrightarrow (\text{NH}_4)_2\text{SO}_4 (\text{aq})$
  - **Dehydrating Agent:**
    - Concentrated sulfuric acid is a strong dehydrating agent; an example of this property being used is the production of ethylene from ethanol.
    - Dehydration of *ethanol*:
      - ethanol  $\xrightarrow{\text{H}_2\text{SO}_4}$  ethylene + water
      - $\text{C}_2\text{H}_5\text{OH} (\text{l}) \xrightarrow{\text{H}_2\text{SO}_4} \text{C}_2\text{H}_4 (\text{g}) + \text{H}_2\text{O} (\text{l})$
  - **Polymers:**
    - Sulfuric acid is used in the production of many polymers (mainly condensation polymers), such as rayon and cellophane.
    - It is used to extrude the liquid mass into fibrous polymer threads.
- *Describe the processes used to extract sulfur from mineral deposits, identifying the properties of sulfur which allow its extraction and analysing potential environmental issues that may be associated with its extraction:*
  - *Mineral deposits* refers to sulfur found in its elemental form; uncombined.
  - These deposits of sulfur are often underground and must be extracted; the process of extraction is called the FRASCH process.
  - **The Frasch Process:**
    - Three *concentric* pipes are forced down to the underground sulfur deposits .
    - *Superheated* steam (which is pressurised to 160°C) is inserted into the outermost pipe, directly into the sulfur, causing it to melt.

- Pressurised air is forced down the inner-most tube, which then pushes the molten sulfur & water foam through the middle-tube, back to the surface.
- The mixture is then cooled, and the sulfur readily separates from the water.
- **PROPERTIES** of sulfur that allow for this extraction:
  - Sulfur has a low melting point of  $113^{\circ}\text{C}$  and melts under superheated steam.
  - Sulfur is insoluble in water, and hence extraction requires only cooling, and produces a very pure product (99.5% sulfur).
  - The low density of sulfur means it readily forms a foamy mixture with water, and also allows it to be easily forced back to the surface.
- **Environmental Issues:**
  - While sulfur itself is non-toxic and odourless, it oxidises easily to sulfur dioxide and is reduced easily to hydrogen sulfide, both of which are serious air pollutants; care must be taken to avoid these reactions.
  - The water used to make superheated steam cannot be discharged into the environment, as it contains contaminants, and will cause *thermal pollution* due to its intense heat; it must be reused.
  - Extraction of large amounts of sulfur creates large underground caverns which can possibly collapse upon themselves. These are called earth *subsidence*s.
- *Outline the steps and conditions necessary for the industrial production of  $\text{H}_2\text{SO}_4$  from its raw materials:*
  - Production of sulfuric acid from raw materials is called the CONTACT process.
  - The raw materials used are *sulfur*, *oxygen* and *water*.



– **The Contact Process:**

▪ Sulfur Dioxide Production:

- Molten sulfur is sprayed into a combustion furnace.
- Air that has been dried, with excess oxygen, is pumped into the furnace.
- The sulfur reacts ('burns') in the oxygen, forming sulfur dioxide:
  - ◆ sulfur + oxygen  $\longrightarrow$  sulfur dioxide
  - ◆  $S_{(l)} + O_{2(g)} \longrightarrow SO_{2(g)}$
- *Alternatively*, some chemical plants source their sulfur dioxide from waste gases produced by metal refineries;
  - ◆ **EG:** Lead is extracted from galena (PbS), which produces sulfur dioxide during the metal extraction:  $PbS + O_2 \longrightarrow Pb + SO_2$

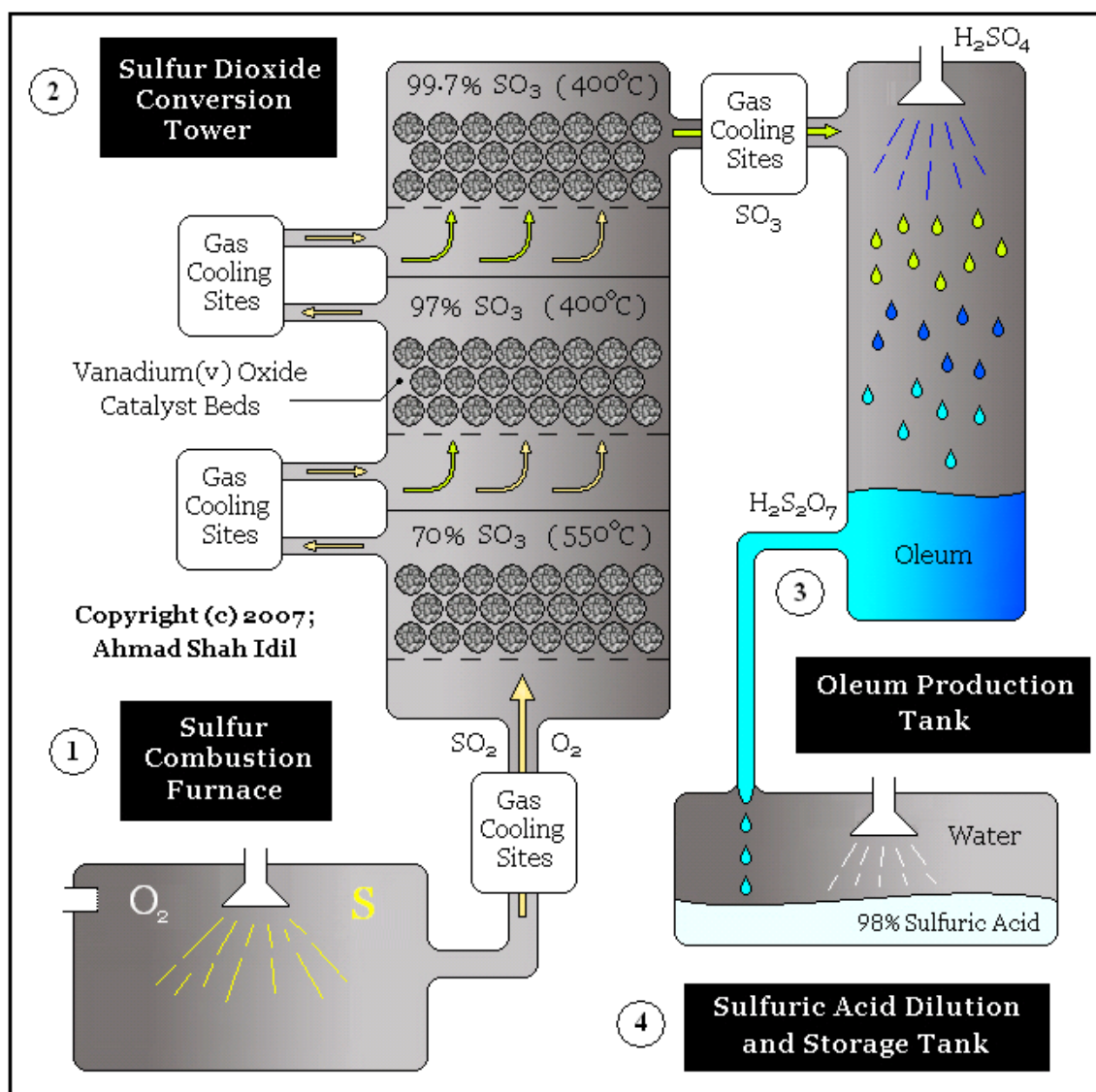
▪ Sulfur Trioxide Conversion:

- The combustion furnace leads to the *conversion tower*.
- Sulfur dioxide is fed into this multi-layered tower, where it is converted into sulfur trioxide; the process is called **catalytic oxidation**.
- It is an equilibrium reaction:
  - ◆ sulfur dioxide + oxygen  $\rightleftharpoons$  sulfur trioxide
  - ◆  $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$
- The reaction conditions used are:
  - ◆ One atmosphere of pressure, 400-550°C and an excess of oxygen.
- The reaction uses a catalyst, vanadium(V) pentoxide.
- The reaction proceeds in stages, in the different levels of the tower, until it reaches about a 99.7% conversion rate. SEE below for more details...

▪ Oleum Absorption:

- When sulfur trioxide is dissolved in water, it forms sulfuric acid.
- However, the reaction is extremely exothermic, reacting explosively and spraying sulfuric acid mist in all directions. This is not suitable for industrial production, as it is dangerous, and the separation of the mist from the air is expensive.
- Instead, the sulfur trioxide is then dissolved in a stream of concentrated sulfuric acid, forming *oleum* ( $H_2S_2O_7$ ).

- This is a stable reaction:
    - ◆ sulfur trioxide + sulfuric acid  $\longrightarrow$  oleum
    - ◆  $\text{SO}_3(\text{g}) + \text{H}_2\text{SO}_4(\text{l}) \longrightarrow \text{H}_2\text{S}_2\text{O}_7(\text{l})$
  - Oleum Dilution:
    - Lastly, the oleum is diluted with purified water in a dilution tank.
    - This is stable reaction, which forms sulfuric acid:
      - ◆ oleum + water  $\longrightarrow$  sulfuric acid
      - ◆  $\text{H}_2\text{S}_2\text{O}_7(\text{l}) + \text{H}_2\text{O}(\text{l}) \longrightarrow 2\text{H}_2\text{SO}_4(\text{l})$
- The final product of the Contact Process is 98% concentration sulfuric acid:





- Describe the reaction conditions necessary for the production of SO<sub>2</sub> and SO<sub>3</sub>:
  - Production of SULFUR DIOXIDE:
    - This involves the oxidation of *sulfur* to *sulfur dioxide*.
    - The reaction is exothermic, and goes to completion:
      - sulfur + oxygen  $\longrightarrow$  sulfur dioxide + heat
      - $S_{(l)} + O_{2(g)} \longrightarrow SO_{2(g)}$
    - **Conditions for Production:**
      - The reaction is carried out in a combustion furnace.
      - Molten sulfur is sprayed into *dry, oxygen-rich* air and burned.
  - Production of SULFUR TRIOXIDE:
    - This involves a second oxidation of *sulfur dioxide* to *sulfur trioxide*.
    - It is also exothermic, BUT it is a reversible reaction that reaches equilibrium:
      - sulfur dioxide + oxygen  $\rightleftharpoons$  sulfur trioxide + heat
      - $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$
    - **Conditions for Production:**
      - Reaction is carried out at about 400-550°C with about 1-2 atm. of pressure.
      - An EXCESS of oxygen is used.
      - *Catalyst:* Vanadium(V) pentoxide (V<sub>2</sub>O<sub>5</sub>) on porous silica pellets.
    - The Conversion Tower (See *diagram* above):
      - The conversion occurs in a multi-layered tower in a series of steps.
      - Firstly, the sulfur dioxide/oxygen mixture from the furnace, which is at about 1000°C is cooled to 550°C, and passed through the first bed of catalyst; 70% converts almost instantly.
      - As it is an exothermic reaction, the gas is then cooled again, but to 400°C this time, and passed through the second catalyst bed; a 97% conversion rate is achieved.
      - The gas is cooled again to 400°C, and passed through the beds until 99.7% conversion rate is achieved, and the residue gas released to atmosphere.
    - Note that the 400°C beds achieve HIGH yield, while the 550°C achieve a FAST rate of reaction; it is a delicate *balancing* act.

- *Apply the relationship between rates of reaction and equilibrium conditions to the production of SO<sub>2</sub> and SO<sub>3</sub>:*
  - **Sulfur Dioxide:**
    - The production of SO<sub>2</sub> is a reaction that proceeds to completion; there are no equilibrium considerations to be made.
    - However, to increase the rate of reaction, the sulfur is liquefied (which increases its surface area), and an excess of oxygen is used.
  - **Sulfur Trioxide:**
    - The production of SO<sub>3</sub> is a reversible reaction, and the conditions chosen for its production are made after considering equilibrium factors.
    - The reaction:
      - sulfur dioxide + oxygen  $\rightleftharpoons$  sulfur trioxide + heat
      - $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$
    - EQUILIBRIUM Considerations (according to Le Chatelier's Principle):
      - The forward reaction is *exothermic*, hence lower temperatures favour the forward reaction, to oppose the change.
      - There are less *moles of gas* as products compared to reactants; hence high pressures will favour the forward reaction.
      - An excess of oxygen is used to further encourage the forward reaction.
    - RATE Considerations:
      - High temperatures are favourable, as the *rate of reaction* will increase due to more molecular collisions.
      - A catalyst of vanadium(V) oxide on silica pellets greatly increases the rate.
    - The Compromise:
      - Thus, a compromise temperature range of 400-550°C is used, which provides a balance between yield and rate of reaction.
      - However, high pressure equipment is expensive and dangerous; a compromise pressure of 1 or 2 atm is sufficient for this reaction.
      - The conditions chosen give an *economically* practical balance between *yield* of products at equilibrium and the *rate* of chemical reaction .

- *Describe, using examples, the reactions of sulfuric acid acting as an oxidising agent and as a dehydrating agent:*
  - RECALL: An oxidising agent (or *oxidant*) brings about oxidation in another substance, and in the process, is itself reduced.
  - *Sulfuric acid* has two important uses:
    - It is a strong **oxidising** agent.
    - It is a strong **dehydrating** agent.
  - The half-equation that demonstrates its oxidising abilities is:
    - $\text{H}_2\text{SO}_4 + 2\text{H}^+ + 2\text{e}^- \longrightarrow \text{SO}_2 + 2\text{H}_2\text{O}$
    - Note that this is the *reduction* half, as electrons are gained.
  - **EG:** The oxidation of *copper* into *copper ions*:
    - Full chemical equation:
      - $\text{Cu}_{(s)} + 2\text{H}_2\text{SO}_{4(aq)} \longrightarrow \text{CuSO}_{4(aq)} + \text{SO}_{2(g)} + 2\text{H}_2\text{O}_{(l)}$
    - One of the sulfates is a spectator ion:
      - $\text{Cu}_{(s)} + \text{H}_2\text{SO}_{4(aq)} + 2\text{H}^+_{(aq)} \longrightarrow \text{Cu}^{2+}_{(aq)} + \text{SO}_{2(g)} + 2\text{H}_2\text{O}_{(l)}$
    - Hence, the two half equations are:
      - $\text{Cu}_{(s)} \longrightarrow \text{Cu}^{2+}_{(aq)} + 2\text{e}^-$
      - $\text{H}_2\text{SO}_{4(aq)} + 2\text{H}^+_{(aq)} + 2\text{e}^- \longrightarrow \text{SO}_{2(g)} + 2\text{H}_2\text{O}_{(l)}$
  - **EG:** The dehydration of *sucrose*:
    - In this reaction, sulfuric acid dehydrates sucrose, leaving behind a tower of spongy carbon:
      - sucrose  $\xrightarrow{\text{H}_2\text{SO}_4}$  carbon + water
      - $\text{C}_{12}\text{H}_{22}\text{O}_{11(s)} \xrightarrow{\text{H}_2\text{SO}_4} 12\text{C}_{(s)} + 11\text{H}_2\text{O}_{(l)}$
- *Describe and explain the exothermic nature of sulfuric acid ionisation:*
  - **RECALL:** *Breaking* bonds absorbs energy, *creating* bonds releases energy.
  - When molecular sulfuric acid (*concentrated*) is diluted (*ionised*), a great amount of heat is released; in a small beaker, the acid may spit and boil.
  - **Explanation:**
    - When a molecule of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) is placed in water, it ionises.
    - It separates into its component ions, i.e.  $\text{H}^+$ ,  $\text{HSO}_4^-$  and  $\text{SO}_4^{2-}$ .

- In water, the  $\text{H}^+$  ions then combine with the water, forming  $\text{H}_3\text{O}^+$  ions.
- In this particular ionisation, the energy released when  $\text{H}_3\text{O}^+$  is formed is *much* GREATER than the energy absorbed when  $\text{H}_2\text{SO}_4$  is broken.
- Hence, the ionisation is strongly exothermic.
- There are two stages in sulfuric acid ionisation:
  1.  $\text{H}_2\text{SO}_4(\text{l}) + \text{H}_2\text{O}(\text{l}) \longrightarrow \text{HSO}_4^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \quad \Delta\text{H} = -90 \text{ kJ/mol}$
  2.  $\text{HSO}_4^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{SO}_4^{2-}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
- The first ionisation goes to completion, and is strongly exothermic.
- The second ionisation only occurs slightly, and is negligible.
- Hence, the ionisation of sulfuric acid molecules is strongly exothermic.
- *Identify and describe safety precautions that must be taken when using and diluting concentrated sulfuric acid:*
  - Concentrated sulfuric acid (98%) is almost completely *molecular* - no free ions.
  - Hence, as it is diluted, the molecular sulfuric acid will be ionised.
  - From above, we know that the ionisation is strongly exothermic, and hence certain safety precautions must be taken when diluting concentrated sulfuric acid.
  - When DILUTING concentrated sulfuric acid:
    - Wear protective clothing, especially safety glasses.
    - Add small amounts of ACID to larger amounts of WATER (this allows the heat of ionisation to disperse throughout the water, to prevent boiling).
    - Continuously stir the mixture to aid a smooth dilution.
    - Clean up any spills immediately, by using sodium hydrogen carbonate.
  - When USING concentrated sulfuric acid:
    - The strictest safety measures must be employed, as it is highly dangerous; full safety-wear must be worn, including lab coat and glasses.
    - It is also extremely important not to allow any water to enter the concentrated sulfuric acid bottle, as it may trigger a reaction that can create enough heat to cause the bottle to explode.
- *Use available evidence to related the properties of sulfuric acid to safety precautions necessary for its transport and storage:*

- **Concentrated Sulfuric Acid:**
  - This is 98% sulfuric acid, sourced directly from production plants.
  - At this high a concentration, sulfuric acid is virtually all *molecular*, i.e. there are no *free ions* (such as  $H^+$  or  $SO_4^{2+}$ ).
  - Hence, concentrated sulfuric acid will not react with iron or steel, as it is only the  $H^+$  ions that take part in acid/metal reactions.
  - Thus, it is safe to store and transport concentrated sulfuric acid in steel or iron containers, instead of glass or plastic containers (which do not react with  $H^+$ ).
  - In addition, iron and steel are stronger than glass or plastic; it would be unsafe to store or transport concentrated sulfuric acid in large glass bottles, which can break very easily.
  - Great care must be taken to prevent any moisture from being present in vessels used to transport concentrated sulfuric acid, as rapid exothermic ionisation may occur.
  - Keep the lid of the container tightly shut, as sulfuric acid can absorb water from the air, leading to a dangerous reaction.
- **Dilute Sulfuric Acid:**
  - Dilute sulfuric acid is *completely ionised* and hence has free  $H^+$  ions which vigorously react with iron and steel; hence iron and steel are unsuitable for its storage or transport.
  - Instead, dilute sulfuric acid must be stored in glass or plastic bottles, which do not react with sulfuric acid; this limits our ability to transport it.
- **PRACTICAL** – *Perform first-hand investigations to observe the reactions of sulfuric acid acting as an oxidising agent and as a dehydrating agent:*
  - As an OXIDISING agent:
    - In a *fume cupboard*, a granule of copper is placed in a small test-tube.
    - Using a dropper, 10 drops of concentrated sulfuric acid were placed onto the copper and the test-tube shaken.
  - As a DEHYDRATING agent:
    - Also done in the *fume cupboard*; 10 mL of concentrated sulfuric acid was added to a beaker containing 50 grams of sugar (sucrose) and stirred.

- **RESULTS:**
  - In the test-tube (*oxidation*), bubbles formed, and slowly the solution began to turn blue:
    - The bubbles indicated the production of a gas.
    - Moist BLUE litmus paper placed over the gas turned RED.
    - Hence the gas was an acidic oxide, that is, sulfur dioxide (SO<sub>2</sub>).
    - The blue signified the production of copper sulfate (CuSO<sub>4</sub>).
  - Hence, this reaction occurred, demonstrating its oxidising abilities:
    - $\text{Cu}_{(s)} + 2\text{H}_2\text{SO}_{4(aq)} \longrightarrow \text{CuSO}_{4(aq)} + \text{SO}_{2(g)} + 2\text{H}_2\text{O}_{(l)}$
  - In the beaker (*dehydration*), the sugar turned black, and then began to smoke, and form a large tower of black carbon. This proved that dehydration occurred:
    - $\text{C}_{12}\text{H}_{22}\text{O}_{11(s)} \xrightarrow{\text{H}_2\text{SO}_4} 12\text{C}_{(s)} + 11\text{H}_2\text{O}_{(l)}$
- **SAFETY:**
  - It was undertaken in a fume cupboard to contain the toxic sulfur dioxide gas.
  - Small quantities were used to prevent too much heat forming; these are exothermic reactions.
- **JUSTIFY:**
  - Copper was used, as the formation of a blue solution is a clear and vivid sign of copper ions, and hence the oxidation of copper.
  - Litmus paper indicated that the gas formed was sulfur dioxide.
  - Sugar dehydration was used, as the formation of carbon is dramatic and clearly a dehydration reaction, as steam is formed.
- **REPORT** – *Gather, process and present information from secondary sources to describe the steps and chemistry involved in the industrial production of H<sub>2</sub>SO<sub>4</sub> and use available evidence to analyse the process to predict ways in which the output of sulfuric acid can be maximised:*
  - See ABOVE for a very thorough examination of the production of sulfuric acid.

#### 4. The industrial production of sodium hydroxide requires the use of electrolysis:

- **RECALL:**

- **Electrolysis** is the process whereby an electrical current is used to bring about a non-spontaneous chemical reaction.
- This often involves the *decomposition* of a compound into its component elements.

- *Explain the difference between galvanic cells and electrolytic cells in terms of energy requirements:*

- *Electrolytic cells* are used to carry out electrolysis reactions.
- *Galvanic cells* are used to create electrical current.

Galvanic Cell	Electrolytic Cell
Chemical $\longrightarrow$ Electrical energy	Electrical $\longrightarrow$ Chemical energy
Produces electrical current	Requires an input of electrical current
Spontaneous reaction	Reaction is forced
Anode is NEGATIVE (-)	Anode is POSITIVE (+)
Cathode is POSITIVE (+)	Cathode is NEGATIVE (-)
$E_0$ is positive	$E_0$ is negative

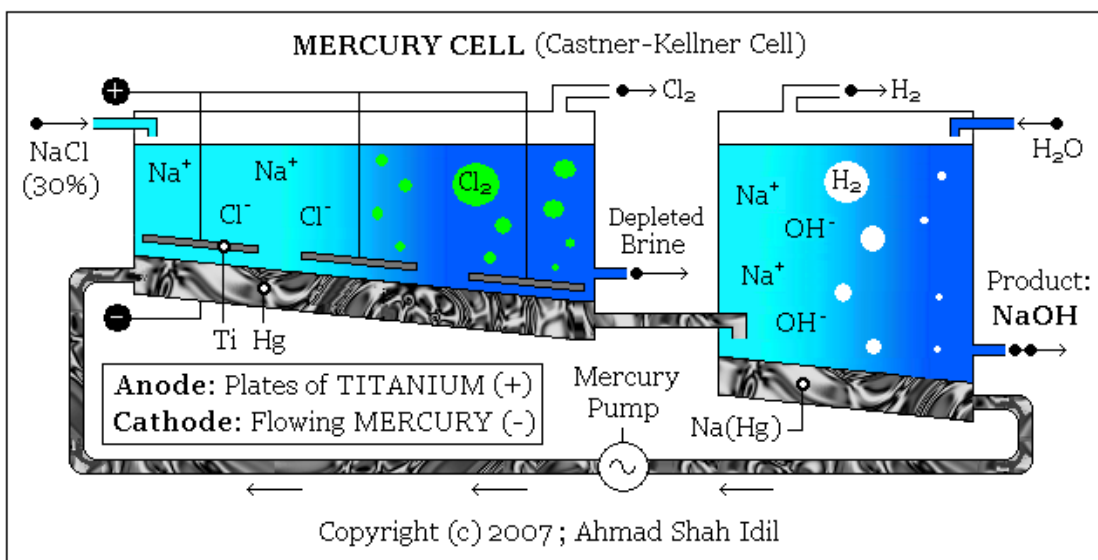
- NOTE: **AN OX** (anode-oxidation) and **RED CAT** (cathode-reduction) holds true in both types cells, *but* the sign of the electrodes is swapped.
- Remember that electrons flow from the negative to the positive terminal, despite what the silly physics people might say...
- *Outline the steps in the industrial production of sodium hydroxide from sodium chloride solution and describe the reaction in terms of net ionic and full formulae equations:*
  - Sodium hydroxide (NaOH) is an extremely commercially significant alkali.
  - It is produced by the *electrolysis* of **salt** (NaCl) and **water**.
  - It is classified as a “strong base” as it undergoes complete ionisation.
  - There are three methods used to industrially produce sodium hydroxide from sodium chloride solution, and they are explained in detail below.

- Distinguish between the three electrolysis methods used to extract sodium hydroxide (i.e. the Mercury Process, the Diaphragm Process and the Membrane Process) by describing each process and analysing the technical and environmental difficulties involved in each process:

– THE MERCURY CELL (Castner-Kellner Process):

▪ **Structure:**

- The mercury-cell is composed of two tanks, connected by a stream of flowing mercury, which is continuously pumped through a series of pipes.
- This cell produces NaOH by the electrolysis of brine (30% NaCl solution).
  - ◆ Other important by-products are chlorine and hydrogen gas.
- The brine is purified, and pumped into the first tank.
- The chloride ions are oxidised on the titanium anodes, and the sodium ions reduced on the mercury cathode:
  - ◆ The chlorine gas is bubbled out and collected.
  - ◆ The sodium dissolves in the mercury, forming an *amalgam*.
- The amalgam then flows into another tank which contains purified water.
- The sodium spontaneously reacts with the water (is *hydrolysed*) and very pure sodium hydroxide and hydrogen gas are formed.
- The hydrogen is bubbled out and collected, and the NaOH tapped-off.
- The mercury is then pumped back to the first tank.



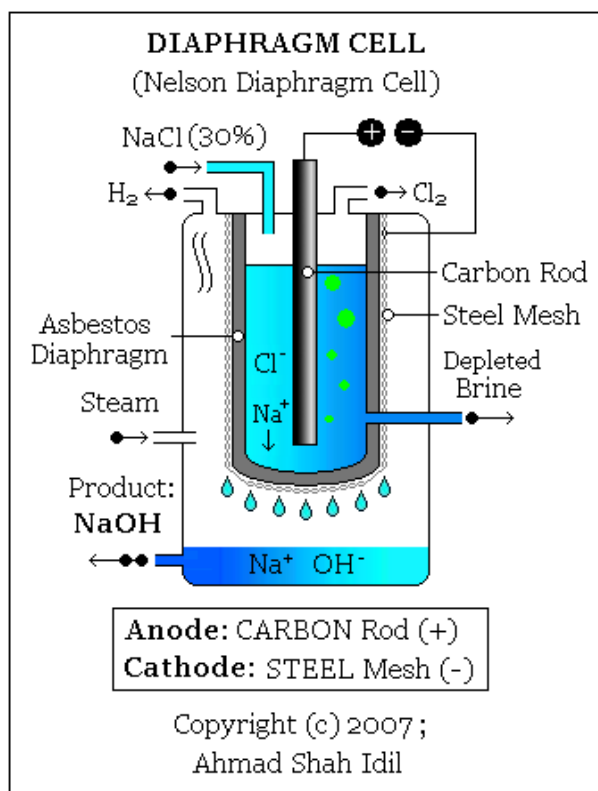


- **Chemistry:**
  - Complete chemical equation:
    - ◆ salt + water  $\longrightarrow$  sodium hydroxide + chlorine + hydrogen
    - ◆  $2\text{NaCl}_{(\text{aq})} + 2\text{H}_2\text{O}_{(\text{l})} \longrightarrow 2\text{NaOH}_{(\text{aq})} + \text{Cl}_{2(\text{g})} + \text{H}_{2(\text{g})}$
  - *Electrolytic* half-equations:
    - ◆ ANODE (*titanium*):  $2\text{Cl}^{-}_{(\text{aq})} \longrightarrow \text{Cl}_{2(\text{g})} + 2\text{e}^{-}$
    - ◆ CATHODE (*mercury*):  $\text{Na}^{+}_{(\text{aq})} + \text{e}^{-} \longrightarrow \text{Na}_{(\text{Hg})}$
  - *Hydrolysis* of sodium:
    - ◆ sodium + water  $\longrightarrow$  sodium hydroxide + hydrogen
    - ◆  $2\text{Na}_{(\text{s})} + 2\text{H}_2\text{O}_{(\text{l})} \longrightarrow 2\text{NaOH}_{(\text{aq})} + \text{H}_{2(\text{g})}$
- **Technical Considerations:**
  - At the anode, chlorine gas is evolved; it is a corrosive, powerful oxidising agent. Hence an INERT anode of *titanium plates* is used.
  - For the cathode, *mercury* is used because:
    - ◆ It is a liquid, and can be pumped around a system.
    - ◆ It readily forms alloys (*amalgams*) with many metals (e.g. sodium).
    - ◆ When using a mercury cathode, sodium ions, not water molecules, are preferentially reduced, as opposed to using *other* cathodes.
  - The titanium plates are held very close to the mercury surface to allow for very large current flows; this promotes electrolysis:
    - ◆ 3 to 4 volts are used, but with tens of thousands of amperes of current.
  - The raw materials (brine and water) must be *purified* before use.
  - The *depleted* brine must be continuously replaced with fresh brine.
  - All products are (i.e. NaOH, Cl<sub>2</sub> and H<sub>2</sub>) are commercially important, and form the basis of the chlor-alkali industry. All are collected and sold.
- **Environmental Issues:**
  - Although the system appears to be closed, small mercury losses to the environmental are inevitable; 100-200g of mercury is released into the environment (e.g. oceans) for every tonne of NaOH produced.
  - Mercury compounds can be passed on to humans by biomagnification.
  - This is of a great concern; mercury is a heavy-metal, and a neurotoxin.

– THE DIAPHRAGM PROCESS (Nelson Diaphragm Cell):

▪ **Structure:**

- The electrolytic cell consists of a carbon anode, within a solution of brine, which is housed in an *asbestos* diaphragm shell.
- The asbestos diaphragm is lined by a steel-mesh cathode.
- When the electrolyte solution soaks through the asbestos diaphragm to the steel mesh, the electrolysis reaction occurs.
- Positive sodium ions ( $\text{Na}^+$ ) are attracted to the negative cathode, and are able to pass through the asbestos.
- Steam is passed over the cathode continuously to wash off a solution of sodium hydroxide, which drips to the bottom of the cell, and is collected.
- Chlorine gas and hydrogen gas are collected separately.



▪ **Chemistry:**

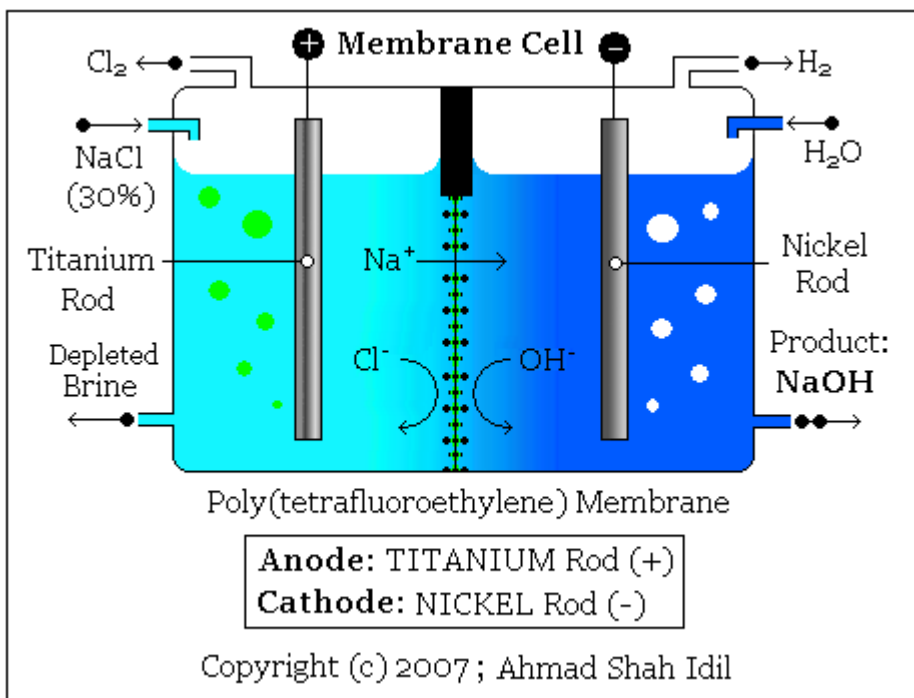
- Complete chemical equation:
  - ◆ salt + water  $\longrightarrow$  sodium hydroxide + chlorine + hydrogen
  - ◆  $2\text{NaCl}_{(aq)} + 2\text{H}_2\text{O}_{(l)} \longrightarrow 2\text{NaOH}_{(aq)} + \text{Cl}_{2(g)} + \text{H}_{2(g)}$

- *Electrolytic half-equations:*
  - ◆ ANODE (*carbon*):  $2\text{Cl}^-_{(\text{aq})} \longrightarrow \text{Cl}_{2(\text{g})} + 2\text{e}^-$
  - ◆ CATHODE (*steel*):  $2\text{H}_2\text{O}_{(\text{aq})} + 2\text{e}^- \longrightarrow 2\text{OH}^-_{(\text{aq})} + \text{H}_{2(\text{g})}$
- **Technical Considerations:**
  - Again, chlorine gas is evolved at the anode, and hence a suitable material must be used; in this case, carbon. Also, the pipes carrying the chlorine must be resistant to *chemical attack*.
  - Chlorine must be separated from the hydrogen, as they react vigorously to form corrosive HCl gas; this was not a concern in the mercury cell as the reaction was separated into two tanks, with one gaseous product each.
  - A large system of many small cells is employed, instead of one large cell, in order to keep the distance between the anode and cathode small, in order to maximise current:
    - ◆ 3.5-5 volts used, with tens of thousands of amperes of current.
  - The *asbestos* is supposed to act as a barrier for the movement of ions, allowing only the movement of  $\text{Na}^+$  ions into the steel mesh, and preventing the movement of hydroxide and chloride ions.
  - However, some unwanted ion movement occurs:
    - ◆ Small amounts of  $\text{Cl}^-$  ions cross the asbestos, and react with the  $\text{Na}^+$  (forming salt, NaCl, which is an impurity in the final product) and also react with the  $\text{OH}^-$  (forming the chlorite ion,  $\text{ClO}^-$ , a strong oxidant).
    - ◆ Small amounts of  $\text{OH}^-$  ions also move back into the brine, forming NaOH and  $\text{ClO}^-$  in the depleted brine.
  - Due to the nature of the diaphragm the final product always contains NaCl, which is only partially removed by crystallisation.
- **Environmental Issues:**
  - Asbestos fibres are quite dangerous, and inhalation of these fibres can cause a range of lung diseases, such as asbestosis and mesothelioma.
  - The depleted brine cannot be released immediately back into the environment, due to the presence of small quantities of basic NaOH, and oxidising  $\text{ClO}^-$  ions, which have to be removed.

– THE MEMBRANE PROCESS:

▪ **Structure:**

- A single cell is divided into two halves by an ion-exchange polymer membrane made of *polytetrafluoroethylene*.
- This membrane is selectively permeable, and allows the diffusion of water and sodium ions ONLY. Chloride and hydroxide ions cannot pass.
- In the first half, brine is pumped in, and water in the second half.
- On the titanium anode, chlorine is produced, and on the nickel cathode, hydrogen and hydroxide ions are produced.
- The sodium ions pass through the membrane, and combine with the hydroxide ions, forming very pure NaOH, which is continuously removed.



▪ **Chemistry:**

- Complete chemical equation:
  - ◆ salt + water  $\longrightarrow$  sodium hydroxide + chlorine + hydrogen
  - ◆  $2\text{NaCl}_{(aq)} + 2\text{H}_2\text{O}_{(l)} \longrightarrow 2\text{NaOH}_{(aq)} + \text{Cl}_{2(g)} + \text{H}_{2(g)}$
- *Electrolytic half-equations:*
  - ◆ ANODE (*titanium*):  $2\text{Cl}^{-}_{(aq)} \longrightarrow \text{Cl}_{2(g)} + 2e^{-}$
  - ◆ CATHODE (*nickel*):  $2\text{H}_2\text{O}_{(aq)} + 2e^{-} \longrightarrow 2\text{OH}^{-}_{(aq)} + \text{H}_{2(g)}$

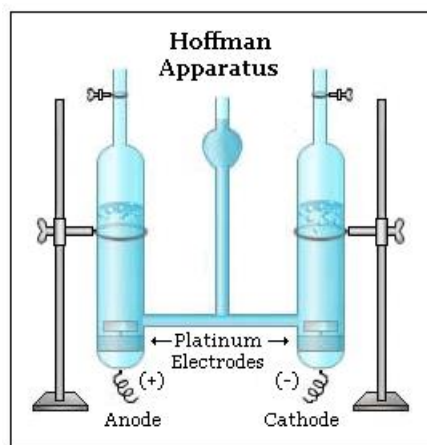
- **Technical Considerations:**
  - This cell solves the problems of both the mercury and diaphragm cells:
    - ◆ There are no toxic materials used, such as mercury or asbestos; a very inert polymer is used as the membrane.
    - ◆ Very pure NaOH is formed, as with the mercury cell, as there is no contamination of the product with chloride ions, and the depleted brine is just NaCl solution.
    - ◆ Titanium is used as anode as it withstands chlorine attack.
  - The polymer has many useful properties, such as its selective permeability, as well as its ability to resist chemical attack in a strongly basic solution.
  - Just as with the diaphragm cell, a large system of many small cells is employed, instead of one large cell, in order to maximise the current:
    - ◆ 3.5-5 volts used, with tens of thousands of amperes of current.
- **Environmental Issues:**
  - Because of the nature of the membrane, and the inert electrodes used, there are very few environmental issues associated with this cell.
  - Issues include the leakage of chlorine gas and NaOH into the environment.
  - Excess brine must not be deposited into waterways, as this will increase the salinity and upset the natural balance.
- NON-SPECIFIC TECHNICALITIES:
  - The location of the plant is a technical consideration that must be in accordance with the availability of the following:
    - Cheap electricity (as this is THE major cost).
    - There must be cheap brine as well as freshwater sources.
    - A local workforce willing to work at suitable expenditure.
    - It must be built away from urban and residential areas, due to the large amounts of noise and heat that the plants emit.
    - Suitable waste disposal must be available.
- *Analyse information from secondary sources to predict and explain the different products of the electrolysis of aqueous and molten sodium chloride:*

- Electrolysis of molten, concentrated solutions and dilute solutions of sodium chloride yields different products.
- The electrolysis products can be predicted using two concepts:
  - The more concentrated an ion, the more likely it will be oxidised or reduced.
  - Certain species are always oxidised or reduced *more readily* than others; by looking at the table of standard reduction potentials, reactions can be predicted.
- **Molten NaCl:**
  - The only ions present in a sample of molten NaCl are  $\text{Na}^+$  and  $\text{Cl}^-$ , and thus they are the only ions that will be oxidised and reduced.
  - Thus, the products will be chlorine gas, and sodium metal.
  - Half-equations:
    - $2\text{Cl}^-_{(l)} \longrightarrow \text{Cl}_{2(g)} + 2e^-$
    - $\text{Na}^+_{(l)} + e^- \longrightarrow \text{Na}_{(s)}$
- **Concentrated NaCl:**
  - This refers to a solution  $\geq 2\text{molL}^{-1}$ .
  - In a solution of concentrated NaCl there are also water molecules present.
  - From the *table of standard reduction potentials*, we see that:
    - Oxidation reactions:
      - ◆ (-1.36 V) :  $2\text{Cl}^-_{(aq)} \longrightarrow \text{Cl}_{2(g)} + 2e^-$
      - ◆ (-1.23 V) :  $2\text{H}_2\text{O}_{(l)} \longrightarrow \text{O}_{2(g)} + 4\text{H}^+_{(aq)} + 4e^-$
    - Reduction reactions:
      - ◆ (-2.71 V) :  $\text{Na}^+_{(aq)} + e^- \longrightarrow \text{Na}_{(s)}$
      - ◆ (-0.83 V) :  $2\text{H}_2\text{O}_{(l)} + 2e^- \longrightarrow \text{H}_{2(g)} + 2\text{OH}^-_{(aq)}$
  - NOTE: *Negative*  $E_0$  values imply that current must be applied for the reaction to occur. A lower  $E_0$  value means the reaction is more likely to occur.
  - As you can see, chloride ions are almost just as likely to be oxidised compared to water molecules; however, due to the high concentration of chloride ions in a concentrated solution, chloride ions are preferentially oxidised at the anode.
  - However, water is much more readily reduced than sodium ions, as can be seen, and hence sodium ions simply migrate to the cathode, but water is reduced.

- Half-equations:
  - $2\text{Cl}^-_{(\text{aq})} \longrightarrow \text{Cl}_{2(\text{g})} + 2\text{e}^-$
  - $2\text{H}_2\text{O}_{(\text{l})} + 2\text{e}^- \longrightarrow \text{H}_{2(\text{g})} + 2\text{OH}^-_{(\text{aq})}$
- Hence, this is the main reaction of the chlor-alkali industry, forming NaOH, hydrogen and chlorine gas.
- **Dilute NaCl:**
  - This refers to a solution  $\leq 0.1\text{molL}^{-1}$ .
  - Referring back to the above data, the products can be predicted.
  - Water is reduced over sodium ions, as above, but ALSO water is oxidised over chloride ions; this is because the concentration of chloride is too low.
  - Hence, the two half-equations are:
    - $2\text{H}_2\text{O}_{(\text{l})} \longrightarrow \text{O}_{2(\text{g})} + 4\text{H}^+_{(\text{aq})} + 4\text{e}^-$
    - $2\text{H}_2\text{O}_{(\text{l})} + 2\text{e}^- \longrightarrow \text{H}_{2(\text{g})} + 2\text{OH}^-_{(\text{aq})}$
  - Doubling the reduction half, and combining the two together, we get:
    - $6\text{H}_2\text{O}_{(\text{l})} \longrightarrow 4\text{H}^+_{(\text{aq})} + 4\text{OH}^-_{(\text{aq})} + 2\text{H}_{2(\text{g})} + \text{O}_{2(\text{g})}$
  - Recognising that  $4\text{H}^+ + 4\text{OH}^- = 4\text{H}_2\text{O}$ , and cancelling them out, we get:
    - $2\text{H}_2\text{O}_{(\text{l})} \longrightarrow 2\text{H}_{2(\text{g})} + \text{O}_{2(\text{g})}$
  - HENCE, the electrolysis of dilute solutions of sodium chloride is simply the electrolysis of water, as only hydrogen and oxygen gas are produced.
- **PRACTICAL** – *Identify data, plan and perform a first-hand investigation to identify the products of the electrolysis of sodium chloride:*

- Using a HOFFMAN apparatus, solutions of *different concentration* of sodium chloride solution were electrolysed and various methods were employed to determine the products the reactions.

- Two solutions were made:
  - **0.01 M** and **2 M** of sodium chloride.
- The two solutions were then electrolysed, using the apparatus, hooked up to a DC power supply at 4V, for 10 minutes each.



– **RESULTS:**

- For the 0.01 M (dilute solution), colourless bubbles were observed on the electrodes very quickly, and gas began to build up in the glass tubes:
  - In the oxidation (+) tube, the gas made a *glowing splint* burn brightly; hence, the gas identified was oxygen.
  - In the reduction (–) tube, the gas burned with a loud *pop*. This identified the gas as hydrogen.
- For the 2 M (concentrated solution), bubbles were also observed instantly, however, the bubbles from the anode were not colourless:
  - In the oxidation tube (+), the gas was observed to have a slight yellow tinge. Also, litmus paper placed in this gas was *bleached* to white. Thus, the gas was identified as being chlorine.
  - In the reduction tube (–), the colourless gas was lit, and made a loud pop. Hence, it was hydrogen gas, as above.
  - *ALSO*, *phenolphthalein* indicator was placed in the solution after reaction, and it turned a vivid pink, indicating a very basic solution. This indicated (but did not prove) the presence of NaOH in the solution.
- Hence, electrolysis of DILUTE solution forms *oxygen* and *hydrogen*, while electrolysis of CONCENTRATED solution forms *chlorine*, *hydrogen* and *sodium hydroxide*.

– **JUSTIFY:**

- The electrolysis of MOLTEN sodium chloride would have been most appropriate, however the conditions required are hard to attain in the school laboratory.
- A Hoffman apparatus was used, as it contained the reaction very well, as well as contained harmful gases, such as chlorine.
- The concentration used were chosen as they were hypothesised to produce different products, and the voltages used were correct.
- Appropriate identification methods were used.



## 5. Saponification is an important organic industrial process:

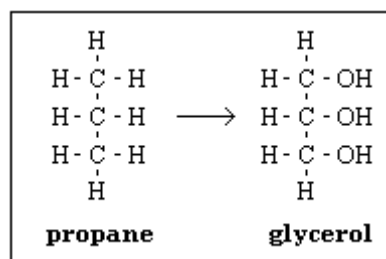
### • **RECALL:**

- Esterification is the reaction that occurs between a *carboxyl group* (-COOH) and a *hydroxyl group* (-OH), forming an *ester bond* (-COOC-) and *water*.
- **Esters** are any compounds that contain the *ester bond*.

### • Describe saponification as the conversion in basic solution of fats and oils to glycerol and salts of fatty acids:

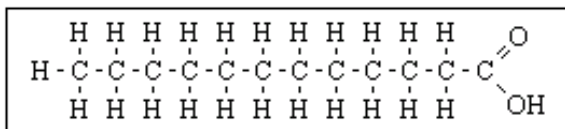
#### - **Glycerol:**

- GLYCEROL is a tri-alcohol compound derived from propane; it contains an alcohol group (a *hydroxyl*) on every carbon.
- Using IUPAC nomenclature, another name for *glycerol* is 1,2,3-propanetriol.

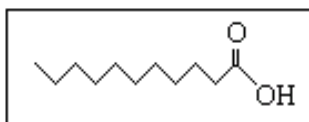


#### - **Fatty Acids:**

- FATTY ACIDS are simply long *carboxylic acids* that occur in fats and oils.
- There are many types of fatty acids, which vary in the number of carbons (which commonly range from about 12-18 carbons), as well as in the degree of *saturation* (that is, whether or not there are double bonds in the chain).
- **EG: Lauric Acid (12-C):**
  - Molecular Formula:
    - ◆  $\text{CH}_3-(\text{CH}_2)_{10}-\text{COOH}$
  - Structural Formula:



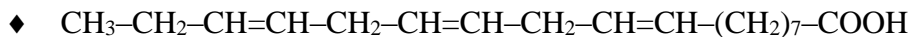
- Simplified Structural Formula:



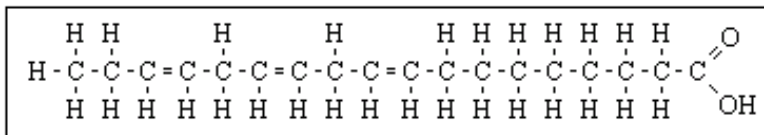
- ◆ **NOTE:** For the simplified diagram, assume there is a carbon at every corner; hydrogens are omitted, other functional groups are shown.

- **EG: *Linolenic Acid* (18-C):**

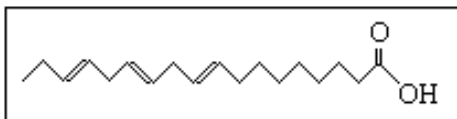
- Molecular Formula:



- Structural Formula:



- Simplified Structural Formula:



– **Fats and Oils:**

- *Fats and oils* are a type of organic compound known as TRIGLYCERIDES:

- At room temperature, *fats* are solid, while *oils* are liquid.

- A triglyceride is a compound in which all 3 *hydroxyl* groups of a glycerol molecule have been ESTERIFIED with *carboxyl* groups from three fatty acid chains; water is a by-product.

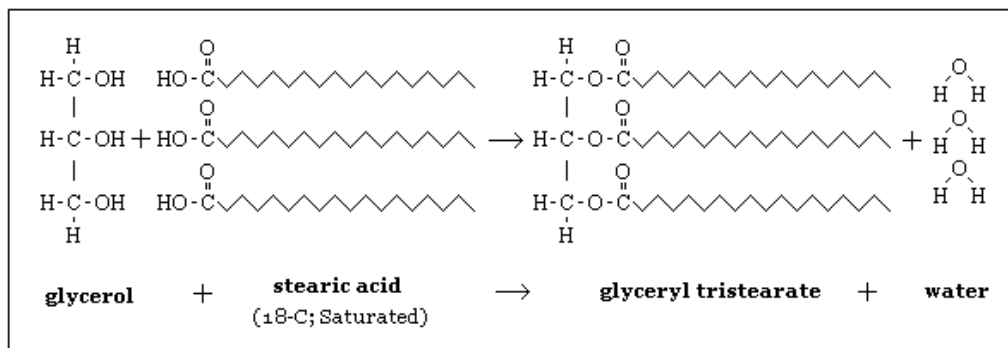
- Three ester bonds are formed; triglycerides are tri-esters.

- **EG: *Glyceryl Tristearate*:**

- NOTE: When naming triglycerides; the glycerol is changed to glyceryl, and the acid is changed from “-ic” to “-ate”, and the prefix “tri-” is added.

- Hence, by applying these rules, we can deduce that this fat was formed by the reaction of glycerol with 3 chains of *stearic acid*.

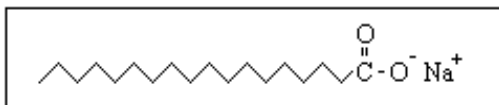
- 3 water molecules are also formed.



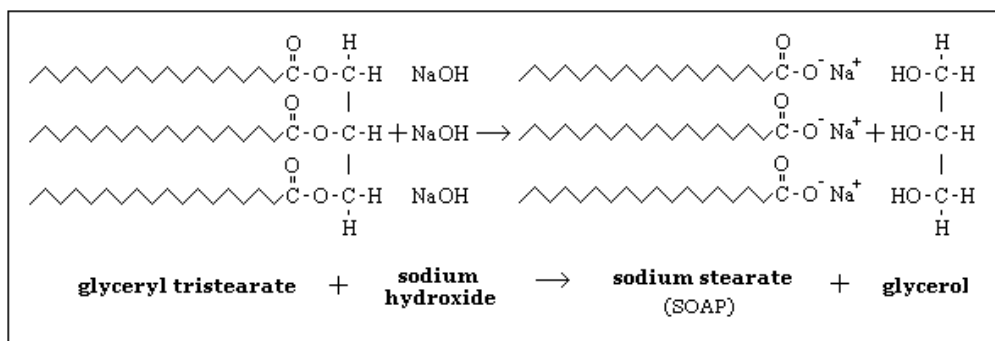
- Hence, the natural formation of fats and oils is an esterification reaction.

– SAPONIFICATION:

- **Saponification** is the reversal of the process that forms *fats* and *oils*.
- It is defined as the conversion, in *basic* solution, of fats and oils into *glycerol* and the *salts of fatty acids*.
- NaOH and KOH solutions are commonly used.
- Salts of fatty acids, such as sodium stearate, are SOAPS.
- Hence saponification is the process of chemically producing soaps.
- **EG:** *Forming sodium stearate*;  $(\text{CH}_3-(\text{CH}_2)_{16}-\text{COO}-\text{Na})$ :



- Sodium stearate is the most common ingredient of soaps used in personal hygiene; it is produced by saponifying the fat *glyceryl tristearate*.



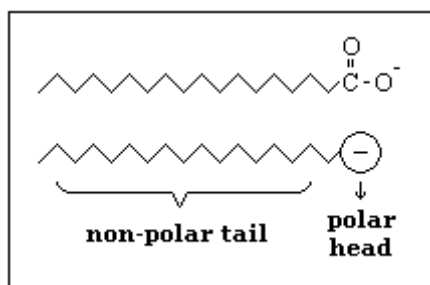
- The sodium hydroxide (NaOH) *splits* the triglyceride (*hydrolysis*) along the ester bond ( $-\text{COOC}-$ ):
    - ◆ The 3 *hydroxyl* groups ( $\text{OH}^-$ ) attach to the glyceryl, forming glycerol.
  - The fatty acids (carboxylate ions) react with the  $\text{Na}^+$  ions, forming the 3 “salts of fatty acids” (in this case sodium stearate).
- *Describe the conditions under which saponification can be performed in the school laboratory and compare these with the industrial preparation of soap:*

– **School Laboratory Saponification:**

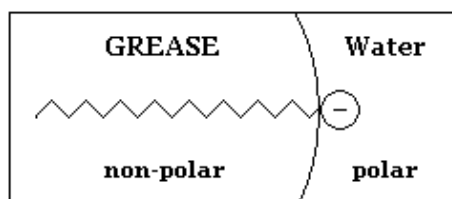
- In a glass beaker, a very pure fat or oil (such as *olive oil* or lard) is mixed with an *excess* of sodium hydroxide solution.
- This mixture is gently heated using a Bunsen burner.

- The soap curds are salted-out using excess saturated sodium chloride solution:
  - Note that the fatty acids are partially soluble.
  - By greatly increasing the concentration of ions in the solution (using large amounts of NaCl), the salts of the fatty acids (i.e. *soap*) are encouraged to precipitate and form the layer of soap curds.
- The soap is then *washed* with water, and the aqueous solution is discarded.
- A paper towel is used to partially dry the soap.
- There is no attempt made to recover the glycerol, perfume, colour or shape the soap, and there is possibly large wastage of reagents (as sodium hydroxide and sodium chloride were used in excess).
- **Industrial Saponification:**
  - The starting fat or oil used in industry is very far from pure; waste fats from butcher shops and abattoirs are collected and used.
  - The fat/oil is cleaned to a standard level, and then mixed with a carefully measured amount of sodium hydroxide; expensive reagents are carefully used in industrial processes, to lower costs.
  - The saponification occurs in “kettles” (large steel containers) in batches, under high pressure and high temperature.
  - After the soap is salted out, it is separated from the solution and dried.
  - Perfume and colours are added, and it is then shaped and packaged.
  - The residue aqueous solution is not discarded; glycerol is distilled out of it and sold as a useful product. Excess NaCl is reused.
- *Account for the cleansing action of soap by describing its structure:*
  - **RECALL** that like *dissolves* like:
    - Polar substances dissolve in other polar substances.
    - Non-polar substances dissolve in other non-polar substances.
  - Water is polar, while grease and dirt are non-polar; they do not mix (dissolve):
  - The *force* that keeps two immiscible (non-mixing) liquids separated from each other (such as water and oil) is called INTERFACIAL TENSION.
  - A **surfactant** (surface acting agent) is a chemical “wetting-agent” that lowers the *interfacial tension* between two liquids, and hence, allows them to mix.

- SOAP is a surfactant; it allows polar *water* and non-polar *grease/dirt* to mix.
- Its chemical property as a surfactant is a result of its structure.
- **Structure of Soap:**
  - Soap is the salt of a fatty acid (e.g. *sodium stearate*)
  - In solution, soap disassociates into its positive cation (such as  $\text{Na}^+$ ), and its negative fatty-acid chain.
  - The surfactant (cleansing) property of soap is caused **ONLY** by the structure of the negatively charged fatty-acid chain; the cation has no effect:

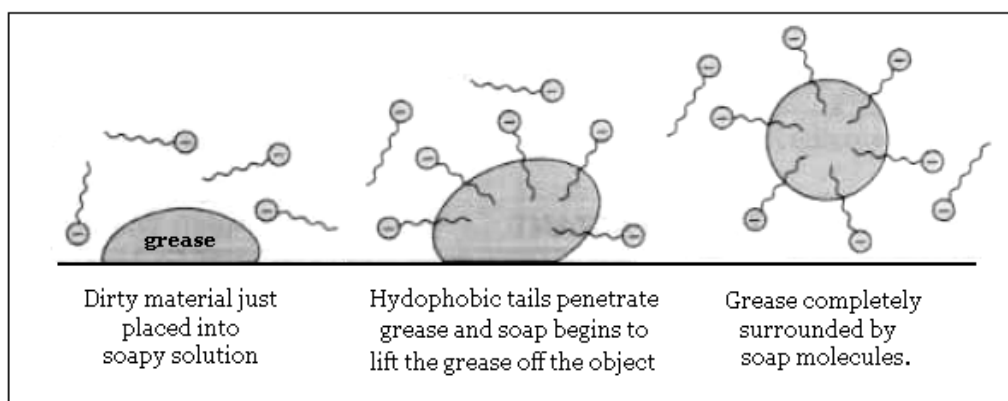


- As you can see, the fatty acid chain is made up of a negatively-charged polar head, and an uncharged, non-polar tail:
  - The head is said to be **HYDROPHILIC** (water-loving), as it is able to dissolve into water (i.e. form hydrogen bonds with water).
  - The tail is said to be **HYDROPHOBIC** (water-hating), as the non-polar tail does not dissolve into water (i.e. dissolves in grease).



- **Cleansing Action of Soap:**
  - Soap cleans and removes grease/dirt from objects by the following steps:
    1. A dirty object is placed in soapy water.
    2. The soap immediately begins to attach to the grease (the hydrophobic tails penetrate the grease **BUT** the hydrophilic head remains in the water).
    3. The grease is lifted off the object as the soap surrounds the grease.
    4. The grease is completely lifted off the object, and is surrounded by soap.

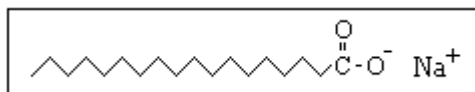
- The grease molecule is completely encased within a sheath of soap molecules with their hydrophilic heads in contact with water, while the hydrophobic tails contain the grease molecule; this sheath allows it to dissolve in water.
- As the mixture is agitated, more grease is lifted off the surface of the dirty object, and more grease/soap particles are formed.
- The grease/soap particles are negatively charged (due to the negative head of the soap), and hence they repel each other, preventing the grease from clumping back together.
- These water soluble particles are then simply washed off with water:



- Hence, the structure of soap accounts for its cleaning (surfactant) properties.
- *Explain that soap, water and oil together form an emulsion with soap acting as an emulsifier:*
  - An **emulsion** is a *stable* mixture of 2 immiscible liquids, with tiny droplets of one liquid evenly dispersed throughout the other.
  - Normally, mixtures of 2 immiscible liquids rapidly separate (such as oil and water); emulsions are stabilised by the action of **EMULSIFIERS**:
    - Emulsifiers are the same as surfactants.
    - They reduce the *interfacial tension* to allow immiscible liquids to mix.
  - In the example of a water/oil emulsion, the emulsifier used is soap; hence a soapy oil/water mixture consists of oil particles evenly dispersed throughout the water.
  - In this case, there is more water than oil, and hence the oil is dispersed throughout the water; if there was more oil than water, the water would be dispersed throughout the oil, as is the case with *butter*.

- *Distinguish between soaps and synthetic detergents in terms of:*
  - *the structure of the molecule*
  - *chemical composition*
  - *effect in hard water*
- As stated above, soaps are salts of fatty acids; soap is a *natural* surfactant.
- *Synthetic* surfactants are called **detergents**.
- There are three types of detergents: ANIONIC, CATIONIC and NON-IONIC.
- Soaps and detergents have different structures and properties.
- Recall: *Hard water* is water that has high levels of  $Mg^{2+}$  and  $Ca^{2+}$  ions.
- **Soap:**

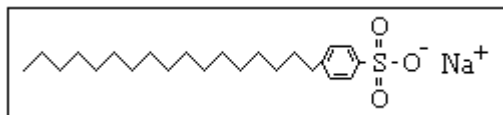
- **STRUCTURE:**



- The cation (i.e.  $Na^+$ ) has no effect on the cleaning action of soap, and so we mainly consider the structure of the fatty acid ion.
- It is made of a hydrophilic head connected to a long hydrophobic tail.
- **CHEMICAL COMPOSITION:**
  - Soap is the salt (usually the sodium or potassium salt) of a fatty acid.
  - Most soaps are *sodium stearate*.
  - It is a hydrocarbon molecule (consists only of H, C and O).
  - The *head* is a carboxylate anion ( $-COO^-$ ), which is negatively charged.
  - The *tail* is a long uncharged hydrocarbon chain.
- **EFFECT IN HARDWATER:**
  - Soap (*sodium stearate*) does not function well in hard-water.
  - When soap is used in hard water, the stearate ion reacts with the high levels of  $Mg^{2+}$  and  $Ca^{2+}$  ions, forming magnesium and calcium stearates.
  - These molecules are not water soluble; they form precipitates.
  - These precipitates occur as a greyish '*soap scum*'.
  - Soap-scum stains ceramic sinks, baths as well as clothes; also, as it removes stearates from the water, it reduces the effectiveness of the soap.

– **Anionic Detergents:**

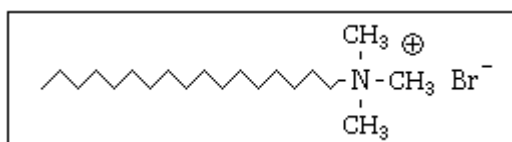
▪ **STRUCTURE:**



- These detergents are called ‘anionic’ because the actual surfactant ion (everything except the  $\text{Na}^+$ ) has a *negative* charge.
- The structure is similar to soap; the surfactant ion consists of a long hydrocarbon tail connection to an anionic head.
- However, the structure and chemical composition of the head is different.
- **CHEMICAL COMPOSITION:**
  - Anionic detergents are mostly the salts of *alkyl benzene sulfonates*.
  - That is, they consist of a hydrocarbon tail (*alkyl* group) connected to a benzene ring, bonded to a ‘sulfonate’ group ( $-\text{SO}_3^-$ ).
  - The sulfonate group is polar, and hence, hydrophilic.
- **EFFECT IN HARDWATER:**
  - The efficiency of anionic detergents is decreased to a very slight extent by hard-water, but not nearly as great as for soap.
  - This is not due to the formation of insoluble precipitates, but rather because the surfactant anions form ‘soluble complexes’ with  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ . This reduces the amount of available surfactant.
  - However, anionic detergents are still very effectively cleaning agents, even in high-ion hard water.

– **Cationic Detergents:**

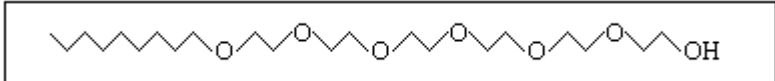
▪ **STRUCTURE:**



- Called ‘cationic’ because the surfactant ion has a net positive charge (as opposed to the negative charge of soap and anionic detergents)
- Like most surfactants, they consists of a hydrophobic, hydrocarbon tail connected to a charged, hydrophilic head.



- CHEMICAL COMPOSITION:
  - These detergents are mainly *halide* salts of *quaternary ammonium cations*.
  - Quaternary ammonium cations are ammonium ( $\text{NH}_4^+$ ) derivatives; that is, the four hydrogens (hence *quaternary*) of an ammonium ion have been replaced by alkyl groups; usually, 3 hydrogens are replaced by methyl groups, and one hydrogen is replaced by a long hydrocarbon chain.
  - Ammonium cations have a permanent positive charge; they are neutralised by halogens (e.g.  $\text{Cl}^-$  or  $\text{Br}^-$ ), and hence are halide salts.
- EFFECT IN HARDWATER:
  - Cationic detergents do not react with the cations in hard-water.
  - Hence, they are completely effective even in hard-water.
- **Non-Ionic Detergents:**
  - STRUCTURE:
 



    - Unlike ionic detergents, non-ionic detergents have no distinct head or tail and do not ionise in water.
    - They consist of a long hydrocarbon chain, connected to another hydrocarbon chain containing oxygen atoms, ending in a hydroxyl group.
  - CHEMICAL COMPOSITION:
    - Non-ionic surfactants are also called *ethoxylates*, because they are formed by joining together many 'ethoxy' groups ( $-\text{CH}_2-\text{CH}_2-\text{O}-$ ).
    - The presence of oxygen makes certain sections of the molecule polar (i.e. hydrophilic); the oxygen atoms form hydrogen bonds with water, while the non-polar tail bonds to the grease.
    - The detergent molecules then surround the grease molecule, similar to the way ionic detergents surround grease.
  - EFFECT IN HARDWATER:
    - Non-ionic detergents do not react at all with ions in the water
    - Hence they are completely unaffected by hard-water.

- *Distinguish between anionic, cationic and non-ionic detergents in terms of chemical composition and uses:*
  - See ABOVE for in-depth coverage of the different types of detergents.
  - Uses:
    - **Anionic Detergents:**
      - These detergents are much more efficient cleaning agents than soap.
      - They are also able to generate large amounts of foam.
      - Anionic detergents are the most common cleaning agents; used in liquid and powder laundry detergents, hand-soaps, shampoo, toothpaste, etc.
    - **Cationic Detergents:**
      - These detergents are a much smaller group than anionic detergents.
      - They are used in fabric softeners, as they bond to the negative fabric fibres leaving a soft, smooth feel, as well as in hair conditioners, where the positive heads attach to the negative hair scales, and the alkyl tail sticks out, leaving a smooth, waxy feel and shiny appearance.
      - The ammonium group is also slightly disinfecting, and so cationic detergents are used in antiseptics, disinfectants and biocides.
    - **Non-Ionic Detergents:**
      - These detergents clean effectively but produce very little foam.
      - Hence they are used in applications such as front-loading washing machines and dishwashers, where excess foam would cause over-flowing.
      - Their main use, however, is as an emulsifying agent in paints, adhesives, pesticides and cosmetics (e.g. lipstick stabilizers).
- *Gather, process and present information from secondary sources to identify a range of fats and oils used for soap-making:*
  - **Tallow**; processed animal-fats (usually waste). It produces common soap.
  - **Coconut Oil**; pressed out of dried coconuts (copra); it is a relatively pure oil. This produces a hard soap that lathers very well.
  - **Shea Butter**; the fat derived from the fruit (or nut) or the Shea tree. It produces a soft soap that is very moisturising and gentle on skin.

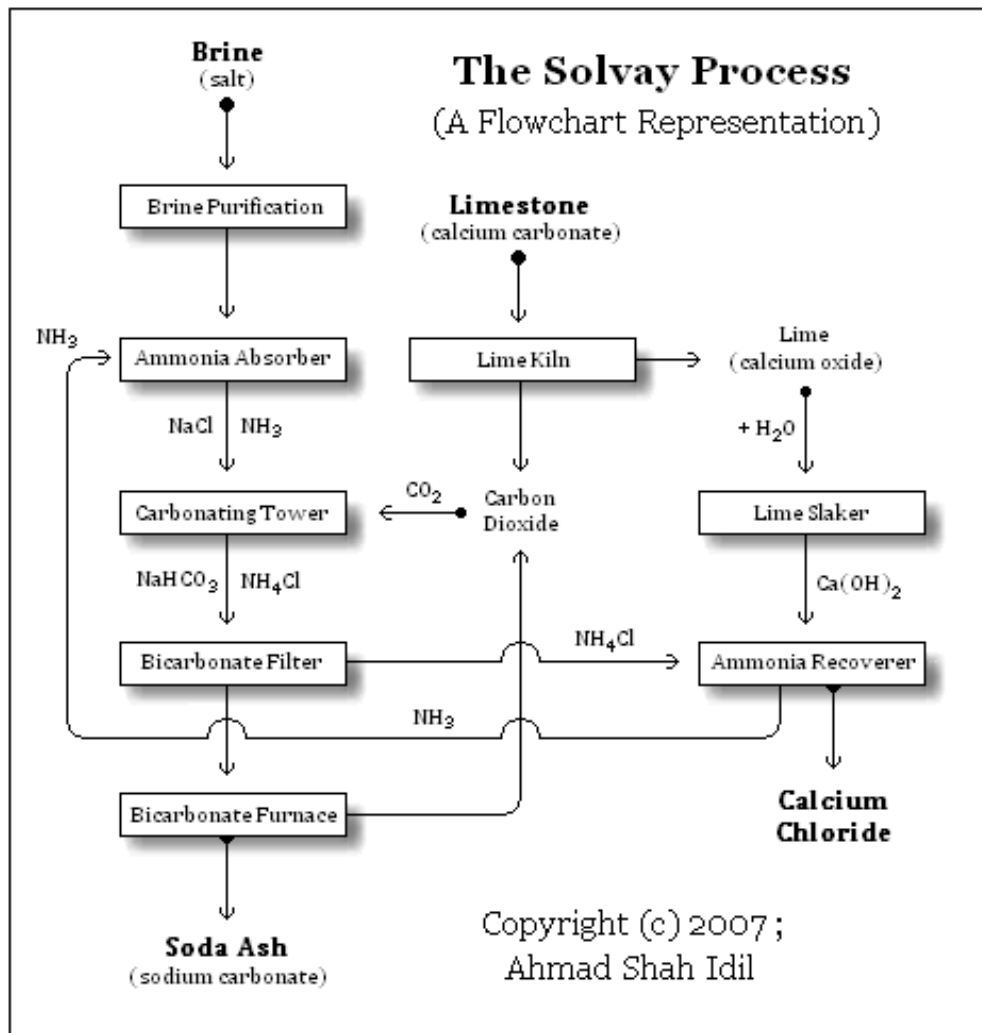
- *Solve problems and use available evidence to discuss, using examples, the environmental impacts of the use of soaps and detergents:*
  - **Biodegradability:**
    - *Soap* has very little environmental impact because it is very easily broken down into carbon dioxide and water due to the action of bacteria.
    - There are two types of *anionic* detergents: detergents with branched chains, and detergents with unbranched (*linear*) chains:
    - *Branched-chain anionic detergents* were the first detergents formed. They were *not* biodegradable, and led to considerable environmental problems:
      - Detergent built up in waterways, and rivers and dams were constantly covered in layers of foam.
      - It was aesthetically and environmentally unwanted.
      - The foam reduced sunlight entering the water, affecting the photosynthesis of water plants. This led to a drop in dissolved oxygen levels.
    - The *linear detergents* were then created; these are much more biodegradable than the branched detergents and solved the foam problem.
  - **Excess Levels of Phosphates:**
    - *Soaps* do not contain any phosphates (or only trace amounts).
    - As stated above, anionic detergent are affected slightly by the presence of  $Mg^{2+}$  and  $Ca^{2+}$  ions in hard-water.
    - Substances called '*builders*' are added to detergents to increase their efficiency; builders (such as *sodium tripolyphosphate*:  $Na_5P_3O_{10}$ ) react with the ions in hard-water, softening the water. Builders also increase the alkalinity of the water, which increases the detergents cleaning power.
    - However, the increasing level of phosphates in waterways as a result of phosphate builders is a major environmental problem.
    - Excess phosphates in waterways lead to eutrophication and algal blooms.
    - These are a major environmental concern, as this will lead to the depletion of oxygen in the system.
    - This causes severe degradation of water quality, the promotion of anaerobic conditions and the disturbance of a natural ecosystem.

- **PRACTICAL** – *Plan and perform a first-hand investigation to carry out saponification and test the product:*
  - This saponification was performed in a 250 mL beaker.
  - 30 mL of 6 mol/L NaOH solution was placed in the beaker.
  - 10 mL of olive oil was added to the beaker.
  - Boiling chips were added, and the mixture heated with a Bunsen burner.
  - The mixture was boiled, while stirring, until the oil layer disappeared.
  - The mixture was cooled, and then 40 mL of saturated NaCl solution was added.
  - The beaker was cooled in a water bath, and then the mixture was filtered using muslin cloth. The residue was washed with water, and then collected and dried.
  - **RESULTS:**
    - An off-white spongy mass of soap was collected.
  - **SAFETY:**
    - Safety glasses, gloves and lab-coats must be used, as dangerous concentrated sodium hydroxide is used. The mixture may spit during boiling.
    - Boiling chips were used to encourage gentle heating.
    - The soap was washed to remove any traces of corrosive NaOH.
  - **JUSTIFY:**
    - Saponification was done in a beaker rather than a reflux apparatus as none of the reactants were volatile.
    - Olive oil was used because it is a cheap and pure oil.
- **PRACTICAL** – *Perform a first-hand investigation to demonstrate the effect of soap as an emulsifier:*
  - Vegetable oil, water and the soap produced from the ABOVE practical were used.
  - First 50 mL water and 20 mL oil were placed in a beaker and mixed vigorously.
  - The two liquids rapidly separated into 2 distinct layers; they were immiscible.
  - Then, the soap mass was broken into small pieces and added to the mixture.
  - It was again mixed vigorously; however, this time, the layers did not separate, but formed a cloudy ‘emulsion’.
  - Hence soap acted as an emulsifier, and emulsified the 2 liquids.

- **PRACTICAL** – *Perform a first-hand investigation to gather information and describe the properties of a named emulsion and relate these properties to its uses:*
  - **Mayonnaise:**
    - Mayonnaise is an emulsion of vegetable oil and egg yolks, with the emulsifier being the lecithin found naturally in the egg yolk.
    - Other additions may be made for flavour, such as vinegar, mustard or salt, but the basic composition of mayonnaise is oil and egg yolks.
    - Mayonnaise is made by slowly adding oil to an egg yolk, while whisking vigorously to disperse the oil; the lecithin stabilises the mixture.
  - **Properties in Relation to Uses:**
    - Mayonnaise is a very STABLE emulsion, due to the strong emulsifying properties of lecithin. It does not separate into its component liquids even when stored for long periods of time.
      - This property is useful as it is a food product; it needs to stay in an edible condition, in storage, for relatively long periods of time.
    - Mayonnaise also has the property of having a creamy ‘mouth-feel’, and not feeling oily. Most people find the sensation of eating pure oil unpleasant, but find the creamy taste of mayonnaise enjoyable. However, mayonnaise is actually on average 75% oil. The property of the emulsion as having a creamy texture adds to its use as a food.

## 6. The Solvay process has been in use since the 1860s:

- *Identify the raw materials used in the Solvay process and name the products:*
  - The SOLVAY PROCESS is the major chemical industrial process used to synthesise sodium carbonate ( $\text{Na}_2\text{CO}_3$ ).
  - **Raw Materials:**
    - *Limestone* (calcium carbonate;  $\text{CaCO}_3$ ).
    - *Brine* (saturated sodium chloride solution;  $\text{NaCl}$ ).
    - *Ammonia* ( $\text{NH}_3$ ).
  - **Products:**
    - *Soda Ash* (sodium carbonate;  $\text{Na}_2\text{CO}_3$ ).
    - *Calcium chloride* ( $\text{CaCl}_2$ ).
- *Describe the uses of sodium carbonate:*
  - The *main* use of sodium carbonate is in the manufacture of *glass*. About 50% of the total production of  $\text{Na}_2\text{CO}_3$  is used to produce for this purpose:
    - Sand (silicon dioxide), soda ash (sodium carbonate) and limestone (calcium carbonate) are heated together, at extremely high temperatures.
    - They are melted together, and then cooled rapidly to form glass.
  - Many other uses of  $\text{Na}_2\text{CO}_3$  stem from its property of being a base; it creates alkaline solutions when dissolved in water:
    - It is used as a cheap alkali in neutralising excess acids from chemical labs.
    - It is sometimes used as an alternative base in saponification (instead of  $\text{NaOH}$ ).
  - Sodium carbonate is also used to soften hard-water, as it precipitates  $\text{Ca}^{2+}$  ions out of solution, forming insoluble calcium carbonate ( $\text{CaCO}_3$ ).
  - It is also used to bleach paper, make pigments, as well as pharmaceuticals.
- *Identify, given a flow chart, the sequence of steps used in the Solvay process and describe the chemistry involved in:*
  - *brine purification*
  - *hydrogen carbonate formation*
  - *formation of sodium carbonate*
  - *ammonia recovery*

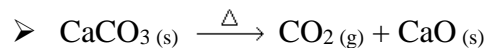


– **BRINE PURIFICATION:**

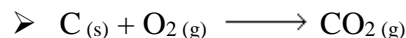
- The first step in the process is gathering raw materials.
- Limestone ( $\text{CaCO}_3$ ) is mined as a relatively pure mineral.
- However, brine must be concentrated and purified.
- Firstly,  $\text{NaCl}$  solution is sourced from *seawater* (or underground brine-wells), and using solar evaporation ponds, the concentration is increased to 30%.
- The brine is then purified to remove  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions; sodium carbonate and sodium hydroxide are added to precipitate out insoluble calcium carbonate ( $\text{CaCO}_3$ ) and magnesium hydroxide ( $\text{Mg}(\text{OH})_2$ ):
  - $\text{Ca}^{2+}_{(\text{aq})} + \text{CO}_3^{2-}_{(\text{aq})} \longrightarrow \text{CaCO}_3(\text{s})$
  - $\text{Mg}^{2+}_{(\text{aq})} + \text{OH}^{-}_{(\text{aq})} \longrightarrow \text{Mg}(\text{OH})_2(\text{s})$
- A **floculant** is added and the precipitates are skimmed off the brine.

– HYDROGEN CARBONATE FORMATION:

- *Carbon dioxide* is formed by the thermal decomposition of calcium carbonate in the **lime kiln**, leaving *calcium oxide* as a by-product:



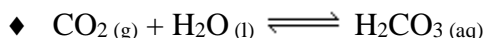
- Also, *coke* (carbon) is present in the kiln, which combusts exothermically to produce more heat, as well as provides more carbon dioxide:



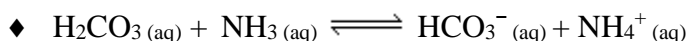
- Then, in the **ammonia absorber** (or *ammonia saturator*), the brine solution is saturated with ammonia ( $\text{NH}_3$ ).
- This ammonia/brine solution is fed into the **carbonating tower**, where it is cooled to about  $0^\circ\text{C}$ .

- Carbon dioxide (from the above reactions) is bubbled into this solution, and through a series of reversible reactions, sodium hydrogen carbonate is formed:

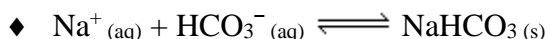
- Firstly, the *carbon dioxide* reacts with water, forming *carbonic acid*:



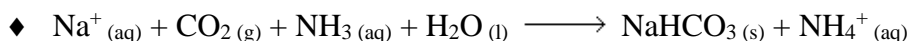
- This weak acid then reacts with the weak base *ammonia*, forming the *hydrogen carbonate* ion, and *ammonium*:



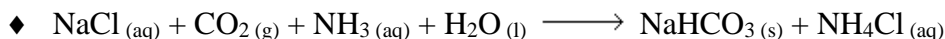
- The *sodium* ion then reacts with the hydrogen carbonate ion, and this forms a precipitate that is very insoluble at low temperatures; this is why the solution is cooled to about  $0^\circ\text{C}$ :



- Hence, the overall ionic equation that occurs in the *carbonator tower* is:

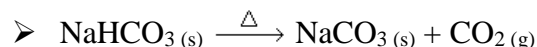


- Adding in the *chloride* spectator ion ( $\text{Cl}^-$ ) gives you the complete equation:



– FORMATION OF SODIUM CARBONATE:

- The solution leaving the *carbonator* is filtered and the  $\text{NaHCO}_3$  collected.
- The sodium hydrogen carbonate is then taken to a **furnace** and finally converted into *sodium carbonate* by heating; the  $\text{CO}_2$  formed is recycled:





- **AMMONIA RECOVERY:**
  - *Ammonia* is considered to be a catalyst of the Solvay Process because it is not consumed in the reaction, but allows the reaction to proceed.
  - It is also the most expensive reagent, and hence efficient recycling is exercised.
  - The **lime** waste (calcium oxide; CaO) from the lime kiln is ‘slaked’ (reacted with water) to form **slaked lime** (calcium hydroxide; Ca(OH)<sub>2</sub>):
    - $\text{CaO}_{(s)} + \text{H}_2\text{O}_{(l)} \longrightarrow \text{Ca(OH)}_{2(aq)}$
  - The residue solution from the bicarbonate filter is an *ammonium chloride* solution; this is reacted with the calcium hydroxide, reclaiming the *ammonia*:
    - $\text{NH}_4\text{Cl}_{(aq)} + \text{Ca(OH)}_{2(aq)} \longrightarrow \text{CaCl}_{2(aq)} + \text{NH}_3(aq) + \text{H}_2\text{O}_{(l)}$
  - The ammonia is recycled back to the ammonia absorber, the water joins the solution, and the only waste produced is the calcium chloride.
- **Overall:**
  - Adding up all the above equations, the Solvay Process can be summarised as:
    - $2\text{NaCl}_{(aq)} + \text{CaCO}_3(s) \longrightarrow \text{Na}_2\text{CO}_3(s) + \text{CaCl}_{2(aq)}$
- *Discuss environmental issues associated with the Solvay process and explain how these issues are addressed:*
  - **Disposal of Calcium Chloride:**
    - Vast amounts of waste calcium chloride are produced by operating Solvay Plants around the world.
    - Although a small portion of calcium chloride is useful, such as in de-icing roads, as a concrete additive, and as a drying agent, most of it is useless.
    - The disposal of CaCl<sub>2</sub> into waterways poses a significant environmental issue.
    - If it is disposed into oceans, with suitable dilution, it poses little risk; however, disposal into rivers and lakes because the increase in chloride ions would be extremely detrimental to freshwater life.
    - In some cases, the solutions are evaporated to dryness, and the minerals buried underground; it is suitable, but very expensive.
  - **Thermal Pollution:**
    - Some of the reactions produce large amounts of heat; water is used as a coolant for these reactions.

- This heated water cannot be directly released back into the waterways it was taken from, as this would cause significant thermal pollution.
- Hence, the water is cooled in cooling tanks, and then discharged.
- **Ammonia Leakages:**
  - Despite the efficient ammonia recycling process, small amounts are released into the environment; ammonia is an air pollutant, particularly if discharged around urban areas.
  - Careful design and monitoring of Solvay Plants greatly reduces this problem.
- *Process information to solve problems and qualitatively analyse the relative quantities of reactants and products in each step of the process:*
  - **EG:** What masses of limestone (88.7% CaCO<sub>3</sub>) and brine (30.9% NaCl) are needed to produce a tonne of SODIUM CARBONATE?
    - Firstly, we state the chemical equation to determine the reaction ratios:
      - $2\text{NaCl}_{(aq)} + \text{CaCO}_{3(s)} \longrightarrow \text{Na}_2\text{CO}_{3(s)} + \text{CaCl}_{2(aq)}$
    - Finding the molar mass of sodium carbonate:
 
$$\begin{aligned} \text{molar mass (Na}_2\text{CO}_3) &= 2(22.99) + (12.01) + 3(16.0) \\ &= 106.0 \text{ g/mol} \end{aligned}$$
    - Finding the number of moles of Na<sub>2</sub>CO<sub>3</sub> in tonne:
 
$$\begin{aligned} \text{moles (Na}_2\text{CO}_3) &= \text{mass} / \text{molar mass} \\ &= (1000000) / (106.0) \\ &= 9433.96 \end{aligned}$$
    - Finding the mass of **limestone** used:
 
$$\begin{aligned} \text{moles (CaCO}_3) &= \text{moles (Na}_2\text{CO}_3) \text{ ; reaction ratio of 1:1} \\ &= 9433.96 \\ \text{molar mass (CaCO}_3) &= (40.1) + (12.0) + 3(16.0) \\ &= 100.1 \text{ g/mol} \\ \text{mass (CaCO}_3) &= \text{moles} \times \text{molar mass} \\ &= 9433.96 \times 100.1 \\ &= 944339.40 \text{ g} \end{aligned}$$
      - BUT limestone is 88.7% CaCO<sub>3</sub>. Hence, the mass of limestone is:
 
$$\text{mass (limestone)} = 944339.40 / 88.7 \times 100 = \mathbf{1.06 \text{ tonnes \#}}$$

- Similarly, finding the mass of **brine** used:

$$\begin{aligned} \text{moles (NaCl)} &= 2 \times \text{moles (Na}_2\text{CO}_3) \text{ ; reaction ratio of 2:1} \\ &= 2 \times 9433.96 \\ &= 18867.92 \end{aligned}$$

$$\begin{aligned} \text{molar mass (NaCl)} &= (23.0) + (35.5) \\ &= 58.5 \text{ g/mol} \end{aligned}$$

$$\begin{aligned} \text{mass (NaCl)} &= \text{moles} \times \text{molar mass} \\ &= 18867.92 \times 58.5 \\ &= 1103773.32 \text{ g} \end{aligned}$$

- BUT *brine* is 30.9% NaCl. Hence, the mass of brine is:

$$\text{mass (brine)} = 11.3773.32 / 30.9 \times 100 = \mathbf{3.57 \text{ tonnes \#}}$$

- *Use available evidence to determine the criteria used to locate a chemical industry using the Solvay process as an example:*
  - The criteria for selecting a **location** for an industrial plant are:
    - *Availability of raw materials*; in the case of Solvay Process, this might mean building the plant close to either the sea (for brine) or a limestone quarry.
    - *Availability of sufficient energy at competitive prices*; this is not so much an issue for the Solvay Process (as compared to electrochemical processes), as stages where energy input is required are just the furnaces.
    - *Locations of markets for the product*; sodium carbonate has a universal market, as it is a much in demand product. Transportation of product easy.
    - *Suitable sites for waste disposal*; this is a MAJOR consideration when finding a location of Solvay plants, as vast amounts of calcium chloride are made.
    - *Availability of a workforce at reasonable cost.*
- **PRACTICAL** – *Perform a first-hand investigation to assess risk factors and then carry out a chemical step involved in the Solvay process, identifying any difficulties associated with the laboratory modelling of the step:*
  - The chemical steps of the Solvay Process modelled in this practical were the ammonia saturator and the carbonating tower.
  - Various techniques were used to safely model the two industrial steps.

- **Ammonia Saturator:**
  - To model this step, 10 mL of concentrated *ammonia* solution (30%) was mixed with 10 mL of brine (saturated *sodium chloride* solution).
  - 10g of *ammonium chloride* crystals were dissolved into the solution, and then more continuously added until no more would dissolve.
  - The clear solution was then *decanted* into a conical flask.
  - RISK FACTORS:
    - *Ammonia* is highly toxic. It was handled in the fume cupboard.
  - DIFFICULTIES:
    - A higher concentration of ammonia is used in the Solvay Process.
    - This is hard to attain in the school laboratory (and unsafe), so instead, ammonium crystals were used to facilitate the carbonation.
- **Carbonating Tower:**
  - 15g of *dry ice* was placed into the conical flask, and it was allowed to melt.
  - After about 15 minutes of bubbling ( $\text{CO}_2$ ) a precipitate began to form.
  - This precipitate was identified as *sodium hydrogen carbonate*.
  - RISK FACTORS:
    - *Dry ice* is extremely cold and can cause frostbite. Handle with tongs.
  - DIFFICULTIES:
    - $\text{CO}_2$  is produced by calcium carbonate decomposition in the Solvay Process, but this method is not suitable in the lab; the high temperatures would make it unsafe, and collecting the  $\text{CO}_2$  would be difficult.
    - Instead, dry ice is used as a concentrated form of  $\text{CO}_2$ .