Chem Factsheet

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The Solvay Process - Manufacturing Sodium Carbonate

At the height of *The Industrial Revolution, 1760-1840*, there was an increasing demand for sodium carbonate. This was, and still is, used in large quantities in the manufacture of soaps and glass. An industrial process was required to convert sodium chloride (common salt) into sodium carbonate to meet these changing social and economic demands. At the end of the eighteenth century, a Frenchmen, Nicolas Leblanc, invented the Leblanc process where sodium chloride was reacted with concentrated sulphuric acid to produce sodium sulphate and hydrogen chloride.

$$2\ NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2HCl$$

The sodium sulphate was then treated with calcium carbonate (limestone) and coal to produce a mixture containing sodium carbonate.

$$Na_2SO_4 + 2C \rightarrow Na_2S + 2CO_2$$

$$\text{then } Na_2S + CaCO_3 \rightarrow Na_2CO_3 + CaS$$

This process remained popular throughout the nineteenth century but was very energy intensive, produced considerable environmental pollution and had a very poor atom economy and % yield.

The Leblanc process was superseded by the ammonia-soda process. This is also known as the Solvay process, after Ernest Solvay who developed the process in the 1860s. It is this process that still continues to produce the majority of the world's supply of sodium carbonate.

The principle resources required for the Solvay process are: salt brine (a source of sodium chloride) and limestone (a source for calcium carbonate).

The industrial process involves four chemical reactions, which can be summarised by the following overall reaction:

$$2NaCl + CaCO_3 \rightarrow Na_2CO_3 + CaCl_2$$

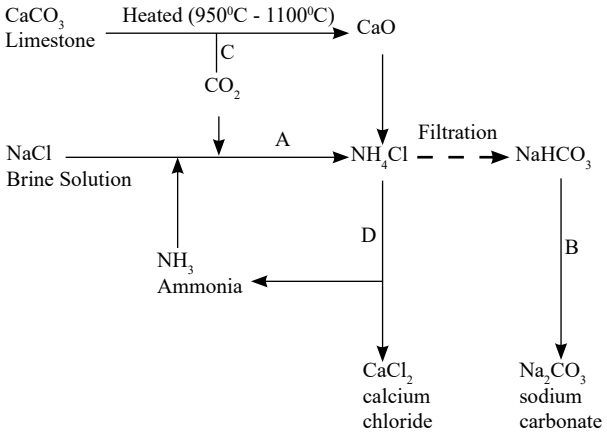
Fig. 1 outlines the stages of the Solvay Process. The main reaction follows path A.

Carbon dioxide, CO_2, reacts with a concentrated aqueous solution of sodium chloride, NaCl, and ammonia, NH_3. The ammonia is first passed through and absorbed into the concentrated brine solution. The carbon dioxide is then bubbled through the ammoniated brine leading to the precipitation of sodium hydrogen carbonate, $NaHCO_3$, from the solution.

Step 1: $NaCl + CO_2 + NH_3 + H_2O \rightarrow NaHCO_3 + NH_4Cl$

The ammonia buffers the solution at a high pH, which facilitates precipitation of the sodium hydrogen carbonate. Without the ammonia, the solution would be acidic and precipitation would not occur.

Fig. 1



This key stage of the process is completed in the Solvay Tower. The ammoniated brine solution is passed down through a tall tower, while carbon dioxide, CO_2, is passed up the tower. A series of mushroom shaped baffles helps to slow down the flow of liquid, allowing the carbon dioxide to be absorbed. The least soluble substance in the solution is sodium hydrogencarbonate, $NaHCO_3$, which precipitates as a solid in the lower section of the Solvay Tower.

The carbon dioxide for this reaction is provided by path C. This is the thermal decomposition of limestone, $CaCO_3$, by heating it to temperatures between 950°C and 1100°C.

$$CaCO_3 \rightarrow CO_2 + CaO$$

When the sodium hydrogencarbonate is precipitated and filtered from the hot ammonium chloride solution, NH_4Cl, this filtrate is then reacted with calcium oxide, CaO, (from path C) to produce calcium chloride, $CaCl_2$ and ammonia for re-used in path A.

$$2NH_4Cl + CaO \rightarrow 2NH_3 + CaCl_2 + H_2O$$

This stage (path D) reclaims much of the 'catalytic' ammonia. Only a small quantity of ammonia is consumed in the reaction, which is recycled for reuse with the brine solution.

The sodium hydrogencarbonate precipitate is then finally converted to sodium carbonate, Na_2CO_3, by calcination, at a temperature between 160°C and 230°C as shown in path B.

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$$

The ammonia, NH_3, produced in path D and the carbon dioxide, CO_2, produced in path C are both recovered for re-use in path A.

Note that the traditional or common name of sodium carbonate is "soda ash" and the chemical is often referred to by this name in many industrial processes and uses.

The principle use of sodium carbonate is in glass-making. This includes the production of bottle and window glass, when the sodium carbonate, Na_2CO_3, is heated with silicon dioxide, SiO_2, and calcium carbonate, $CaCO_3$ at about 1500°C.

Sodium carbonate is often used to soften water as it precipitates hard water agents, magnesium and calcium ions. It is used in some washing powders for this purpose.

$$\text{e.g. } Mg^{2+}(aq) + CO_3^{2-}(aq) \rightarrow MgCO_3(s)$$

It is also used in the paper-making industry where it is converted to sodium hydrogen sulphite, $NaHSO_3$. This is used to separate lignin from cellulose before the paper is manufactured. Lignin is a complex organic polymer commonly found in the cell walls of wood and tree bark and causes paper to yellow very rapidly if not removed.

Scientists developing new techniques of Carbon Capture and Storage (CCS), have devised tiny capsules consisting of sodium carbonate and a permeable polymer shell that reacts with and absorbs carbon dioxide, CO_2. This potentially offers a cheaper and environmentally friendly method of carbon capture.

Concerns over increased emissions of carbon dioxide have led to scientists proposing a variation in the Solvay process for carbon sequestration. The carbon dioxide produced in industrial processes could be reacted to form solid carbonates, such as sodium hydrogencarbonate. This could be permanently stored, thus reducing the amount of carbon dioxide in the atmosphere.

Sodium carbonate is hygroscopic, which means it readily absorbs water. This allows anhydrous sodium carbonate to be used as a drying agent. One form of the hydrated salt is sodium carbonate decahydrate, $Na_2CO_3.10H_2O$.

Questions

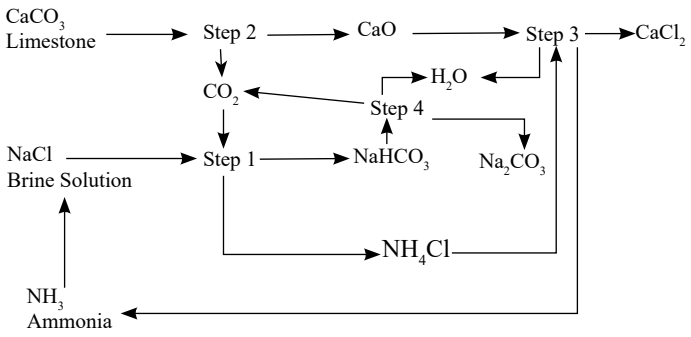
1. Complete a simple schematic flow-diagram describing the different chemical reactions involved in the Solvay Process. Ensure you correctly label each of the four reactions involved in the process.

2. In step 4 of the Solvay process (see answer 1), solid $NaHCO_3$ is heated producing washing soda, water, and carbon dioxide.
   (a) Complete the chemical equation describing this reaction and identify the type of reaction observed.
   (b) Explain why the entropy of the products is greater than the entropy of the reactant.
   (c) 5000kg of sodium hydrogen carbonate, $NaHCO_3$, is heated producing 1310kg of carbon dioxide, CO_2. Confirm that the reaction has gone to completion, and hence, determine the mass of soda ash produced.

3. Summarise how the following raw materials are used in the Solvay Process. Use chemical equations where appropriate:
   (a) Limestone
   (b) Ammonia
   (c) Brine

Answers

1.



2. (a) $2NaHCO_3(s) \xrightarrow{heat} Na_2CO_3(s) + H_2O(g) + CO_2(g)$

   Thermal decomposition

   (b) Solid $NaHCO_3$ reacts producing two gases, H_2O and CO_2, which have greater disorder, leading to an increase in the entropy of the system.

   (c) Mol ($NaHCO_3$) = mass ÷ M_r
   = 5000×10^3g ÷ (23+1+12+(3×48)) = 59.5×10^3 mol
   Mol (CO_2) = mass ÷ M_r = 1310×10^3g ÷ (12+(2×16))
   = 29.8×10^3 mol
   Mol stoichiometric ratio is therefore 1:($59.5 \times 10^3 \div 29.8 \times 10^3$)
   = 1:2 as per equation.
   → reaction is complete.

3. (a) Limestone is a cheap source of calcium carbonate, $CaCO_3$, which is heated to produce calcium oxide, CaO, and carbon dioxide, CO_2. The carbon dioxide is used in step 1 (see answer 1) of the Solvay Process. $CaCO_3 \rightarrow CaO + CO_2$

   (b) Ammonia acts as a catalyst in step 1 (see answer 1) of the Solvay Process, most of which is reclaimed in Step 3 and recycled for use with the initial brine solution.
   $NaCl + CO_2 + NH_3 + H_2O \rightarrow NaHCO_3 + NH_4Cl$
   $2NH_4Cl + CaO \rightarrow 2NH_3 + CaCl_2 + H_2O$

   (c) Brine is a concentrated solution of sodium chloride, providing a source for sodium chloride, NaCl, for the ammoniated brine solution

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