RS•C

Part 5
The thermodynamics and equilibria involved in the Solvay process for producing sodium carbonate

Material for post-16 students

The thermodynamics and equilibria involved in the Solvay process for producing sodium carbonate

Thermodynamic aspects of the process

This is an old process dating from the late 19th century. It is also known as the ammonia-soda process. It uses two raw materials: sodium chloride and calcium carbonate.

The overall reaction:

$2NaCl(aq) + CaCO_3(s) \rightleftharpoons Na_2CO_3(aq) + CaCl_2(aq)$

is endothermic (ΔH = +20 kJ mol^{-1}, ΔG = +60 kJ mol^{-1})

and the equilibrium lies well to the left. So the production of sodium carbonate must be undertaken by an indirect route. The actual series of reactions used is:

1) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ ΔH = +178 kJ mol^{-1}

2) $2NaCl(aq) + 2NH_3(aq) + 2H_2O(l) + 2CO_2(g) \rightleftharpoons 2NH_4Cl(aq) + 2NaHCO_3(s)$ ΔH = -158 kJ mol^{-1}

3) $2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(l)$ ΔH = +85 kJ mol^{-1}

4) $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s)$ ΔH = -65 kJ mol^{-1}

5) $Ca(OH)_2(s) + 2NH_4Cl(aq) \rightarrow CaCl_2(aq) + 2NH_3(aq) + 2H_2O(l)$ ΔH = -20 kJ mol^{-1}

Questions

1. (*a*) Show that the overall effect of the five reactions above is the same as:
$2NaCl(aq) + CaCO_3(s) \rightleftharpoons Na_2CO_3(aq) + CaCl_2(aq)$

You can do this by adding up the five equations above – *ie* adding all the species on the left of the arrows, adding all the species on the right of the arrows and then cancelling all the species that occur on both the left and the right.

(*b*) Hess's Law states that the enthalpy change for any reaction is independent of the route by which that reaction occurs. So adding the enthalpy changes of the five reactions above should give the enthalpy change of

$2NaCl(aq) + CaCO_3(s) \rightleftharpoons Na_2CO_3(aq) + CaCl_2(aq)$

Add up the enthalpy changes of reactions 1 – 5 above to calculate a value for ΔH for the overall reaction. Comment on the value you obtain.

The overall reaction requires an input of heat energy. This is provided by burning coke.

$C(s) + O_2(g) \rightarrow CO_2(g)$

Questions

2.	What is coke and where does it come from? What other products are formed in the coke-making process?
3.	Use the table of data at the end of this sheet to find $\Delta H^{\ominus}$, the standard enthalpy change for the burning of coke.

The heat energy produced is used to decompose calcium carbonate (limestone, $CaCO_3$) according to the following equation:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

Questions

4.	Use the table of data at the end of this sheet to calculate $\Delta H^{\ominus}$, the standard enthalpy change for the above reaction.
5.	Using the two $\Delta H^{\ominus}$ values you have obtained above, deduce (to the nearest whole number) how many moles of calcium carbonate can be decomposed by the energy produced on burning 1 mole of carbon (coke).
6.	Burning coke is the preferred energy source for the Solvay process rather than other fossil fuels or even electrical heating. Look at the set of reactions which make up the Solvay process and suggest why coke is used.

Coke and limestone are burned together in a kiln and the resulting carbon dioxide is used in the next stage of the process.

Sodium chloride solution (brine) is extracted from underground deposits by 'solution mining'. This involves pumping water down into the salt strata. The salt dissolves, and the saturated brine is pumped to the surface. Here it is purified and mixed with ammonia before entering a tower – called the Solvay tower – where the the reaction with carbon dioxide takes place, *Figure 1*. Here it reacts with the carbon dioxide according to the following equation:

$$NaCl(aq) + NH_3(aq) + H_2O(l) + CO_2(g) \rightleftharpoons NH_4Cl(aq) + NaHCO_3(s) \quad \Delta H = -79\ kJ\ mol^{-1}$$

Sodium hydrogencarbonate is less soluble than ammonium chloride at low temperatures. It precipitates out and is separated by vacuum filtration. Since this is an exothermic reaction careful temperature control is necessary to keep the temperature low enough for the sodium hydrogencarbonate to precipitate, *Figure 1*.

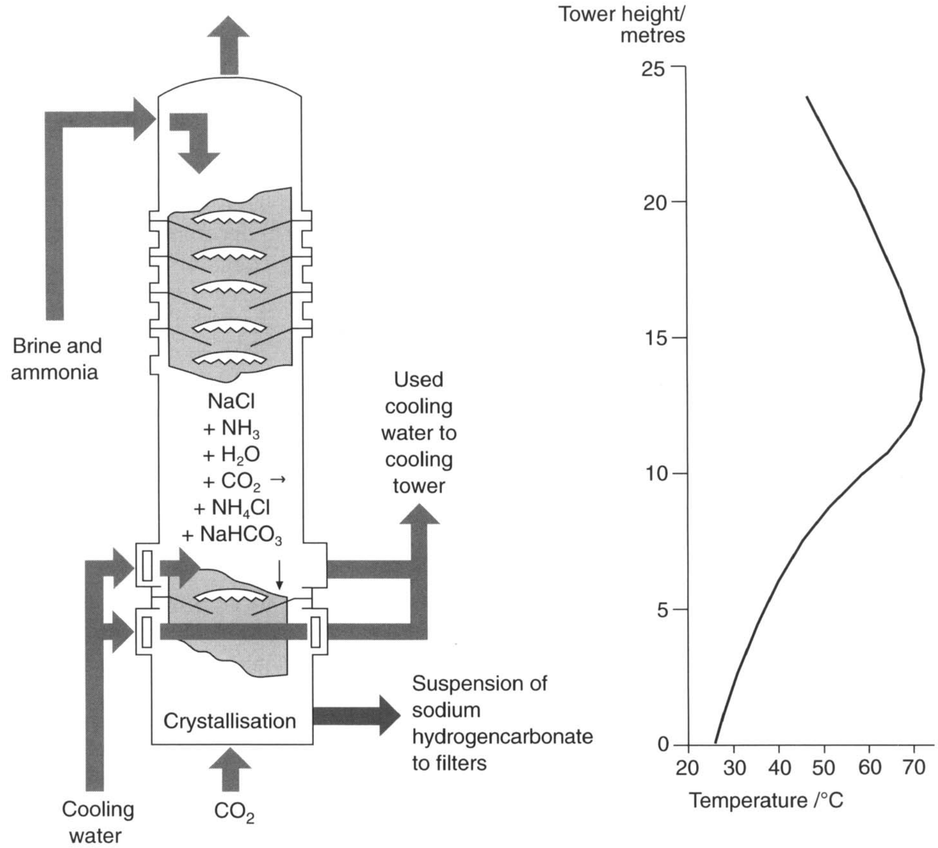

Fig 1 The temperature profile of a Solvay tower

Questions

7. (*a*) Describe the advantages in obtaining salt from underground deposits, up to 500 m deep, by solution mining rather than by conventional mining.
8. Explain the shape of the graph of temperature against tower height in *Figure 1*.
9. The crystal size of the final product is important. When crystallising a product, what factors determine the size of the crystals produced?

The solid sodium hydrogencarbonate is transferred to driers, called secheurs, where thermal decomposition takes place to form sodium carbonate.

Questions

10. Write a balanced equation and calculate the standard enthalpy change for the decomposition of sodium hydrogencarbonate using data from the table at the end of this sheet.

Question

11. Look at *Figure 2* and describe in words or in chemical equations the processes that are occurring in the areas labelled A, B and C? What substances are represented by the arrows labelled a, b, c and d?

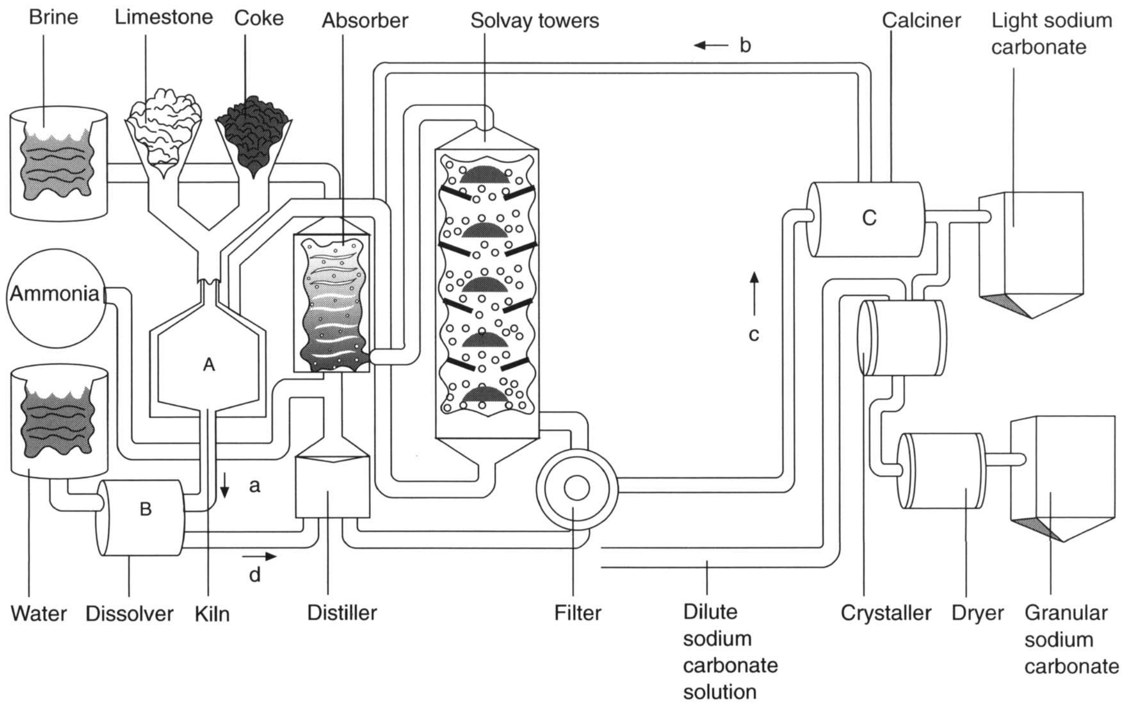

Fig 2 The Solvay process

Acid and base aspects of the process

The Brønsted Lowry definitions of acids and bases are that an acid is a proton (H^+ ion) donor and that a base is a proton (H^+ ion) acceptor.

Questions

12. Using the definition of acids and bases given above, identify the acids and the bases in the following reactions from the Solvay process.

    (*a*) $NaCl(aq) + NH_3(aq) + H_2O(l) + CO_2(g) \rightleftharpoons NH_4Cl(aq) + NaHCO_3(s)$

    (*b*) $Ca(OH)_2(s) + 2NH_4Cl(aq) \rightarrow CaCl_2(aq) + 2NH_3(aq) + 2H_2O(l)$

13. Sodium carbonate is the salt of a strong base and a weak acid.

    (*a*) Will a solution of sodium carbonate be acidic, neutral or alkaline? Explain your answer.

    (*b*) (This part is much harder)

What will be the pH of a 1 mol dm^{-3} solution of sodium carbonate?

This involves the two equilibria

1. $CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$

$K_b = 2.08 \times 10^{-4}$ mol dm^{-3}

and

2. $HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$

$K_b = 2.2 \times 10^{-8}$ mol dm^{-3}

You will first have to use the expression

$$2.08 \times 10^{-4} = \frac{[HCO_3^-(aq)]_{eq}\,[OH^-(aq)]_{eq}}{[CO_3^{2-}(aq)]_{eq}}$$

to calculate $[OH^-(aq)]$ produced by equilibrium 1,

then you will need to use the expression

$$2.22 \times 10^{-8} = \frac{[H_2CO_3(aq)]_{eq}\,[OH^-(aq)]_{eq}}{[HCO_3^-(aq)]_{eq}}$$

and the $[HCO_3^-(aq)]$ you have worked out above to calculate

$[OH^-(aq)]$ produced by equilibrium 2.

The total $[OH^-(aq)]$ will be the sum of these two values.

You will then need to use the expression

$[H^+(aq)]_{eq} \times [OH^-(aq)]_{eq} = 1.0 \times 10^{-14}$ mol^2 dm^{-6}

to calculate the corresponding value of $[H^+(aq)]$ and hence the pH of the solution.

Uses of sodium carbonate

The major use for sodium carbonate is in manufacturing glass. Here, sodium carbonate is heated with sand and other materials. Often the sodium carbonate supplied can contain an impurity of sodium chloride and this produces hydrogen chloride gas during the glass making process which pollutes the environment. So it is important that the sodium carbonate does not contain a high level of sodium chloride.

Question

> 14. Using the information from the titration curve in *Figure 3* and the information about some indicators in Table 1, plan in detail a method for determining the purity of a sodium carbonate sample obtained from the manufacturers.
>
> If possible, check your method with your teacher and carry out an analysis of a sample of sodium carbonate.

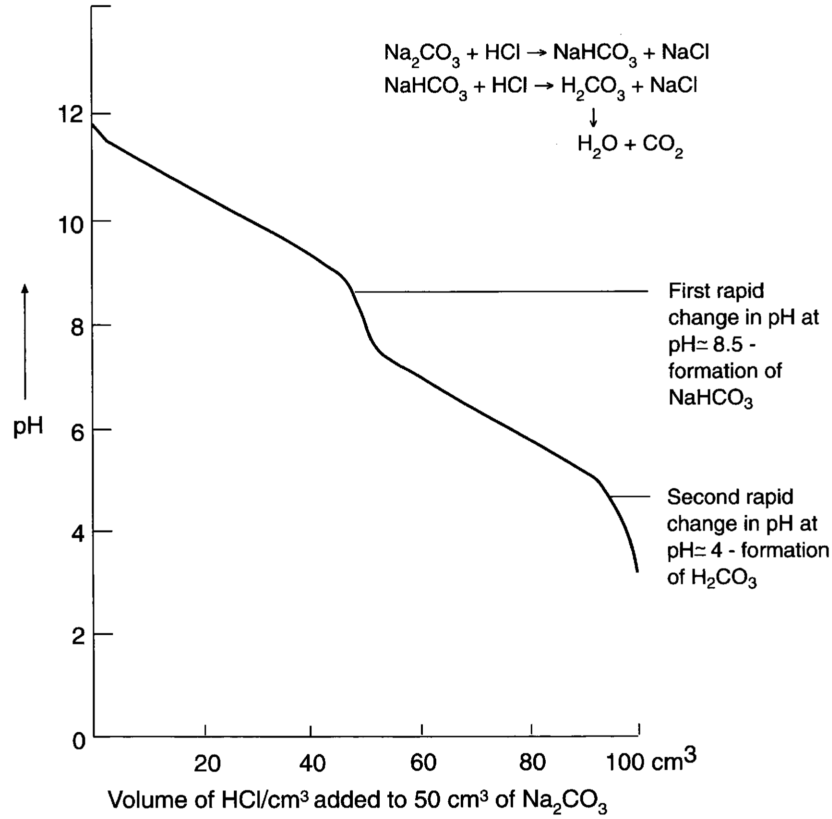

Fig 3 Titration curve for sodium carbonate (0.100 mol dm^{-3}) with hydrochloric acid (0.100 mol dm^{-3})

Indicator / pH	1	2	3	4	5	6	7	8	9	10	11
Thymol blue	Red	Change			Yellow			Change		Blue	
Methyl orange		Red		Change	Yellow						
Methyl red				Red	Change		Yellow				
Litmus					Red	Change		Blue			
Bromothymol blue					Yellow	Change		Blue			
Phenolphthalein							Colourless		Change	Red	
Universal indicator		Red		Orange	Yellow	Green		Blue		Violet	

Table 1 The colour changes of some indicators

Data

$\Delta H_f^\ominus$ /kJ mol^{-1}	
CO_2(g)	-393
CaO(s)	-635
$CaCO_3$(s)	-1207
H_2O(l)	-286
$NaHCO_3$(s)	-951
Na_2CO_3(s)	- 1131