# CII.—*The Interaction of Sodium Chloride and Alumina.*

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Sodium chloride is known to react with alumina and with silica in a similar manner. Tilghman (Brit. Pat. 11556, 1847), Gossage (*ibid.* 2050, 1862), Hargreaves (*ibid.* 2121, 1867), and Grüneberg and Vorster (*ibid.* 2639, 1874) were aware of the reaction in presence of moisture yielding sodium aluminate and hydrochloric acid, whilst De Lande and Prud'homme (*Bull. Soc. chim.*, 1872, [ii], **17**, 290) and Schultze (*J. pr. Chem.*, 1880, [ii], **21**, 407) observed

the reaction in presence of air or oxygen yielding sodium aluminate and chlorine. The subject was deemed worthy of a more quantitative investigation.

## Experimental.

The heating element consisted of a nichrome-wound silica tube the temperature of which was controlled to $\pm 10°$ over long periods by means of an adjustable resistance in conjunction with an automatic regulator designed to overcome variations in temperature due to fluctuations in the voltage supplied. The furnace temperatures were measured by a standardised platinum–platinum rhodium thermocouple. The reactions were carried out in alundum* tubes which, being somewhat pervious to gases, were enclosed in a slightly larger silica tube.

*Products and Course of the Reaction.*—The following reactions have been observed :

(*a*) $4x\mathrm{NaCl} + y\mathrm{Al_2O_3} + x\mathrm{O_2} = 2x\mathrm{Na_2O},y\mathrm{Al_2O_3} + 2x\mathrm{Cl_2}$.
(*b*) $2x\mathrm{NaCl} + y\mathrm{Al_2O_3} + x\mathrm{H_2O} = x\mathrm{Na_2O},y\mathrm{Al_2O_3} + 2x\mathrm{HCl}$.
(*c*) $4\mathrm{HCl} + \mathrm{O_2} = 2\mathrm{H_2O} + 2\mathrm{Cl_2}$.

Reaction (*b*) is reversible at about 1000°. The formation of aluminium chloride has not been observed in these experiments, which have been restricted to reactions in the presence of water. This does not preclude its formation under anhydrous conditions.

*Materials.*—Pure, dry sodium chloride was used and the alumina was prepared by igniting recrystallised ammonium alum, free from iron, in a muffle, extracting for 2 days in a Soxhlet extractor with dilute hydrochloric acid, re-igniting in the muffle for 6 hours, followed by a fresh extraction for 2 days. The pulverulent product showed no traces of sulphate on testing after fusion with sodium carbonate.

*Effect of Rate of Flow of Gas over the Reaction Mixture.*—A purified stream of moist air was passed at a constant rate over 0·5 g. of a mixture of equal parts by weight of alumina and sodium chloride placed in a platinum boat and heated in the furnace in a silica-jacketed alundum tube. The gaseous products of the reaction were absorbed in a U tube filled with fragments of glass moistened with sodium bicarbonate and potassium iodide. The reaction tube was finally swept out with a current of dried air. The experiments were duplicated and the results are shown in Table I.

The results indicate that reaction (*b*) predominates, and that the chlorine produced is to be attributed more to reaction (*c*) than reaction (*a*), since it is dependent on the rate at which air and water

* 15·42% $SiO_2$; 83·25% $Al_2O_3$; 0·49% $Fe_2O_3$; 0·52% $TiO_2$; 0·76% CaO.

TABLE I.

Duration of experiment ..... 5 hours.
Mean temperature of furnace ..... 1009°.
Temperature of saturation of air with water vapour 50°.

| C.c. of air passed. | $Cl_2$ (c.c. of $N/20$). | HCl (c.c. of $N/20$). | $\frac{Cl_2}{HCl}$ | $\frac{Cl_2}{HCl + Cl_2}$ |
|---|---|---|---|---|
| 9400 | 10·8 | 74·6 | 0·145 | 0·126 |
| 8450 | 10·5 | 67·5 | 0·156 | 0·135 |
| 6500 | 18·5 | 63·9 | 0·290 | 0·225 |
| 3000 | 24·0 | 51·6 | 0·465 | 0·317 |
| 1600 | 26·2 | 49·9 | 0·525 | 0·344 |
| 1250 | 22·1 | 35·6 | 0·621 | 0·383 |
| 1050 | 17·9 | 37·4 | 0·479 | 0·324 |

are supplied. Examination of equation (*c*) shows that a proportionate increase in the concentration of water and oxygen would lead to a displacement of equilibrium to the left.

*Effect of Proportion of Sodium Chloride and Alumina.*—The results are shown in Table II.

TABLE II.

Duration of experiment ..... 5 hours.
Volume of air passed ..... 6500 c.c.
Temperature of saturation of air with water ... 50°.
Temperature of furnace ..... 1009°.

| 0·5 G. of | HCl (c.c. of $N/20$). | $Cl_2$ (c.c. of $N/20$). | $\frac{Cl_2}{HCl + Cl_2}$ |
|---|---|---|---|
| 100% NaCl | 64·6 | 16·4 | 0·202 |
| 75% NaCl | 76·2 | 26·0 | 0·254 |
| 50% NaCl | 63·9 | 18·5 | 0·225 |
| 25% NaCl | 36·6 | 6·6 | 0·150 |

*Effect of Temperature on Reaction* (b).—0·5 Gram of an intimate mixture of equal weights of sodium chloride and alumina was heated as previously described in an atmosphere of water vapour produced by allowing water to drip at a very slow constant rate from a capillary tube into the silica tube. The hydrochloric acid produced was collected and titrated with $N/10$-alkali. Reactions (*a*) and (*c*) were excluded. The composition of the residue was determined by gravimetric analysis, the sodium oxide being determined by Smith's method (*Amer. J. Sci.*, 1871, [ii], **50**, 269).

At the higher temperature very little of the resulting sodium aluminate was soluble or hydrolysable. The results are summarised in Table III.

The results indicate that above 1000°, for a given quantity of sodium chloride, the reaction with alumina is virtually complete, as would be expected, since the method of supplying the water for the reaction precludes the reverse one.

In these experiments the amount of sodium oxide produced in the platinum boat was always less than that equivalent to the

TABLE III.

Duration of experiment ..... 5 hours.

| Temp. | HCl (c.c. of $N/10$). | Composition of residue. % NaCl. | % $Na_2O$. | % $Al_2O_3$. | $\frac{Na_2O}{Al_2O_3}$. |
|---|---|---|---|---|---|
| 1075° | 46·65 | 0·2 | 3·7 | 96·1 | 0·0385 |
| 1008 | 42·20 | 0·97 | 11·8 | 87·2 | 0·135 |
| 952 | 35·20 | 12·1 | 6·8 | 81·1 | 0·0838 |
| 897 | 29·55 | — | — | — | — |
| 838 | 20·30 | 32·3 | 5·5 | 62·2 | 0·0883 |
| 785 | 8·93 | 44·6 | 3·8 | 51·6 | 0·0737 |
| 707 | 3·35 | — | — | — | — |
| 605 | 0·50 | — | — | — | — |

hydrochloric acid absorbed, particularly at the higher temperatures. This is to be attributed to the reaction of sodium chloride vapour with the alundum tube in addition to the reaction of the unvolatilised reagents in the boat. Thus we find that the reaction at 1075°, although productive of the greatest yield of hydrochloric acid, does not give the greatest yield of sodium oxide in the residue.

*Equilibrium Experiments.*—(*A*). An attempt was now made to determine the effect of varying proportions of water and hydrogen chloride on the proportion of sodium chloride, sodium aluminate, and alumina in equilibrium with the vapours at a temperature (830°) where sodium chloride is not markedly volatile.

Equilibrium was approached from both sides. In one platinum boat was placed a mixture of equal weights of sodium chloride and alumina, and in another, a mixture of 40% sodium chloride, 40% alumina, and 20% sodium aluminate, made by previously calcining equal weights of alumina and sodium carbonate. The two boats were heated in a stream of water vapour and hydrogen chloride, obtained by allowing a solution of hydrochloric acid to drip slowly through a capillary tube into the silica reaction tube. A blank experiment with an empty tube showed that the acid condensing after passing through the furnace had the same composition as that entering it. The results showed that equilibrium was imperfectly attained in the solid mixtures, since differences of about 1% were obtained in the proportions of sodium oxide present. The results given in Table IV are mean values.

A noticeable feature is the almost constant proportion of sodium oxide in the solid mixture in equilibrium with the gaseous phase, irrespective of the composition of the latter.

(*B*). Similar experiments were made to ascertain the composition of the sodium aluminate in equilibrium with varying gaseous mixtures of hydrogen chloride and water vapour saturated with sodium chloride vapour at 1045°. The procedure was similar to that just described, but to render the alundum reaction tube inert

TABLE IV.

Mean temperature 829°

| Composition of gaseous phase. | Composition of solid phase. | | |
|---|---|---|---|
| $\frac{[H_2O]}{[HCl]}$. | $\frac{[NaCl]}{[Al_2O_3]}$. | $\frac{[Na_2O]}{[Al_2O_3]}$. | $\frac{[NaCl]}{[Na_2O]}$. |
| 57·4 | 1·65 | 0·067 | 24·6 |
| 505·0 | 1·64 | 0·080 | 20·5 |
| 2740·0 | 1·56 | 0·075 | 20·8 |
| 5480·0 | 1·53 | 0·074 | 20·7 |

to the gaseous reagents it was first treated with concentrated sodium hydroxide and dried. The boats were then introduced and heating was commenced in an atmosphere of the required composition. Thus the alundum tube as well as the contents of the two platinum boats was finally in equilibrium with the vapours. Equilibrium was assumed to be obtained when the composition of the condensed acid was the same as that of the original, which was usually after 20 to 24 hours' heating. Table V shows the results obtained.

TABLE V.

Mean temperature 1045°.

| Composition of gaseous phase $[H_2O]/[HCl]$. | | | | | |
|---|---|---|---|---|---|
| 13·7 | 27·6 | 66·9 | 105·0 | 529·0 | 1590·0 |
| **Composition of solid phase $[Na_2O]/[Al_2O_3]$.** | | | | | |
| 0·017 | 0·026 | 0·070 | 0·107 | 0·102 | 0·117 |

The stability of sodium aluminate with reference to hydrochloric acid decreases rapidly at 1045° when the molecular ratio $Al_2O_3/Na_2O$ is less than 10 to 1 (see Table V), and at 830° when the ratio is less than 12 to 1 (see Table IV). In this reaction, no quantitative relationship between the composition of the gaseous phase and of the solid phase is apparent from these results. For the complete reaction of sodium chloride with alumina in the presence of water, an excess of alumina appears to be of greater moment than an excess of water.

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