

Steel.	Drown's method. Per cent.	Swedish method. Per cent.
A	0.190	0.190
"	0.190	0.196
"	0.196
"	0.192
B	0.178	0.184
"	0.178	0.182
"	0.182
"	0.190
C	0.204	0.202
"	0.202	0.204
"	0.202	0.200

LABORATORY OF HENRY DISSTON & SONS'
STEEL WORKS, PHILADELPHIA.

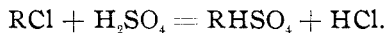
ON THE DECOMPOSITION OF THE CHLORIDES OF ALKALI METALS.

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Received February 23, 1901.

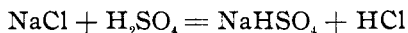
PART I.

THE action of sulphuric acid on the chlorides of the alkali metals is usually expressed by

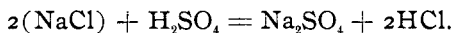


It has been observed that concentrated sulphuric acid acts with considerable violence on the alkaline chlorides at the common temperature; that an acid, which has been diluted with one-quarter or one-third of its weight of water, acts with less violence, developing hydrochloric acid gas on the application of heat; and it is known that, if less acid than as above is used, the hydrochloric acid gas is developed only on applying considerable heat. Thus we observe that in the manufacture of sulphate by the Leblanc process, 2 molecules of salt are used with 1 molecule of sulphuric acid (60° Bé) and that, whereas, only about 70 per cent. of the hydrochloric acid gas is driven off in the pans, the mass has further to be calcined at a high temperature in the calcining furnaces, to complete the decomposition. We have, therefore, *a priori* to conclude that, in order to effect a thorough decomposition of the chloride by sulphuric acid, the application of heat is necessary; that the decomposition takes place periodically, as the temperature is raised, and that it is generally presumed that

the entire decomposition is effected at a lower temperature when the materials are used in quantities corresponding with



than with



But it may be stated here that the operation does not take place quite in accord with this theory. If we bring concentrated sulphuric acid in contact with sodium chloride at the common temperature, the action takes place at once; the mass foams under development of hydrochloric acid gas, and ultimately ceases. When the quantities used correspond with the bisulphate formulation, a considerable portion of the gas is driven out, but hardly one-half of the theoretical quantity. If the mass is not heated, the process is ended, so that even with sufficient acid to form the bisulphate, only about one-half of the chloride is decomposed; the other half can be decomposed only by the application of heat.

For the purpose of investigating this matter, I undertook first to determine the quantity of hydrochloric acid gas, which is developed during the indicated phases of the process.

I effected the decomposition of the chlorides in an apparatus very much like those usually described for the preparation of hydrochloric acid. As the mass foams very much, when concentrated acid is used, the flask is of ample proportion and provided with a thermometer, safety funnel, and gas delivery tube. Between the absorption vessel and the development flask I inserted an empty bottle with safety tube, serving as receiver of substances carried over from the flask, and also as a safety valve.

At each phase I drew through the apparatus a sufficient quantity of air, to carry the gas from the apparatus into the absorbing water. An aliquot portion of the solution of hydrochloric acid gas in water served for the determination of hydrochloric acid by normal soda solution. In this process, equivalent proportions of the chlorides and sulphuric acid in grams were used.

The temperatures in the flask during the periods of gas development were noted.

I. DECOMPOSITION OF SODIUM CHLORIDE.

To 117 grams sodium chloride, 200 grams sulphuric acid (sp. gr. 1.84) were added.

The evolution of gas is violent; the mass foams. Temperature,

18°. No rise of temperature is observed. In the absorption vessel was a liter of water, of which, after the reactions were finished, aliquot portions (100 cc.) were used for the determination of hydrochloric acid.

It was found that the flask, containing the salt and sulphuric acid, should be frequently shaken to effect the reaction, otherwise only an imperfect decomposition of the chloride takes place. This is shown by the following two series of determinations, one resulting from the flask left at rest, and the other frequently shaken. From 117 grams sodium chloride, one-half of the theoretical quantity of HCl (73), that is, 36.5 grams, should be set free and found in the absorbing water :

Percentages found.	
I.	II.
26.49	33.58
25.91	32.12
27.61	34.31
26.50	33.58
26.50	34.42
27.31	33.60
26.00	34.12
....	34.30
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Average 26.6	33.7

Theoretical amount, 36.5.

This shows that 95 per cent. of the theoretical amount of hydrochloric acid has been developed ; and that only 46 per cent. of the total amount of the acid has been set free at the common temperature by an excess of sulphuric acid.

The residue in the flask solidifies almost entirely to a salt cake, when left for a length of time undisturbed. Shortly after the gas development ceases, it shows a mixture of an oily liquid with undecomposed sodium chloride, and in the liquid, needles of crystallization begin to form. If at this time the liquid is poured off from the forming salt cake and filtered, crystals are obtained, which show the composition $\text{NaH}_3 \cdot 2\text{SO}_4$, and as it appears somewhat difficult to effect a separation of these crystals from the remaining sodium chloride and free sulphuric acid, I will describe an improvement on the filtering apparatus, which I have used on former occasions for similar purposes.¹ The bell-jar was connected with a Woulfe bottle containing sulphuric acid in such

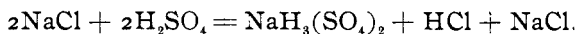
¹ This Journal, 23, 490.

a way as to admit dry air to the jar through a tube with stop-cock.

The liquid or salt mixture is poured on a platinum cone, which is finely perforated, and placed into the funnel of the filtering apparatus, which is placed into the bell-jar. When the air is exhausted, the faucet is opened sufficiently to let a very slow stream of air pass through the apparatus. This air is dried by sulphuric acid. By means of this filtration in a vacuum, the superfluous sulphuric acid is removed from the crystals on the platinum cone, and, as I have found by comparative tests, the salt on the filter may be washed with concentrated sulphuric acid to remove any traces of sodium chloride, without changing the crystallization on the filter. This is owing to the fact that the polysulphates, formed in the salt cake of the flask, are not affected by concentrated sulphuric acid. In this manner material for analysis was obtained, and the parts of the salt crystallizing from sulphuric acid, or from the oily liquid in the flask before solidifying, gave, on analysis, the following results :

	I.	Found. II.	III.	Average.	Theory for NaH ₃ (SO ₄) ₂ .
Na,	9.31	8.100	8.70	10.550
H ₃ ,	2.11	11.8	1.6	1.85 ¹	1.376
SO ₄ ,	87.50	89.9	92.3	89.9	88.073
	98.92	101.7	102.00	100.45	99.999

The irregularities in these results the writer can ascribe only to the difficulty in separating the different salts, which necessarily exist in the mixture. From the foregoing, I conclude that the action of concentrated sulphuric acid on sodium chloride at 18° can be expressed thus :

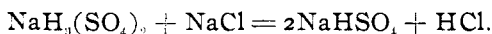


This reaction takes place without any development of heat, and with its termination the development of hydrochloric acid gas ceases.

The second period of the development of the gas commences when heat is applied to the mass. From the fact that gas develops as soon as the flask becomes warm, and that the salt cake in the flask melts easily, and the gas development continues until the cake becomes hard and dry, the reaction may be considered

¹ Omitting II.

as taking place between the polysulphate and the remaining sodium chloride and may be expressed thus :



The mass in the flask showed, at the end of this part of the process, nearly 120° . The salt cake is now the usual bisulphate. The hydrochloric acid gas absorbed in the same manner as described in the first part of the process, measured by titration with normal alkali, corresponds within from 2 to 7 per cent. in excess with the calculation. This great difference is evidently owing to the fact that quantities of the sodium chloride escape contact with the sulphuric acid, in the measure, as the salt cake becomes thick or solid. The difficulties in the practical manipulation in this investigation consist mainly in the impossibility, so far, of separating the trihydrogen sodium disulphate from the remaining sodium chloride, or from any other sulphates, which may be formed during the first period or phase of the action of the sulphuric acid on the chloride. On contact with atmospheric air, water is very quickly absorbed by the liquid and also by the polysulphates, and the result is then always sodium bisulphate and diluted sulphuric acid.

2. DECOMPOSITION OF POTASSIUM AND AMMONIUM CHLORIDES.

In the continuation of the experimental part of this investigation, the action of concentrated sulphuric acid on potassium chloride and ammonium chloride, during the first phase of the reaction, has been examined. The quantities brought in contact at the common temperature, 17° - 18° , complied with $\text{RCl} + \text{H}_2\text{SO}_4$. The temperature of the mixture of potassium chloride and acid remains stationary until the acid has come well in contact with the chloride, when the temperature rises from 17° to 30° , receding again to 17° after the corresponding reaction is finished. When sulphuric acid reacts on ammonium chloride under the same conditions, the temperature falls quickly from 18° to 1° .

This work is to be continued.

Reference to Literature :

Carl Schultz : "Ueber saure Salze der Schwefelsäure," *Pogg. Ann.*, 1868.