XXVII.—*On Chlorhydrated Sulphuric Acid.*

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IT will be recollected that about fourteen years ago, Professor Williamson discovered that by acting on hydric sulphate with phosphoric chloride, chlorhydrated sulphuric acid was produced. In his hands this reaction became very important from a theoretical point of view, and went far to establish the theory of types. He explained it as the replacement of half the hydroxyl in hydric sulphate by univalent chlorine, thus—

$$(1).\quad \begin{matrix}HO\\HO\end{matrix}SO_2 + PCl_5 = \begin{matrix}Cl\\HO\end{matrix}SO_2 + POCl_3 + HCl,$$

the chlorhydrate being formed together with phosphoric oxichloride and hydric chloride.

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* Pages 254—259 of this volume.

My colleague, the Rev. J. Maclaurin, in preparing some of this chlorhydrate, called my attention to a well-defined crystalline body in the neck of the retort. This anomaly determined me, as time did not permit him to continue the work, to investigate more fully the reaction of phosphoric chloride and hydric sulphate.

In the first instance an excess of hydric sulphate was used, and the yield of chlorhydrate was small. After all the chlorhydrate had been distilled over, a liquid followed which, when cool, crystallised in the ordinary form, and was found to possess all the properties of sulphuric acid, SO_3. On raising the temperature, a distillate was obtained which crystallised in plates exactly similar to those obtained by Mr. Maclaurin. As these last crystals could not then be freed from adhering liquid, the analysis was thought unadvisable. But qualitative observation has shown the probability that they are a definite hydrate of sulphuric acid containing more acid than Nordhausen sulphuric acid. The residue in the retort was next submitted to examination, and, after evaporating the excess of hydric sulphate, the glacial metaphosphate remained. The reaction, therefore, was shown to go further than was originally found by Dr. Williamson. As the distillate on decomposition with water was found to contain no phosphate, it was clear that the phosphoric oxichloride first formed again reacted on the hydric sulphate. This may be represented in two successive steps :—

$$(2).\quad POCl_3 + H_2SO_4 = PO_2Cl + HCl + HClSO_3,$$

and then

$$(3).\quad PO_2Cl + H_2SO_4 = HPO_3 + HClSO_3.$$

It was found that the chlorhydrate was yielded in the largest quantities when the substances were used in proportions corresponding to three molecules of hydric sulphate to one of phosphoric chloride, a slight excess of hydric sulphate being added to ensure the complete decomposition of the phosphoric oxichloride. The whole reaction may be represented then by the equation—

$$(4).\quad 3H_2SO_4 + PCl_5 = 2HCl + HPO_3 + 3HClSO_3.$$

When a very large excess of hydric sulphate was used, no chlorhydrate was obtained, but hydric chloride was given off in great quantities followed by sulphuric acid SO_3.

The fact of sulphuric acid being obtained was explained by the discovery that the chlorhydrate is broken up by normal hydric sulphate, hydric chloride being given off with great violence, and Nordhausen acid being left.

$$(5.)\quad HClSO_3 + H_2SO_4 = HCl + H_2SO_4.SO_3$$

Having prepared a quantity of the chlorhydate which gave a satisfactory analysis,

	Calculated.	Found.	
SO_3	68·67	—	69·20
HCl	31·33	31·28	30·72
	100·00		99·92

it was determined to take its vapour-density. This was done by Dumas's method, as the substance attacks mercury with great energy.

The first determination gave the following results :—

Calculated density $HClSO_3$ = 4 vols.	Found.
29·125	48·813

There were many reasons for doubting the accuracy of this determination. Firstly, the bulb was shown not to be absolutely free from moisture, as some of chlorhydrate was decomposed on entering; secondly, too much of the liquid was taken; and lastly, the analysis of the contents of the globe gave 78·241 per cent. SO_3 instead of 68·721, showing that probably decomposition had taken place from the presence of moisture. Another determination was accordingly made. The bulb was sealed at 216° C., *circa* 71° above the boiling point of the liquid. The numbers corresponded to about 3½ volumes.

Calculated density $HClSO_3$ = 4 vols.	Found.
29·125	32·857

This result confirmed the surmise founded on its analogy to hydric sulphate, that in the state of vapour it breaks up into hydric chloride and sulphuric acid. To separate the mixed vapour into its constituents, diffusion was attempted. Many forms of apparatus were tried, but without success, and as yet the separation has not been effected. The mere fact that small quantities of hydric chloride are liberated would not be evidence that diffusion was taking place. For Dr. Williamson has proved that by continued heating the chlorhydrate is decomposed into chlorosulphuric acid and hydric sulphate, thus—

$$2HClSO_3 = Cl_2SO_2 + H_2SO_4.$$

Now, this hydric sulphate would, as has been shown, break up some chlorhydrate, setting free hydric chloride, and retaining the sulphuric acid. This difficulty, however, is not insurmountable.

This investigation was carried on in the laboratory of University College, London, under the direction of Dr. Williamson.