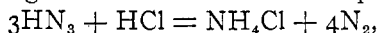


## VI. The Reaction between Hydronitric Acid and Hydrochloric Acid.

Curtius has already described the reaction between dilute aqueous solutions of hydrochloric acid and hydronitric acid, ammonium chloride being formed and nitrogen given off. He writes the equation,



although he obtained only 130 cc. of nitrogen, instead of a theoretical 270 cc. He found no trace of a reducing substance, showing that no hydrazine nor hydroxylamine is formed.

To ascertain whether the concentration of the acid was a governing factor in the nature of the resulting reduction product, dry hydronitric acid, hydrochloric acid gas and air were passed through a glass tube cooled by ice and salt. There appeared a transparent crystalline deposit, closely adhering to the walls of the glass. The crystals were well formed icositetrahedrons, showing no reducing action with potassium iodate. Analyses for ammonia and hydrochloric acid gave

Theory for $\text{NH}_4\text{Cl}$ per cent.		Found per cent.
$\text{NH}_3$	31.85	31.11
$\text{HCl}$	68.15	68.24

showing that the salt is ammonium chloride.

The ratio of nitrogen evolved to nitrogen retained as ammonia was determined by passing hydrochloric acid through a U-tube filled with anhydrous hydronitric acid, then to a nitrometer filled with water. There was a very slight deposit of crystals on that part of the tube with which the hydronitric acid had been in actual contact. This was washed out and distilled into standardized hydrochloric acid and found to contain 0.00087 gram nitrogen as ammonia. 5.3 cc. of nitrogen under standard conditions was evolved, equivalent to 0.00665 gram nitrogen. The ratio of evolved nitrogen to nitrogen retained as ammonia was consequently 0.00665:0.00087 or 7.64:1. Inasmuch as very small quantities of material were used, the results may be regarded as within the limits of experimental error and the equation of Curtius which calls for a ratio of 8:1, may be accepted.

CORNELL UNIVERSITY,  
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## PENTAVALENT BISMUTH

By E. B. HUTCHINS, JR., AND VICTOR LENHER.  
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Peculiar interest has been attached to investigations of a higher state of valence than that of three with bismuth. Its many analogies to the other members of the fifth group of the periodic system have caused the pentavalent condition to be sought for repeatedly. Pentavalent arsenic

and pentavalent antimony are well known, both the oxides and types of the halides exist with these elements. With bismuth as the element having the highest atomic weight in this series, pentavalent derivatives might reasonably be expected.

Since 1818 when Brandes and Bucholz<sup>1</sup> prepared an oxide of bismuth containing more oxygen than the trioxide, many attempts have been made to prepare the pentoxide, a bismuthic acid or a bismuthate. Gutbier<sup>2</sup> has recently reviewed the various methods which other investigators have used and with his own work has questioned the acidic character of the higher oxides of bismuth. The authors have repeated most of the methods given for the preparation of these oxides and have obtained products by the various reactions whose analyses corresponded to the tetroxide, potassium bismuthate, and impure bismuthic acid. It appears that although none of the higher products of oxidation of bismuth except the tetroxide are stable, yet under the proper conditions, it is possible to have a higher state of oxidation than the valence of three.

Very little attention has, however, been directed to the study of other derivatives than the oxygen type. Muir<sup>3</sup> fused together sulphur and bismuth trichloride and obtained  $\text{BiSCl}$  but not  $\text{BiSCl}_3$ . He also treated  $\text{Bi}_2\text{O}_3$  with chlorine with the view of obtaining  $\text{BiOCl}_3$  analogous to  $\text{POCl}_3$ , but obtained only  $\text{BiCl}_3$ . Rauter<sup>4</sup> states that when he treated bismuth pentoxide, with silicon tetrachloride he obtained bismuth trichloride as the product.

In order to ascertain the action of chlorine on bismuth trichloride, at very low temperatures, some of the dry powdered salt and some clear crystals were introduced into a test tube which was placed in a Dewar bulb containing liquid air. Chlorine gas was passed into the tube and it at once assumed the solid state. When a large excess of the solid chlorine had collected in the tube, it was withdrawn from the bulb and the solid chlorine allowed to melt. The trichloride was then well shaken with the liquid chlorine and the two returned to the liquid air bulb, where it was kept for an hour. The trichloride remained unchanged in appearance during the entire course of the experiment. After the chlorine had been allowed to spontaneously evaporate, analysis of the powdered material showed it to contain 33.2 per cent. of chlorine. From this experiment it is evident that bismuth pentachloride is not formed by the action of solid or liquid chlorine upon the trichloride. Other similar experiments were conducted in which the trichloride was kept in contact with chlorine at  $-15^\circ$  for several hours. In no case was the chlor-

<sup>1</sup> Schweiggers J. Chem. Phys., 22, 27.

<sup>2</sup> Z. anorg. Chem., 48, 162; 48, 298; 49, 432; 50, 210.

<sup>3</sup> J. Chem. Soc. 39, 22.

<sup>4</sup> Liebig's Anal., 270, 251.

ide changed in appearance by the action of the chlorine, nor could an excess of chlorine above that required for the trichloride be detected by analysis.

A small quantity of impure bismuth pentoxide was maintained at a temperature of  $-10^{\circ}$  and dilute hydrochloric acid added. The pentoxide dissolved at that temperature with the evolution of chlorine gas. Experiments looking to the formation of double halides of pentavalent bismuth likewise proved fruitless. A hydrochloric acid solution of bismuth trichloride was saturated with chlorine at  $-10^{\circ}$  and solid ammonium chloride added; the solution was then concentrated over sulphuric acid. Colorless crystals separated, which on analysis proved to be  $\text{BiCl}_2\text{NH}_4\text{Cl}$ . This salt is described by Deherain<sup>1</sup>.

$\text{CsICl}_2$ , the perhalide of Wells and Penfield<sup>2</sup> was dissolved in water and a molecular quantity of bismuth trichloride added; chlorine was passed through the hot solution, when a yellow crystalline salt separated at once. Analysis showed this substance to contain 35.05 per cent. caesium, 37.0 per cent. of bismuth, and 27.8 per cent of chlorine. The compound is therefore  $2\text{BiCl}_3\text{CsCl}$ , which has been described by Brigham<sup>3</sup>. In a similar manner bromine was added to a hot solution of caesium tribromide and bismuth tribromide in hydrobromic acid. In this experiment a finely divided yellow precipitate was obtained which was quite insoluble in hydrobromic acid, but readily soluble in hydrochloric and nitric acids. Analysis showed this to be a new salt corresponding to the formula  $2\text{BiBr}_3\text{CsBr}$ , as it contained 46.9 per cent. bromine, 27.0 per cent. caesium, while the theoretical for  $2\text{BiBr}_3\text{CsBr}$  is 46.8 per cent. bromine, 27.1 per cent. bismuth, and 26.1 per cent. caesium.

It is evident from the preceding work and from the experiments of others that while bismuth can exist in a higher state of valence than three with oxygen, thus far the halogens have not been combined with bismuth in any higher ratio than that of the valence of three.

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## THE ACTION OF THIONYL AND SULPHURYL CHLORIDES ON SELENIUM AND SELENIUM DIOXIDE

BY VICTOR LENHER AND H. B. NORTH.

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When selenium dioxide and thionyl chloride are brought together the two begin to react immediately, considerable heat is liberated and the needle-like crystals of the dioxide are quickly changed to a white and

<sup>1</sup> Compt. rend. 54, 726.

<sup>2</sup> Am. J. Sci. 43, 27.

<sup>3</sup> Am. Chem. J. 14, 181.