

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° 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° and solid ammonium chloride added; the solution was then concentrated over sulphuric acid. Colorless crystals separated, which on analysis proved to be $\text{BiCl}_3 \cdot 2\text{NH}_4\text{Cl}$. This salt is described by Delherain¹.

CsICl_2 , the perhalide of Wells and Penfield² 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 $2\text{BiCl}_3 \cdot 3\text{CsCl}$, which has been described by Brigham³. 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 $2\text{BiBr}_3 \cdot 3\text{CsBr}$, as it contained 46.9 per cent. bromine, 27.0 per cent. caesium, while the theoretical for $2\text{BiBr}_3 \cdot 3\text{CsBr}$ 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

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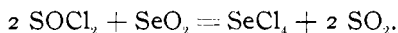
When selenium dioxide and thionyl chloride are brought together the two begin to react immediately, considerable heat is liberated and the needle-like crystals of the dioxide are quickly changed to a white and

¹ Compt. rend. 54, 726.

² Am. J. Sci. 43, 27.

³ Am. Chem. J. 14, 181.

finely divided crystalline powder. When the reaction is carried out in a sealed tube and heat applied, larger crystals can be obtained. Examination of these crystals showed them to be selenium tetrachloride, the reaction being as follows,



When the tubes are opened the sulphur dioxide escapes and the excess of thionyl chloride can be removed from the crystals of the selenium tetrachloride by extraction with carbon bisulphide.

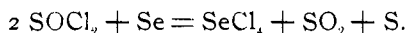
A more satisfactory method of carrying out this reaction consists in placing the selenium dioxide in a porcelain boat in a glass tube and heating in the vapor of thionyl chloride.

Selenium tetrachloride prepared in this manner gave on analysis

	I	II	Calculated for SeCl_4
Se	35.76	36.05	35.83
Cl	64.01	64.10	64.17

Selenium and Thionyl Chloride.—When selenium is brought in contact with thionyl chloride at the ordinary temperature only very slight action takes place, but when the two are sealed together in a tube and heated they react on each other more readily as the temperature is raised. In two weeks' time by continuous heating at 200° a few grams of selenium tetrachloride can be produced, while at 300° the same quantity of substance can be formed in a few hours. In carrying out this experiment, it is more convenient both for readiness in carrying out the reaction and for obtaining a purer product, to heat the elementary selenium in a porcelain boat in a glass tube in the vapor of thionyl chloride.

The reaction takes place as follows:



Analysis of the product formed gave

	I	II	Calculated for SeCl_4
Se	35.63	35.66	35.83
Cl	64.51	64.31	64.17

Selenium and Sulphuryl Chloride.—When these two substances are brought together, reaction immediately ensues, a large amount of heat is liberated, and on cooling selenium tetrachloride deposits in crystals. This reaction like the previously described ones can be advantageously carried out by heating the selenium in the vapor of sulphuryl chloride. The reaction takes place as follows:



Analysis of the tetrachloride showed

	I	II	Calculated for SeCl_4
Se	35.95	35.79	35.83
Cl	64.51	64.17

Selenium Dioxide and Sulphuryl Chloride.—When these two substances

are brought together, no reaction takes place even at elevated temperatures or under strong pressure. Several tubes containing these substances were allowed to stand for a year but at the end of this time no reaction had taken place. The two when heated together in tubes of very heavy glass, which had been obtained for work of this character, would not react, all of the tubes exploding when the temperature was sufficiently raised, but without previously showing any signs of change in the contents. After numerous attempts to bring the two to react the dioxide of selenium was vaporized from a porcelain boat in a glass tube in the vapor of sulphuryl chloride, and was condensed in a cooler portion of the tube. Analysis of the sublimed dioxide showed it to be chlorine-free, thus showing that it is possible to sublime selenium dioxide in the vapor of sulphuryl chloride without any reaction taking place.

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ON THE MERCURY NITROGEN COMPOUNDS

(THE MERCURIAMMONIUM SALTS AND BASES)

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Notwithstanding the considerable attention which has been given to the study of the mercury nitrogen compounds, widely diverse views are still held concerning their constitution as will be evident from consultation of the dictionaries of chemistry, scarcely any two of which agree in their methods of formulating these compounds. Most frequently, however, they are assumed to be substituted ammonium bases and salts. According to the view of Rammelsberg, which has been followed by Fehling¹ and by Dammer² in their classification of the mercury nitrogen compounds, and which in recent years has been defended especially by Pesci³ and his pupils, and also by Rây,⁴ all the mercury ammonia compounds are referred to the one type of mercuriammonium compounds in which the four ammonium hydrogen atoms of an ammonium salt are substituted by two atoms of mercury as indicated, for example, by the formulas, Hg_2NOH and Hg_2NCl , for dimercuriammonium hydroxide and chloride respectively. According to Pesci the salts of dimecuriammonium are especially prone to the formation of hydrates, and to union with ammonium and mercuric compounds to form double and complex salts. In accordance with this theory the well known fusible white precipitate is given the formula, $\text{Hg}_2\text{NCl} \cdot 3\text{NH}_4\text{Cl}$; the infusible precipitate, the formula, $\text{Hg}_2\text{NCl} \cdot \text{NH}_4\text{Cl}$; the chloride of Millon's base, the

¹ Handwörterb. Chem. (1890) 5, 1091.

² Handb. anorg. Chem. (1894) 2.2, 896 and (1903) 4, 630.

³ Z. anorg. Chem. 21, 361.

⁴ Ibid. 33, 193 and J. Chem. Soc. 81, 645.