4. $4NH_4Cl + 6HCl + 2K_2Cr_2O_7 = 4KCl + Cr_2O_3 + 2CrCl_3 + 2N + 11H_2O$.

5. $2NH_4Cl + 8HCl + 2K_2Cr_2O_7 = 4KCl + 2Cr_2O_3 + N_2 + 3Cl_2 + 8H_2O$.

At a high temperature and especially where an excess of the dichromate is used, chlorine is liberated as indicated in equations 2 and 3.

Some of the above equations are only possible, of course, when a part of the dissociated ammonia has been eliminated from the reaction as for instance by the phosphoric anhydride bulb. Any free ammonia left would react with the oxides of nitrogen and chlorine, liberating free nitrogen.

The substances above mentioned are by no means the only ones formed when the above mixtures are heated. There is formed in addition to the above substances, a small amount (representing about one per cent.) of a substance which, when brought in contact with water, liberates pure nitrogen. This substance appears to be a chromyl nitride, and is now under further investigation.

A summary of the principal facts noted above may be stated as follows:

1. The reaction between ammonium chloride and potassium dichromate when heated is not correct as ordinarily given.
2. The oxides of nitrogen are always present in the gas liberated.
3. Both ammonia and chlorine are liberated under certain conditions.
4. Other chromium compounds besides the common oxide are formed.
5. A nitride, presumably trichromyl nitride is formed.
6. The complex nature of this reaction is due in very large measure to the dissociation of ammonium chloride.

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THE ACTION OF THIONYL AND SULPHURYL CHLORIDES ON MERCURY AND MERCURIC OXIDE.

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The action of sulphuryl chloride on mercuric oxide has already been studied by Spelta.[1] He states that red oxide of mercury and sulphuryl chloride do not react in the cold or even after prolonged heating in sealed glass tubes.

Yellow oxide of mercury, on the contrary, was found by Spelta to react with sulphuryl chloride when the two are heated together in sealed glass tubes at 150°. He indicates that the reaction proceeds according to the equation

$$(a) \quad 2HgO + SO_2Cl_2 = HgCl_2 + HgSO_4$$

or

$$(b) \quad HgO + SO_2Cl_2 = HgCl_2 + SO_3$$

[1] *Gazz. chim. ital.*, **34**, 262 (1904).

depending upon the relative quantities of oxide and reagent employed.

During the course of a general research on the action of thionyl and sulphuryl chlorides on metals and metallic oxides, the author has had occasion to repeat the work of Spelta. The results, however, do not entirely concord with those obtained by the latter, as no great difficulty was experienced in causing sulphuryl chloride and red mercuric oxide to react.

Sulphuryl Chloride and Mercuric Oxide.—When *yellow* mercuric oxide and sulphuryl chloride were brought together at the ordinary temperature and pressure, reaction commenced immediately, but proceeded very slowly. After standing several days the yellow color had entirely disappeared. The white powder which remained consisted of a mixture of mercurous and mercuric chlorides.

Small quantities of the yellow oxide with an excess of sulphuryl chloride were then heated together in sealed glass tubes at a temperature of about 150°. Reaction was complete after a few hours. The solid contents of the tubes appeared in the form of clear, colorless crystals, some of which were over 1 cm. in length. When the tubes were opened, considerable pressure was noted and dense white fumes, consisting in part of sulphur trioxide, were given off.

The crystals were dried between filter papers and analyzed. Qualitative tests failed to show more than mere traces of sulphate, and this was probably due to sulphur trioxide formed in the reaction. Quantitative analysis showed the crystals to be mercuric chloride. From this it is evident that, as reported by Spelta, the reaction proceeds according to the equation "*b*" heretofore given. That no mercuric sulphate was present was of course due to the fact that a considerable excess of sulphuryl chloride was employed.

Red oxide of mercury, in contrast to the yellow compound, did not immediately react with sulphuryl chloride in the cold, but after standing several days, some reaction had taken place for the mixture was found to contain traces of both mercurous and mercuric chlorides. As previously stated, no great difficulty was encountered in causing them to react by heating in sealed glass tubes. Moreover, the temperature necessary was only 160–180°. Reaction was complete after 15 or 20 hours.

The results were the same as those obtained from the experiment with the yellow oxide. The crystals were large and clear, and when the tubes were opened dense white fumes containing sulphur trioxide were evolved. Likewise the crystals analyzed to mercuric chloride and showed a mere trace of sulphate.

Why this result differs from that obtained by Spelta is difficult to explain. It is possible, however, that the oxide used by him had been

prepared at a higher temperature, in which case it would naturally show greater resistance to the action of the reagent.

Sulphuryl Chloride and Mercury.—Sulphuryl chloride was found to have no action upon metallic mercury under ordinary conditions of temperature and pressure. But when heated together in sealed glass tubes at 160–180°, reaction was complete after a few hours and a well crystallized product resulted. Great pressure was developed and much sulphur dioxide was evolved when the tubes were opened. The crystals analyzed to mercuric chloride and contained no sulphate. It is probable that the reaction is a simple one, as expressed by the following equation:

$$Hg + SO_2Cl_2 = HgCl_2 + SO_2.$$

When an excess of mercury was used, the solid product formed was noncrystalline, and consisted entirely of mercurous chloride.

Thionyl Chloride and Mercuric Oxide.—A very strong reaction resulted upon bringing thionyl chloride into contact with *yellow* mercuric oxide. Much heat was evolved and the solid contents of the tube became white. Reaction stopped after a few minutes. The white mass was found to be a mixture of the two chlorides of mercury. When *red* oxide of mercury was employed, the same reaction took place, but much more slowly.

In order to obtain better products, both reactions were carried out in sealed glass tubes at about 160°. After heating several hours the tubes presented the same appearance. The crystals were large, and the supernatant liquid was clear but slightly yellowish in color.

Upon opening the tubes they were found to be under no pressure and no sulphur dioxide was evolved. The crystals were mercuric chloride and contained no sulphate. The author is of the opinion that reaction takes place with the formation of sulphuryl chloride and sulphur monochloride according to the following equation:

$$HgO + 5SOCl_2 = HgCl_2 + 3SO_2Cl_2 + S_2Cl_2.$$

The fact that no gaseous products were formed seems to substantiate this view. Furthermore, the supernatant liquid, after decomposition by water, gave a strong test for sulphuric acid. When thionyl chloride is decomposed by water the products are hydrochloric acid and sulphur dioxide.

If the above reaction is true, it can take place only when a large excess of thionyl chloride is present. To ascertain the truth of this, other tubes were prepared, care being taken to employ less of the reagent. In these tubes considerable pressure was developed due to sulphur dioxide formed. The reaction probably proceeds according to the equation

$$HgO + SOCl_2 = HgCl_2 + SO_2.$$

Thionyl Chloride and Mercury.—Thionyl chloride, like sulphuryl chloride, was found to have no reaction upon metallic mercury in the cold. But

after heating in sealed glass tubes for a few hours at 150°, reaction was complete. As in the case of thionyl chloride and mercuric oxide, when a large excess of reagent was employed, no sulphur dioxide was formed and the tubes were therefore under no pressure. But when only a slight excess was employed, considerable pressure was developed. In both cases a strong odor of sulphur monochloride was noticeable while the crystals were being dried, and the filter paper was colored slightly yellow, evidently by this compound. Reaction probably proceeds according to one of the two following equations, depending upon the amount of thionyl chloride used:

$$Hg + 4SOCl_2 = HgCl_2 + 2SO_2Cl_2 + S_2Cl_2$$
$$3Hg + 4SOCl_2 = 3HgCl_2 + 2SO_2 + S_2Cl_2.$$

When an excess of mercury was employed, mercurous chloride, sulphur dioxide and sulphur monochloride were the products.

The author has heretofore investigated many reactions between thionyl chloride and metals or oxides, but the two above-mentioned reactions, in which a large excess of thionyl chloride was used, are the first he has found in which no pressure is developed or in which sulphur dioxide is not one of the final products. It has not been possible to positively identify sulphuryl chloride inasmuch as the amount of thionyl chloride used was small, and the boiling points of the two liquids are too close to allow of definite tests by fractional distillation of small quantities. However, considering the facts heretofore given, the author has little doubt that the reaction proceeds with the formation of sulphuryl chloride, according to the equations given.

The two reactions with sulphuryl chloride are also noteworthy inasmuch as they are the first reactions found for this reagent in which sulphur trioxide or a sulphate is produced.

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[CONTRIBUTION FROM THE LABORATORIES OF GENERAL AND PHYSICAL CHEMISTRY OF THE UNIVERSITY OF CHICAGO.]

DOES CALOMEL FURNISH ANOTHER CONTRADICTION OF THE THEORY OF HETEROGENEOUS DISSOCIATION EQUILIBRIUM?

BY ALEXANDER SMITH.

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As is well known, undried ammonium chloride gives, at 360°, values for the vapor density corresponding to the formula ½ NH_4Cl, and indicating complete dissociation. Brereton Baker,[1] however, using the Victor Meyer and the Dumas methods found that the salt, when elaborately dried, gave at the same temperature values corresponding very nearly

[1] *J. Chem. Soc.*, 65, 615; 73, 475.