ACTION OF AMMONIUM CHLORIDE ON CERTAIN CHLORIDES.

PART I. ACTION ON METALLIC CHLORIDES.

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THE study of the action of ammonium chloride on phosphorus pentachloride, when the two bodies are heated together in a sealed tube, was fruitful in results, leading, as it did, to the discovery, by H. N. Stokes,[1] of a whole series of polymeric chloronitrides of phosphorus, in addition to the one previously known. It is, therefore, rather strange to note that the allied study of the behavior of other chlorides when similarly treated with sal ammoniac has seemingly been entirely neglected. The present communication is the first contribution to a general research on the action of ammonium chloride on polychlorides, a problem with which I have been grappling, off and on, during the last four or five years.

I. ACTION OF AMMONIUM CHLORIDE ON ANTIMONY PENTACHLORIDE.

Antimony chloride being the nearest accessible analogue of phosphorus pentachloride, it was first taken up. The expectation was, judging by analogy, that antimony pentachloride and sal ammoniac might react as follows:

$$SbCl_5 + NH_4Cl = SbNCl_2 + 4HCl.$$

Accordingly in the first experiments the two substances were digested in equimolecular proportions. On sealing them in tubes and heating, no change was observed until the temperature reached about 200° when the liquid began to diminish and the solid to increase in quantity. If the temperature is not allowed to rise above 200°-215°, the process of solidification may take thirty to forty hours, if 10 to 15 grams of antimonic chloride are digested with corresponding amounts of ammonium chloride. The total contents will become solid in ten to twelve hours at 230°-250°. The change of the physical state is not accompanied by evolution of hydrogen chloride. Obviously we have here a case of formation of a double salt. Under favorable conditions of digestion (250°-270°) this salt appears as a uniform, compact white mass (with a yellow tinge due probably to impurities), granular in structure.

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[1] *Am. Chem. J.*, 19, 782.

Not before the temperature reaches 350° are considerable quantities of hydrogen chloride given off and the evolution of gas soon slackens even at that temperature. Only between 350° and 400°, and preferably nearer to the latter, a comparatively rapid progress of the reaction can be insured.

It was soon learned that the reaction did not take place in the sense indicated by the above equation: considerably less hydrogen chloride than required in accordance therewith, was evolved and in the reaction product much antimony trichloride was found. In the earlier experiments the digestion was stopped when the evolution of gas became very slow, and since the highest temperatures which could be attained with the furnace then used were below 350°, the reaction (in the light of subsequent experience) had not been brought to a finish. The consequence was that on distilling off the antimonious chloride a residue containing antimony, nitrogen and chlorine was obtained, a residue which, as found later, disappears if the digestion is carried on until the reaction is completed. As it was, the residue unnecessarily complicated matters. And the difficulty was only overcome after an allied study of the action of phosphonium iodide on antimony pentachloride[1] had been completed by Ernestine Fireman and the writer. In that case we found that the following reaction takes place:

$$3SbCl_5 + 3PH_4I = 2SbCl_3 + SbI_3 + 9HCl + PH_3 + P_2.$$

It suggested itself that between antimony pentachloride and ammonium chloride, analogously, this reaction might take place:

$$3SbCl_5 + 3NH_4Cl = 3SbCl_3 + 8HCl + NH_4Cl + N_2.$$

or simpler:

$$3SbCl_5 + 2NH_4Cl = 3SbCl_3 + 8HCl + N_2.$$

New experiments at higher temperatures soon proved the reaction to proceed as represented by these equations.

Of the numerous experiments, a somewhat detailed description will be given only of the last one, which was made with two tubes. One tube (I) received 13.1 grams (3 mols.) of antimony pentachloride and 1.57 grams (2 mols.) of ammonium chloride, and another (II) 15.2 grams (1 mol.) of the former and 2.73 grams (1 mol.) of the latter body. On heating the sealed tubes from

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[1] *Am. Chem. J.*, 30, 118.

ten to twelve hours at 380°-390°, tube I lost 1.63 grams and tube II 1.73 grams of gaseous products. The contents of the tubes became solid. Further digestion for from seventeen to eighteen hours at 380°-405° caused tube I to lose 1.37 grams and tube II 1.33 grams by escaping gases. The somewhat softened solid mass of the tubes foamed up as the gases rushed out. After renewed heating for twenty-two hours at 380°-410° the losses of tubes I and II were 1.51 and 2.58 grams, respectively. The foaming in the latter tube was very violent, causing the throwing out of a slight amount of the solid product. Further digestion for forty hours at the same temperature occasioned only the losses 0.05 and 0.1 gram. The contents of the tubes were now a water-clear mass consisting of prismatic crystals with pyramidic base.

The total loss of tube I was 4.56 grams instead of 4.69 grams, as calculated for hydrogen chloride and nitrogen according to the above equation; that of tube II, 5.65 instead of 5.44 grams. The excessive loss in the latter tube was due, as indicated above. to some of the product having been thrown out by the outrushing gases. It will perhaps not be superfluous to give the data of another experiment in which 15.5 grams (1 mol.) of antimonic chloride and 2.79 grams (1 mol.) of sal ammoniac were used. On heating until no more gases were evolved the total loss was 5.49 grams instead of 5.55 grams (theory).

The crystalline residue in the tubes was easily identified as antimonious chloride by its ready fusibility and by its boiling-point. The contents of tube I (without excess of ammonium chloride) distilled almost entirely at 218° (boiling-point of the trichloride of antimony) and that of tube II (with excess of ammonium chloride) passed over for the most part at 218°, but in part, towards the end, at up to 230°, leaving a small residue identified as sal ammoniac.

To ascertain whether the gaseous product actually contains nitrogen as well as hydrochloric acid, the evolved gases were in one experiment collected and examined, the tube having been, after digestion, opened under water, after the procedure of Stadel.[1] In that case the tube (of about 50 cc. capacity) with the reacting bodies was heated for some time and then cooled and opened as usual; these operations were repeated until about 3

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[1] *Ann. Chem.* (Liebig), **195**, 190.

grams of the gases escaped. After the most of the air had thus been swept out of the tube the latter was once more heated. On cooling, the tube was immersed in a 12-gallon jar filled with water. The tip of the tube pointing to the cylinder was then filed in under the water until the gas bubbles began to gently break through The discharge of the gases lasted more than ten minutes. The hydrochloric acid was absorbed by the water in the jar while in the cylinder collected 118 cc. (reduced to normal temperature and pressure) of a gas not absorbed by water. The acid required 44 cc. of normal potash for neutralization, hence amounting to 1.6148 grams, while the 116 cc. of nitrogen (allowing 2 cc. for admixed air) weighed 0.1457 gram. The ratio of 1.6148 : 0.1457 is equal to 11.1, while the ratio of hydrochloric acid to nitrogen, according to the above equations, is 10.4.

These figures, though very rough, accord well with the sense of the reaction in question. Thus the equation

$$3SbCl_5 + 2NH_4Cl = 3SbCl_3 + 8HCl + N_2$$

accurately represents the reaction between antimony pentachloride and ammonium chloride.[1]

II. ACTION OF AMMONIUM CHLORIDE ON TIN TETRACHLORIDE.

These two bodies apparently do not exert the slightest influence upon one another even when heated for several days at temperatures of 400° and upward.

III. ACTION OF AMMONIUM CHLORIDE ON TITANIUM TETRACHLORIDE.

After heating the two substances for twenty hours at 260°-270° a greenish yellow solid began to appear. The formation of the new body proceeds very slowly. After digestion for sixty hours at 260°-270° and for twenty more hours at 360° there still remained some unchanged liquid which only entirely disappeared after further heating for eighteen hours at 400°-410°. During all the above and renewed heating at the highest temperatures attainable in the tube furnaces, scarcely any gaseous products were evolved. Obviously no other reaction takes place between titanium tetrachloride and sal ammoniac than the formation of a double salt.

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[1] The subject of this section of the article was begun by the writer in cooperation with E. G. Portner, in 1899, at the Columbian University, Washington, D. C., but their joint work was soon discontinued, the former having left the institution before the nature of the reaction in question was cleared up.

Seeing that antimony pentachloride is completely reduced by ammonium chloride to a lower chloride while stannic and titanic chloride are not reduced in the slightest under the same conditions, it occurred to the writer that the reaction between antimonic chloride and sal ammoniac is not a direct reduction of the former by the latter, but primarily a decomposition of ammonium chloride by the free chlorine due to the dissociation of antimony pentachloride. Stannic and titanic chlorides are not known to be dissociated even at higher temperatures and, therefore, remain unaltered when heated in the presence of ammonium chloride. If this conjecture is correct, then we should expect, *e. g.*, ferric chloride and cupric chloride which dissociate at higher temperatures, to be reduced by ammonium chloride and mercuric chloride, which is not known to dissociate, to remain unchanged. The following experiments were undertaken to test these inferences.

IV. ACTION OF AMMONIUM CHLORIDE ON FERRIC CHLORIDE.

Ferric chloride does not, according to Victor Meyer and Grünbaum,[1] show any signs of dissociation at 448°, the temperature of boiling sulphur, but breaks up appreciably as the temperature approaches 500°. It was interesting to find out whether the chlorine of ferric chloride will be available for the decomposition of ammonium chloride at the temperatures attainable in "bomb" furnaces. Expecting that the two bodies would react in accordance with the equation

$$3FeCl_3 + NH_4Cl = 3FeCl_2 + 4HCl + N,$$

5 grams (3 mols.) of anhydrous sublimed ferric chloride and 0.636 gram (1 mol.) of sal ammoniac were sealed up in a glass tube and digested.

14 hours at about 400° caused the escape of 0.35 gram of gases.
36 " " " 420° " " " " 0.55 " " "
40 " " " 420° " " " " 0.33 " " "
30 " " " 420° " " " " 0.43 " " "
20 " " " 420° " " " " 0.10 " " "
48 " " " 420° " " " " 0.04 " " "

During the digestion the original brown-black mass gave rise at the first stages to the formation (on cooling) of beautiful red hexagonal plates, which gradually disappeared at the later stages,

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[1] *Ber. d. chem. Ges.*, **21**, 687.

the contents of the tube becoming at the end greenish yellow, with a brown tinge in some places. The total loss in gaseous products was 1.8 grams, instead of 1.9 grams, which should have been lost in accordance with the above equation.

V. ACTION OF AMMONIUM CHLORIDE ON CUPRIC CHLORIDE.

Cupric chloride, we learn in chemical handbooks, decompose into cuprous chloride and chlorine at a red heat. Two experiments were made bringing together in one tube 5.9 grams of anhydrous cupric chloride and 2.357 grams of ammonium chloride according to the equation

$$3CuCl_2 + 3NH_4Cl = 3CuCl + 4HCl + N + 2NH_4Cl,$$

and in the other (using rather too small amounts of the reacting bodies) 2.3 grams of cupric chloride and 0.305 gram of ammonium chloride according to the equation

$$3CuCl_2 + NH_4Cl = 3CuCl + 4HCl + N.$$

The rate of the progress of the reaction will be shown in the case of the former experiment. The heatings and losses were as follows:

	Gram.
6 hours at about 400°	0.93
9 " " " 400°	0.65
24 " " " 400°	0.46
30 " " " 410	0.25

The total loss in evolved gases was 2.29 grams instead of 2.33 grams, calculated. In the other experiment 0.81 gram was lost in place of 0.91 gram. After the digestion was completed, the contents of the tube with excess of ammonium chloride was a crystalline mass, gray to brown-black, while that in the other tube was blue-black with streaks of yellow and of a copper luster.

VI. ACTION OF AMMONIUM CHLORIDE ON CORROSIVE SUBLIMATE.

The two bodies in equimolecular proportions were heated for eighteen hours at 300° and then at once withdrawn from the furnace. The contents of the tube presented a homogeneous liquid, which on cooling solidified to beautiful interlacing strands of silky fibers. The formation of this crystalline mass, as well as additional prolonged heating at the highest temperatures attainable in the "bomb" furnaces, did not cause the evolution of gases. Evidently the only reaction in this case is the formation of a double salt.

Thus the experiments with ferric chloride and cupric chloride fully corroborate, by positive results, and that with mercuric chloride, by a negative result, the conjecture expressed above. We may consider, therefore, as well established the rule that only those metallic chlorides, which more or less readily dissociate are reduced to a lower degree of chlorination when heated in a closed tube with ammonium chloride, the latter breaking up completely thereby with the setting free of nitrogen.

In the chemical literature I find only one instance which has a direct bearing on the rule in question. H. Moissan[1] prepared chromous chloride by heating chromic chloride in ammonium chloride vapor. Neither chromic nor chromous chloride being volatile below a red heat, it was not necessary to heat the reacting substances in a sealed tube, but obviously the reaction in this case has to be represented by the equation

$$3CrCl_3 + NH_4Cl = 3CrCl_2 + 4HCl + N,$$

and falls under the rule formulated above; chromic chloride is reduced by ammonium chloride because it dissociates.

In closing, I may say that while studying the action of ammonium chloride on metallic chlorides, a subject which will continue to occupy me in the immediate future, I have been devoting considerably more attention to the more interesting study of the action of ammonium chloride on the chlorides of some non-metallic elements, *viz.*, of carbon, silicon and sulphur, and I hope to be able to publish the results soon.

THE ACTION OF CHLORIC ACID ON METALS.

By W. S. Hendrixson.

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In the course of my work a year ago on "Silver as a Reducing Agent," in which the action of finely divided silver on chloric, iodic and chromic acids was studied quantitatively, there was occasion to study the literature regarding the action of chloric and related acids on other metals. It soon appeared clear that the amount of information to be gained about the action of chloric acid, in particular, on the metals was very meager, and it appeared

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[1] *Ann. chim. phys.* [5], **25**, 401.