

which was totally unexpected. He had denied ever having had any mental disease when catechised previous to his acceptance as a juror. A second trial was therefore necessary. It resulted in a verdict of imprisonment for life.

The wife of the prisoner was held in custody for many months, but was finally released on her own recognizance. She had presented herself at the insurance offices dressed in appropriate mourning and claiming to be the widow of "Baum." Several of the companies made payments which she accepted.

It is a noteworthy circumstance that the history of antimonial poisoning is so frequently connected with the destruction of lives heavily insured. Taylor,¹ in a monograph, gives some remarkable cases. In some of these a second poison was administered. Though there have been cases where arsenic has been found along with antimony its presence has been due to the impure nature of the antimony. We have not been able to find the record of any case of chronic antimonial poisoning followed by the use of arsenic as a toxic agent.

BELLEVUE HOSPITAL MEDICAL COLLEGE,
May 10, 1895.

[CONTRIBUTIONS FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY. NO. 4.]

ACTION OF HYDROCHLORIC ACID GAS UPON SALTS OF THE ELEMENTS OF GROUP V OF THE PERIODIC SYSTEM.

BY EDGAR F. SMITH AND JOS. G. HIBBS.

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IN a former number of this Journal (*Vol. XI, 578*) we took occasion to call attention to the rather interesting behavior of sodium vanadate, when gently heated in an atmosphere of hydrochloric acid gas. The results obtained by us proved that vanadic acid is entirely expelled from its salt by this means. This behavior naturally suggested a line of investigation, which we hoped to begin at once, but it was not until very recently that we were able to resume the study. The idea as to whether the salts of the acids of other elements of Group V of the Periodic System were similarly transposed by hydrochloric acid gas, or by the gaseous haloid acids in general, constantly obtruded itself.

¹ On Poisoning by Tartarized Antimony. A. S. Taylor, M.D., F.R.S., *Guy's Hospital Reports*, Third Series, 3, 369, 1857.

We accordingly turned to sodium nitrate and submitted it to the action of hydrochloric acid gas, aiding the reaction by a gentle heat. The gas was evolved by dropping concentrated sulphuric acid from a funnel tube into commercial hydrochloric acid. From the evolution flask it passed through an empty bottle and then through sulphuric acid, from which it entered a combustion tube carrying a boat containing the salt to be acted upon. The products of the reaction were conducted into water, contained in a bulb-receiver, to which was attached a small Erlenmeyer flask containing water.

When the gas came in contact with pure sodium nitrate, action set in even in the cold. The salt assumed a brown-yellow color and a yellow liquid condensed in the cooler portion of the combustion tube. On the application of heat this was driven into the receiver. The action was continued for fifteen minutes, after which the boat was allowed to cool in the gas and then transferred to a vacuum desiccator, where it remained for an hour before it was weighed. An examination of its contents revealed the presence of nothing but sodium chloride. That the conversion was quantitative is evident from the following data:

Experiment 1.—0.1878 gram of carefully dried nitrate gave 0.1289 gram of sodium chloride, while the calculated quantity of the latter is 0.1290 gram.

Experiment 2.—0.3536 gram of nitrate gave 0.2429 gram of chloride, instead of the theoretical 0.2428 gram.

Experiment 3.—0.2971 gram of nitrate gave 0.2040 gram of chloride, while the required quantity is 0.2041 gram.

Experiment 4.—0.6462 gram of nitrate gave 0.4440 gram of chloride, instead of 0.4439 gram, as required by theory.

In experimenting with phosphates we used pure sodium pyrophosphate. We found that this salt was not affected when subjected to the action just described. Nothing was expelled from it. When sodium pyroarsenate was substituted for the phosphate action did occur; the arsenic was completely volatilized and collected in the water contained in the bulb-receiver. The contents of the latter were carefully poured into a beaker glass and oxidized with a few drops of nitric acid. Later a "magnesiâ mixture" was added to the neutralized solution, which was permit-

ted to stand fifteen hours before the magnesium ammonium arsenate was filtered. It was finally weighed as magnesium pyroarsenate. The contents of the boat were also dissolved and tested for arsenic, but none was found.

Experiment 1.—0.3844 gram of sodium pyroarsenate gave 0.3355 gram of magnesium pyroarsenate, instead of 0.3361 gram, the quantity required by theory.

Experiment 2.—0.1093 gram of sodium pyroarsenate gave 0.0959 gram of the magnesium salt, instead of 0.0956 gram, the calculated quantity.

In these experiments a colorless liquid collected in the cooler portions of the tube beyond the boat, but this disappeared upon the application of a gentle heat.

In a third trial the aqueous arsenic solution was not oxidized, consequently the arsenic obtained by precipitation with the "magnesia mixture" was far from the required quantity. From this we infer that the arsenic is not volatilized wholly as a derivative of its higher oxide. The latter doubtless suffers partial reduction. We are striving at present to ascertain in what form it is removed. When it is considered that vanadic acid is expelled as an oxychloride, analogy would suggest some similar form for the arsenic. Of this, however, we expect to speak more definitely in the future.

Care should be exercised in heating the sodium pyroarsenate in the hydrochloric acid gas, as the salt when heated in it fuses very readily, and after fusion sets in the acid acts rather slowly. Magnesium pyroarsenate and lead arsenate were found to be converted quite as readily, by the gas, into their chlorides and the arsenic as completely eliminated as in the case of the sodium salt. The corresponding phosphates remained unchanged.

The separation of the two acids, when associated as sodium salts, as magnesium salts, and lead salts, was tried.

Experiment 1.—A mixture, consisting of one-tenth gram of sodium pyroarsenate and an equal amount of sodium pyrophosphate, was treated as just described. The arsenic found in the bulb-receiver and weighed as magnesium pyroarsenate, was 0.0869 gram. Theory required 0.0874 gram. The phosphate remaining in the boat was dissolved in water and the acid finally

weighed as magnesium pyrophosphate. It equaled 0.0830 gram instead of 0.0834 gram, the theoretical quantity.

Experiment 2.—In this trial 0.1100 gram of each salt was used. The volatilized arsenic, weighed as pyro-salt, equaled 0.0957 gram, instead of 0.0961 gram. The non-volatilized phosphorus, weighed in the same form, equaled 0.0909 gram, instead of the theoretical 0.0918 gram.

We next prepared magnesium pyroarsenate and magnesium pyrophosphate. Mixtures of these salts were then acted upon by the acid gas. Two separations were made with the following results:

Experiment 1.—0.1100 gram of each salt brought into a boat was acted upon by the acid. No difference from the behavior of the sodium salts was observed, excepting that the tendency to fusion was not so marked in this case as with the sodium salts. The volatilized arsenic acid gave 0.1094 gram of magnesium pyro-salt, thus falling short of the theoretical amount by 0.0006 gram. The residual magnesium pyrophosphate weighed 0.1105 gram. This approaches the theoretical (0.1100 gram) so closely that the separation must be viewed as complete.

Experiment 2.—The same quantities of the two salts were taken in this trial. Instead of 0.1100 gram of pyrophosphate actually taken the found salt equaled 0.1108 gram. The difference between the arsenic salt used and the quantity of it, which was carried out of the mixture by the gas, equaled 0.0009 gram. An examination of the non-volatilized phosphate showed it to be free from arsenic. Lead arsenate was very readily transposed by the acid into lead chloride, and the volatile arsenic derivative.

Lead arsenate.	Obtained.	Lead chloride. Required.
<i>Experiment 1.</i> —0.2965 gram	gave 0.2746 gram	0.2747 gram.
" 2.—0.3608 "	" " 0.3347 "	0.3343 "

The residual lead chloride was dissolved in water, and the aqueous solution introduced into a Marsh apparatus. Not a trace of arsenic was found in this way. Upon adding a very slight amount of lead arsenate to the solution the mirror and spots of arsenic were almost immediately observed. The complete transposition of this salt induced us to execute a third trial in which we not only weighed the residual lead chloride and

found it satisfactory, but also determined the arsenic which had been volatilized.

Lead arsenate.

Magnesium pyroarsenate.
Found. Calculated.

0.2965 gram gave.....0.1022 gram. 0.1028 gram.

Two portions of a mineral containing lead, arsenic acid, and phosphoric acid, were exposed to the action of the acid gas. The volatilized arsenic equaled in (a) 10.42 per cent, and in (b) 10.39 per cent. None remained in the residue contained in the boat.

Experiments have not yet been made with antimonates.

Separations of vanadic and arsenic acids from tungstic and chromic acids are now being carried out, and with encouraging results. The action of hydrobromic, hydriodic and hydrofluoric acid in gas form upon vanadates, nitrates, arsenates and phosphates, has received attention with results which will appear later.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF
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URANIUM OXYNITRIDE AND URANIUM DIOXIDE.

BY EDGAR F. SMITH AND J. MERRITT MATTHEWS.

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THE action of ammonia upon molybdenyl (MoO_2Cl_2) and tungstyl (WO_2Cl_2) chlorides has received attention in this laboratory. To complete the study of Group VI in this direction, uranyl chloride (UO_2Cl_2) was prepared, placed in a porcelain boat and heated in a glass tube in a current of dry ammonia. At a comparatively moderate temperature the material began to take on a dark color, and copious fumes of ammonium chloride were evolved. The heat was raised and continued until the ammoniacal salt was no longer produced. The residue was dull black in color. When fused in a nickel crucible with caustic potash, ammonia was slowly evolved. A portion of the substance introduced into aqueous silver nitrate caused the separation of a beautiful deposit of brilliant crystals of metallic silver. Chlorine was not found in the compound. When it was heated with sulphuric acid (1:2) in a sealed tube, complete solution ensued. Upon titration with standardized potassium permanganate, the presence of 6.83 per cent. of dioxide was disclosed. No hydro-