difference in feeding methods pursued in America and Europe. They are no doubt right, though the mode of rendering also differs.

At the present time the writer is aware of no method of analysis approaching the modified method of Muter for accuracy, and invariably applies it in doubtful cases.

G. Halphen[1] gives results of a method of separating the fluid and solid fatty acids based on difference in solubility of zinc salts in carbon bisulphide. Their results show that very imperfect separations are obtained and the process has little practical utility. The writer tried the same method in 1888, using gasoline, and obtained better but not satisfactory results.

In conclusion, I would say that working with the best analytical methods at our command, unless the origin of samples is known, the analyst is frequently at a loss to interpret results, in much the same manner as in passing upon a potable water of unknown history, and often when we see the self-confident manner in which small percentages of cotton oil are announced on very questionable data, we feel like exclaiming with the poet,

"Fools rush in where angels fear to tread."

March 12, 1895.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY. NO. 7.]

THE ACTION OF HALOID ACIDS IN GAS FORM UPON THE SALTS OF ELEMENTS OF GROUP V OF THE PERIODIC SYSTEM.

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Received May 3, 1895.

AFTER observing the conduct of salts of the acids of elements of Group V toward hydrochloric acid gas, it was but natural that we should, with some interest, note the results arising when the other haloid acids, in gas form, were substituted for hydrogen chloride. It was useless to predict what might occur, and, therefore, the slight variations from preconceived notions were in no wise surprising. Taking up the study of the haloid acids and the various salts in the order of increasing molecular magnitude, we began with

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[1] *J. de Pharm. et Chim.*, 30, 241-247, *1894*.

1. THE ACTION OF HYDROFLUORIC ACID GAS UPON SODIUM NITRATE.

The salt was exposed to the action of the gas in a platinum boat, carried in an iron tube. The temperature at which the reaction was conducted did not exceed 250° C. Not more than twenty minutes were allowed, or required, for the change which, from the analytical result given below, is evidently complete.

Experiment.—0.1052 gram of sodium nitrate gave 0.0530 gram of sodium fluoride, instead of 0.0520 gram, the theoretical amount.

A second trial gave a similar quantitative result.

2. THE ACTION OF HYDROFLUORIC ACID UPON PHOSPHATES.

The gaseous acid expelled nothing from sodium pyrophosphate. The boat contents sustained no less in weight. The water in the receiver gave no evidence of the presence of phosphorus when tested for it.

3. HYDROFLUORIC ACID AND VANADATES.

Sodium vanadate, thoroughly dried, was heated to 250° C., for one-half hour in an atmosphere of the acid vapor. Vanadium was found both in the receiver and in the boat. Upon repeating the experiment, increasing the temperature, and continuing the action of the acid vapor through an hour, about one-half of the vanadic acid was volatilized.

4. HYDROFLUORIC ACID AND ARSENATES.

In these trials sodium pyroarsenate was heated to about 400° C., while exposed to a brisk current of the acid vapors.

Experiment 1.—0.1893 gram of sodium pyroarsenate was used. When the boat-contents were examined 0.0872 gram of the pyro-salt was found unvolatilized.

Experiment 2.—0.2015 gram was treated in the same manner, with practically the same result. The volatilization, therefore, of the arsenic compound must be considered as incomplete.

To summarize, nitrates are entirely converted into fluorides by the vapors of hydrofluoric acid; with vanadates and arsenates the conversion is incomplete, while phosphates remain intact.

1. HYDROBROMIC ACID AND NITRATES.

Apparently no change occurs when these compounds are brought together in the cold. When gently heated aqueous vapor and bromine appear. In the course of half an hour the conversion into bromide is finished.

Experiment.—0.1887 gram of sodium nitrate gave 0.2286 gram of sodium bromide, instead of the theoretical 0.2273 gram.

2. HYDROBROMIC ACID AND PHOSPHATES.

Not even traces of phosphoric acid were expelled on heating sodium pyrophosphate in an atmosphere of hydrobromic acid.

3. HYDROBROMIC ACID AND VANADATES.

Sodium vanadate was acted upon in the cold. It became brown in color, and when the temperature was raised to almost 300° C., vapors escaped and condensed to an oily, reddish liquid beyond the heated portion of the tube. By the continued action of the acid this liquid acquired a green color, and small, green-colored crystals appeared. After the lapse of half an hour the liquid had completely solidified to a mass of radiating needles, having a beautiful green color. Several analyses of this compound showed the presence of 59.40 per cent. bromine and 14.65 per cent. vanadium, which would closely approximate the formula $V_2O_3Br_2.3HBr.7H_2O$, requiring 58.91 per cent. bromine and 15.02 per cent. vanadium. That such an oxybromide is not improbable may be inferred from the fact that Ditte (*Comptes rendus*, **102,** 1310) prepared the compound $V_2O_3Br_2.2HBr.7H_2O$, by boiling vanadic oxide (V_2O_5) with hydrobromic acid. It required 53.51 per cent. bromine and 17.06 per cent. vanadium. The conversion into bromide was not complete.

4. HYDROBROMIC ACID AND ARSENATES.

Quite a distinct reaction was evident with pure, dry, sodium pyroarsenate even in the cold. The salt assumed a dark-grey color. When a gentle heat was applied to it vapors were expelled; these condensed in the anterior portion of the tube to a pale-yellow, oily liquid, soluble in water. The temperature at which the reaction was carried out did not exceed 300° C. The boat contained pure sodium bromide.

Experiment 1.—0.5440 gram of pyroarsenate gave 0.6335 gram of sodium bromide, instead of 0.6331 gram, the theoretical quantity.

Experiment 2.—0.4277 gram of pyrophosphate gave 0.4984 gram of sodium bromide, while theory requires 0.4981 gram.

With this complete, quantitative expulsion of arsenic, and the non-volatilization of phosphoric acid before us, we next proceeded to the separation of the two acids, both being present as sodium pyro-salts.

Experiment 3.—0.1572 gram of sodium pyroarsenate and 0.1897 gram of sodium pyrophosphate were mixed and gently heated in hydrobromic acid gas. The phosphate remaining in the boat, when determined and calculated into pyro-salt, equaled 0.1903 gram. As it was free from arsenic, we did not estimate the arsenic contained in the receiver.

Through both hydrobromic acid and hydrochloric acid vapors, acting upon a mixture of arsenates and phosphates, a separation of the two acids may be effected.

The succeeding experiments relate to the conduct of nitrates, arsenates, and phosphates toward hydriodic acid gas. This was prepared by dropping water upon a mixture of amorphous phosphorus and iodine. It was carefully dried before it came in contact with the salts.

I. HYDRIODIC ACID AND NITRATES.

Sodium nitrate was changed by the gas into iodide. One approximate result may be given:

0.1039 gram of sodium nitrate gave 0.1886 gram of sodium iodide, instead of the theoretical 0.1833 gram.

Not one experiment could be completed, since explosions of considerable violence invariably occurred. A dark sublimate, apparently iodine, appeared in the tube, and after the lapse of a quarter of an hour a flash of fire ran through the tube, accompanied by a loud report. Not succeeding in finding a method to prevent this, further work was abandoned. These explosions were doubtless due to the production of some unstable derivative of nitrogen and iodine.

Phosphates were not altered by contact with hydriodic acid gas.

2. HYDRIODIC ACID AND ARSENATES.

Sodium pyroarsenate was employed. In the cold the acid gas produced a change. Thus, 0.1592 gram of pyro-salt gave 0.2672 gram of sodium iodide, instead of 0.2689 gram. The arsenic volatilized, determined, and calculated into pyro-salt gave 0.1583 gram instead of 0.1592 gram. As explosions occurred in all the trials made we concluded to abandon the study.

It may not be uninteresting to present a scheme of the elements, composing Group V of the periodic system,

Nitrogen	Phosphorus	Arsenic	Antimony	——	Bismuth
14	31	75	120	164?	208
	Vanadium	Columbium		Didymium	Tantalum
	51	94		142	182,

and briefly review their deportment so far as known, when acted upon by the gaseous haloids. Nitrogen is fully expelled by all of them from nitrates. Phosphorus, existing as phosphates, apparently is absolutely uninfluenced and remains unaltered in the salts with which experiments were tried. Arsenic is only partially volatilized from arsenates by hydrofluoric acid gas, but is completely removed by any one of the remaining haloid acids. Antimony is fully expelled from antimonates by hydrochloric acid gas. No experiments have been tried with bismuth. Hydrofluoric and hydrobromic acid gas volatilize vanadium in part, while its removal from sodium vanadate by hydrochloric acid gas is complete. We have no knowledge of the action of hydriodic acid. Columbium yields volatile products with both hydrochloric and hydrobromic acid vapors. Didymium has never been subjected to this treatment. Tantalum is but slightly affected by the vapors of hydrochloric acid, although it has long been known that both the oxide of columbium and that of tantalum are volatilized to a marked degree when heated with aqueous hydrofluoric acid.

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