XXI.—*On the Bichromate of Ammonia, and some of its Double Salts.*

BY MESSRS. HENRY R. RICHMOND AND JOHN S. ABEL,
Of the Royal College of Chemistry.

Being engaged, a few weeks since, in preparing some of the double salts of chromic acid, described by Mr. S. Darby, in the Quarterly Journal of the Chemical Society,† we were struck by the unusual and somewhat improbable nature of the formula, $\text{NH}_3 \cdot 2\text{CrO}_3$, assigned by him to the bichromate of ammonia. We, therefore, prepared a specimen of the salt, and made several analyses of it, the details of which are given below. We also prepared and analysed several double compounds which the bichromate of ammonia forms with protochloride of mercury.

BICHRIMATE OF AMMONIA.

The bichromate of ammonia was prepared according to the directions given by Mr. Darby. A strong solution of chromic acid was

* In the construction of these formulæ, the oxide of iron and silica were not taken into consideration, as it was supposed that all soils contain these substances in sufficient quantity to supply the wants of any plant not belonging to the *gramineæ*.

† Including the alkaline chlorides, and regarding them as free alkalis.

‡ Vol. I. p. 20.

divided into two equal portions, one of which was saturated with ammonia; the two solutions were then mixed and evaporated.

As the chromic acid employed contained a large quantity of sulphuric acid, the product of the first crystallization was very impure. It was of a brown colour, but became perfectly yellow and opaque on drying. This curious change could also be produced at once by pouring water over the crystals.

After several recrystallizations, the colour changed to a beautiful red, and the crystals no longer became opaque under any circumstances. For analysis, they were powdered and dried *in vacuo* over sulphuric acid.

In determining the quantity of chromic acid, we availed ourselves of the remarkable deportment of this salt when exposed to the influence of heat. Under these circumstances, the salt is decomposed with evolution of nitrogen and water, according to the following equation:

or, if we take the formula $\text{NH}_3 \cdot 2 \text{CrO}_3$,

This decomposition was observed at an early period by Hayes, and lately again by Böttger, who noticed that the sesquioxide, separated in this reaction, presents a very peculiar appearance, closely resembling mixed tea.

In order to avoid all loss from the violent evolution of steam and nitrogen, which was apt to scatter portions of the sesquioxide, it was found convenient to insert a plug of asbestos into the glass tube in which the operation was performed: the tube was subsequently drawn out, so as to leave only a small opening for the escape of the gases.

The ammonia determinations were made in the following manner: a weighed portion of the substance was dissolved in a small quantity of water in a porcelain dish; hydrochloric acid and alcohol were added to reduce the chromic acid; and the ammonia was precipitated by means of bichloride of platinum. After evaporating nearly to dryness, the residue was thrown on a filter, and the sesquichloride of chromium was removed by washing in the usual way with a mixture of alcohol and ether, in which it is readily soluble.

Several other methods of determining the ammonia were tried without success. One of these consisted in distilling the bichromate with a solution of potassa, the liberated ammonia being collected in the ordinary nitrogen bulbs. The results of this process were always too low, owing to a portion of the ammonia remaining in the solution.

In addition to the determinations of chromic acid and ammonia, several hydrogen determinations were made by burning the salt with chromate of lead.

We have given below the calculated percentages of chromic acid and of ammonia for the formulæ $\text{NH}_3 \cdot 2 \text{CrO}_3$, and $\text{NH}_4\text{O} \cdot 2 \text{CrO}_3$. It will be seen that the results of all the analyses agree pretty closely with the latter formula.

Theoretical percentages :

	Formula $\text{NH}_3 \cdot 2 \text{CrO}_3$.		Formula $\text{NH}_4\text{O} \cdot 2 \text{CrO}_3$.	
Chromic acid . . .	104.30	85.98	104.30	80.05
Ammonia	17.00	14.02	17.00	13.05
Water	—	—	9.00	6.90
	<hr/>	<hr/>	<hr/>	<hr/>
	121.30	100.00	130.30	100.00

Details of analyses:

CHROMIC ACID DETERMINATIONS.

- I. 0.8753 grm. of salt gave 0.5393 grm. of sesquioxide of chromium
 II. 0.624 " " " 0.385 " " "
 III. 0.2273 " " " 0.1409 " " "

AMMONIA DETERMINATIONS.

- IV. 0.3682 grm. of salt gave 0.641 grm. of the platinum-salt
 V. 0.1198 " " " 0.2043 " " "
 VI. 0.2185 " " " 0.3767 " " "
 VII. 0.2515 " " " 0.4332 " " "

The percentage of chromic acid and ammonia calculated from these analyses is tabulated below.

Calculated percentages :

	I.	II.	III.	IV.	V.	VI.	VII.
Chromic acid	80.03	80.14	80.40	—	—	—	—
Ammonia	—	—	—	13.11	12.99	13.09	13.08

HYDROGEN DETERMINATIONS.

- VIII. 2.8217 grm. of the salt gave 0.8165 grm. of water

- IX. 2.0455 " " " 0.5752 " "

The theoretical percentage of hydrogen for the formula $\text{NH}_3 \cdot 2 \text{CrO}_3$ is 2.47.

The theoretical percentage of hydrogen for the formula $\text{NH}_4\text{O} \cdot 2 \text{CrO}_3$ is 3.07.

Analyses VIII. and IX. give respectively 3.21 and 3.12 per cent, agreeing with the latter formula.

In all the calculations, we have taken the equivalent of chromium as 28.15, instead of 26.3, which is the number adopted by Mr. Darby. The latter supposition reduces the theoretical percentage of chromic acid, according to either formula, by about 0.5, and slightly increases the percentage of chromic acid deduced from the amounts of sesquioxide of chromium found in the analyses. These discrepan-

cies, however, are by no means sufficient to account for the great difference between our results and those of Mr. Darby. We have made a few experiments, in order to ascertain whether the compound in question might lose an equivalent of water at 100° , and thus give rise to the formation of the substance which has been analysed by Mr. Darby: we have not, however, succeeded in obtaining such a compound. Leaving it, therefore, doubtful whether such a body actually exists, we do not hesitate to conclude, from the results of our own analyses, that a compound of the formula $\text{NH}_4 \text{O} \cdot 2\text{CrO}_3$ does exist, exactly corresponding to the potassa-salt, $\text{KO} \cdot 2\text{CrO}_3$, with which it is most likely isomorphous.

DOUBLE COMPOUNDS OF BICHROMATE OF AMMONIA WITH PROTOCHLORIDE OF MERCURY.

Having satisfied ourselves with respect to the constitution of the bichromate of ammonia, we next turned our attention to the double salt which it forms with protochloride of mercury, and to which Mr. Darby has assigned the formula $\text{NH}_3 \cdot 2 \text{CrO}_3 \cdot \text{HgCl}$.

This salt presents itself in very different forms, according to the strength of the solution from which it is crystallized. The first specimen which was prepared was deposited from a concentrated solution in the form of small red needles, closely resembling those of the bichromate of chloride of potassium. Several analyses of this salt gave rather uncertain results, approaching, however, most nearly to Mr. Darby's formula. As it seemed probable that a small quantity of uncombined protochloride of mercury was mixed with the salt, we prepared another specimen in the following manner. About equal weights of the two salts were dissolved together in rather a large quantity of water; the solution being allowed to cool, a portion of the protochloride of mercury separated and was removed. The solution was then evaporated down just sufficiently to cause the formation of a few crystals on cooling. The salt obtained in this manner crystallized in beautiful, large, six-sided prisms of a splendid red colour. The crystals were dried on blotting-paper, and afterwards *in vacuo* over sulphuric acid.

On further evaporation, the liquid yielded a second crop of crystals, in appearance exactly the same as the first, which were likewise removed and dried. The mother-liquor was once more evaporated, and on cooling deposited some more beautiful red crystals, very much resembling the other crops, but rather more inclined to the needle-shape; these crystals were also preserved and dried. On attempting to recrystallize portions of these salts, it was found that a part of the protochloride of mercury crystallized out by itself,—

whence it appears that it is necessary to have an excess of bichromate of ammonia in the solution, to obtain the salts free from uncombined protochloride of mercury.

The products of these three crystallizations were analysed successively in the order in which they were deposited. They all deflagrated on heating, the protochloride of mercury being driven off, together with the water of the nitrogen resulting from the decomposition of the bichromate of ammonia, and pure sesquioxide of chromium remaining behind: the first two salts deflagrated gently, leaving the sesquioxide of chromium in the form of a dark powder, which became green when strongly heated; the third salt deflagrated violently, swelling up to a great bulk, and leaving the sesquioxide in large flakes of a dull green colour, assuming the most fantastic shapes.

CHROMIC ACID DETERMINATIONS BY IGNITION.

The chromic acid in these salts was determined in nearly the same manner as in the bichromate of ammonia; but as they did not deflagrate with such violence as the latter salt, and as it was necessary to apply a strong heat to drive off the whole of the protochloride of mercury, the operation was performed in a porcelain crucible instead of a glass tube.

DETERMINATIONS OF MERCURY AND CHROMIC ACID.

The mercury was determined as protosulphide, the chromic acid being reduced by means of hydrochloric acid and alcohol before passing the hydrosulphuric acid, in order to avoid the precipitation of free sulphur. The chromic acid was also determined, in the usual way by precipitating the sesquioxide by means of ammonia, in the filtrate from the protosulphide of mercury.

HYDROGEN DETERMINATIONS.

In making the hydrogen determinations, some precautions were necessary, for if the chloride of calcium tube had been placed as usual, close to the combustion furnace, the mercury would have been driven into it, together with the water.

To avoid this, the combustion tube was drawn out in two places so as to form a kind of bulb in which all the mercury and the greater part of the water condensed. The chloride of calcium tube was attached in the usual manner beyond the bulb.

After the combustion was completed, all that portion of the combustion tube which projected from the furnace was cut off by means of a file at one of the narrow necks; the chloride of calcium tube remaining attached to it. The water was then swept into the chloride of calcium tube by means of a current of dry air drawn through by an aspirator. The mercury was dissolved and determined as sulphide.

Details of analyses of the first salt :

CHROMIC ACID DETERMINATIONS BY IGNITION.

- I. 0·210 grm. of the salt gave 0·0614 grm. of sesquioxide of chromium.
 II. 0·2205 „ „ 0·0645 „ „
 III. 0·2155 „ „ 0·0634 „ „

DETERMINATIONS OF MERCURY AND CHROMIC ACID.

- IV. 0·2565 grm. of the salt gave 0·1085 grm. of protosulphide of mercury and 0·0762 grm. of sesquioxide of chromium.
 V. 0·434 grm. of the salt gave 0·183 grm. of protosulphide of mercury and 0·1267 grm. of sesquioxide of chromium.
 VI. 0·2243 grm. of the salt gave 0·0940 grm. of protosulphide of mercury.

DETERMINATION OF HYDROGEN AND MERCURY.

- VII. 0·6390 grm. of the salt gave 0·1080 grm. of water (mercury lost.)
 VIII. 0·6440 „ „ 0·1060 „ „ and 0·2720 grm. of protosulphide of mercury.

The following are the percentages calculated from these analyses :

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Chromic acid	38·00	38·00	38·19	38·08	37·9	—	—	—
Mercury . .	—	—	—	36·49	36·36	36·20	—	36·40
Hydrogen .	—	—	—	—	—	—	1·87	1·83

We had not anticipated the presence of more than one equivalent of water in this substance, and it was on this account that we repeated the determinations of the various constituents several times.

The formulæ $\text{NH}_4\text{O} \cdot 2 \text{CrO}_3 \cdot \text{HgCl}$,
 and $\text{NH}_3 \cdot 2 \text{CrO}_3 \cdot \text{HgCl}$,

appeared at the first glance to be the most probable; the former as an ordinary double salt of the bichromate of oxide of ammonium with protochloride of mercury, corresponding to the potassa-salt, to which Millon has assigned the formula $\text{KO} \cdot 2 \text{CrO}_3 \cdot \text{HgCl}$, the latter as representing a compound analogous to the bichromate of chloride of potassium, containing, in the place of potassium, the hypothetical metal mercurammonium.

The formula of the potassa-salt being $\text{KCl} \cdot 2 \text{CrO}_3$, we should have :

The comparison, however, of the percentages deduced from our analyses, with those calculated from the preceding formulæ, and

from the formula $\text{NH}_4\text{O} \cdot 2 \text{CrO}_3 \cdot \text{HgCl} + \text{HO}$, leave no doubt that the latter is the constitution of the salt as we obtained it.

$\text{NH}_4\text{O} \cdot 2 \text{CrO}_3 \cdot \text{HgCl}$; $\text{NH}_3 \cdot 2 \text{CrO}_3 \cdot \text{HgCl}$; $\text{NH}_4\text{O} \cdot 2 \text{CrO}_3 \cdot \text{HgCl} + \text{HO}$.		
Chromic acid . .	39·24	40·61
Mercury . .	37·62	38·94
Chlorine . .	13·35	13·83
Nitrogen . .	5·27	5·45
Hydrogen . .	1·51	1·17
Oxygen (as water) 3·01	—	5·82
	<hr/> 100·00	<hr/> 100·00

The product of the second crystallization proved to be identical with the preceding.

I. 0·4215 grm. of salt gave 0·1215 grm. of sesquioxide of chromium corresponding to 37·94 per cent of chromic acid.

II. 0·463 grm. of salt gave 0·1954 of protosulphide of mercury, corresponding to 36·39 per cent of mercury, and 0·1354 grm. of sesquioxide of chromium, corresponding to 37·97 per cent of chromic acid.

Another specimen of the salt was prepared which yielded the same results.

Lastly, the product of the third crystallization was analysed and yielded the following numbers:

I. 0·1880 grm. of salt gave 0·0862 grm. of sesquioxide of chromium

II. 0·2093	„	„	0·0958	„	„	„
III. 0·2068	„	„	0·0454	„	protosulphide of mercury	
IV. 0·2190	„	„	0·0480	„	„	„

Calculated percentages:

	I.	II.	III.	IV.
Chromic acid . .	59·52	59·43	—	—
Mercury . . .	—	—	18·91	18·90

Theoretical percentages for the formula $3(\text{NH}_4\text{O} \cdot 2 \text{CrO}_3) \cdot \text{HgCl}$:

Chromic acid	59·44
Mercury	18·99
Ammonia	9·69
Water	5·13
Chlorine	6·75

100·00

It will be seen that the calculated percentages agree very closely with those required by this formula.