[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, NO. 171.]

ON THE NATURE OF CERTAIN SODIUM-URANIUM COMPOUNDS.

BY F. J. METZGER AND M. HEIDELBERGER.

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This investigation was undertaken for the purpose of determining whether the final product obtained in the analysis of uranium by Patera's method[1] was correctly represented by the formula $NaO(U_2O_3)_2$. In this connection it was also thought advisable for purposes of comparison, to prepare pure sodium uranate and analyze it, both in the ignited and air-dried condition.

The literature of uranium, while replete with analyses of the crystallized uranates of sodium and potassium, contains very little quantitative work on the amorphous uranates of these metals, or such as are precipitated from uranyl solutions by the addition of sodium or potassium hydroxides. The results obtained by Zimmerman[2] and Ditte,[3] who prepared crystalline $Na_2U_2O_7$ and $K_2U_2O_7$ in the dry way, appear to have been applied directly to the amorphous compounds, as agreeing with the few analyses previously made of the latter. These early analyses,[4] however, appear to have been of little value, for, as none of the analysts mentioned the great difficulty of completely washing out the alkali from the uranates, it is reasonable to consider that this point was overlooked, and the results therefore showed a high value for sodium.

The authors have observed that this analogy between the crystallized and amorphous uranates does not hold when the excess of alkali has been entirely washed out, as the results given below will show.

Patera's method[5] for the determination of uranium is as follows: The uranium, in solution as nitrate, is separated from iron, aluminum, manganese, zinc, calcium, etc., by treating with an excess of sodium carbonate solution, and boiling so as to completely dissolve the double carbonate of sodium and uranium. After acidifying and boiling out the carbon dioxide, the filtrate is treated with an excess of sodium hydroxide, and the precipitate washed a few times with hot water. After drying, the precipitate and the filter are separately ignited at redness in a platinum crucible, and then transferred to a small filter, where they are washed free from any remaining soda. The residue is then dried and reignited at redness, after which, according to Patera, the composition is NaO

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[1] *K. k. Geol. Reichsanstalt, Sitzungs Verhandl.*, Mar. 20, 1866.

[2] *Ann.*, **213**, 290.

[3] *Ann. chim. phys.*, [6], **1**, 338

[4] Wertheim, *J. prakt. Chem.*, **29**, 219; Patera, *Ibid.*, **61**, 397; Priwoznik, *Berg.-Hüttenänn. Jahrb.*, **1878**, 208.

[5] *Loc. cit.*

$(U_2O_3)_2$. The advantage claimed for this method is that the alkali is very readily washed out after the ignition of the precipitate of sodium uranate. This, however, is not the case unless an expedient is resorted to which is not mentioned by Patera or any of the subsequent workers using the method, namely, that of thoroughly grinding the precipitate in a mortar before attempting to wash out the alkali. The authors have observed that as many as thirty washings are insufficient if this is not done.

Through some curious oversight, Patera's formula $NaO(U_2O_3)_2$ is still in use, although it ought long since to have been changed to $Na_2U_2O_7$ at the time when the formula for water was changed from HO to H_2O. Bornträger[1] writing in 1898, and Kern[2] in 1901 used the old formula, although the former recognized the compound as sodium uranate. It was the curious ratio of sodium to uranium in this formula, namely, 1:4, that prompted the work in hand, and while the analytical results obtained at once made the apparent absurdity of the old formula evident, it was not until the formula had been traced down through the literature from Patera's time to the present that this apparent absurdity was solved by translating the formula to its modern form.

Experimental.

For the preparation of sodium uranate, six portions of Kahlbaum's uranyl nitrate, $UO_2(NO_3)_2.6H_2O$, weighing approximately 2.3 g. each, were dissolved in 150 cc. water, and the slight insoluble residue which remained in each case filtered off. The solutions were then diluted to about 450 cc. with hot water, and the uranium precipitated by an excess of hot sodium hydroxide solution. After boiling fifteen to twenty minutes, the precipitates were allowed to settle, and after pouring off the supernatant solution, were washed three times by decantation, and then on filters with hot water containing a little sodium chloride. After the washings began to show only a weak alkaline reaction, the use of sodium chloride in the wash water was discontinued; this, however, caused some of the precipitate to become colloidal. Washing was continued until the filtrates showed no test for chlorides, and no test for alkali with phenolphthalein within five minutes, showing that all the sodium chloride, and all but an unweighable trace of alkali had been removed. The resulting portions of pure sodium uranate were allowed to dry in the air, and each divided into two parts. Small portions of each of these were used in making up sample No. 13. Portions 1 to 6 were ignited in open porcelain crucibles with the full Bunsen flame to constant weight (40 to 50 minutes), while portions 7 to 13 were analyzed without previous ignition.

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[1] *Zeit. anal. Chem.*, **37**, 436.

[2] THIS JOURNAL, **23**, 714.

The analytical procedure was as follows: The weighed samples 1 to 12 were dissolved in concentrated hydrochloric acid, the uranium precipitated by ammonia, and weighed as U_3O_8 in the usual manner.

In the filtrate the sodium was determined by evaporation to dryness in platinum dishes, driving off ammonium salts and weighing as sodium chloride, every precaution being observed.

A small correction (0.0006 g. per 10 g. NH_4Cl) was deducted from each of the sodium chloride weighings, based on the amount of non-volatile, soluble matter found in the Kahlbaum's ammonium chloride used in the precipitation and washing of the uranium.

No. 13 was analyzed in the same way, except that a double precipitation of the uranium was made. The result showed that, while some sodium may be held back with the uranium the first time, the amount is so minute if the precipitate is thoroughly washed, that it does not affect the values for the ratio of sodium to uranium—the ultimate object of the analyses.

The preparation of Patera's precipitate was accomplished as follows, using the conditions for the precipitation of sodium uranate found best by Kern:[1] Four portions of uranyl nitrate, weighing about 0.7 g. each, were dissolved in 175 cc. water, filtered from the small insoluble residue, and 6.5 g. sodium nitrate and 36 g. sodium chloride added to each. The solutions were again filtered, 3 cc. of concentrated hydrochloric acid added to each, and the uranium precipitated from the hot solutions by a slight excess of sodium hydroxide. After boiling for about ten minutes, the precipitates were washed twice by decantation, and three times on the filters with hot water, except No. 14, which was washed until entirely free from alkali, and the air-dried product analyzed to determine whether the composition of the uranate was affected by the conditions of precipitation. In all four cases the precipitate became slightly colloidal after the first washing on paper. Precipitates 15, 16, and 17 were then dried in an air bath at 107°, separated from the paper, ground to a fine powder in an agate mortar, and ignited in platinum crucibles at redness for half an hour. The ash of the filter paper was then added, and the ignition continued for five minutes. The residues were then transferred to small filters, and ten washings with hot water found sufficient to remove all the alkali. After drying, the precipitates were transferred to platinum crucibles, and the ash of the separately ignited filters added to each, and the whole ignited at redness for ten minutes. The weighed residues were then analyzed in the same manner as 13 and 14.

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[1] *Loc. cit.*

Results of Analyses.

No.	Wt. of uranate.	Wt. U_3O_8.	Wt. NaCl.	Ratio Na:U.	Wt. oxygen (by diff.).	Ratio Na:U:O.
1....	0.4761	0.4319	0.0725	81:100	0.0812	81:100:330
2....	0.32815	0.2974	0.0518	84:100	..	....
3....	0.3868	0.3502	0.0605	82:100	..	....
4....	0.3450	0.3108	0.0537	83:100	..	....
5....	0.4593	0.4162	0.07045	81:100	0.0786	81:100:332
6....	0.4055	0.3678	0.0617	81:100	0.0692	81:100:331
					Wt. H_2O (by diff.).	No. molecules H_2O.
7[1]...	0.3893	0.3301	0.0604	88:100		
8....	0.5726	0.4795	0.0806	81:100	0.0412	7
9....	0.5135	0.4304	0.0751	84:100	..	
10....	0.4669	0.3907	0.0658	81:100	0.0339	7
11....	0.4546	0.3803	0.0653	83:100	..	....
12....	0.4924	0.4109	0.0713	84:100	..	....
13....	0.3519	0.2945	0.05055	83:100	..	....
					Wt. oxygen (by diff.).	Ratio Na:U:O.
14....	0.3548	0.2969	0.0466	75:100		
15....	0.4288	0.3853	0.0699	88:100	0.0748	88:100:342
16....	0.4497	0.3997	0.0741	89:100	0.0813	89:100:358
17....	0.4980	0.4443	0.0819	93:100	0.0890	93:100:353

Conclusions.

From the above results, it will readily be seen that the ratio of sodium to uranium does not in any case approach 1 : 1, as is required by the formula $Na_2U_2O_7$, or, written in the old style heretofore in use, $NaO(U_2O_3)_2$. On the contrary, the ratios obtained for the pure sodium uranate approximate 80: 100, or 4: 5; or, if we include the average oxygen ratio for the three analyses of the ignited precipitate nearest to this ratio, we have 80: 100: 331, or 4: 5: 17. The formula would thus be $Na_4U_5O_{17}$.[2]

If we consider the air-dried sodium uranate to possess the same formula as the ignited, except for the addition of some water, this being in agreement with the figures obtained from the analyses, the complete formula would be $Na_4U_5O_{17}.7H_2O$, the number of molecules of water being calculated from Nos. 8 and 10 by difference after calculating and deducting the weight of oxygen.

As for the pure Patera's precipitate obtained, its formula, instead of being $Na_2U_2O_7$ (old style $NaO(U_2O_3)_2$) as Patera suggests, appears to be $Na_9U_{10}O_{35}$.

It is interesting to note the close relationship existing between these formulas and $Na_2U_2O_7$, the one heretofore used. Multiplying $Na_2U_2O_7$

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[1] The authors are unable to explain the high ratio found in No. 7.

[2] It is to be understood that these formulas are intended merely to express the analytical results in a readily comparable form and are not to be taken as indicating the exact composition of the compounds. Indeed, the precipitates may be complex mixtures of compounds differing widely from the composition found.

by 5 we get $Na_{10}U_{10}O_{35}$. leaving the formula found for Patera's precipitate as it is we have $Na_9U_{10}O_{35}$. and multiplying the formula found for sodium uranate by 2 we get $Na_8U_{10}O_{34}$. We thus see that there is actually very little difference between these formulas, the high results previously obtained for sodium being attributable to an incomplete removal of the free sodium hydroxide from the precipitate.

The authors believe that the formulas $Na_4U_5O_{17}$ and $Na_9U_{10}O_{35}$ may be satisfactorily explained according to the ionic theory by the following hypothesis. As actually thrown down from solution in the presence of an excess of sodium hydroxide, sodium uranate may correspond to the formula $Na_2U_2O_7$. As soon as this excess is removed, however, an entirely new set of conditions prevails. This may be illustrated ionically by either of the following diagrams:

$$U_2O_7^{--} + 2H^+ + H_2O \rightleftarrows 2UO_2^{++} + 4OH^-$$

(1)

$$\begin{tikzcd}
 & Na_2U_2O_7 \arrow[d, shift right] \\
2Na^+ & U_2O_7^{--} \arrow[u, shift right] \arrow[d, shift right] \\
 & 2UO_2^{++}\ 3OH^- \arrow[u, shift right]
\end{tikzcd}$$

(2)

Both of these diagrams illustrate the same reaction, (2) showing the mechanism more clearly. The reaction is plainly a reversible one, proceeding (1) from left to right when the hydrogen ion is in excess, resulting in the formation of a uranyl compound; and going from right to left when the hydroxyl ion is in excess, resulting in the formation of a uranate. Now, when sodium uranate is precipitated by an excess of sodium hydroxide, the high concentration of hydroxyl ion inhibits any tendency of the minute amount of sodium uranate in solution to dissociate into uranyl and hydroxyl ions (diagram 2). The washing away of the excess of sodium hydroxide, however, results in the gradual lowering of the concentration of the hydroxyl ion, and at the same time causes an increase in the concentration of the hydrogen ion furnished by the hot water used for washing. When *all* the sodium hydroxide has been washed out, there remains only a slight concentration of hydroxyl ion from the ionization of the water, equal to the concentration of hydrogen ion which is of course higher than before. The reaction therefore tends to swing from left to right (diagram 1) with the formation of uranyl ion. As $U_2O_7^{--}$ and OH^- are the only anions in solution, uranyl uranate (not known to exist) or uranyl hydroxide, or both, would then be precipitated as soon as the solubility product of either is exceeded. As soon as this precipitation occurs, the accompanying reduction in concentration of the $U_2O_7^{--}$ ion results in an increase in concentration of sodium ion, which is washed away. It is the loss of the sodium ion that reduces the ratio of Na to U in $Na_2U_2O_7$ below 1 : 1.

The extent to which the reversibility of the reaction proceeds will depend upon two factors. In the first place, if the solubility products of the uranyl compounds formed are near that of sodium uranate, the formation of the former can not proceed very far before equilibrium is established. Besides this, the more the sodium uranate is washed, the more will it tend to pass over into the insoluble uranyl compounds up to a certain point where equilibrium is again reached.

In the light of this, then, the various formulas deduced are readily explained. The sodium uranate used for the preparation of Patera's precipitate was not thoroughly washed free of alkali until in a different physical form (*i. e.*, after ignition); hence the ratio of sodium to uranium in Patera's precipitate would naturally be different from the corresponding ratio found for the pure sodium uranate, from which all but an unweighable trace of alkali had been removed. The ratio 3 : 4 obtained in the case of No. 14 is also explained, as in this case the sodium uranate was washed longer, that is, until absolutely no alkali was left.

To sum up, then, it has been found that, while sodium uranate may actually be precipitated as $Na_2U_2O_7$, on completely removing the excess of alkali by washing with water, the precipitate undergoes a partial hydrolysis or reversal of the reaction by which it was formed, the extent of this reversal depending upon the amount of washing and upon certain physical constants not yet determined.

There is still a necessity for more work in this field to determine definitely what compounds are formed by the reversal of the reaction, the limit to which the reversal can proceed, and the solubility products of the compounds formed. It would also be of interest to determine whether the uranates of the other metals act in a manner analogous to sodium uranate.

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THE DETERMINATION OF THALLIUM IN THE ELECTROLYTIC WAY.

BY GILBERT W. MORDEN.

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The analytical behavior of thallium salts toward the electric current has been the subject of investigation by Schucht,[1] Heiberg[2] and Neumann.[3] The former used a nitric acid solution but the separation

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[1] *Berg. und Hüttenzeitung*, **39**, 122 (1880).

[2] *Z. anorg. Chem.*, **35**, 346

[3] *Ber.*, **21**, 356.