minations are indicated by asterisks. The other values are those of Kerp and Böttger, which are given for the sake of comparison.

TABLE II.

t°.	Cs.	Rb.	K.	Na.	Li.	Ba.	Sr.	Ca.[1]
0	*1.96	0.92	0.31	0.54	0.04	0.15	0.73	....
18	*2.61	....	....	....	....	0.32	1.04	....
19.5	....	*1.21	....	....	....	....	....	....
20	....	0.47 *0.46	....	....	....	....	....	....
22	....	....	....	0.63	*0.047	....	....	....
23	....	....	....	....	....	....	*1.12	=or>*0.09
24	....	....	....	....	....	*0.32	....	....
25	....	1.37	0.53	0.65	....	0.34	....	....
26	*2.98	....	....	....	....	....	....	....
30	....	....	0.56	0.67	....	0.43	1.27	....
64.5	....	....	....	....	0.10	....	....	....

In conclusion, it is desired to offer an explanation of the well-known fact that, although mercury itself will not adhere to such metals as iron and platinum, even very dilute alkali and alkali-earth amalgams do readily adhere to them. Upon dipping a platinum wire covered with adhering amalgam into dilute hydrochloric acid, the alkali metal is extracted and the resulting mercury does not continue to adhere to the platinum. It has been shown[2] that, in the decomposition of these amalgams with hydrochloric acid, a point is reached at which there is a sudden increase in the surface tension of the amalgams, accompanied by the sudden evolution of a cloud of minute hydrogen bubbles, and by a sudden decrease in the solution pressure of the amalgams. It would appear, therefore, that the adhesion of the amalgams to platinum and to iron is due rather to the inferior cohesion of the amalgams than to any chemical reaction.

URBANA, ILL.

[CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL CHEMISTRY, OF THE COLLEGE OF THE CITY OF NEW YORK.]

SOME NEW DOUBLE ARSENATES.[3]

BY LOUIS J. CURTMAN.

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The work on double phosphates[4] suggested the preparation of corresponding arsenates, especially as reference to the literature showed that

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[1] We were unable to prepare an amalgam containing more than 0.09 per cent. of calcium. It was filtered at 23°, and was entirely liquid.

[2] THIS JOURNAL, **31**, 31 (1909).

[3] Presented in abstract before the Boston Meeting of the American Chemical Society, December, 1909.

[4] THIS JOURNAL, **29**, 714 and 1194 (1907).

such compounds had not been prepared. The method which was found to yield these salts was similar to that employed in the preparation of the double phosphates, except as regards the acidity of the solution, which in this case was somewhat greater.

Preparation.—A solution consisting of 100 cc. of 10 per cent. ferric chloride, 50 cc. of hydrochloric acid (sp. gr. 1.2) and 50 cc. of water was heated to 70°. To this was added gradually and with constant stirring a hot solution of diammonium arsenate containing 105 grams in 175 cc. of water. The addition of the arsenate was followed by the formation of a temporary precipitate which, dissolving on stirring, had the effect of weakening the color of the iron solution: the latter became perfectly colorless when nearly the entire quantity of the arsenate had been added. On adding the last few cc., a slight white gelatinous precipitate formed, which, on heating and stirring, increased in amount and at the same time changed to a finely granular form resembling chalk. The mixture was continuously heated with stirring on an asbestos pad until the temperature rose to 100°, after which it was digested on a boiling water bath for one hour and then allowed to stand overnight. The next day the clear, colorless, supernatant liquid was siphoned off and the residual, perfectly white, compact mass washed twice by decantation with an alcoholic solution (1 part 95 per cent. alcohol to 2 parts of water) containing 0.1 per cent. of ammonium chloride, and then finally with alcohol (1–1) till the washings were free of chlorides.[1] The filtrate was acid to litmus and gave strong tests for ammonium and arsenate, showing that an excess of the precipitant had been used; it did not contain any iron.

The precipitate was first allowed to partially dry in the air, then pulverized, and finally dried to constant weight in a water oven. The yield was 12 grams.

Analysis.—The ammonium was determined by direct distillation with caustic soda into a standard acid solution. The arsenic and the iron were determined in another portion by the following procedure: About one gram of the material was dissolved in 10–15 cc. of conc. hydrochloric acid; when solution was complete, 50–75 cc. of a strong solution of sulphurous acid were added, the whole transferred to a small pressure bottle, and the latter stoppered and heated in a boiling water bath for one hour. After cooling, the contents of the pressure bottle were transferred to an Erlenmeyer flask and without heating, the arsenic was precipitated with a rapid stream of hydrogen sulphide. The filtrate and washings were at once treated with filtered compressed air to drive out the hydrogen sulphide, evaporated to a small bulk, filtered, and the iron determined gravimetrically as Fe_2O_3, or volumetrically with a standard

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[1] The final washings, though free of chlorides, gave a test for AsO_4.

potassium permanganate solution by the Zimmerman-Rheinhart method. The well washed precipitate of As_2S_3 and S was dissolved in concentrated hydrochloric acid with the addition of potassium chlorate, boiled to expel the excess of chlorine, filtered from the undissolved sulphur into a standard volumetric flask and diluted to the mark. Aliquot portions were then pipetted out, rendered alkaline with ammonia, and the arsenic precipitated in the usual way with magnesia mixture and ultimately weighed in a Gooch crucible as $Mg_2As_2O_7$.

	Found.		Theory for $(NH_4)H_2AsO_4.FeAsO_4$.
NH_4	4.71	4.66	5.08
Fe	15.45	15.63	15.81
As	42.12	42.06	42.37

Properties of $NH_4H_2AsO_4.FeAsO_4$.—The double arsenate of ferric iron and ammonium is a white powder possessing a faint greenish-yellow tint. It readily dissolves in cold conc. hydrochloric acid with the formation of a yellow solution; it is also soluble in hot nitric and in hot dilute sulphuric acids. Arsenic acid containing 75 per cent. arsenic pentoxide readily dissolves it on heating, yielding a colorless solution from which ammonia, even when added in excess, failed to reprecipitate the arsenate, but instead gave a reddish brown solution, the color of which varied with the amount of double salt originally dissolved. It is insoluble in 50 per cent. acetic acid, also in a strong solution of ammonium chloride. Caustic alkalies completely hydrolyze the compound, the final product being ferric hydroxide; hot water has a similar effect, only to a smaller degree. Hot strong ammonia dissolves the double salt with the formation of a deep red solution. On gentle ignition the double arsenate decomposes, giving off ammonia and water.

Action of Water.—As the chief characteristic of the corresponding double phosphates is their readiness to undergo hydrolysis when washed excessively with water,[1] it was thought worth while to determine whether or not this was the case with the double arsenate and thus explain the difficulty of obtaining a product of a high degree of purity. Accordingly, about two grams of the analyzed salt were treated in a bottle of two liters capacity with 1500 cc. of water at the laboratory temperature, repeatedly shaken, and finally allowed to stand overnight. The next day nearly all the material had settled to the bottom; a very small portion, however, remained in suspension in the colloidal form, which could not be removed by the usual process of filtration. As standing for three days did not cause the colloidal material to settle, recourse was finally had to a porcelain filter operated by strong suction; this proved effective. The residual solid material after the water treatment was notice-

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[1] THIS JOURNAL, 29, 717. "Ueber die Phosphate des Kupfers," Doctor's Dissertation, Halle, 1890.

ably yellow, thus indicating hydrolysis. It was returned to the bottle and treated again with 1500 cc. of water, shaken, allowed to stand overnight, and filtered. The residue which was dried over sulphuric acid possessed a light brown color. Analysis of the clear concentrated aqueous extract showed the presence of AsO_4 and ammonium, but contained no iron. Analysis of dried brown residue after the two treatments with water gave: NH_4, 2.27; Fe, 19.24; As, 31.11.

Comparison of these figures with those obtained for the normal salt shows that the action of water on the salt consists in dissolving out arsenic acid and ammonium, accompanied by a change in color of the compound due to the formation of ferric hydroxide. The action is one of *hydrolysis*, precisely similar to that observed with the corresponding phosphates.

Action of Ammonia.—The solubility of the double salt in ammonia suggested the possibility of the formation of basic double arsenate of ferric iron and ammonium similar to that prepared from the corresponding double phosphate. A small quantity of freshly prepared double ammonium ferric arsenate was treated in an Erlenmeyer flask with concentrated ammonia and the mixture heated on a boiling water bath; the white precipitate first became yellow, then brown, and finally, on further heating, dissolved completely to a beautiful reddish brown solution. On adding 95 per cent. alcohol to this solution, a curdy, reddish brown precipitate settled to the bottom and was at once filtered from the overlying cloudy liquid. A portion of the reddish brown material, nearly completely dried in the air, was treated with water; it entirely dissolved to a yellow solution. The ammoniacal filtrate containing an excess of alcohol possessed a very pale yellow color and gave a strong test for arsenic acid with silver nitrate after neutralization of the ammonia with acetic acid. Another portion was evaporated to dryness, taken up with hydrochloric acid and tested for iron. The slight tests obtained indicated that the filtrate contained only traces of iron. Qualitative analysis of the dried precipitate obtained with alcohol showed the presence of iron, arsenic, and ammonium, but the amount was too small for a quantitative analysis. Its qualitative analysis taken, together with its physical properties, namely, color and solubility in water, strongly suggest the corresponding phosphate which forms under the same condition. This will be further investigated.

When dipotassium arsenate was used in place of the ammonium compound, under the same conditions which were found favorable for the formation of the double arsenate of iron and ammonium, a white precipitate was obtained. The result of a qualitative analysis of this substance indicates the existence of the corresponding double alkali arsenate. This compound, together with the double arsenates of aluminium and chromium, are under investigation at the present time.

Summary.

If to a hot ferric chloride solution, strongly acid with hydrochloric acid, diammonium arsenate solution be added to incipient precipitation, and the mixture heated, there forms a white, finely divided precipitate, which analysis showed to be a double arsenate of ammonium and iron of the formula $NH_4H_2AsO_4.FeAsO_4$. Like the corresponding phosphate prepared by the author, the double arsenate readily hydrolyzes when washed with water. It readily dissolves in mineral acids, but is practically insoluble in 50 per cent. acetic acid. Ammonia dissolved it on heating to a deep reddish brown solution, from which 95 per cent. alcohol precipitates a basic double ammonium ferric arsenate. When potassium arsenate was used under the same conditions, a precipitate was obtained which, from the results of a qualitative analysis, appears to be the corresponding double alkali arsenate.

NEW YORK CITY, February, 1910.

A STUDY OF THE PHENOLSULPHONIC ACID METHOD FOR THE DETERMINATION OF NITRATES IN WATER.

[SECOND PAPER.]

THE COMPOSITION OF THE YELLOW COMPOUND.

BY E. M. CHAMOT AND D. S. PRATT.

Received February 22, 1910.

In our first paper[1] we discussed the composition of the various sulphonic acid reagents which have been suggested for use in this method[2] and showed that the standard phenolsulphonic acid generally used in the United States (Method Am. Pub. Health Association)[3] made by heating a mixture of 15 grams of phenol and 128 cc. of concentrated sulphuric acid for six hours in a flask immersed in boiling water, consists of phenoldisulphonic acid 1-2-4, with always small but appreciable quantities of phenolmonosulphonic acid (para) and a large excess of sulphuric acid. It was also stated that the yellow color obtained by treating a nitrate-containing water residue with this reagent, diluting and making alkaline, was not due, as had long been taken for granted, to salts of picric acid,[2],[3] nor could it be due to salts of mononitro phenols, as believed by Hazen and Clark,[4] nor to salts of dinitro phenols as Montanari supposed.[5]

It had already been shown by Andrews[6] that the mononitro and dinitro

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[1] THIS JOURNAL, 31, 922.

[2] Sprengel, *Pogg. Ann.*, 121, 188 (1863); Grandval and Lajoux, *Compt. rend.*, 62, 101 (1885); Kekulé, *Lehrbuch*, III, 236; Fox, *Tech. Quart.*, 1, 54 (1887); Rideal, *Chem. News*, 60, 261 (1889); Pagnoul, *J. Soc. Chem. Ind.*, 23, 135 (1904); Smith, *Analyst*, 10, 199 (1885).

[3] Gill, THIS JOURNAL, 16, 122 (1894).

[4] Hazen and Clark, *J. Anal. Appl. Chem.*, 5, 301 (1891).

[5] Montanari, *Gazz. chim. Ital.*, 22, I, 87 (1902).

[6] Andrews, THIS JOURNAL, 26, 388 (1904).