THE ACTION OF NITRATE OF SILVER ON DISODIUM ORTHOPHOSPHATE IN DILUTE SOLUTION.

BY WILLIAM ROBERT LANG AND WILLIAM PEROT KAUFMANN.

Received July 14, 1905.

THE generally accepted text-book expression for the reaction which takes place between solutions of disodium orthophosphate and nitrate of silver is given as being

$$(1)\qquad \underbrace{Na_2HPO_4}_{142.1} + \underbrace{3AgNO_3}_{509} = Ag_3PO_4 + 2NaNO_3 + HNO_3,$$

indicating the complete precipitation of phosphoric acid as a silver salt and the setting free of nitric acid.

From the molecular weight in (1) it will be seen that 1 gram of disodium orthophosphate should react with 3.57 grams of silver nitrate.

In order to determine the correctness of this expression, decinormal solutions of these were made up and the phosphate titrated with the silver nitrate, using potassium chromate as an outside indicator. As the result of from 200 to 300 determinations it was found that the "end-point" of the reaction, as indicated by the first appearance of the red silver chromate, invariably occurred when an amount of silver solution had been added corresponding to the proportion of 1 gram of disodium orthophosphate to only 1.447 grams of silver nitrate. These proportions would indicate that a reaction had taken place as expressed by the equation

$$(2)\qquad 2Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + NaH_2PO_4 + 2NaNO_3.$$

Ostwald, in his "Scientific Foundations of Analytical Chemistry" (second English edition, 1900), on page 204, gives this equation (2) as being probably the more correct expression of the reaction taking place between these substances, but adds that, ". . . . . it no doubt also fails to express all that goes on."

The analyses of types of the resulting silver phosphates may be tabulated as follows:

The figures in column (*e*) comparing the even with the odd, show that a greater yield of precipitate is obtained from the neutralized solutions than from those reacting acid, and a comparison of the yield of precipitate *obtained* and *calculated* in the case of the

TABLE I.

a. Reaction of solution.	Grams Na_2HPO_4 used. *b*.	Grams $AgNO_3$ used when "end-point" with K_2CrO_4 was reached. *c*.	End-point" overstepped. *d*.	Grams precipitate yielded. *e*.	Calculated yield of precipitated Ag_3PO_4 from grams $AgNO_3$ in columns *c* and *d*. *f*.	Calculated yield from grams Na_2HPO_4 in column *b*. *g*.	Grams' Na_2HPO_4 not acted on by $AgNO_3$. *h*.	Percentage of silver in precipitated phosphates. *j*.
(1) Acid	0.7105	1.17872	......	0.9608	0.9700	2.09	0.4 (=57%)	76.96
(2) Neutralized by dilute KHO	0.7105	1.17872	......	0.9655	0.9700	2.09	0.4 (=57%)	75.82
(3) Acid	0.7105	....	1.696 (excess)	1.0630	1.734	.....	....	76.19
(4) Neutralized by dilute KHO	0.7105	....	1.696 (excess)	1.4070	1.734	.....	....	76.80
(5) Acid	0.7105	....	2.544 (large excess)	1.1350	2.601	.....	....	76.65
(6) Neutralized as No. 4	0.7105	....	2.544 (large excess)	2.3841	2.601	.....	....	77.36

neutralized solution makes it evident that even in such menstrua the phosphate enters appreciably into solution.

It will be seen from (1) and (2), which are typical of a large number of determinations, that the "end-point" occurs at a stage in the reaction where only a partial separation of the phosporic acid as the silver salt has taken place. The resulting solution is acid to litmus, which acidity is due to the dihydrogen sodium orthophosphate; no free nitric acid could in any case be detected at this stage. It is evident, however, from these determinations and from Nos. 3, 4, 5 and 6 that equation (2) only expresses accurately what takes place when silver nitrate is added to disodium orthophosphate and the completion of the reaction taken as being indicated by the first formation of argentic chromate.

As from these results it was evident that there remained a considerable quantity of phosphoric acid in combination as (presumably) dihydrogen sodium orthophosphate, silver nitrate was added in excess to effect its complete precipitation, if possible, and the precipitates analyzed. The results are expressed in percentages of silver which was determined first of all gravimetrically, but later on Volhard's method was substituted on account of the close agreement of the gravimetric estimations. The only one of the percentages in column (*f*) which *accurately* corresponds to the substance Ag_3PO_4 is No. 6, the others showing a deficiency in their silver content of from 0.4 to 1.54 per cent. But in the earlier stages of this investigation in four cases precipitates were obtained which yielded, on analysis, respectively:

	Silver. Per cent.
(1) "End-point" reaction	73.76
(2) "End-point overstepped	74.19
(3) Large excess of silver nitrate	73.88
(4) Deficiency of silver nitrate	73.62
Average	73.862

These precipitates evidently correspond exactly to the formula $Ag_5H(PO_4)_2$ which contains 73.86 per cent. of silver. The others in Table I, numbered (1) to (5), lie between somewhere Ag_3PO_4 with 77.32 per cent. and $Ag_5H(PO_4)_2$ with 73.86 per cent. of silver.

The following table contains the percentage of silver found in a number of precipitates obtained under similar conditions of temperature and concentration, but in different total quantities of the reacting salts. We have found it so far impossible to produce at will the phosphate of any desired composition but hope that further investigation will enable us to accomplish this.

TABLE II.—SILVER CONTENT IN PERCENTAGES.

73 per cent. and below 74 per cent.	75 per cent. and below 76 per cent.	76 per cent. and below 77 per cent.	77 per cent. and above.
73.49	75.34	76.47	77.01
	75.23	76.17	
	75.95	76.77	
	75.01	76.47	
	75.78	76.25	
		76.70	
		76.43	
		76.52	
		76.35	
		76.82	
		76.57	
		76.96	
		76.25	
		76.23	

It will be seen from this that the most commonly occurring precipitates nearly approach that of the composition Ag_3PO_4 *but not quite.*

Having obtained the "end-point" with potassium chromate (the reaction expressed by

$$2Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + NaH_2PO_4 + 2NaNO_3),$$

and having filtered off the precipitate, an excess of silver nitrate was added, causing further precipitation of a phosphate containing 76.25 per cent. to 76.5 per cent. of silver. The filtrate from this further precipitate was found to contain free nitric acid and also responded to tests for phosphoric acid. Following the equation given above, it would seem that the dihydrogen sodium phosphate reacted further with the silver nitrate possibly in accordance with the following equations:

(3) $$NaH_2PO_4 + AgNO_3 = AgH_2PO_4 + NaNO_3,$$

(4) $$AgH_2PO_4 + AgNO_3 = Ag_2HPO_4 + HNO_3,$$

(5) $$Ag_2HPO_4 + AgNO_3 = Ag_3PO_4 + HNO_3.$$

Combining these equations there would be obtained the expression

(6) $$NaH_2PO_4 + 3AgNO_3 = Ag_3PO_4 + NaNO_3 + 2HNO_3,$$

which does not account for the presence of phosphoric acid in the filtrates; but if (4) and (5) are coupled, the precipitate will have the composition $Ag_5H(PO_4)_2$ which was obtained in the four cases previously quoted, the production of which can be expressed by the equation

$$(7)\quad 2Na_2HPO_4 + 5AgNO_3 = \underbrace{Ag_5H(PO_4)_2}_{Ag_3PO_4.Ag_2HPO_4} + 4NaNO_3 + HNO_3.$$

For an expression which would account for the presence in the filtrate from the complete (?) precipitation of the silver, of both nitric acid and of phosphoric acid the following is suggested:

$$(8)\quad 4Na_2HPO_4 + 6AgNO_3 = 2Ag_3PO_4 + 4NaNO_3 + HNO_3 + H_3PO_4$$

It would appear then that the reaction between silver nitrate and disodium orthophosphate takes place in several distinct stages, and that the formation of a phosphate containing about 76 per cent. of silver is the most constant resultant. Also that free nitric acid and phosphoric acid remain in the solution from which no further precipitate can be obtained on the addition of the nitrate. It is our intention to further investigate this matter specially as regards the quantitative composition of these filtrates with a view to determining whether or not the last six equations suggested (Nos. 3 to 8) adequately express the reaction.

THE CHEMICAL LABORATORIES,
THE UNIVERSITY OF TORONTO.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, DEPARTMENT OF AGRICULTURE, NO. 59.]

A CONSTANT TEMPERATURE BATH FOR LOW TEMPERATURES.

BY A. GIVEN.

Received October 12, 1905.

THE usual temperature at which specific gravity determinations are made is 15.6° C. (60° F.), and it was for this temperature that this bath was primarily intended, and at which the bath has been used, though modifications of it are in use at 20° C. The advantage of such a bath lies in the fact that the whole body of the pycnometer is immersed, after cooling to 14° C. or below, and therefore rises to the desired temperature more quickly and uniformly than in any other way. Moreover, the pycnometer can be left in the bath as long as may be desired without change