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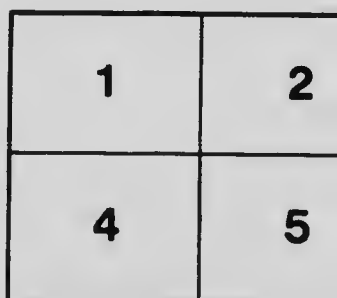
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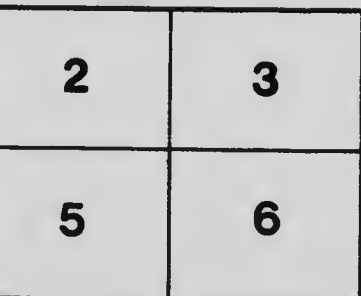
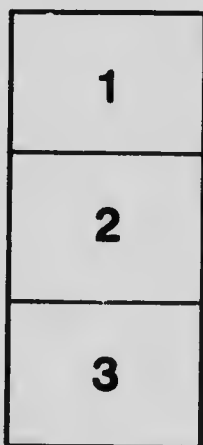
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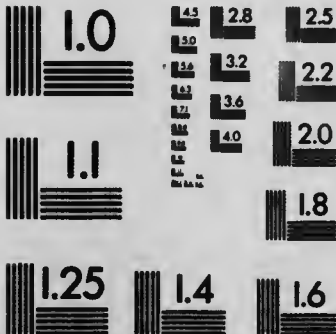
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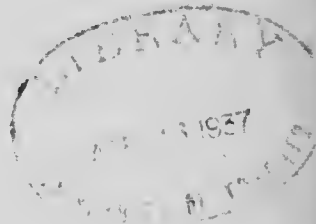
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(REPRINTED FROM THE JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, VOL. XXVII.)

**No. 55: THE INTERACTION OF HYDROGEN SULPHIDE AND SULPHUR DIOXIDE, BY W. R. LANG AND C. M. CARSON**

(REPRINTED FROM THE PROCEEDINGS OF THE CHEMICAL SOCIETY, VOL. XXI.)



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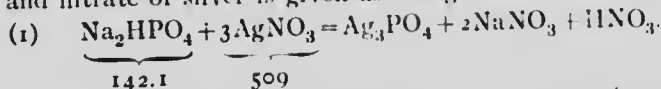
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## THE ACTION OF NITRATE OF SILVER ON DISODIUM ORTHOPHOSPHATE IN DILUTE SOLUTION.

BY WILLIAM ROBERT LANG AND WILLIAM PEROT KAUFMANN.

Received July 14, 1905.

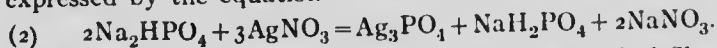
THE generally accepted text-book expression for the reaction which takes place between solutions of disodium orthophosphate and nitrate of silver is given as being



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



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



TABLE I.

a. Reaction of solution.	b. Grams $\text{Na}_2\text{HPO}_4$ used.	c. Grams $\text{AgNO}_3$ used when "end-point" with $\text{K}_2\text{CrO}_4$ was reached.	d. "End-point" "overshopped."	e. Grams precipitate yielded.	f. Calculated yield of precipitated $\text{Ag}_3\text{PO}_4$ from grams $\text{AgNO}_3$ in columns c and d.	g. Calculated yield from grams $\text{Na}_2\text{HPO}_4$ in column b.	h. Grams $\text{Na}_2\text{HPO}_4$ not acted on by $\text{AgNO}_3$ .	i. Percentage of silver in precipitated phosphate.
(1) Acid .....	0.7105	1.17872	....	0.9608	0.9700	2.09	0.4 (=57%)	76.96
(2) Neutralized by dilute $\text{KHO}$ .....	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 $\text{KHO}$ .....	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

case of the 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 phosphoric 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 (j) which accurately corresponds to the substance  $\text{Ag}_3\text{PO}_4$  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  $\text{Ag}_5\text{H}(\text{PO}_4)_2$  which contains 73.86 per cent. of silver. The others in Table I, numbered (1) to (5), lie between somewhere  $\text{Ag}_3\text{PO}_4$  with 77.32 per cent. and  $\text{Ag}_5\text{H}(\text{PO}_4)_2$  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

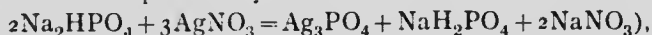
of the reacting salts. We have found it so far impossible to produce at will the phosphate of any desired composition but hope that further investigation will enable us to accomplish this.

TABLE II.—SILVER CONTENT IN PERCENTAGES.

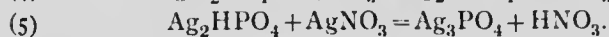
73 per cent. and below 74 per cent.	75 per cent. and below 76 per cent.	76 per cent. and below 77 per cent.	77 per cent. and above.
73.49	75.34	76.47	77.01
	75.23	76.17	
	75.95	76.77	
	75.01	76.47	
	75.78	76.25	
		76.70	
		76.43	
		76.52	
		76.35	
		76.82	
		76.57	
		76.96	
		76.25	
		76.23	

It will be seen from this that the most commonly occurring precipitates nearly approach that of the composition  $\text{Ag}_3\text{PO}_4$  but not quite.

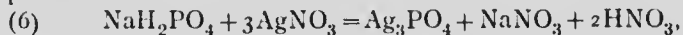
Having obtained the "end-point" with potassium chromate (the reaction expressed by



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:

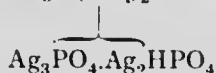


Combining these equations there would be obtained the expression



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  $\text{Ag}_5\text{H}(\text{PO}_4)_2$  which was obtained in the four cases previously quoted, the production of which can be expressed by the equation



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 :



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.

86. "The interaction of hydrogen sulphide and sulphur dioxide."  
By William Robert Lang and Charles Macdonald Carson.

When hydrogen sulphide is passed into an aqueous solution of sulphur dioxide for several periods of from two to three hours on successive days, a milky solution is obtained which is termed Wackenroder's solution (Wackenroder, "On Pentathionic Acid," *Arch. Pharm.*, 1846, 48, 272, 140; Berzelius, *Jahresbericht*, 1847, 27, 36). This has been investigated by Debus (*Trans.*, 1888, 53, 278), who proved the pre-

sence therein of sulphur, and sulphurie, trithionie, tetrathionie, and pentathionie acids, and probably hexathionie acid. The salts of these acids were examined by Hertlein (*Zeit. physikal. Chem.*, 1896, **19**, 287), who described methods for their separation and their physical properties. The explanation given by Debus for the formation of the polythionie acids is that tetrathionie acid is a direct product of the reaction of hydrogen sulphide on sulphurous acid, and that the other acids are formed from it by various subsequent reactions.

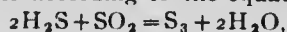
In order to investigate this, the reaction was effected, not in solution, but in the presence of a very little moisture, without which the gases do not interact. A large flask was surrounded with snow, a little moisture blown in, and the two gases then passed in at about equal rates for from two to three hours. A heavy yellow deposit, formed in the body of the flask, but not in the neck, was probably due to condensation of water having taken place only on the colder portions of the glass. This yellow material resembled ordinary sulphur, was dry to the touch, and quite brittle. On treatment with cold water, a milky liquid was obtained and the substance became stringy; this product, when boiled with water, was rendered soft and elastic.

Deposits formed by the above methods at different times, on being heated to  $100^{\circ}$  for an hour, lost from 25—30 per cent. by weight, and on estimating the sulphur compounds contained in them (as sulphurie acid) the amount never exceeded 1 per cent. Weighed quantities of the yellow material were allowed to remain in both open and closed tubes for several days at temperatures below  $0^{\circ}$ , but no change was noticeable in any case. When heated at  $100^{\circ}$ , the same loss of weight was observed as before; the presence of hydrogen sulphide could in no case be detected. Since the residue, after heating, contained more than 99 per cent. of free sulphur, it may be concluded that the polythionie acids were present in extremely small amounts.

Several quantities of the yellow material were next placed in stoppered bottles at the temperature of the room. After one day, the sulphur had become pliable and elastic and was covered with an oily liquid having an acid reaction, while a strong odour of sulphur dioxide was perceptible on removing the stoppers. The amount of this liquid seemed to increase after the second day, and this was proved to be the case on estimating the sulphuric acid present in quantities which had stood for one and two days respectively, and which had afterwards been heated at  $100^{\circ}$ . This liquid was then obtained in larger quantities, and was found to have a sp. gr. usually above 1.35, and to correspond with what is commonly called pentathionie acid, and which Debus showed to be a mixture of polythionie acids. Around the neck of the bottles, while below  $0^{\circ}$ , colourless crystals were formed: these were in such small amounts that their composition was not

determined, although, on warming, they gave off sulphur dioxide and left a deposit of sulphur.

It would appear from the above experiments that the action of gaseous hydrogen sulphide on gaseous sulphur dioxide produces first sulphur and water according to the equation,



with sulphur dioxide present in the sulphur in considerable quantities. The last two substances slowly interact at comparatively higher temperatures, giving rise to polythionic acids.

An attempt was made to investigate the action of anhydrous liquid hydrogen sulphide on liquid sulphur dioxide, but the drying of the gases was probably not thorough enough. About 5 c.c. of liquid hydrogen sulphide were collected in a thick-walled glass tube surrounded by a freezing mixture, dry sulphur dioxide passed in until the volume of the mixed liquids measured some 15 c.c., and the tube then sealed at the blowpipe. A slight yellow deposit was formed where the tube was sealed. After one day, a thin yellow film had formed at the upper part of the tube which gradually increased, and when the tube was opened after one week there was found in the bottom a solid lump of sulphur covered by a clear liquid. This liquid when allowed to evaporate, gave off sulphur dioxide and left a small quantity of water containing dissolved sulphur dioxide.

Methods for the detection and estimation of the different polythionic acids which will, it is hoped, enable the composition of the oily mixture of acids to be accurately determined are at present being investigated.





