the oxidation of ferrous in some cases is known[1] but this is hardly a case of that sort since nitric acid alone oxidizes ferrous solution in the cold easily, as is seen from the results above. This peculiar result will be thoroughly and carefully investigated.

Taking a survey of all of this preliminary work as a whole, it seems that there is some ground, then, for the following conclusions:

1. Dilute nitric acid and dilute mixtures containing hydrogen, nitrate and chloride ions may effect the oxidation of certain substances at different rates, even when the final products of the two oxidations do not differ in their energy content.
2. This difference may be due (*a*) to the influence of excess of hydrogen ions where chloride ion is absent, and (*b*) when chloride ion is present, to a possible catalytic action of this ion.
3. The most striking example of chloride ion acting as a catalytic agent is in the oxidation of ferrous salts, when it acts as a negative catalytic agent.[2] Finally it must again be emphasized that this work here reported is purely preliminary, and serves to outline a field of work in which it is hoped some important results may be achieved, in the future.

NEW YORK CITY.

A VOLUMETRIC ESTIMATION OF PHOSPHORIC ACID.

BY J. ROSIN.

Received April 26, 1911.

The reaction between silver nitrate and a soluble phosphate whereby silver phosphate is precipitated has served as the basis of several attempts at a volumetric estimation of phosphoric acid. Perrot,[3] who was the first to propose a method based on this reaction, precipitated the phosphoric acid with silver nitrate in the presence of acetic acid and determined the residual silver by sodium chloride. Holleman[4] converted the phosphoric acid or the mono-alkali salt into the dialkali salt by means of caustic soda and precipitated the phosphoric acid with silver nitrate in the presence of sodium acetate. The residual silver was then titrated in an aliquot portion by Volhard's method. Lieberman[5] adds a considerable amount of nitric acid to the solution of the phosphate, then adds an excess of silver nitrate and follows this with ammonia water until blue litmus paper is no longer affected. He then determines residual silver by Volhard's method.

Holleman's method recommends itself and it is in fact the best of the

---

[1] Benson, *J. Physic. Chem.*, **7**, 1–14; **7**, 356–77 (1903).

[2] See also in this connection, Benson (*loc. cit.*) with respect to the influence of iodide ion, and for other theories.

[3] *J. Soc. Chem. Ind.*, **1888**, 311.

[4] *Z. anal. Chem.*, **1895**, 85.

[5] *Analyst*, **1909**, 361.

methods above cited. However, results obtained by it are far from satisfactory. If a considerable excess of sodium acetate is used, silver acetate is co-precipitated and too high results are obtained. With a moderate excess only of sodium acetate, the acetic acid liberated, although very dilute, dissolves sufficient silver phosphate to yield results from 0.5–1 per cent. too low. It is evident that if phosphoric acid is to be completely precipitated, any free acid present must be neutralized.

The products resulting from the interaction of disodium hydrogen phosphate and silver nitrate are frequently represented in the text books by the equation:

$$Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + 2NaNO_3 + HNO_3. \quad (A)$$

Ostwald[1] and Treadwell[2] express the reaction by the equation

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

Neither of these equations is correct. If a solution of sodium phosphate be precipitated with an excess of silver nitrate, the filtrate from the silver phosphate contains from 35–38 per cent. of the phosphoric acid originally used. According to equation (A) very little,[3] if any, phosphoric acid should be found in the filtrate, while according to equation (B) 50 per cent. of the original phosphoric acid should be found in the filtrate. If the filtrate from the silver phosphate is distilled after the excess of the silver nitrate has been removed by sodium chloride, very little nitric acid will be found in the distillate. In two experiments quantities of sodium phosphate which, according to equation (A) should yield nitric acid equivalent to 92.3 and 85.8 cc. 0.1 *N* caustic soda respectively, were precipitated with an excess of silver nitrate, the excess of the latter removed from the filtrate with a slight excess of sodium chloride, and the filtrate from the silver chloride repeatedly distilled with water into standard alkali, carrying the final distillation almost, but not quite, to dryness. Upon titrating the excess of alkali 3.40 and 2.95 cc. respectively of 0.1 *N* alkali were found to have been neutralized by the acid that had distilled over. This acid proved to be nitric acid. These facts show that the reaction will be represented more correctly if expressed by the equation

$$3Na_2HPO_4 + 6AgNO_3 = 2Ag_3PO_4 + 6NaNO_3 + H_3PO_4. \quad (C)$$

According to this equation no nitric acid is formed. The small quantities of it obtained in the experiments just described probably resulted from the action of the phosphoric acid formed, on the sodium nitrate, at the end of the distillation when the phosphoric acid became concentrated.

---

[1] "Principles of General Chemistry."

[2] "Qualitative Analysis."

[3] Enough silver phosphate will, of course, remain dissolved to maintain the equilibrium suggested by the equation.

I have observed that when a solution of free phosphoric acid containing sodium nitrate is concentrated on the water bath, nitric acid is lost.

Equation (C) requires one-third of the original phosphoric acid to be found in the filtrate from the silver phosphate. The presence of more than one-third—35–38 per cent.—is probably due to the solvent action of the liberated phosphoric acid on the silver phosphate. The amount of silver phosphate dissolved is dependent upon the time of contact between it and the phosphoric acid.

That the reaction proceeds in the sense indicated by equation (C) was confirmed by the following experiment: 3.0164 grams of Na_2HPO_4 were precipitated with an excess of silver nitrate and made up to 202 cc.—allowing 2 cc. for the volume occupied by the silver phosphate (taking the specific gravity of silver phosphate to lie between 4 and 5) and filtered. From 100 cc. of the filtrate the excess of the silver nitrate was precipitated with a slight excess of sodium chloride, filtered, washed, and filtrate and washings, containing the free acid, divided into two equal parts. One part when titrated with 0.1 *N* alkali, using methyl orange as indicator, required 18.0 cc. The other part, with phenolphthalein as indicator, required 35.5 cc. With the latter indicator practically twice as much alkali was required. This is in accordance with the behavior of phosphoric acid towards these indicators.[1]

It is also seen that the quantity of alkali consumed corresponds almost theoretically to the amount required by equation (C)—17.7 cc. with methyl orange and 35.4 cc. with phenolphthalein. The fact that the filtrate from the silver phosphate is acid to methyl orange conclusively proves that equation (B) is incorrect, since according to this equation there is NaH_2PO_4 formed and this substance is not acid to methyl orange. The experiment just described was repeated several times and the same results obtained—with the phenolphthalein twice as much alkali was required as with methyl orange, and the amount of alkali corresponded very closely to that required by equation (C). The results of these experiments are presented here. The figures in the first line represent the amount of Na_2HPO_4 used for the quantity titrated.

	1.	2.	3.	4.
Na_2HPO_4 used, gram	0.7541	1.0322	0.8691	0.4346
Cc. 0.1 *N* KOH used, phenolph. ind	35.5	48.5	41.5	20.6
Cc. 0.1 *N* KOH used, methyl orange ind	18.0	24.5	20.1	10.2
Cc. 0.1 *N* KOH required by equation (C), phenolph. ind	35.4	49.4	40.8	20.4
Cc. 0.1 *N* KOH required by equation (C), methyl orange ind	17.7	24.7	20.4	10.2
Cc. 0.1 *N* KOH required by equation (A)	53.1	74.1	61.2	30.6

---

[1] See Ostwald "Scientific Foundations of Analytical Chemistry," Engl. edition, p. 128.

While the method presented in this paper was being worked out, Wilkie[1] published a modification of Holleman's method. He neutralizes the phosphoric acid or its solution in nitric acid with caustic soda, using phenolphthalein indicator, adds an excess of 0.1 *N* silver nitrate and then runs in dilute caustic soda till just pink. He then adds 2 cc. 0.1 *N* H_2SO_4, makes up to volume and titrates an aliquot portion of the filtrate for residual silver by Volhard's method.

A procedure almost the same as Wilkie's was tried before Wilkie's method was published, but, on account of the precipitation of silver oxide when the alkali is added, the neutralization is difficult, as Wilkie himself admits, and failing to obtain a sharp end-point, I abandoned further attempts along this line. A method was sought where the use of sodium acetate could be avoided by neutralizing the free acid formed in the interaction of sodium phosphate and silver nitrate with a substance, a moderate excess of which would have no effect upon the excess of silver nitrate. Still under the impression that at least most of the acid is nitric acid, calcium carbonate at once suggested itself. It was, however, soon found that the precipitated carbonates of the alkaline earths, and even the naturally occurring carbonates of these earths, limestone, spar, strontianite and witherite, are transposed by silver nitrate solution into silver carbonate and the corresponding nitrate of the alkaline earth. Owing to their finer state of division, the precipitated carbonates are much more readily transposed than the natural. Precipitated basic zinc carbonate is also transposed, although slowly. Zinc oxide was tried and found to answer the purpose.

In a preliminary series of experiments with disodium hydrogen phosphate a rather large excess of zinc oxide was added, as it was thought that it would have no effect on the excess of silver nitrate. The results were too high and not in accordance with each other. The excess of the zinc oxide acts upon the silver nitrate, precipitating it as the oxide. Experiments have proven this. On allowing 0.2 gram of zinc oxide to stand in contact with 25 cc. 0.1 *N* silver nitrate for half an hour, 0.3 cc. of the silver nitrate was found to have been precipitated. Evidently a large excess of zinc oxide cannot be used.

The method as finally adopted, and which has given good results, is as follows: The solution of the phosphoric acid contained in a graduated (200 cc.) flask is neutralized, if necessary, to phenolphthalein, with caustic soda free from chloride,[2] an excess of 0.1 *N* silver nitrate added and the mixture well shaken. Zinc oxide, or a suspension of it in water, is then added little by little, shaking vigorously for two or three minutes after

---

[1] *J. Soc. Chem. Ind.*, 1910, 794.

[2] If chloride-free soda is not at hand, it can be neutralized with standard alkali of known chloride content.

each addition and testing for free acid each time by dropping in a very small piece of blue litmus paper. When the color of the litmus paper is no longer affected, the solution is made up with water to the mark well mixed and allowed to subside for a few minutes. It is then filtered through a dry filter and the excess of the silver determined in an aliquot portion of the filtrate (100 cc.) by Volhard's method. Some of the results obtained by this method with sodium and ammonium phosphates and phosphoric acid are here given:

	P_2O_5 present. Gram.	P_2O_5 found. Gram.	Error. Gram.
1	0.0620	0.0618	—0.0002
2	0.0620	0.0622	+0.0002
3	0.0930	0.0928	—0.0002
4	0.0604	0.0604	0.0000
5	0.1208	0.1210	+0.0002
6	0.0613	0.0613	0.0000
7	0.0919	0.0916	—0.0003
8	0.0805	0.0807	+0.0002
9	0.1343	0.1342	—0.0001
10	0.2015	0.2018	+0.0003
11	0.0692	0.0692	0.0000
12	0.1037	0.1039	+0.0003

The points to be observed in this method are: (1) A minimum excess of 30 per cent. of the theoretical amount of silver nitrate required must be added, otherwise the results are apt to be too low. A large excess of silver nitrate, even as much as two and a half times the theoretical quantity required, does not interfere. (2) After the zinc oxide has been added, the mixture should not be allowed to stand long before filtering, as otherwise the excess of the zinc oxide—and an excess of the latter must necessarily be added in order to combine with all the acid—will precipitate some of the silver and thus vitiate the results. It is best to filter as soon as possible. The final volume to which the solution is made up has no effect. Using the same quantities of sodium phosphate and silver nitrate, but varying the final volume from 100–250 cc., no appreciable difference of results could be observed.

The method is available in the presence of sulfates, nitrates, chlorides and calcium, but cannot be used for the determination of the total phosphoric acid in the presence of more than traces of iron and aluminum. If a chloride is present, a correction must be applied.

Since, as has been shown, phosphoric acid is liberated in the interaction of sodium phosphate and silver nitrate, the action of the zinc oxide is probably this: it combines with the phosphoric acid, forming zinc phosphate which is then transposed by the silver nitrate into silver phosphate and zinc nitrate. This assumption has led to an investigation of the action of a solution of silver nitrate on the precipitated phosphates. The results may be summarized in the rough generalization that "precipitated phosphates soluble in acetic acid are transposed, more or less readily, by a solution of silver nitrate into silver phosphate and the corresponding nitrate, while those insoluble in acetic acid are not so transposed." Thus, the phosphates of the alkaline earths, magnesium, zinc, manganese, nickel, cobalt, copper and cadmium, are transposed, but those of iron, aluminum, lead and bismuth are not.

Quantitative examination of the action of silver nitrate on precipitated phosphates was limited to that of calcium, as this is the only phosphate that has any commercial value. It was found that precipitated calcium phosphate is quantitatively transposed into silver phosphate and calcium nitrate when it is shaken up for a few minutes with at least twice the theoretical amount of 0.1 *N* silver nitrate required. The procedure is the same as given under soluble phosphates. In case of the tri-basic phosphate, no zinc oxide is required, as there will be no acid formed. The commercial phosphate is usually a mixture of the di- and tribasic, and some acid will be formed when silver nitrate is added to it and consequently zinc oxide will have to be added. Below are given some results obtained by this method with two samples of calcium phosphate. Both contained chloride, which was determined and corrected for. The figures given in the first column were obtained gravimetrically.

	Per cent. P_2O_5 present.	Per cent. P_2O_5 found.	Error found.
1	47.20	47.12	—0.08
2	47.20	49.07	—0.11
3	48.52	48.36	—0.16
4	48.52	48.34	—0.18

The fact that the results obtained by this method are slightly lower than the gravimetric is probably due to the presence of a little iron in the phosphate.

The operation by the described method should not be performed in direct strong sunlight, as the yellow silver phosphate is liable to blacken somewhat and thus give rise to doubts as to the correctness of the procedure.

LABORATORY OF POWERS-WEIGHTMAN-ROSENGARTEN CO.,
ANALYTICAL DEPARTMENT, PHILADELPHIA.

THE OXIDATION OF FERROUS SALTS.

BY CHARLES BASKERVILLE AND RESTON STEVENSON.

Received April 26, 1911.

In the course of an examination of commercial oxygen, it was observed with surprise that a slightly acid solution of ferrous ammonium sulfate (Mohr's salt) was not appreciably oxidized by bubbling oxygen through it for three hours. Subsequent tests with variations were made and this communication records our findings.