ART. VII.—*The Estimation of Phosphorous, Hypophosphoric and Phosphoric Acids in Mixture;* by R. G. VAN NAME and WILBERT J. HUFF.

(Contributions from the Kent Chemical Laboratory of Yale Univ.—ccxcvii.)

Since hypophosphoric acid solutions undergo a gradual hydrolytic decomposition with the formation of phosphorous and phosphoric acids, the possession of a dependable method for the quantitative analysis of the resulting mixture is of fundamental importance for any extended study of the properties of hypophosphoric acid. The standard methods for determining phosphorous acid, as ordinarily carried out, would be inapplicable in the presence of hypophosphoric acid, while both the iodometric method proposed by Rupp and Fink[1] and the essentially equivalent method of Rosenheim and Pinsker,[2] which the last named authors claim to be accurate in the presence of hypophosphoric acid, are unfortunately unsound. In both the phosphorous acid is oxidized by an excess of iodine in the presence of potassium bicarbonate, and the iodine remaining is titrated with thiosulphate in the bicarbonate solution. Since, however, it has been conclusively proved that the estimation of iodine by thiosulphate in the presence of an alkali bicarbonate gives wholly inaccurate results,[3] it is evident that these methods are of little value.

In connection with a study of the reducing properties of hypophosphorous and phosphorous acid, Sieverts[4] estimated phosphorous acid by a modification of the method of Rupp and Fink, in which the excess of iodine was determined by arsenic in the bicarbonate solution, thus avoiding the objection above mentioned. This method, though not used or recommended by Sieverts for such a purpose, would in fact be applicable in the presence of hypophosphoric acid, but, as will be shown later, there is an inherent source of error in the method which limits its accuracy. In anything but a very thorough search of the literature this method might easily be overlooked, since the description of it is merely incidental, in an article upon a wholly different subject.

[1] Ber. chem. Ges., 35, 3691, 1902.
[2] Zs. anorg. Chem., 64, 327, 1909, also Pinsker, Dissertation, Berlin, 1909.
[3] Topf, Zs. anal. Chem., 26, 183-188, 1887; Ruff and Jeroch, Ber. chem. Ges., 38, 409, 1905; Ashley, this Journal, 19, 237, 1905.
[4] Zs. anorg. Chem., 64, 29, 1909.

The methods of analysis to be described were developed to meet the need for accurate analytical processes for the special purposes of a research upon hypophosphoric acid, the results of which will be published in subsequent articles.

I. *The Estimation of Phosphorous Acid in the Presence of Hypophosphoric Acid.*

A solution of phosphorous acid, slightly less than tenth normal in reducing power, was prepared by dissolving in water the crystallized acid (furnished by Baker and Adamson). This solution, which contained a little phosphoric acid as impurity, was standardized by three independent methods as follows:

(a) *As Magnesium Pyrophosphate.*—To estimate the phosphoric acid present, measured portions of the solution were treated with magnesium chloride mixture under the conditions recommended by Gooch and Austin.[5] The precipitate was dissolved in a little hydrochloric acid and reprecipitated by ammonia. Rupp and Fink[6] have shown that a double precipitation is necessary to free the precipitated ammonium magnesium phosphate from phosphite. The precipitates were ignited and weighed as magnesium pyrophosphate. Other measured portions of the original solution were treated with aqua regia and evaporated as far as possible over a water bath, thus oxidizing the phosphorous acid to phosphoric acid, which was then precipitated as above and weighed as magnesium pyrophosphate. From the difference in the results before and after oxidation the phosphorous acid content of the solution was calculated. Two determinations, using 45 cm^3 portions of the solution gave, respectively, 0.2524 — 0.0366 = 0.2188, and 0.2523 — 0.0366 = 0.2187 grm. $Mg_2P_2O_7$, equivalent to 0.003583 and 0.003582 grm. H_3PO_3 per cm^3.

(b) *As Mercurous Chloride.*—Adherence to the directions for this method of estimating phosphorous acid, as given in the standard text-book of Treadwell-Hall[7] led to several failures from incomplete precipitation. Pro-

[5] This Journal, 7, 187, 1899.

[6] Ber. chem. Ges., 35, 3692, 1902.

[7] "Analytical Chemistry", 3rd English ed., pp. 374 and 372. The conditions recommended are the same for phosphorous as for hypophosphorous acid.

longed heating at a fairly high temperature is essential, acidity accelerating the reaction.[8] Success was finally attained by adding an excess of mercuric chloride, then concentrated hydrochloric acid in quantity sufficient to make up about two per cent of the total volume, and finally heating the liquid at 80°-85° for seven hours. The precipitates were collected on asbestos and dried at 100°-105°.

From two 45 cm³ portions of the solution 0.9331 and 0.9302 grm. Hg_2Cl_2 were obtained, equivalent to 0.003604 and 0.003593 grm. H_3PO_3 per cm³.

(c) *Oxidation by Permanganate.*—The method employed was a modification of that of Kühling.[9] Portions of the phosphorous acid solution were measured into conical flasks, and to each was added 40 cm³ of 10% solution of crystallized zinc sulphate, and an excess of a potassium permanganate solution containing about 3.16 grams of that salt per liter. The zinc sulphate serves to prevent the solution from becoming alkaline. The flasks were heated on the steam bath for 90 minutes, cooled and treated with an excess of acidified potassium iodide solution, and the iodine thus liberated was titrated with thiosulphate in the presence of starch. Kühling filtered off the manganese dioxide and estimated the latter by treatment with potassium iodide, but the modification described above is more rapid and convenient. We would also emphasize the importance of a precaution not mentioned by Kühling, that of determining the standard of the permanganate, or, rather, the ratio of the permanganate to the thiosulphate, by means of blank experiments carried out under precisely the same conditions as the determinations themselves. This procedure tends to cancel out a possible error resulting from decomposition of the permanganate during the heating. The results obtained by this method are recorded in full in Table I. Their average gives for the standard of the solution the value 0.003594 grm. H_3PO_3 per liter, as compared with 0.003591 for the average of the results of (a) and (b).

Although the volumetric method is probably equally accurate, we shall give the benefit of the doubt to the older methods and accept the value 0.003591 as the

[8] Linhart, this Journal, 35, 353, 1913.
[9] Ber. chem. Ges., 33, 2914, 1900.

TABLE I.

Standardization of Phosphorous Acid Solution, Oxidation by Permanganate. Kühling's Method Modified.

Sodium Thiosulphate Solution, 1·008 N/10.

H_3PO_3 solution taken cm^3	$KMnO_4$ solution taken cm^3	$Na_2S_2O_3$ solution required cm^3	H_3PO_3 found grm.	H_3PO_3 found grm./cm^3
0·00	50·00	47·22	.....	.....
10·00	50·00	38·50	0·03607	0·003607
15·00	50·00	34·20	0·05385	0·003590
20·00	50·00	29·82	0·07197	0·003599
25·00	50·00	25·57	0·08954	0·003582
72·00	150·00	79·15	0·2585	0·003591

standard of the solution. It should be noted that hypophosphates, though they are readily oxidized by hot permanganate, can not be estimated by this method. Low and irregular values are obtained, probably because of the insolubility of zinc hypophosphate under the conditions.

Iodometric Estimation of Phosphorous Acid in the Presence of Potassium Bicarbonate.—In Table II are the

TABLE II.

Estimation of Phosphorous Acid—Method of Sieverts.

Iodine solution 1·133 N/10. Arsenite solution 0·9812 N/10.

H_3PO_3 taken cm^3	H_3PO_3 taken grm.	Iodine solution taken cm^3	Arsenite solution required grm.	H_3PO_3 found grm.	Per cent of theory
5·00	0·01795	25·00	24·39	0·01804	100·50
10·00	0·03591	24·50	19·31	0·03617	100·72
15·00	0·05387	45·07	38·58	0·05420	100·61
20·00	0·07182	44·32	33·18	0·07247	100·91
20·00	0·07182	28·35	14·80	0·07219	100·52
30·00	0·1077	48·03	28·52	0·1085	100·74
50·00	0·1795	48·05	10·77	0·1800	100·28

results of a series of determinations obtained by the method of Sieverts,[10] already referred to. Measured volumes of the standard phosphorous acid solution were placed in glass-stoppered flasks, to each of which was added two grams of potassium bicarbonate and a known excess of standard iodine solution. The flasks were then

[10] Zs. anorg. Chem., 64, 29, 1909.

set aside in the dark for periods varying from 2 to 24 hours,[11] after which the iodine remaining was titrated with standard arsenite, using starch as indicator.

The results are fairly accurate but show, throughout, a small positive error. That this was chiefly due to an interaction between the iodine and bicarbonate is proved by Table III, which gives the results of a series of blank

TABLE III.

Error due to Iodide and Iodate Formation.

Iodine solution 0·9438 N/50. Arsenite solution 1·000 N/50.

$KHCO_3$ grm.	Iodine solution taken cm³	Time hours	As_2O_3 solution to bleach cm³	Iodine total to color cm³	Volume N/50 Iodine absorbed cm³
2	49·05	2	45·35	49·15	1·04
1*	49·00	2	46·00	49·07	0·31
5	49·00	2	45·20	49·03	1·08
In solution† cm³					
5‡	49·00	2	46·18	49·07	0·13
100‡	49·00	2	44·00	49·10	2·34
5	49·00	2	44·88	49·10	1·46
10	49·00	2	45·90	50·10	1·39

* One drop of dilute HCl added after the bicarbonate.

† The solution was prepared by dissolving 250 grams of potassium bicarbonate in a liter of water, and thoroughly saturating the liquid with carbon dioxide.

‡ This portion of the bicarbonate solution was further treated with a current of carbon dioxide gas for 20 minutes just before using.

experiments in which no phosphorous acid was present, but which in other respects were conducted like those of Table II. The solutions of iodine and of thiosulphate, however, were made fiftieth normal, so that small losses of iodine could be detected with greater certainty, and the influence of the hydroxyl-ion concentration of the solution was tested by employing varying quantities of bicarbonate (1 to 25 grams), and by saturating the solution in some cases with carbon dioxide before mixing with the iodine.

As the results show, there was in every case a marked loss of iodine. This is easily explained, for it is known that iodine on standing with potassium bicarbonate forms a little iodide and iodate with consequent loss of titrable iodine. Washburn mentions this reaction as a

[11] By heating in a pressure flask at 70°, Sieverts was able to complete the oxidation within 30 minutes.

possible source of error even in the direct titration of an arsenite by iodine in the presence of a bicarbonate, and states that for accuracy it is absolutely necessary that the solution be kept saturated with carbon dioxide.[12] It is obvious that the danger is far greater in a process in which an excess of iodine is left in prolonged contact with the bicarbonate, as in the present case.

Since all the iodine which enters into this reaction is set free again when the solution is acidified, it should be possible to improve upon Sieverts' method by carrying out the final titration of the iodine in acid solution by means of thiosulphate. In practice, however, this is inconvenient because of the effervescence produced when the solution is acidified, and the special precautions necessary to prevent consequent loss of iodine.

For this reason we have adopted disodium hydrogen phosphate as a substitute for the bicarbonate. As solutions of this salt have a higher alkalinity than alkali bicarbonate solutions which are saturated with carbon dioxide, the amount of iodate formed during the first stage of the process may be much greater, but this does not affect the results because the solution is acidified before the final titration of the iodine. The absence of effervescence is a great advantage. The amount of the sodium phosphate used must, of course, be great enough to neutralize the hydriodic acid formed, and to keep the solution alkaline during the oxidation of the phosphorous acid. In an initially neutral solution, 11 grams of $Na_2HPO_4.12H_2O$ for every 100 cm^3 of N/10 iodine reduced, will just suffice to leave the solution neutral at the end.[13] This quantity represents the absolute minimum which must not be overstepped. In practice it is a safe rule to add twice as much, or at least 11 grams for each 50 cm^3 of N/10 iodine to be introduced. It is immaterial whether the amount used exceeds this or not, but it is desirable that the total be known as an aid in estimating the amount of acid needed for the acidification. A rough estimate is quite sufficient, for it is well known that the degree of acidity may vary over quite a wide range without affecting the accuracy of the thiosulphate titration.

That this procedure eliminates the iodate error is

[12] J. Am. Chem. Soc., 30, 43, 1908.
[13] Washburn, loc. cit., p. 44.

shown by the experiments of Table IV, in which the titration of a N/50 iodine solution with thiosulphate gave practically the same result whether the titration was performed in neutral solution in the ordinary way, or in acid solution, after the iodine had previously stood for 2½ hours with the amount of disodium phosphate recommended above.

The details of the procedure finally adopted for the estimation of phosphorous acid in the presence of hypo-

TABLE IV.

Iodine solution approximately N/50.

Iodine solution taken cm^3	Na_2HPO_4 110 grams per liter cm^3	Time hours	H_3PO_4 85% solution cm^3	Thiosulphate solution required cm^3
50·00	....	...	..	49·21
50·00	....	...	..	49·20
50·00	50·00	2½	5	49·16
50·00	50·00	2½	5	49·18

NOTE:—One gram of potassium iodide was added in the final titration to increase the sensitiveness of the starch reaction.

phosphoric acid are as follows: A suitable quantity of the solution to be analyzed is measured into a glass-stoppered conical flask of 300 cm^3 capacity. If strongly acid or strongly alkaline the solution is brought approximately to the neutral point toward litmus by cautious addition of sodium hydroxide or hydrochloric acid. This adjustment need only be very rough, but the litmus paper must be used very sparingly, and in such a way as to avoid the introduction of paper fiber, or of appreciable quantities of the indicator, into the solution. When phosphorous acid is the only acid present, this preliminary neutralization may be omitted if the quantity of disodium hydrogen phosphate employed is not less than that recommended above. This salt is now added, either as crystals or in solution, and an excess of a standard solution of iodine is measured into the flask,[14] which is then stoppered and set aside in the dark for at least two hours. Finally the solution is acidified by adding a measured quantity of phosphoric acid[15] (which must be

[14] If a number of determinations are to be made much time can be saved by adding the iodine solution with an accurately calibrated pipette. When this is done, it is best to use the same pipette in determining the ratio between the thiosulphate and iodine solutions.

[15] Though not tested, it is probable that hydrochloric or sulphuric acid could be used for this purpose.

free from impurities which reduce iodine), and the excess of iodine is at once titrated in the usual way with thiosulphate, adding starch just before the end point is reached. If the iodine solution is more dilute than N/10 about a gram of potassium iodide should be added before or during the titration to increase the sharpness of the end point. The amount of acid taken for the acidification should be slightly more than twice the quantity, as determined by a rough preliminary test, which will just suffice to give an acid reaction toward litmus to a solution of disodium phosphate containing the same weight of that salt as has actually been added.

A number of test analyses of standard phosphorous acid solutions by this method are recorded in Table V and VI. For Table VI the solution used was the same as

TABLE V.

Iodometric Estimation of Phosphorous Acid.

Iodine solution 1·022 N/50. Thiosulphate solution 1·010 N/50.

H_3PO_3 taken		Iodine solution	$Na_2S_2O_3$ solution required	H_3PO_3 found	Found
cm³	grm.	cm³	cm³	grm.	%
15	0·01077	45·00	32·53	0·01078	100·09
20	0·01436	45·00	28·22	0·01435	99·93
25	0·01796	45·02	23·85	0·01799	100·17
30	0·02155	45·00	19·52	0·02156	100·05
35	0·02514	45·00	15·21	0·02513	99·96
40	0·02873	45·00	10·80	0·02879	100·21
0	0	45·00	45·52	.....	.....
0	0	45·00	45·58	.....	.....

Reagents used in each determination. 25 cm³ of an 11% solution of $Na_2HPO_4.12H_2O$. 5 cm³ of 42% H_3PO_3 solution. 10 cm³ of 10% KI solution.

in Table II, and a portion of the same solution, carefully diluted to five times its volume with the aid of a certified burette and a certified flask, was employed in the experiments of Table V. The results of Table V, obtained with N/50 solutions of iodine and of thiosulphate, show a very satisfactory accuracy. Those of Table VI, for which N/10 solutions were used, though remarkably concordant, all show a small positive error. Whether this is due in some way to the fact that in this series of experiments the solution was acidified with acetic instead of

TABLE VI.

Iodometric Estimation of Phosphorous Acid.

Iodine solution 1·049 N/10. Thiosulphate solution 1·008 N/10.

H_3PO_3 taken cm³	H_3PO_3 taken grm.	Iodine solution cm³	$Na_2S_2O_3$ solution required cm³	H_3PO_3 found grm.	Found %
15	0·05387	45·00	33·75	0·05411	100·45
20	0·07182	45·00	29·37	0·07223	100·57
25	0·08978	45·00	25·03	0·09018	100·44
30	0·1077	45·00	20·68	0·1082	100·46
35	0·1257	45·00	16·35	0·1261	100·32
40	0·1436	45·00	11·93	0·1443	100·49

Reagents used in each determination. 11 grams of $Na_2HPO_4.12H_2O$. 8 cm³ of glacial acetic acid.

phosphoric acid, or is the result of an error in the standard of one of the N/10 solutions, we are unable to say. On account of lack of time this point was not further investigated.

Table VII is a study of the effect produced by the presence of a hypophosphate upon such analyses. The exact standard of the phosphorous acid solution was unknown. Its equivalent reducing power was approxi-

TABLE VII.

Estimation of Phosphorous Acid in Presence of Hypophosphoric Acid.

Phosphorous acid solution approximately N/50. Hypophosphate solution approximately N/20. Iodine 1·022 N/50. Thiosulphate 1·006 N/50.

H_3PO_3 taken cm³	$Na_2H_2P_2O_6$ taken cm³	Iodine taken cm³	$Na_2S_2O_3$ required cm³	Error per 10 cm³ of hypophosphate cm³ of I_2	H_3PO_3 found grm.
25·00	....	45·00	21·38	...	0·02009
25·00	10·10	45·00	21·26	0·12	0·02019
30·00	....	45·00	16·58	...	0·02405
30·00	9·90	45·00	16·35	0·23	0·02424
35·00	....	45·00	11·61	...	0·02815
35·00	20·00	45·00	11·43	0·09	0·02831
....	....	45·00	45·70	...	.....
....	10·00	45·00	45·58	0·12	.....

Reagents used in each determination. 25 cm³ of an 11% solution of $Na_2HPO_4.12H_2O$. 5 cm³ of 42% H_3PO_4 solution. 10 cm³ of 10% KI solution.

mately N/50, while that of the sodium acid hypophosphate solution, as determined by the permanganate method, was a little over N/20.

In this series a slight reduction of the iodine by the

hypophosphate solution is plainly evident, though the results are in other respects very concordant with one another. As the sample of acid sodium hypophosphate from which the solution was prepared had been recrystallized but once, it seems reasonable to conclude that the reduction of iodine was due to the presence of a little phosphite[16] in the hypophosphate, and not to oxidation of the hypophosphate itself.

This conclusion is supported by the following experiments: Salzer,[17] in 1886, stated that normal sodium hypophosphate, $Na_4P_2O_6$, is partly oxidized by iodine, though neither hypophosphoric acid nor the acid sodium hypophosphate are attacked. To test this point a solution prepared from a sample of the salt which had been recrystallized three times was treated with sodium hydroxide (free from carbonate) in quantity slightly greater than that calculated to be necessary to form the normal sodium salt. Two portions of this solution were each treated with a measured quantity of standard iodine more than sufficient to completely oxidize all the hypophosphate. After two hours' standing in the dark both of these solutions were colorless, but upon acidifying and titrating, the iodine found was practically equal to that taken, the deficiencies being only 0.04 cm^3 and 0.08 cm^3 of the iodine solution, respectively, though the hypophosphate present had a reducing power sufficient to call for about 50 cm^3 of iodine. Losses as small as these might easily be due to experimental error, or to slight impurities in the reagents used, and certainly do not show that the hypophosphate has been attacked. It seems probable, therefore, that Salzer mistook the disappearance of iodine caused by iodide and iodate formation, which necessarily takes place in the rather strongly alkaline solution of the normal sodium hypophosphate, for an actual oxidation of the latter.

It is evident, in any case, that under the conditions recommended above for the determination of phosphorous acid, no appreciable oxidation of the hypophosphate is to be feared. We have used the method for many analyses in the course of a study of the hydrolysis of hypophosphoric acid,[18] and have found it entirely satisfactory.

[16] This impurity is always present in the crude hypophosphate as first prepared, and can only be eliminated by repeated crystallization.

[17] Ann. Chem., 232, 116, 1886.

[18] See the following article.

II. *The Estimation of Hypophosphoric Acid in the Presence of Phosphorous and Phosphoric Acids.*

Since the hydrolysis of hypophosphoric acid gives an equimolecular mixture of phosphorous acid and phosphoric acid according to the equation:

$$H_4P_2O_6 + H_2O = H_3PO_3 + H_3PO_4,$$

it is obvious that the estimation of unknown quantities of hypophosphoric acid can be accomplished by first hydrolyzing completely and then estimating the phosphorous acid so formed by the method described in the foregoing section. Hypophosphates can be quantitatively hydrolyzed, as was first shown by Amat,[19] by

TABLE VIII.

Estimation of Hypophosphoric Acid.

Iodine solution 1·029 N/50. Thiosulphate solution 1·088 N/50.

$Na_2H_2P_2O_6$ solution taken cm³	Iodine solution taken cm³	$Na_2S_2O_3$ solution required cm³	$H_4P_2O_6$ found grm.	$H_4P_2O_6$ taken grm.	Found %
20·02	50·00	28·96	0·03233	0·03245	99·63
25·00	50·00	24·37	0·04042	0·04053	99·73
35·00	50·00	15·27	0·05648	0·05674	99·54
40·00	50·00	10·62	0·06467	0·06484	99·74
45·00	50·00	5·91	0·07298	0·07295	100·04

evaporating the solution to dryness with concentrated hydrochloric acid. Phosphorous acid is remarkably resistant toward atmospheric oxidation[20] and under these conditions undergoes no loss of reducing power.

Table VIII gives the results of a series of analyses, by this method, of measured portions of a hypophosphate solution, which was prepared of definite strength by weighing out the very stable, and beautifully crystalline, acid sodium hypophosphate, $Na_2H_2P_2O_6.6H_2O$, using a sample of the salt which had been carefully purified by seven recrystallizations. In these experiments measured portions of the solution were evaporated nearly to dryness in small beakers over the steam bath. To each beaker 50 cm³ of hydrochloric acid was then added, and the liquid again evaporated as before. To insure complete hydrolysis the treatment with hydrochloric acid

[19] Comptes rendus, **111**, 676, 1890.

[20] Sieverts, Zs. anorg. Chem., **64**, 32, 1909. Luther and Plotnikow, Zs. phys. Chem., **61**, 513, 1908.

and subsequent evaporation was then repeated, after which the residue was taken up with water, transferred to a glass-stoppered flask, and the iodometric analysis carried out as already described.

If phosphorous acid is present at the outset, the iodometric analysis must be carried out upon separate portions of the solution before and after hydrolyzing with hypophosphoric acid, and the amount of the latter calculated from the difference. This presents no difficulty, and appears to be the most satisfactory method available for the estimation of hypophosphoric acid in the presence of phosphorous and phosphoric acids.[21]

III. *Complete Analysis of a Mixture of the Three Acids.*

Three portions of the solution are measured out. In the first the phosphorous acid is determined as described in section I. In the second the hypophosphoric acid is hydrolyzed according to section II and the phosphorous acid then estimated as before, the gain as compared with the first portion giving the content of hypophosphoric acid. In the third portion the reducing acids are completely oxidized by treatment with hot aqua regia and evaporation nearly to dryness, and the total phosphoric acid then estimated by any one of the standard methods. The phosphoric acid originally present is calculated by difference.

Summary.

1. An iodometric method for the estimation of phosphorous acid is described, which is applicable in the presence of hypophosphoric and phosphoric acids.

2. Hypophosphoric acid can be estimated by first hydrolyzing completely and then following the method just mentioned.

3. A mixture of phosphorous, hypophosphoric, and phosphoric acids can be completely analyzed by the above processes, combined with the determination (after oxidizing the reducing acids) of the total phosphoric acid.

4. Incidentally, another volumetric process for the estimation of phosphorous acid is described. This process, which is a more rapid modification of Kühling's method, is applicable in the presence of phosphoric but not of hypophosphoric acid.

[21] For criticisms of the method proposed by Rosenheim and Pinsker, Zs. anorg. Chem., 64, 333 ff., see the following article.