molecules in the solution, and a definite chemical equilibrium between the ions and undissociated molecules. In order for such combination to occur, in which, according to the conceptions of Knorr,[12] Pauling[13] and others, electronic orbits may surround both atomic nuclei, it is first necessary to have an effect similar to the Stark effect which deforms one or both of the ions. Thus, since the lithium ion lowers the dielectric constant of the medium and deforms the hydroxyl ion to a greater extent than the sodium ion, the formation of non-polar bonds would be more probable in the case of lithium than sodium hydroxide, and much more probable in the case of water. Very similar considerations would also apply to the activity coefficient of formic acid in the salt solutions, in which case a similar effect would have to be assumed in the case of the formate ion which we have premised in the case of the hydroxyl ion.

Summary

1. From the results of Manning and the assumption that the velocity of hydrolysis of ethyl formate in neutral salt solutions is proportional to the hydrogen-ion concentration, the activity-coefficient products of formic acid in salt solutions of various kinds and strengths have been calculated.

2. The values thus obtained parallel very satisfactorily the behavior of the ionic activity-coefficient product of water in salt solutions.

3. A theory of the thermodynamic behavior of hydroxyl and formate ions has been discussed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ARIZONA]

THE REACTION BETWEEN ELEMENTARY PHOSPHORUS AND POTASSIUM IODATE AND ITS UTILIZATION IN THE VOLUMETRIC DETERMINATION OF PHOSPHORUS[1,2]

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When either white or red phosphorus is mixed with potassium iodate, and a few drops of water are added, the mixture reacts violently, sometimes even explosively, liberating iodine and evolving a considerable quantity of heat. When more water is initially taken, the rate of the reaction is greatly decreased. Since the reaction starts slowly and gradually speeds

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[12] Knorr, *Z. anorg. allgem. Chem.*, **129**, 109 (1923).

[13] Pauling, THIS JOURNAL, **48**, 1132 (1926).

[1] Presented by O. E. Schupp, Jr., before the Physical Sciences Section at the Spring Meeting of the Southwestern Division of the American Association for the Advancement of Science, February 15–18, 1926, Phoenix, Arizona.

[2] The initial work on this method was carried out by one of us at the University of California during the session 1919–1920 in conjunction with solubility studies under Professor J. H. Hildebrand.

up, it appears probable that the iodine formed is responsible for the rapidity of the reaction rather than the iodate ion. Experimental evidence advanced by Steele[3] and Brukl and Behr[4] indicates that phosphorous acid reacts but slowly with iodine. Since phosphorous acid is formed to a considerable extent under these conditions, the rate of the entire reaction is determined solely, perhaps, by the rate at which it is oxidized to phosphoric acid. It is possible, however, under suitable conditions, to render this oxidation complete by means of potassium iodate.

These observations served as a starting point in the development of a satisfactory volumetric method of determining elementary phosphorus, especially in connection with solubility studies. The method to be described was originally employed by Hildebrand and Buehrer[5] to determine the concentration of white phosphorus in various organic solvents. It consists essentially in allowing the phosphorus to react with a known weight of potassium iodate in acid solution, boiling under a reflux condenser for a time and titrating the iodine formed with standard thiosulfate.

Theoretical Part

The need of a satisfactory volumetric method for elementary phosphorus arises from the fact that all of the methods thus far proposed are gravimetric, involving time-consuming precipitation and ignition. The oxidation process prior to precipitation with magnesium ammonium phosphate or phosphomolybdate is generally carried out by means of nitric acid, iodine or bromine; in each case considerable care must be taken (a) to insure complete oxidation to phosphoric acid and (b) to prevent loss of volatile phosphorus compounds during the oxidation. Christomanos,[6] in his determinations of the solubility of white phosphorus in ether and benzene, apparently succeeded in fulfilling these conditions by first precipitating the phosphorus as copper phosphide with copper sulfate solution, filtering and oxidizing the phosphide formed by means of bromine and nitric acid, and determining the phosphorus gravimetrically. While this method applies to the white modification, it would fail with the red; furthermore, it is satisfactory only when relatively small amounts of phosphorus are taken.

Before the iodate method can be accepted as satisfactory several points must be definitely established: (a) the nature of the reactions involved; (b) the effect of acidity on the speed and completeness of the reaction; (c) whether the iodine produced or the residual iodate will yield the true percentage of phosphorus. Certain factors which affect the experimental procedure will also be discussed.

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[3] Steele, *J. Chem. Soc.*, **93**, 2203 (1908).

[4] Brukl and Behr, *Z. anal. Chem.*, **64**, 23 (1924).

[5] Hildebrand and Buehrer, This Journal, **42**, 2213 (1920). Details of the method were not included in this paper.

[6] Christomanos, *Z. anorg. Chem.*, **45**, 132 (1904).

Nature of the Reactions Involved

The reactions involved in the oxidation of phosphorus by potassium iodate have been found to take place as follows.

$$5P + 3IO_3^- + 3H^+ + 6H_2O = {}^3/_2\,I_2 + 5H_3PO_3 \quad (1)$$

This reaction is slow, and goes partially to phosphoric acid.

$$2P + 3I_2 + 6H_2O = 6H^+ + 6I^- + 2H_3PO_3 \quad (2)$$

This reaction is quite rapid.

$$5H_3PO_3 + 2IO_3^- = I_2 + 3H^+ + 5H_2PO_4^- + H_2O \quad (3)$$

This reaction is very slow, as is strikingly shown by adding potassium iodate to a phosphorous acid solution. Very little iodine is liberated even on refluxing the solution for some time.

$$H_3PO_3 + I_2 + H_2O = 3H^+ + 2I^- + H_2PO_4^- \quad (4)$$

This reaction has been studied by Steele[3] who finds that "two distinct reactions occur. . . .one of which preponderates in acid solution and the other in the absence of strong acid," the one in acid solution being catalyzed by hydrogen ion. This reaction has been shown by a number of authors to be slow, and to depend in large measure upon the acid concentration.[7,8,9,10] It appears probable that the oxidation of the phosphorous acid by iodine determines the rate of the reaction as a whole.

$$5I^- + IO_3^- + 6H^+ = 3I_2 + 3H_2O \quad (5)$$

This reaction is known to be instantaneous and complete.

Experimental Part

Red phosphorus was used because it could be handled in dry form and because any experimental conditions applying to this modification would apply to the white also. It was first ground very fine in an agate mortar and suspended in water, and the suspension poured through a 200-mesh sieve. It was then boiled with dil. potassium hydroxide solution to remove both white phosphorus and oxides of phosphorus, washed several times by decantation, and the suspension centrifuged to settle the fine material. It was finally dried over phosphorus pentoxide in a vacuum. A gravimetric analysis showed it to contain 95.03 and 95.25% of phosphorus; av., 95.1%. The remaining 4.9% of the material was not quantitatively analyzed; qualitative tests, however, showed negligible amounts of phosphorous and phosphoric acids.

The potassium iodate was twice recrystallized from hot water, dried over phosphorus pentoxide in a vacuum and screened through a 200-mesh sieve. On adding potassium iodide and sulfuric acid and titrating with thiosulfate, it was found to be 100% pure within the limits of error of this titration.

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[7] Rupp and Fink, *Chem. Zentr.*, **11**, 1432 (1902).

[8] Federlin, *Z. physik. Chem.*, **41**, 565 (1902).

[9] Orlov, *J. Russ. Phys.-Chem. Soc.*, **46**, 535 (1914); *C. A.*, **8**, 3144 (1914).

[10] Boyer and Bauzil, *C. A.*, **13**, 992 (1919).

Apparatus and Method

In the light of the foregoing reactions, the determinations were made so as to yield data which would permit the calculation of the amount of phosphorus by titration of the iodine distilled, the residual iodate and the gravimetric determination of the phosphorus itself, if necessary or desirable. The apparatus devised for this purpose which made possible both refluxing and distillation of the iodine is shown in Fig. 1.

One-tenth g. of phosphorus (or an equivalent weight of phosphorus compound) and about 0.8000 g. of potassium iodate (solid or in solution) are weighed into the glass-stoppered Erlenmeyer flask A, and a few glass beads added to prevent bumping. The requisite amount, 10 cc., of 4 *N* sulfuric acid, 65 cc. of water and 2 cc. of carbon tetrachloride are added at once from a 100cc. graduated cylinder and the flask *quickly* attached to the condenser to prevent loss of iodine. Since digestion under the reflux condenser involves possible condensation of iodine, it was decided to add a small amount of a non-polar solvent, for example, carbon tetrachloride, in which the iodine readily dissolves. This solvent washes the iodine constantly down into the flask, thus enabling it to take part in the main oxidation reaction. To avoid the possibility of removing most of the iodine from the aqueous phase and thus slowing down the reaction greatly, only a small volume, 2 cc., of carbon tetrachloride is used, this quantity being sufficient to accomplish its purpose.

With water passing through the condenser jacket B, the solution is refluxed for at least three and preferably four hours, is then distilled by draining the cooling water from B but allowing it to continue to flow through Jacket C, which is very easily accomplished by proper manipulation of the screw clamps. The cooling effect of the second condenser prevents loss of iodine by volatilization. The iodine is caught in an Erlenmeyer flask D containing a known (but not an excess) volume of standard thiosulfate solution to which is added some cracked ice. This solution prevents any loss of iodine throughout the entire refluxing and distillation process.[11] It is preferable not to employ an excess of thiosulfate solution in Flask D,

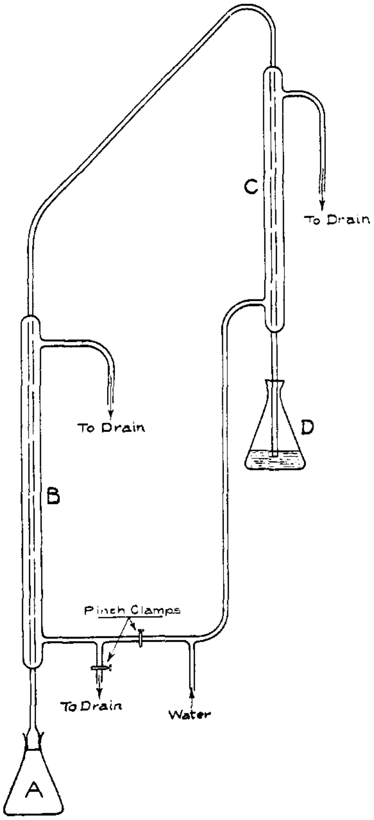

Fig. 1.—Apparatus for analysis of phosphorus by means of potassium iodate.

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[11] The distilling apparatus, obtained from a chemical supply house, consisted of a Pyrex Erlenmeyer flask into which was ground the condenser tube of ordinary *soft glass* of much higher coefficient of expansion. An absolutely tight joint was thus assured at this point, and no loss of iodine could be detected at any time during the distillation.

so as to eliminate back titration with iodine solution. At times during the distillation, the iodine tends to collect in the second condenser and stick, but it can readily be loosened by removing the flame from Flask A, thus allowing the solution in D to suck up into the condenser and dissolve the iodine. After the iodine has apparently been entirely driven over, the distillation is again allowed to proceed in order to permit the condensed water to wash out the condenser C. The iodine in D is then titrated with standard thiosulfate solution.

To rinse Condenser B the water is once more turned into its jacket and refluxing continued; the condensed water washes down any iodate which may have spattered during the distillation. Flask A is then cooled with a beaker containing water and cracked ice, lumps of ice and potassium iodide are added (the solution being already acid) and titration is at once completed with thiosulfate solution. If desired, the iodine may simply be boiled from the original flask and titration of the residual iodate completed in the usual way.

The Effect of Acidity on Speed and Completeness of the Reaction

On the basis of the known reaction between phosphorus and potassium iodate given above, it should be possible to predict the optimum conditions for the quantitative method under consideration. The large number of experiments carried out in this connection have shown that the elementary phosphorus reacts completely within the first five minutes after the reaction starts. We may, therefore, consider 4 and 5 to be the principal reactions taking place. It will be seen from the respective equations that Reaction 4 will be favored by low acidity, whereas Reaction 5 requires considerable acidity to go to completion. Since the system is complicated by both reactions occurring simultaneously, the rate constants obtained by Steele[3] could not be used for calculating the time required for the reaction to go to completion. It was, therefore, necessary to study experimentally the relation of initial acidity to speed and completeness of reaction. This was accomplished in a single series of experiments by carrying out determinations with the same amounts of phosphorus, of iodate and of initial acidity, but refluxing the mixtures for different lengths of time. The same type of experiment was then carried out by varying the initial acidity as follows: (a) solution neutral; (b) 0.25 *N* in sulfuric acid; (c) 1.25 *N* in sulfuric acid. In each case, after refluxing had been continued for the chosen period of time, the flask containing the mixture was cooled with ice to stop the reaction. The iodine formed was then extracted with carbon tetrachloride and titrated with thiosulfate solution. The curves are shown in Fig. 2, where percentages of phosphorus (obtained from the iodine titration) are plotted as ordinates against time in hours as abscissas.

From the curves thus obtained it appears that in an initially neutral solution the reaction is entirely too slow to reach completion within any reasonable length of time. When the acidity is only 0.25 *N*, the reaction is complete within about three hours, and in even less time at an acidity of 1.25 *N*. To be certain that the low results invariably obtained when the solution was initially neutral were not due to reduction of some of the iodine to iodide ion and not reacted upon by iodate ion due to insufficient acidity, a little sulfuric acid was added to the solution after extraction of the iodine but no more iodine was formed. Several experiments in which the initial acidity was increased up to 6 *N* yielded results which were from 5–10% high, both by direct titration of the iodine and by residual titration of iodate. No explanation for this peculiar phenomenon has been found.

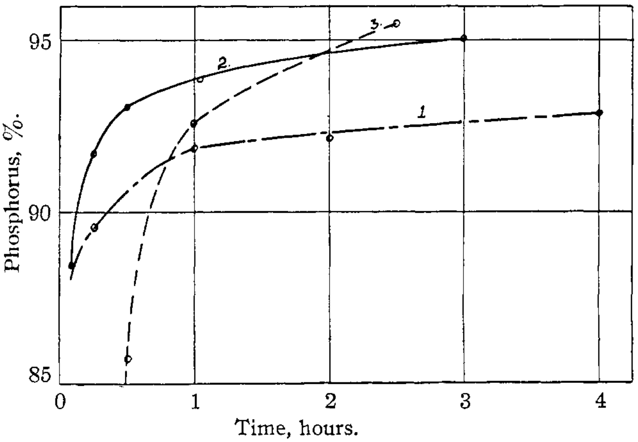

Fig. 2.—Effect of initial acidity on rate of oxidation of phosphorus by potassium iodate. 1. Initially neutral. 2. 0.25 *N* H_2SO_4. 3. 1.25 *N* H_2SO_4. Reaction is complete at 95%.

Test of Accuracy of the Method

The results of a series of determinations are given in Table I.

TABLE I

DETERMINATION OF ELEMENTARY PHOSPHORUS BY MEANS OF POTASSIUM IODATE

Total volume of reaction mixture, 75 cc.

CCl_4, Cc.	Initial acidity, *N*	Time, hrs.	KIO_3 taken, g.	Excess of KIO_3, g.	P taken, g.	P lib. by I_2, g.	Error, %	P by resid. KIO_3, g.	Error, %	Remarks
25	0.25	3	0.8450	0.2172	0.0909	0.0911	+0.22	0.0909	0.0	Refluxing and distillation of iodine. Titration of iodine and residual iodate as given in final method.
25	.25	3	.8450	.0646	.1134	.1132	− .18	.1130	− .35	
10	1.25	2	.8466	.1674	.0979	.0977	− .20	.0985	+ .61	
10	1.25	2	.8466	.1716	.0985	.0979	− .61	.0986	+ .10	
2	1.25	2.5	.9000	Excess	.1037	.1042	+ .48	...	....	
2	0.80	3	.8221	.1221	.1010	.1008	− .19	.1013	+ .29	
2	.80	4	.8106	.0768	.1060	.1063	+ .28	.1062	+ .19	
2	.80	4	.9747	.2326	.1074	.1071	− .28	.1074	+ .00	
2	.5	4	.8481	.1472	.1012	...	....	.1074	+ .49	Samples refluxed and iodine boiled off under the hood, and residual KIO_3 titrated.
2	.5	4	.8495	.0851	.1106	...	....	.1109	+ .27	
2	.5	5	.9553	.2215	.1065	...	....	.1062	− .28	
2	.5	4	.8765	.1634	.1031	...	....	.1032	+ .10	
2	.5	4	.9686	.1823	.1133	...	....	.1135	+ .17	
Av. % error (irrespective of sign).							0.31		0.22	
Average % error (regarding signs).							− .07		+ .19	

Discussion of Results and Sources of Error

The results obtained by both direct titration of iodine and residual titration of iodate are seen to reproduce the quantities of phosphorus taken to about 0.3% and in some instances the agreement is even better. A number of sources of error enter into the determination, however, some of which are apparently unavoidable. In the first place, since we are dealing here with very nearly pure phosphorus, an error of 0.1 mg. alone in weighing the sample would entail an error of 0.1%. Where solutions of phosphorus are analyzed, this error would, however, be much less. When 0.1 *N* thiosulfate solution is used for titration, and a 0.1000g. sample of phosphorus is taken, an error of 0.04 cc. in the volume of solution used involves an error of 0.1%. In the residual titration of iodate, the magnitude of the error would be expected to be less, since 1 gram ion of iodate liberates 6 gram atoms of iodine. The chief source of error in the method, which may lead to low results, is the volatilization of iodine, which is minimized by using ice in all solutions containing it. At 0° the vapor pressure of iodine from a potassium tri-iodide solution is negligibly small. A third factor is the acidity which, though necessary for its catalytic effect and for the completeness of the reaction, cannot be impressed to an indefinitely high value as indicated earlier in this paper.

Application of Method to Solubility Determinations of Phosphorus

For the purpose of analyzing solutions of phosphorus in solubility determinations, this method commends itself because iodic acid does not act upon the common non-polar solvents and only very slowly with many of the polar solvents. Boiling an acidified iodate solution with carbon tetrachloride, chloroform, ether, benzene, hexane, naphthalene, *p*-dibromobenzene, for considerable periods of time yielded no more iodine than an amount equivalent to one drop of 0.1 *N* thiosulfate solution. Methyl alcohol, ethyl alcohol and carbon disulfide react slightly after long-continued boiling.

Summary

1. The reaction between phosphorus and potassium iodate is utilized as the basis of a new volumetric method of determining elementary phosphorus.

2. It is found experimentally that the oxidation of phosphorus to phosphoric acid goes to completion only in an initially acid solution (at least 0.25 *N* in sulfuric acid), which is refluxed for at least three hours.

3. The reactions involved and the sources of error in the method are discussed.

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