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THE IONIZATION RELATIONS OF ORTHO- AND PYROPHOSPHORIC ACIDS AND THEIR SODIUM SALTS.

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1. Purpose of the Investigation and Review of Previous Work.

The ionization relations of the polybasic acids are at present imperfectly understood. This is true even of such important acids as phosphoric acid and the less hydrated acids derived from it. Therefore an investigation of these acids was undertaken in the hope that an exhaustive study of their ionization relations might contribute toward a better understanding of their chemical behavior in inorganic reactions. The general scope of this investigation may be seen by reference to the table of contents given above.[1]

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[1] The experimental work described in this article was carried out by one of the authors alone (G. A. A.). It was begun in October, 1904, and completed two years later, at which time the calculations were first made and the results interpreted. After his departure, work in this laboratory along other lines led to the adoption of a more satisfactory method than that first employed of estimating concentrations of ions and undissociated substances; the calculations were therefore completely revised by the other author (W. C. B.). This revision by the new method has given more concordant results and enabled some additional conclusions to be drawn.

The knowledge already existing consists, for the most part, of more or less fragmentary physico-chemical data obtained by numerous experimenters in connection with other investigations. Conductivity measurements have been made by Kohlrausch,[1] Ostwald,[2] Walden,[3] Foster,[4] Noyes and Eastman,[5] and others. Arrhenius[6] has also calculated from these the heat of ionization of the first equivalent of hydrogen in orthophosphoric acid by the van't Hoff equation; he gives for 25° the value 1820 calories.

The heats of neutralization of ortho- and of pyrophosphoric acids have been measured by Berthelot and Louguinine,[7] and by Thomsen.[8] The results are given in the following table:

Orthophosphoric acid.			Pyrophosphoric acid.	
	Calories evolved.			Calories.
1 H_3PO_4 Aq +	B. & L.	Thomsen.	1 $H_4P_2O_7$ Aq +	Thomsen.
0.5 NaOH Aq	7180	7330	1 NaOH Aq	14380
1.0 "	14680	14830	2 "	28650
2.0 "	26330	27080	4 "	52740
3.0 "	33590	34030	6 "	54480
6.0 "	35500	35280		.....

In the case of orthophosphoric acid the large heat effects that attend the addition of the third equivalent and of the three extra equivalents of sodium hydroxide indicate that its third equivalent of hydrogen is largely, but far from completely, replaced when the proportions of acid and base are those corresponding to the salt Na_3PO_4. The results with pyrophosphoric acid seem to show that the same is true of its fourth equivalent of hydrogen in a solution of the salt $Na_4P_2O_7$. It is also worthy of note that the replacements of its first and second equivalents are attended with almost the same heat evolution (14380 and 14270 calories), but yet with one which considerably exceeds the value 13700 usual for nearly completely ionized acids.[9]

In measuring the heat of neutralization of orthophosphoric acid by ammonium hydroxide Berthelot and Louguinine discovered the highly remarkable fact that the addition of the third equivalent of base in some experiments gave rise to a heat effect which indicated the quantitative formation of tri-ammonium phosphate, while in other experiments made

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[1] *Ann. Physik*, **26**, 161 (1885).

[2] *Allgemeine Chemie*, **2**, 1, 728 (1893).

[3] *Z. physik. Chem.*, **1**, 529 (1887); and **2**, 49 (1888).

[4] *Phys. Rev.*, **8**, 257 (1899).

[5] *Carnegie Institution Publications*, No. **63**, 239.

[6] *Z. physik, Chem.*, **4**, 105 (1889).

[7] *Ann. chim. phys.* [5], **9**, 26 (1876).

[8] Thomsen, *Thermochemistry*, Ramsay Series, p. 99.

[9] A combination of these results with the ionization values given in Table XV below for 0.05 formular $NaH_3P_2O_7$ leads to the conclusion that the reaction $H_3P_2O_7^- = H^+ + H_2P_2O_7^{--}$ is attended by an evolution of about 1000 calories.

under apparently the same conditions it produced scarcely any heat effect, indicating that no reaction whatever had occurred. It was shown also that after standing several days the two solutions had become identical, at any rate in the respect that they gave the same heat evolution when treated with an excess of sodium hydroxide, indicating that when the tri-ammonium phosphate has been formed it is slowly hydrolyzed upon standing. The heats of neutralization obtained by the authors in the two cases are as follows:

H_3PO_4.	Calories evolved.	
	I.	II.
1 NH_4OH	13460	13840
2 NH_4OH	26320	23140
3 NH_4OH	33170	23330
6 NH_4OH	33100	.....
12 NH_4OH	.....	23700

Loomis[1] obtained values of the freezing-point lowerings caused by orthophosphoric acid, which correspond to a much smaller degree of ionization than that derived from the conductivity of the acid.

D. Berthelot[2] found that when ammonium, sodium, or potassium hydroxide is added to a dilute solution of orthophosphoric acid, the decrease of conductance of the solution may be represented by a straight line up to the point at which one of the hydrogens of the acid is replaced and by another straight line different in direction from the first up to the point corresponding to the replacement of the second hydrogen. Beyond this point further addition of alkali causes a change in the direction of the curve, which can no longer be represented by a straight line. From these facts the conclusions may again be drawn that the first and second equivalents of hydrogen in orthophosphoric acid are almost quantitatively replaced, but that the third equivalent is only gradually neutralized as the proportion of base increases.

J. Shields[3] has determined the quantity of free base in solutions of hydrolyzed salts by measuring the rate at which the solution saponifies ethyl acetate. From his measurements he concluded that tri-sodium phosphate, Na_3PO_4, is at least 98 per cent. hydrolyzed into Na_2HPO_4, and NaOH in 0.02 formular solution, at 24.2°, and that di-sodium hydrogen phosphate, Na_2HPO_4, is probably hydrolyzed only to the extent of 0.07 per cent. in 0.05 formular solution. That the former of these conclusions is far from correct is evident from the results presented below.

2. The Conductance of Ortho- and Pyrophosphoric Acids and Their Sodium Salts. Experimental Data.

Apparatus and Method of Measurement.—The conductance of the solutions was measured by the familiar method of Kohlrausch, using a

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[1] *Ann. Physik*, 51, 517 (1894).

[2] *Compt. rend.*, 113, 851–4 (1891).

[3] *Z. physik. Chem.*, 12, 180–3 (1893).

Wheatstone slide-wire bridge, an alternating current produced by an induction coil, and a telephone as an indicator of zero potential. The bridge was carefully calibrated and the resistances employed were checked against a standard bearing the certificate of the German "Reichsanstalt." A special form of conductivity cell was used (Fig. 1) for which I am indebted to Dr. C. A. Kraus, of this laboratory. This possesses many advantages over the familiar Arrhenius type: it permits the convenient introduction and removal of solutions without danger of contamination from exposure to the air; it can be completely immersed in the liquid of the thermostat so that the temperature of the latter is fully attained, and the electrodes are safe from mechanical disturbances which might cause a change in the conductance capacity of the cell. The large thermostat, in which the cell was securely held by a clamp, was stirred by the rotation of a paddle driven by an electric motor, while the temperature was regulated by an electric heating coil, a cooling coil, and a mercury regulator connected electrically with a relay which controlled the current of the heating coil. With this apparatus it was easy to maintain the temperature constant within 0.01-0.02°. The temperature was determined by a Beckmann thermometer which had been compared with a standard thermometer, certified by the German "Reichsanstalt."

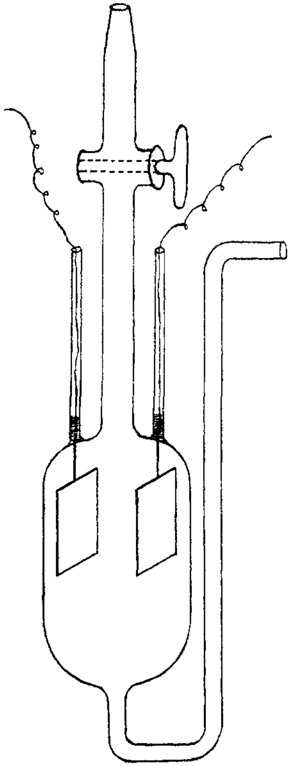
Fig. 1.

THE PREPARATION OF THE SUBSTANCES AND SOLUTIONS.

Orthophosphoric Acid.—The "C. P." acid of the market contained objectionable amounts of impurities, particularly of sodium salts, from which it could not be readily freed; therefore it seemed advisable to prepare the acid by a method which would eliminate such contamination. After investigating various methods, the direct oxidation of phosphorus was selected as the method most likely to yield an acid free from salts and other impurities which would affect its physico-chemical properties. Yellow phosphorus was chosen, because it is usually purer than the red variety, although the latter is safer and more convenient for the purpose. Carefully selected, clean, translucent pieces were put into a two-liter glass-stoppered retort, and heated with about 16 times their weight of pure nitric acid of specific gravity 1.20. The density of the nitric acid employed is important; if greater than 1.20, the action becomes violent, and may even give rise to a dangerous explosion; if less than 1.20, the action is unnecessarily prolonged. During the oxidation of the phosphorus, the heat was so regulated that the mixture was kept at the boiling temperature but not allowed to boil violently, and the distillate which collected in the well-cooled receiver was returned to the retort from time to time. When the oxidation was complete, the contents of the retort were transferred in successive small portions to a platinum dish, enough pure nitric acid was added to insure the complete oxidation of any phosphorous acid, and the liquid was evaporated till it became sirupy and white fumes of metaphosphoric acid appeared. The cooled residue was then treated with conductivity water, and the solution was saturated in the cold with pure hydrogen sulphide gas, warmed in a pressure bottle (made of Whitall, Tatum, and Co.'s "non-sol" glass) for more than an hour, allowed to stand over night to insure the precipitation of any arsenic or platinum (taken up from the dish), again evaporated to a sirup, and redissolved. The solution thus prepared contained metaphosphoric acid and pyrophosphoric acid. To convert these into orthophosphoric acid, the solution was transferred to a large platinum dish of 1500 cc. capacity, and maintained at the boiling temperature for three hours on two consecutive days. At the end of this time it failed to show the ordinary tests for metaphosphoric acid, no precipitate being produced by albumen or barium chloride solution; while, on the other hand, it gave with silver nitrate solution, after careful neutralization, the characteristic yellow precipitate of silver orthophosphate. But to ascertain, if possible, whether or not the transformation into ortho acid was really complete, a portion of the solution was placed in a "non-sol" bottle (with the glass stopper securely wired in) and was heated in the steam bath three hours; then it was quickly chilled in a stream of cold water, after which the conductance was measured. The value was identical with that of the solution before heating. It will, moreover, be shown in the following article that the rate of conversion of pyrophosphoric acid into the ortho acid is complete and rapid at 100°.

The acid solution was next subjected to a thorough examination for impurities. The usual systematic qualitative procedure for the detection of bases gave in every instance a negative result. A portion rendered alkaline and treated with Nessler's reagent gave merely a trace of coloration due to ammonia. The method of preparation at once suggests the possibility of contamination by nitric acid; but not a trace of it could be detected even by the phenol-sulphonic acid test, which shows even minute traces of the acid by the formation of the intensely yellow ammonium picrate. With silver nitrate in nitric acid solution no precipitation or turbidity could be observed. Barium chloride likewise failed to produce the slightest turbidity.

To determine the concentration of the acid solution, weighed samples of it were transferred to beakers and precipitated with a slight excess of magnesium ammonium chloride, after adding to the solution one-half its volume of ammonia water of specific gravity 0.96. After standing twelve hours at room temperature the precipitates were collected, washed with dilute ammonia water containing alcohol, dried, separated from the filter, and ignited. The stock solution was thus found to contain 20.087 grams or 0.2049 formula weights of H_3PO_4 per 1000 grams of solution.[1]

Di-sodium Hydrogen Phosphate.—The best grade of "C. P." di-sodium phosphate was subjected to five recrystallizations from conductivity water. From this salt the stock solution was prepared. It was standardized by carefully evaporating a weighed sample to dryness in a platinum dish, heating the residue to fusion, cooling, and weighing. The stock solution was thus found to yield 54.15 grams Na_2HPO_4 per 1000 grams of solution.

Mono-sodium Di-hydrogen Phosphate.—Solutions of this salt were prepared, when required, by weighing out and mixing the proper amounts of the stock solutions of the acid and the di-sodium salt.

Pyrophosphoric Acid.—Sodium pyrophosphate was first prepared from pure di-sodium hydrogen phosphate by igniting the latter in a platinum dish; the residue was then dissolved and precipitated with a hot, concentrated solution of pure copper sulphate, which was added in excess to avoid the formation of any double salts of copper and sodium. The resulting precipitate of copper pyrophosphate was washed with boiling conductivity water by decantation, until the washings were free from sodium and sulphates. The washed precipitate was suspended in water in a glass-stoppered bottle which was then surrounded by crushed ice, and when the contents were cold, a stream of washed hydrogen sulphide was passed into the bottle, until, after thorough shaking, the liquid possessed a strong odor of the gas. The liquid was then filtered rapidly through a Büchner funnel, and a stream of purified air was forced through the well-cooled filtrate, until a sample of the latter failed to give a dark precipitate with lead acetate solution. It was then refiltered, to remove any turbidity due to precipitated sulphur, and placed in the ice box until ready for use.

The acid prepared in this way was carefully tested for impurities. No sulphuric acid could be detected. The ferrocyanide and ammonia tests for copper gave negative results, and portions of 50 cc. evaporated to dryness in a platinum dish left no weighable residue. As there seems to be no satisfactory test for the ortho acid in the presence of a large

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[1] The International Atomic Weights of 1908 were used.

excess of the pyro acid, the fact (substantiated by data presented below) that nearly identical values of the conductance were obtained from independently prepared samples of the acid was regarded as sufficient evidence of the absence of this impurity in significant amount.

The solution was standardized gravimetrically as follows: 50 cc. portions were treated with an equal volume of nitric acid (sp. gr. 1.20) and heated on the steam bath for five hours, to convert the pyro into the ortho acid; then the acid was neutralized with ammonia, and the solution was cooled, treated with magnesium ammonium chloride, and allowed to stand over night. The stock solution was thus found to contain 0.1051 formula weight of $H_4P_2O_7$ per liter.

The behavior of the pyrophosphoric acid solutions toward indicators was studied with the view of finding a more convenient method of standardization. It was found that 25.00 cc. of the stock solution when titrated with a 0.1224 normal sodium hydroxide solution required 43.00, 42.95, and 43.05 cc., respectively, when methyl orange, Congo red, and cochineal were used as indicators. Assuming that only one-half the hydrogen in the pyro acid is neutralized when the end-point is reached, this result would correspond to a concentration of 0.1053 formula weights $H_4P_2O_7$ per liter, which is nearly identical with the value (0.1051) found gravimetrically. Solutions of the pyro acid subsequently prepared were standardized in this way, using methyl orange as an indicator.

This behavior towards indicators evidently shows that the dissociation of the first two hydrogens of pyrophosphoric acid is fairly large, and that that of the third and fourth hydrogens is extremely small.

Sodium Pyrophosphates.—Solutions of the salts $Na_2H_2P_2O_7$, $Na_3HP_2O_7$, and $Na_4P_2O_7$, were prepared, when required, by weighing out and mixing suitable amounts of the solid $Na_4P_2O_7$ and of the stock solution of pyrophosphoric acid.

Dilute Solutions of the Acids and Salts.—Solutions of concentrations down to 0.01 formular were made up by diluting the stock solutions of the various substances above referred to by means of calibrated flasks. The more dilute solutions were then prepared by weighing out the requisite amounts of the 0.01 formular solutions and of "conductivity water."

THE CONDUCTANCE DATA.

The conductance capacity of the cell was determined by measuring the conductances of it when filled with 0.01 normal solutions of potassium chloride and sodium chloride and with a 0.02 normal solution of potassium chloride. From the results of these measurements the following three values of the conductance capacity of the cell were calculated: 0.2823, 0.2822 and 0.2825. The mean of these, 0.2823, was used in the subsequent calculations, the actual conductance of the various solutions being multiplied by this quantity to give the specific conductance.

The following table contains the results of all the conductance measurements. The temperature was 18° in all cases. The concentration, *C*, is always expressed in formula weights per liter; the specific conductance, *L*, in reciprocal ohms. In the last column is given μ, the "formular conductance," where $\mu = 1000\ L/C$. The results marked I and II were obtained with solutions prepared separately from the stock solutions.

TABLE I. THE CONDUCTANCE DATA.

Substance.	Formula weights per liter (C).	Specific conductance × 10^6.			Formular conductance, μ.
		I.	II.	Mean.	
Na_2HPO_4	0.2	19858	19852	19855	99.27
	0.1	11563	11561	11562	115.62
	0.05	6515	6517	6516	130.32
	0.02	2951	2590	2950	147.5
	0.01	1588	1587	1587	158.7
	0.005	842.8	841.8	842.3	168.5
	0.003	523.0	523.0	523.0	174.3
	0.002	355.6	355.6	355.6	177.8
	0.001	182.17	182.08	182.12	182.1
NaH_2PO_4	0.2	9926	9972	9949	49.74
	0.1	5442	5444	5443	54.43
	0.05	2913	2913	2913	58.26
	0.02	1228	1229	1228.6	61.43
	0.01	655.5	655.1	655.3	65.53
	0.005	337.7	338.1	337.9	67.58
	0.003	207.8	207.6	207.7	69.23
	0.001	71.70	71.66	71.68	71.68
$Na_4P_2O_7$	0.1	15650	15650	15650	156.5
	0.05	9280	9240	9260	185.2
	0.02	4474	4482	4478	223.9
	0.01	2566	2566	2566	256.6
	0.005	1456.8	1456.8	1456.8	291.3
	0.003	943.38	942.6	942.9	314.3
	0.001	374.3	369.9	372.1	372.1
	0.0003	125.1	126.5	126.0	420.0
$Na_3HP_2O_7$	0.1	14890	14904	14897	148.9
	0.05	8600	8607	8603	172.1
	0.02	3980	3980	3980	199.0
	0.01	2201	2202	2201	220.1
	0.003	745.7	746.3	746.0	248.7
	0.001	272.3	270.6	271.4	271.4
	0.0003	87.14	85.88	86.51	288.3
$Na_2H_2P_2O_7$	0.1	10700	10710	10705	107.0
	0.05	6000	6005	6002.5	120.0
	0.02	2665	2665	2665.0	133.2
	0.01	1432	1429	1430.5	143.0
	0.003	468.2	468.6	468.4	156.1
	0.001	165.5	166.5	166.0	166.0
	0.0003	52.87	52.82	52.84	176.1

TABLE I—THE CONDUCTANCE DATA (*Continued*).

Substance.	Formula weights, per liter (C).	Specific conductance × 10^6.			Formular conductance. μ.
		I.	II.	Mean.	
$NaH_3P_2O_7$........	0.1	15270	15260	15265	152.6
	0.05	9090	9087	9088	181.7
	0.02	4576	4575	4575	228.7
	0.01	2691	2693	2692	269.2
	0.003	810.3	807.6	808.9	269.6
	0.001	388.6	388.7	388.6	388.6
	0.0003	125.9	126.0	126.0	420.0
$H_4P_2O_7$..........	0.05	17700	17680	17690	353.8
	0.025	9625	9620.5	9622	384.9
	0.0125	5483	......	5483	438.6
	0.005	2516	2517.0	2516.5	503.3
	0.0025	1391.2	1392.2	1391.7	556.7
	0.00125	752.75	752.25	752.5	602.0

3. The Hydrolysis of Ammonium Salts of Ortho- and Pyrophosphoric Acids, Determined by Distribution Experiments.

Description of the Method.—The method which has been used in this investigation for measuring the degree of hydrolysis is based upon the fact that when an aqueous solution of ammonia is shaken up with chloroform, the ammonia distributes itself between the two non-miscible solvents, so that the ratio of its concentrations—the so-called distribution ratio—is constant at a given temperature.[1] It is obvious that this enables us to determine the concentration of the ammonia existing as free base in a solution of a hydrolyzed ammonium salt. The method has proved to be so simple and accurate that it seems capable of a fairly wide application in the investigation of the ammonium salts of other weak acids.

But, simple in principle as the method is, its successful application requires attention to certain experimental details. The chief difficulty arises from the fact that the aqueous solutions form emulsions with the chloroform layer which remain turbid even after standing several hours in the thermostat. Minute drops of the aqueous solution thus remain suspended in the chloroform layer, making it impossible to obtain concordant results when different samples are titrated. Fortunately it was found that this difficulty may be completely overcome by merely rotating the solutions in glass-stoppered bottles in a thermostat. For this purpose, the bottles were fastened to the axle of the horizontal rotator of the thermostat, such as is used for making solubility measurements,[2] and

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[1] Hantzsch and Sebaldt (*Z. physik. Chem.*, 30, 266 (1899)) have pointed out that chloroform is the most satisfactory non-aqueous solvent for this purpose; fortunately its distribution ratio is of a convenient magnitude.

[2] Noyes, *Z. physik. Chem.*, 9, 606 (1892).

allowed to rotate one to three hours, when the two phases invariably separated perfectly clear, with a sharply defined bounding surface.

Care must also be taken to establish the equilibrium without changing the concentration relations of the hydrolyzed salt, and therefore without changing its hydrolysis. To accomplish this, 500 to 600 cc. of thoroughly washed chloroform were shaken successively with fresh 100 cc. portions of the hydrolyzed solution in a glass-stoppered bottle of 1 liter capacity. Each time after allowing the phases to separate, the water layer is removed as completely as practicable before the next portion of the solution is added. This process is repeated three times; a fourth portion of the solution is then shaken with the same chloroform and rotated as described above.

In removing the sample of chloroform for titration, it is important to avoid contamination by any of the aqueous solution, and to prevent the loss of any of the dissolved ammonia by vaporization. This was done by replacing the glass stopper of the saturation bottle with a rubber stopper through which passes a short straight tube and a longer siphon-shaped tube whose shorter arm reaches nearly to the bottom of the bottle. The end of this arm had been previously sealed in a flame and a small thin bulb blown upon it. This was passed while still closed through the aqueous layer into the chloroform layer beneath, and was then opened by breaking the bulb against the bottom of the bottle. The chloroform was now forced by air pressure into a clean dry vessel, measured in a suitable pipette, and finally titrated with 0.02 normal hydrochloric acid, using methyl orange as indicator. The titration was made in a glass-stoppered bottle of 500 cc. capacity, after adding enough pure water to make a layer of sufficient depth to view the color of the indicator, which does not color the chloroform. After each addition of acid, the stoppered bottle was vigorously shaken. The results obtained in this manner were more satisfactory than those obtained by first shaking the ammonia out of the chloroform with dilute standard acid, and then titrating the excess with standard alkali.

Preparation of the Solutions.—In addition to the stock solutions of ortho- and pyrophosphoric acids and their sodium salts, standard solutions were prepared of pure ammonia, and of hydrochloric acid of two concentrations—approximately 0.1 normal and exactly 0.02 normal. The ammonia used in preparing the solutions was taken from a stock which had been used in a special research on its conductivity, and had been carefully tested for impurities. Solutions of convenient concentration were prepared as required and standardized immediately before use by titrating with standard hydrochloric acid, using methyl orange as indicator. An approximately 0.1 normal solution of hydrochloric acid was prepared from the pure acid and carefully standardized by precipitating with silver nitrate and weighing the silver chloride produced. It was thus found to be 0.09747 normal. The hydrochloric acid solution was also titrated against a 0.2000 normal sodium carbonate solution made up by weighing out the well-ignited "C. P." salt furnished by Baker and Company, and was thus found to be 0.09738 normal. The mean result of the two methods of standardization is 0.097425 normal.

The solutions of the different ammonium salts whose hydrolysis was studied were prepared by weighing out into a calibrated flask the calculated quantity of the stock solution of the appropriate acid salt, adding the requisite amount of the stock solution of ammonia from a burette, and finally making up to the mark with pure water, at 18°.

Determination of the Distribution Ratio.—Solutions of ammonia were shaken with chloroform and finally rotated in the thermostat at 18°, as described above. Both the aqueous and chloroform solutions were then titrated with 0.02 normal hydrochloric acid.

The following table contains the results, all of which were obtained at 18°. In the first column is given under C the concentration of the total ammonium hydroxide in the aqueous phase; in the second column under C_1, the concentration of the un-ionized ammonium hydroxide in that phase calculated with the help of the ionization constant 17.2×10^{-6}; in the third column under C_2 the concentration of the ammonia in the chloroform phase; and in the fourth column under C_1/C_2, the ratio of these two concentrations. All concentrations are in formula weights per liter.

TABLE II. THE DISTRIBUTION RATIO.

C.	$C_1 = C(1 - r)$.	C_2.	C_1/C_2.
0.04811	0.04724	0.001764	26.78[1]
0.04917	0.04823	0.001749	27.58
0.04773	0.04682	0.001705	27.46
0.04803	0.04712	0.001716	27.46
0.04773	0.04683	0.001724	27.16
0.04766	0.04676	0.001699	27.48
0.01999	0.01941	0.0007057	27.50
0.0200	0.01942	0.0007067	27.48
		Mean	27.45

Distribution Data for the Various Salts.—In the following tables, the first column gives the formulas of the salts used; the second, their concentrations at 18° in milli-formula-weights per liter; the third, the number of cubic centimeters of chloroform used; the fourth, the number of cubic centimeters of 0.02 hydrochloric acid required to neutralize the ammonia in this chloroform; the fifth, the concentrations of the ammonia in the chloroform phase in milli-equivalents per liter; and the sixth, the concentrations of the un-ionized ammonium hydroxide in the water phase,

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[1] First value rejected in deriving the mean.

obtained by multiplying the average concentrations in chloroform by the distribution ratio (27.45). From the values thus obtained, the concentrations of the "total base" in the water phase were calculated by adding to them the values of the concentrations of OH^- ion taken from Tables XV–XVIII below; and by dividing these values by the concentrations of the salt given in the second column the values of percentage hydrolysis given in the last column were obtained.

TABLE III.

Substance.	Milli-formula weights per liter	Cc. chloroform titrated.	Cc. 0.02 N HCl used.	Milli-equiv. NH_3 per liter chloroform.	Milli-equiv. un-ionized NH_4OH per liter water.	Percentage hydrolysis.
$Na_2NH_4PO_4$.......	100	400	69.58	3.479	.....	.....
	...	...	69.56	3.478	.....	.....
	...	...	69.54	3.477	.....	.....
	...	...	69.48	3.474	.....	.....
	...	...	69.50	3.475	.....	.....
	...	...	69.48	3.474	.....	.....
	...	...	69.52	3.476	.....	.....
			Mean	3.476	95.42	96.03
	50	300	25.98	1.732	.....	.....
	...	300	26.03	1.735	.....	.....
	..	400	34.60	1.730	.....	.....
	..	400	34.65	1.732	.....	.....
	..	400	34.70	1.735	.....	.....
	..	400	34.60	1.730	.....	.....
	..	400	34.70	1.735	.....	.....
	..	500	43.25	1.730	.....	.....
			Mean	1.732	47.55	96.10
	20	400	13.90	0.6950	.....	.....
	..	...	13.85	0.6925	.....	.....
	..	...	13.90	0.6950	.....	.....
	..	...	13.78	0.6890	.....	.....
	..	...	13.85	0.6925	.....	.....
			Mean	0.6930	19.02	97.30
$NaNH_4HPO_4$......	100	500	2.70	0.1080	.....	.....
	..	...	2.65	0.1060	.....	.....
	..	...	2.70	0.1080	.....	.....
			Mean	0.1073	2.945	2.95
	50	500	1.35	0.0540	.....	.....
	..	...	1.40	0.0560	.....	.....
	..	...	1.35	0.0540	.....	.....
	..	...	1.40	0.0560	.....	.....
			Mean	0.0550	1.510	3.02

TABLE III (*Continued*).

Substance.	Milli-formula weights per liter.	Cc. chloroform titrated.	Cc. 0.02 N HCl used.	Milli-equiv. NH_3 per liter chloroform.	Milli-equiv. un-ionized NH_4OH per liter water.	Percentage hydrolysis.
$Na_3NH_4P_2O_7$.......	100	400	7.70	0.385	.....	.....
	..	...	7.68	0.384	.....	.....
	..	...	7.70	0.385	.....	.....
			Mean	0.3847	10.56	10.57
	50	400	4.78	0.239	.....	.....
	..	...	4.78	0.239	.....	.....
	..	...	4.80	0.240	.....	.....
			Mean	0.2393	6.570	13.15
	20	500	3.15	0.1260	.....	.....
	..	...	3.15	0.1260	.....	.....
	..	...	3.16	0.1264	.....	.....
			Mean	0.1261	3.461	17.34
$Na_2(NH_4)_2P_2O_7$......	50	400	6.50	0.325	.....	.....
	..	...	6.50	0.325	.....	.....
	..	...	6.51	0.325	.....	.....
			Mean	0.325	8.92	17,85
	20	500	4.30	0.172	.....	.....
	..	...	4.30	0.172	.....	.....
	..	...	4.30	0.172	.....	.....
			Mean	0.172	4.721	23,63
$Na_2NH_4HP_2O_7$.....	50	400	0.84	0.0420	.....	.....
	..	...	0.86	0.0430	.....	.....
	..	...	0.85	0.0425	.....	.....
			Mean	0.0425	1.167	2,33
	20	500	0.45	0.0180	.....	.....
	..	...	0.45	0.0180	.....	.....
	..	...	0.45	0.0180	.....	.....
			Mean	0.0180	0.4941	2.47

These results show that in solution the salt $Na_2NH_4PO_4$ is almost completely hydrolyzed, less than five per cent. of the ammonium radical existing in the form of ammonium salt; and that the salts $Na_3NH_4P_2O_7$ and $Na_2(NH_4)_2P_2O_7$ are also from 10 to 20 per cent. hydrolyzed, while the remaining salts are decomposed to the extent of only 2 or 3 per cent. When the hydrolysis is large, this method of measurement yields excellent results, as is evident from the very concordant measurements, and even when it is small the accuracy is probably far greater than that attained by other methods. It will be noted that the percentage hydrolysis of the pyrophosphates shows a marked increase with the dilution, an effect which will be shown to be largely due to the influence of the un-ionized substances in the solutions. The first equivalent of hydrogen in the ortho acid and the first two in pyrophosphoric acid are so highly dissociated that their ammonium salts are not hydrolyzed to a measurable degree.

4. The Ionization of the Successive Hydrogens of Ortho- and Pyrophosphoric Acids and That of Their Sodium Salts.

APPROXIMATE VALUES OF IONIZATION CONSTANTS.

The ionization constants of the successive hydrogens of orthophosphoric acid, which will be designated by K_1, K_2, and K_3, are defined by the following Mass Action equations:[1]

$$K_1 = \frac{(H^+)(H_2PO_4^-)}{(H_3PO_4)}, \quad K_2 = \frac{(H^+)(HPO_4^{--})}{(H_2PO_4^-)}, \quad \text{and} \quad K_3 = \frac{(H^+)(PO_4^{---})}{(HPO_4^{--})}.$$

By combining the last two equations with the Mass Action relations[2] $K_W = (H^+)(OH^-)$ and $K_B = (NH_4^+)(OH^-)/(NH_4OH)$,[3] the following expressions for K_2 and K_3 are obtained:

$$K_2 = \frac{K_W(NH_4^+)(HPO_4^{--})}{K_B(NH_4OH)(H_2PO_4^-)} \quad \text{and} \quad K_3 = \frac{K_W(NH_4^+)(PO_4^{---})}{(NH_4OH)(HPO_4^{--})}.$$

The different ionization constants for pyrophosphoric acid may be formulated in exactly the same way:

$$K'_1 = \frac{(H^+)(H_3P_2O_7^-)}{(H_4P_2O_7)}, \quad K'_2 = \frac{(H^+)(H_2P_2O_7^{--})}{(H_3P_2O_7^-)}, \quad K'_3 = \frac{(H^+)(HP_2O_7^{---})}{(H_2P_2O_7^{--})},$$

and $K'_4 = \dfrac{(H^+)(P_2O_7^{----})}{(HP_2O_7^{---})}$ and the expressions for K'_3 and K'_4 are

$$K'_3 = \frac{K_W(NH_4^+)(HP_2O_7^{---})}{K_B(NH_4OH)(H_2P_2O_7^{--})} \qquad K'_4 = \frac{K_W(NH_4^+)(P_2O_7^{----})}{K_B(NH_4OH)(HP_2O_7^{---})}.$$

The values of these ionization constants, K_2, K_3, K'_3 and K'_4, were calculated from the distribution experiments described above, in which the concentration of undissociated NH_4OH was measured directly. K_3, for example, was obtained as follows from the experiments on $NH_4Na_2PO_4$, which is hydrolyzed according to the equation

$$NH_4Na_2PO_4 + H_2O = NH_4OH + Na_2HPO_4.$$

---

[1] As will be seen later, the ionization of the first hydrogen of orthophosphoric acid, and that of the first two hydrogens of the pyro acid, show in a measure the phenomenon observed with strong electrolytes, and do not obey the Mass Law.

[2] The value $K_W = 0.59 \times 10^{-14}$ at 18° has been assumed in this article, Cf. Heydweiller, *Ann. Physik*, 28, 503 (1909).

[3] $K_B = 1.72 \times 10^{-5}$ at 18°, Noyes and Sosman, Carnegie Institution Publications, No. 63, page 234.

The sum of the concentrations of all substances containing the HPO_4 radical must be equal to that of the total free base, since equal quantities of acid and base must be produced in this reaction. The base exists in the two forms, NH_4OH and OH^-; the OH^- concentration is very small, and can be calculated with sufficient accuracy from K_B the ionization constant of NH_4OH and the estimated NH_4^+ ion concentration. The HPO_4 radical exists not only in the form of the ion, but also in the form of un-ionized salts, such as Na_2HPO_4. Therefore, $(NH_4OH) + (OH^-) = (HPO_4^{--}) +$ (undissociated HPO_4 salts) $= Ch$ where C is the concentration of $Na_2NH_4PO_4$ in formula weights per liter and h is the fraction hydrolyzed. The remainder of the phosphate is present partly as PO_4^{---} ion and partly as undissociated salts containing the PO_4 radical:

$$(PO_4^{---}) + (\text{undissociated } PO_4 \text{ salts}) = C\,(1 - h).$$

The NH_4 radical is present as NH_4^+ ion and as undissociated NH_4OH and ammonium salts:

$$(NH_4^+) + (NH_4OH) + (\text{undissociated } NH_4 \text{ salts}) = C.$$

In order to obtain a preliminary value for K_3 the undissociated salts were neglected, and the correspondingly simplified forms of the above equations used.

The other ionization constants were determined approximately in an exactly similar manner. Thus K_2 was calculated from the distribution experiments on NH_4NaHPO_4 by means of the equations

$$(NH_4OH) + (OH^-) = (H_2PO_4^-) = Ch,$$
$$(HPO_4^{--}) = C\,(1 - h),$$
$$(NH_4^+) + (NH_4OH) = C.$$

In this case (OH^-) was found to be negligibly small.

The preliminary values of the ionization constants so obtained are given in the following table:

TABLE IV.

Orthophosphoric Acid.

From experiments with NH_4NaHPO_4.	K_2.	From experiments with $NH_4Na_2PO_4$.	K_3.
$C = 0.1$	3.7×10^{-7}	$C = 0.1$	7.3×10^{-13}
$C = 0.05$	3.5 "	$C = 0.05$	7.8 "
		$C = 0.02$	6.0 "
Mean	3.6×10^{-7}	Mean	7.0×10^{-13}

Pyrophosphoric Acid.

From experiments with $NH_4Na_2HP_2O_7$.	K_3'.	From experiments with $NH_4Na_3P_2O_7$.	K_4'.
$C = 0.05$	6.0×10^{-7}	$C = 0.1$	2.5×10^{-8}
$C = 0.02$	5.4 "	$C = 0.05$	1.5 "
		$C = 0.02$	0.8 "
Mean	5.7×10^{-7}	Mean	1.6×10^{-8}

By means of these preliminary values of the ionization constants, the conductance data for the various salts were corrected for the effects of hydrolysis or of hydrogen-ion dissociation; the limiting conductances at infinite dilution were found by an extrapolation method, and the percentage dissociation calculated. These results were used, as will be explained later, in estimating the concentrations of the un-ionized salts in the above hydrolysis experiments, and a second set of values of the ionization constants was calculated. This process of approximation was repeated once or twice more until concordant results for the limiting conductances and the ionization constants were obtained. The final results are given in the following sections:

CORRECTION OF CONDUCTANCE DATA FOR HYDROLYSIS OR HYDROGEN DISSOCIATION.

Principle of the Method.—Solutions of Na_2HPO_4, $Na_4P_2O_7$ and $Na_3HP_2O_7$ are alkaline, owing to hydrolysis, while those of NaH_2PO_4 and $Na_2H_2P_2O_7$ are acid owing to hydrogen-ion dissociation. In each case, to get the true conductance of the salt, a correction must be applied.

Thus the hydrolysis of Na_2HPO_4 may be expressed by the equation

$$2\ Na^+ + HPO_4^{--} + H_2O = 2\ Na^+ + H_2PO_4^- + OH^-,$$

from which it is evident that the effect of hydrolysis is to increase the conductance, since the mobile OH^- ion more than compensates for the decrease resulting from the change of HPO_4^{--} ion to $H_2PO_4^-$. Therefore the measured values of the formular conductance must be diminished by an amount equal to

$$h[\Lambda(OH^-) + \mu(H_2PO_4^-) - \mu(HPO_4^{--})].^1$$

The fraction hydrolyzed, h, was calculated from the expression $Ch^2/(1-h) = K_W/K_A$, where C is the concentration of the salt in formula weights per liter, K_W is the ionization constant for water, and K_A (in this case $= K_2$) that for the acid.

In an exactly similar manner the conductances of $Na_4P_2O_7$ and $Na_3HP_2O_7$ were corrected for hydrolysis by means of the corresponding expressions, which are given below.

In the case of NaH_2PO_4 appreciable dissociation takes place in accordance with the equation $H_2PO_4^- = H^+ + HPO_4^{--}$, from which it is evident that the concentrations of H^+ and HPO_4^{--} are equal.

Therefore, $$K_2 = \frac{(H^+)(HPO_4^{--})}{(H_2PO_4^-)} = \frac{(H^+)^2}{(H_2PO_4^-)}.$$

But as long as the H^+ ion dissociation is small the concentration of $H_2PO_4^-$ is practically equal to γC where C is the concentration of the salt and γ

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[1] Λ and μ represent equivalent and formular conductances, respectively; (ΛOH^-), $\mu(H_2PO_4^-)$ and $\mu(HPO_4^{--})$ represent the limiting conductances of the ions at infinite dilution.

is the degree of ionization. Therefore, $K_2 = (H^+)^2/\gamma C$ or $(H^+)/C = \sqrt{\gamma K_2/C}$. In order to correct the conductance of the salt at any concentration C, the value of the product

$$[\Lambda(H^+) + \mu(HPO_4^{--}) - \mu(H_2PO_4^-)]\ [(H^+)/C]$$

was subtracted from the measured conductance.

The conductance measurements of $Na_2H_2P_2O_7$ were corrected in a similar manner by means of the formulae given in the table.

Thus in each case the correction of the conductances of a single salt involves the knowledge of the limiting conductance of this salt and of one other one. Approximate values for the limiting conductances were determined, the corrections for hydrolysis or hydrogen-ion dissociation were made, the values of μ_0 were calculated as described in the following paragraphs, and a comparison made with the values of μ_0 assumed. This process was repeated and concordant results were usually obtained on the second approximation. The final values of μ_0 for the different ions are given in Table VI below.

Method of Determining the Limiting Conductance.—The method used in determining the limiting conductances at zero concentration depends upon the following principles: It is well known that the dissociation of strong acids and bases and of salts in general does not follow the Mass Action Law even approximately; nevertheless, for most salts which have been investigated, the following empirical expression holds between certain concentration limits

$$(C\gamma)^n/C(1-\gamma) = \text{const.}$$

in which, below 0.1 normal, the exponent n has a value between 1.40 and 1.55. Substituting for γ, the degree of ionization, the ratio μ/μ_0, the expression may be transformed into

$$(\mu_0-\mu)/\mu_0 = \text{const. } C^{n-1}\mu^n/\mu_0{}^n,$$

or

$$1/\mu = 1/\mu_0 + \text{const. } (C\mu)^{n-1}.$$

This expression is evidently the equation of a straight line, in which the variables are $1/\mu$ and $(C\mu)^{n-1}$ (*i. e.*, the reciprocal of the formular conductance, and a function of the specific conductance). If the (corrected) values for $1/\mu$ for the different concentrations are plotted as ordinates, and the corresponding values of $(C\mu)^{n-1}$ as abscissas, and the value of the exponent is varied until a straight line is obtained, then the intercept on the ordinate axis is equal to $1/\mu_0$. (In order to compare the curvature of the various lines more easily, the scale used in plotting the abscissae $(C\mu)^{n-1}$ was varied in such a way that all the lines passed through a single point, corresponding to a concentration to say 0.05 formular).

Four of the salts were found to obey the above empirical law very closely, and it was an easy matter to determine approximately a value of n which gave a fairly good straight line over the whole range of concentrations, up to 0.1 formular.[1]

In practice several neighboring values of n were found to give almost equally good results, and as a result the possible values of μ_0 varied between certain limits. Thus in the case of $Na_2H_2P_2O_7$ the values of n were approximately 1.47–1.53 and the corresponding values of μ_0 172–169. The error in μ_0 has been estimated in this way and the values inserted in the tables below along with the values of μ_0 finally chosen. Of course the errors may be even larger if the method of extrapolation is not correct, *i. e.*, if the above law does not continue to hold in the more dilute solutions.[2]

In the following table, in the first row, are given the final values of n used in the extrapolation—those which apply in dilute solutions. For the sake of comparison the approximate value of n in more concentrated solutions (C = 0.01 — 0.1 formular) are given; and also the corresponding values for the two acids H_3PO_4 and $H_4P_2O_7$.

TABLE V.

Values of n.

	Na_2HPO_4.	NaH_2PO_4.	$Na_4P_2O_7$.	$Na_3HP_2O_7$.	$Na_2H_2P_2O_7$.	H_3PO_4.	$H_4P_2O_7$.
Dilute............	1.55	1.50	1.55	1.50	1.50	1.90	1.65
Concentrated....	1.55	1.50	1.45	1.50	1.50	1.70	1.45

It is seen that in the dilute solutions of the salts n lies between 1.50 and 1.55, and that it decreases with increasing concentration in the case of $Na_4P_2O_7$ and the two acids.

The final values of the molecular conductances of the ions at 18° are given in the following table, also the values for Na^+, H^+ and OH^- used in making the calculations. The estimated errors in these μ_0 values for the ions are also given; they have, of course, the same numerical values as the errors estimated for the salts.

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[1] In case of $Na_4P_2O_7$, however, the salt of the highest type considered, no single value of n gave satisfactory results; to obtain a straight line between certain limits of concentration it was necessary to use one value of n in dilute solutions and another, smaller value in the more concentrated solutions. Therefore in extrapolating that value of n was chosen which gave a straight line in the dilute solutions.

In testing this method by means of the conductivity data of Kohlrausch, many other examples were found in which the value of n decreased with increasing concentration, especially in the case of salts of high valence type, such as $MgSO_4$; and the use of the high value of n in extrapolating in such cases was found to be very satisfactory. Further details of this method will be published later.

[2] As an additional guide in choosing the most probable μ_0 value for a given salt, the percentage ionizations of a number of other salts of the same type were plotted against the concentration; and that value of μ_0 was chosen which placed the new curve symmetrically with respect to the other curves (see Fig. 2 below). In only one case was the value of μ_0 appreciably affected by this treatment; the conductance measurement of the most dilute solution of Na_2HPO_4 was neglected and the μ_0 value chosen was somewhat higher than if this value has been considered.

TABLE VI.

Limiting Formular Conductances at 18°.

$H_2PO_4^-$	26.4 ± 1.0	$H_2P_2O_7^{--}$	83.3 ± 1.0	Na^+	43.6
HPO_4^{--}	106.8 ± 2.0	$HP_2O_7^{---}$	179.2 ± 4.0	H^+	315.0
PO_4^{---}	207[1] ± 30.0	$P_2O_7^{----}$	325.6 ± 10.0	OH^-	173.0

These values will be discussed in the summary with respect to the relations between them.

The corrected values of the conductance are summarized in the following tables. In addition, in the last two columns of each table are given the percentage ionizations and equivalent ion concentrations. The values enclosed in brackets were derived by graphical interpolation by means of the $1/\mu$, $(C\mu)^{n-1}$ plot; the corresponding values of $\mu_{\text{obs.}}$ are not in agreement with the other values and are marked with interrogation points.

TABLE VII.

Conductance of Na_2HPO_4 *Corrected for Hydrolysis.*[2]

Form. wts. per liter, C.	μ observed.	Percentage hydrolysis, 100 h.	μ corrected.	Percentage ionization.	Equiv. ion concen.
0.2	99.27	0.039	99.23	51.2	0.2048
0.1	115.62	0.055	115.57	59.6	0.1192
0.05	130.32	0.078	130.25	67.14	0.06714
0.02	147.5	0.122	147.39	76.0	0.03040
0.01	158.7	0.174	158.5	81.7	0.01634
0.005	168.5	0.246	168.3	86.7	0.00867
0.003	174.3	0.317	174.0	89.7	0.00538
0.002	177.8	0.387	177.4	91.5	0.00366
0.001	182.1 (?)	0.547	181.6	(94.1)	(0.00188)
0.0	......	.....	194.0	.....	....

Foster[3] has measured the conductance of solutions obtained by dissolving weighed amounts of the salt Na_2HPO_4, after dehydrating at 120°, but his results do not agree with ours. Thus the measured conductances, obtained by graphic interpolation, at $C = 0.05$ and 0.02 molal are 124.5 and 142 respectively, instead of the values 130.3 and 147.5 given in the table. His concentrations were not checked by direct analysis, and, moreover, his results for certain other salts, such as $MgCl_2$, do not agree with those of Kohlrausch.

Foster's measurements on solutions of the salt KH_2PO_4 were corrected and plotted in the same way. Although the results in dilute solutions were evidently inaccurate, the value $n = 1.50$ was clearly the most satis-

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[1] This is only an estimate, determined as described in Section 5.

[2] $Ch^2/1-h = K_W/K_2 = 3.02\times10^{-8}$; $\Lambda(OH)+\mu(H_2PO_4^-)-\mu(HPO_4^{--}) = 92.6$ and μ corr. = μ obs. — $92.6h$.

[3] *Physic. Rev.*, 8, 257 (1899).

TABLE VIII.

Conductance of NaH_2PO_4 Corrected for Hydrogen Ionization.[1]

Form. wts. per liter, C.	μ observed.	$395.4(H^+)/C$.	μ corrected.	Percentage ioniz., 100γ.	Equiv ion concen.
0.2	49.74	0.33	49.41	70.6	0.1412
0.1	54.43	0.48	53.95	77.1	0.0771
0.05	58.26	0.71	57.55	82.2	0.0411
0.02	61.43 (?)	1.15	60.28	(87.6)	(0.0175)
0.01	65.53	1.67	63.86	91.2	0.00912
0.005	67.58	2.37	65.21	93.2	0.00466
0.003	69.23	3.07	66.16	94.5	0.002835
0.001	71.68 (?)	5.36	66.22	(96.7)	(0.000967)
0.0	....	....	70.0	....	....

factory one, and with its aid μ_0 for KH_2PO_4 was estimated to lie between 90 and 91. The corresponding values for $\mu(H_2PO_4^-)$ are 25.3 and 26.3, which are in unexpectedly good agreement with the value 26.4 determined from the sodium salt. The percentage ionization of KH_2PO_4 is distinctly greater than that of NaH_2PO_4, as is shown by the results given in the following table:

TABLE IX.

KH_2PO_4 (Foster).

Form. wts. per liter, C.	μ observed.	μ corrected.	Percentage ionization.	Equiv. ion concen.
0.333	64.2	64.0	70.3	0.234
0.1667	69.6	69.3	76.2	0.127
0.0333	80.1	79.3	87.1	0.02903
0.01667	83.4	82.2	90.2	0.01503
0.0100	84.6	83.1	91.3	0.00913
0.00333	88.5	85.8	94.2	0.00314
0.0	....	91.1	....	....

Orthophosphoric Acid.—For the sake of completeness the results of Noyes and Eastman[2] on orthophosphoric acid at 18° are also given here, and the values of $K_1 = (H^+)(H_2PO_4^-)/(H_3PO_4)$ calculated. These measurements were made in the platinum-lined bomb which is in use in this laboratory for conductance measurements at high temperatures. On account of the high concentration of H^+ ion, no correction was necessary for the ionization of $H_2PO_4^-$ into H^+ and HPO_4^{--}. The value of μ_0 (341), obtained upon recalculation, agrees within the error of extrapolation with that determined by Noyes and Eastman (338) and with that (341.4) calculated by summation from the H^+ and $H_2PO_4^-$ ions. It is worthy of note that the value of n decreases from 1.90 in dilute solutions to 1.70 in the more concentrated ones. The decrease in the value of K_1

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[1] $[(H^+)/C]^2 = 1.957/10^7\,C$; $\Lambda(H^+) + \mu(HPO_4^{--}) - \mu(H_2PO_4^-) = 395.4$.

[2] A. A. Noyes and G. W. Eastman, Carnegie Institution Publications, No. 63, 262 (1907).

with increasing dilution (as shown in the last column of the table) is in agreement with the small value of n, since K_1 is calculated on the assumption that n is equal to 2.

TABLE X.

H_3PO_4 (Noyes and Eastman).

Form. wts. per liter, C.	μ observed.	Percentage ionization.	Equiv. ion concen.	$K_1 \times 10^2$.
0.1	96.5	28.3	0.0283	1.12
0.08	(104)	(30.5)	(0.0244)	1.07
0.05	122.7	36.0	0.0180	1.01
0.0125	191.2	56.1	0.00701	0.90
0.010	(203)	(59.6)	(0.00596)	0.88
0.002	283.1	83.0	0.00166	0.71
0.0002	330.8	97.1	0.000194	0.63
0.0	341.4	....	....	....

TABLE XI

Conductance of $Na_4P_2O_7$ Corrected for Hydrolysis.[1]

Form. wts. per liter, C.	μ observed.	Percentage hydrolysis, 100 h.	μ corrected.	Percentage ionization.	Equiv. ion concen.
0.1	156.5	0.40	156.4	31.3	0.1251
0.05	185.2	0.57	185.0	37.0	0.0740
0.02	223.9	0.90	223.7	44.7	0.0358
0.01	256.6	1.27	256.3	51.3	0.0205
0.005	291.3	1.77	290.8	58.2	0.01164
0.003	314.3 (?)	2.29	313.7	(63.4)	(0.00761)
0.001	372.1	3.92	371.1	74.2	0.00297
0.0003	420.0	6.88	418.2	83.6	0.001003
0.0	.....	....	500.0	....	....

TABLE XII.

Conductance of $Na_3HP_2O_7$ Corrected for Hydrolysis.[2]

Form wts. per liter, C.	μ observed.	Percentage hydrolysis, 100 h.	μ corrected.	Percentage ionization.	Equiv. ion concen.
0.1	148.9	0.045	148.9	48.0	0.144
0.05	172.1	0.063	172.0	55.5	0.0833
0.02	199.0	0.100	198.9	64.2	0.0385
0.01	220.1	0.141	220.0	71.0	0.0213
0.003	248.7 (?)	0.258	248.5	(80.6)	(0.00725)
0.001	271.4	0.445	271.0	87.4	0.00262
0.0003	288.3	0.81	287.7	92.8	0.000835
0.0	.....	.....	310.0	....	....

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[1] $Ch^2/(1-h) = K_W/K'_4 = 1.64 \times 10^{-6}$; $\Lambda(OH^-) + \mu(HP_2O_7^{---}) - \mu(P_2O_7^{---}) = 26.6$ and $\mu_{corr.} = \mu_{obs.} - 26.6\ h$.

[2] $Ch^2/(1-h) = K_W/K'_3 = 2.0 \times 10^{-8}$; $\Lambda(OH^-) + \mu(H_2P_2O_7^{--}) - \mu(HP_2O_7^{---}) = 77.1$ and $\mu_{corr.} = \mu_{obs.} - 77.1\ h$.

TABLE XIII.

Conductance of $Na_2H_2P_2O_7$ Corrected for Hydrogen Dissociation.[1]

Form. wts. per liter, C.	μ observed.	$410\,(H)/C$.	μ corrected.	Percentage ionization, $100\,\gamma$.	Equiv. ion concen.
0.1	107.0	0.54	106.5	62.5	0.1250
0.05	120.0 (?)	0.81	119.2	(69.2)	(0.0692)
0.02	133.2	1.36	131.8	77.3	0.0309
0.01	143.0	2.0	141.0	82.7	0.01654
0.003	156.1	3.8	152.3	89.3	0.00536
0.001	166.0	6.7	159.3	93.5	0.00187
0.0003	176.1	12.4	163.7	96.0	0.000576
0.0	.....	.....	170.5	....	....

Pyrophosphoric Acid and Sodium Trihydrogen Pyrophosphate.—The values of the formular conductance (μ) of $H_4P_2O_7$ and of $NaH_3P_2O_7$ are of importance, since they enable us to decide whether these solutions contain the ion $H_3P_2O_7^-$ in any considerable amount. From the relation (pointed out in the Summary, Table XXIII) between the limiting conductances of the ions $P_2O_7^{----}$, $HP_2O_7^{---}$ and $H_2P_2O_7^{--}$ it is evident that the probable value for $\mu(H_3P_2O_7^-)$ is 20.4. The upper and lower limits for the limiting formular conductances (μ_0), corresponding to complete and negligible ionization of $H_3P_2O_7^-$ respectively, are

Upper limits: $2\Lambda(H^+) + \mu(H_2P_2O_7^{--}) = 713.3$,
$\Lambda(Na^+) + \Lambda(H^+) + \mu(H_2P_2O_7^{--}) = 441.9$; and

Lower limits: $\Lambda(H^+) + \mu(H_3P_2O_7^-) = 335.4$,
$\Lambda(Na^+) + \mu(H_3P_2O_7^-) = 64.0$.

In the most dilute solutions investigated the following high values of μ were obtained: $H_4P_2O_7$, $C = 0.00125$, $\mu = 602.0$

$NaH_3P_2O_7$ $C = 0.0003$, $\mu = 422.0$

It is evident that in these solutions the ionization of $H_3P_2O_7^-$ must be nearly complete.

A further confirmation of this result was obtained by plotting the conductivity data for $H_4P_2O_7$ in the $1/\mu$, $(C\mu)^{n-1}$ diagram. The exponent n was found to vary from 1.65 in the dilute solutions to 1.45 in the more concentrated ones; and the value of μ_0 obtained was in good agreement with the theoretical number 713.3.[2]

This result does not, however, prove that the first equivalent of hydrogen of pyrophosphoric acid is completely dissociated at the higher concentrations, and we shall see, in fact, that this is not the case, though it is true that the first equivalent of hydrogen dissociates much more readily than

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[1] $(H^+)/C = 2.90\gamma/10^7C$; $\Lambda(H) + \mu(HP_2O_7^{---}) - \mu H_2P_2O_7^{--}) = 410$.

[2] Since measurements were not extended to very dilute solutions, the possible error of extrapolation was large, and this result cannot be regarded as furnishing an accurate independent determination of $\mu(H_2P_2O_7^{--})$.

the second. This conclusion can namely be derived from the two independent sets of conductance measurements for the acid and the salt, to which correspond two simultaneous equations containing as unknowns the two ionization constants K_1' and K_2'. Instead of attempting to solve these equations directly, a method of trial was used, which is illustrated by the following calculations for 0.05 formular solutions of the acid and of the salt.

Let us assume in the first place that the primary ionization of $H_4P_2O_7$ into H^+ and $H_3P_2O_7^-$ is 86 per cent. Then the concentration of un-ionized $H_4P_2O_7$ is 0.0070; and if there were no secondary ionization, that of $H_3P_2O_7^-$, would be 0.0430. and the formular conductance of the solution would be $0.86 \times 335.4 = 288$. If, however, the $H_3P_2O_7^-$ were completely ionized, the formular conductance would be $0.86 \times 713.3 = 613$ or 325 units greater. Since the measured conductance is 358.8, it is evident that the fraction of $H_3P_2O_7^-$ ionized is $(353.8 - 288)/325 = 0.202$. This enables the following concentrations to be calculated:

$$(H_2P_2O_7^{--}) = 0.0087,\ (H_3P_2O_7^-) = 0.0343, \text{ and } (H^+) = 0.0517.$$

The corresponding values of the ionization constants are:

$$K_2' = (H^+)\,(H_2P_2O_7^{--})/(H_3P_2O_7^-) = 0.0132$$
$$K_1' = (H^+)\,(H_3P_2O_7^-)/(H_4P_2O_7) = 0.253.$$

By assuming other percentage values for the primary ionization the following results were obtained:

Percentage primary ionization	80	85	86	87	90
Total ion (equiv.)	0.0514	0.0515	0.0517	0.0517	0.0519
K_2'	0.0205	0.0138	0.0132	0.0120	0.0093
K_1'	0.147	0.230	0.253	0.280	0.396

Similarly, in the case of the salt $NaH_3P_2O_7$ at 0.05 formular concentration, different percentage values were assumed for the primary ionization into $Na^+ + H_3P_2O_7^-$, and the actual concentrations of the ions $H_2P_2O_7^{--}$ and $H_3P_2O_7^-$ were calculated from the conductance measurements. In order to determine the concentration of $H_4P_2O_7$ it was necessary first to estimate the concentrations of the un-ionized sodium salts $NaH_3P_2O_7$ and $Na_2H_2P_2O_7$. This was done by means of the method described below which depends on the assumption that at a given ion concentration the function (anion)(cation)/(undiss. salt) is a constant. The following results were thus obtained:

Percentage primary ionization	78.0	78.9	79.0	79.2	79.6	81.0
Total ion	0.0563	0.0568	0.0569	0.05695	0.0570	0.0577
K_2'	0.0138	0.0138	0.0137	0.0135	0.0130	0.0127
K_1'	0.20	0.236	0.25	0.26	0.30	0.53

From a comparison of the two sets of results it is seen that for a total ion concentration of 0.051–0.057 most nearly concordant values of K_1' (0.0132 and 0.0135) and K_2' (0.253 and 0.26) are obtained for the assumptions that the primary ionization of $H^+(H_3P_2O_7^-)$ is 86 per cent. and that that of $Na^+(H_3P_2O_7^-)$ is 79.2 per cent. These values are therefore the ones that best satisfy all the conditions of the problem and are to be regarded as its mathematical solutions.

Similar calculations were made for nearly all the other concentrations. The values of K_2' and K_1' were found to vary with the total ion concentration, and this variation was considered in choosing the final values for primary ionization. The final results are given in the following tables. All concentrations are expressed in milli-formula-weights per liter (except the total ion concentration, which is in equivalents).

TABLE XIV.

$H_4P_2O_7$.

Acid	50.0	25.0	12.5	5.0	2.5	1.25
μ Observed	353.8	384.9	438.6	503.3	556.7	602.0
Primary ioniz., %	86.0	87.0	90.0	92.0	94.0	96.0
Total ion = (H^+)	51.7	27.9	15.77	7.18	3.95	2.13
$H_3P_2O_7^-$	34.3	15.6	6.73	2.02	0.75	0.27
$H_2P_2O_7^{--}$	8.7	6.15	4.52	2.58	1.60	0.93
$H_4P_2O_7$	7.0	3.25	1.25	0.40	0.15	0.05
K_2'	0.0132	0.0110	0.0106	0.0095	0.0084	0.0073
K_1'	0.253	0.134	0.085	0.036	0.020	0.011

TABLE XV.

$NaH_3P_2O_7$.

Salt	100.0	50.0	20.0	10.0	1.0
μ Observed	152.6	181.7	228.7	269.2	338.6
Primary ioniz., per cent	74.0	79.2	85.0	88.0	96.0
Total ion	101.8	56.9	26.24	14.43	1.825
Na^+	74.0	39.6	17.0	8.8	0.96
$H^+ = H_2P_2O_7^{--}$	27.8	17.3	9.24	5.63	0.865
$H_3P_2O_7^-$	46.2	22.3	7.76	3.17	0.095
$NaH_3P_2O_7$	10.9	4.07	0.89	0.263	0.002
$NaH_2P_2O_7$	11.8	4.85	1.60	0.672	0.032
$H_4P_2O_7$	3.3	1.48	0.51	0.265	0.006
K_2'	0.0168	0.0134	0.0110	0.0100	0.0079
K_1'	0.39	0.26	0.14	0.067	0.013

It is seen that the values of the ionization "constants" decrease with increasing dilution. In the more concentrated solutions the first equivalent of hydrogen of $H_4P_2O_7$ has a much greater ionization tendency than the second equivalent, but the difference is not so great in the dilute solutions. A comparison with Table X above shows that at the same total ion concentration the values of K_2' are almost identical with those of K_1, the ionization constant of the first hydrogen of H_3PO_4. It is also worthy of note that the primary ionization of the salt $NaH_3P_2O_7$ is practically the same as that of the corresponding uni-univalent salt NaH_2PO_4, at the same total ion concentration (Table VIII).

These results, it may be repeated, depend on two assumptions, (1) that the limiting conductance of the ion $H_3P_2O_7^-$ is 20.4, and (2) that the empirical principle involved in the calculation of the concentrations of the un-ionized sodium salts in the mixture is correct; but they would not be greatly altered by moderate errors in these assumptions.

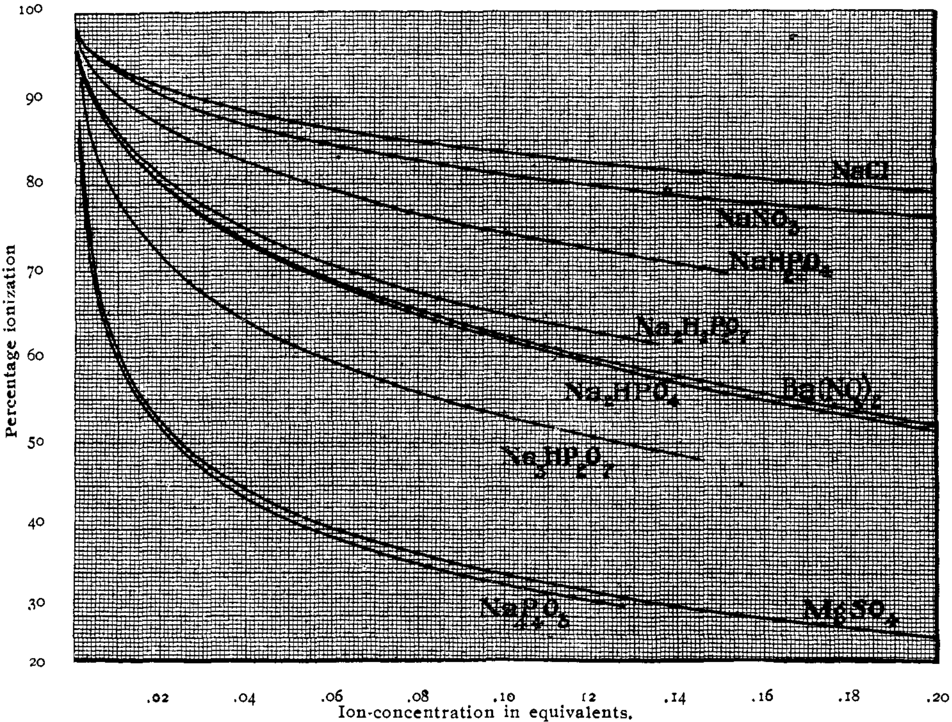

Fig. 2.

Percentage Ionizations.—In Fig. 2 the percentage ionization of each of the salts investigated is plotted against the equivalent ion concentration; and, for the sake of comparison, several other salts, NaCl, $NaNO_3$, $Ba(NO_3)_2$, and $MgSO_4$ are also included. The decrease in ionization with increase in the "valence product" of the salt[1] is shown in a striking manner. It is worthy of note that NaH_2PO_4 and $NaH_3P_2O_7$ are less ionized than nearly all other uni-univalent salts thus far investigated;[2] and that the curves for $Na_2H_2P_2O_7$ and especially Na_2HPO_4 are close to that for $Ba(NO_3)_2$, all three of them lying somewhat lower than the curves for most other salts of the same type. Finally the curves almost coincide in the cases of $Na_4P_2O_7$ and $MgSO_4$, two salts of a different valence type but having the same valence product.

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[1] A. A. Noyes, Carnegie Publication, No. 63, 343 (1907).

[2] A still more striking example of small ionization in a salt of this type is furnished by $AgNO_2$, Niementowski and Roszkowski, *Z. physik. Chem.*, **22**, 147 (1897).

FINAL VALUES OF IONIZATION CONSTANTS.

In order to obtain more accurate values of the various ionization constants of ortho- and pyrophosphoric acids than those given in Table IV, the concentrations of the un-ionized substances in the hydrolysis experiments were estimated by the following empirical principle, suggested by Arrhenius,[1] which appears to be approximately true, at least for mixtures of uni-univalent and uni-bivalent salts.[2]

Between the concentration of an un-ionized salt, such as Na_2HPO_4, and that of each of its ions, Na^+ and HPO_4^{--}, there is a relation expressed by the equation (anion)(cation)/(undissociated salt) = K = $(Na^+)(HPO_4^{--})/(Na_2HPO_4)$ where the "ionization function," K, is a variable which depends on the total equivalent ion concentration, but not upon the nature of the ions present. The form of this expression is independent of the number of ions into which the salt dissociates.

The numerical value of this "ionization function" at a given ion concentration is calculated from the percentage ionization of the pure salt at the same ion concentration. For example, in the experiments with 0.1 mol. $Na_2NH_4PO_4$ (Table XVI) the equivalent ion concentration was finally assumed to be 0.1207; at this concentration the percentage ionization of Na_2HPO_4 as determined from the conductance measurements is 59.4 (Fig. 2) and the value of K reduces to $(0.1207)\ (59.4)/(40.6) = 0.177$. This value was used in calculating the concentration of un-ionized Na_2HPO_4 from the concentrations of Na^+ and HPO_4^{--} given in Table XV.

In the case of ammonium salts, the percentage ionization was assumed to be the same in each case as that of the corresponding sodium salt. Thus the concentration of un-ionized $(NH_4)_2HPO_4$ in the experiment considered above was calculated by means of the value of K found for Na_2HPO_4, 0.177. Similarly the ionization of Na_3PO_4 was assumed to be the same as that of $Na_3HP_2O_7$, a salt of the same type. No serious error can be introduced by these assumptions, since it was found that the values of the ionization constants of the different acids are not greatly altered by small changes in the percentage ionization. In addition to the un-ionized sodium and ammonium salts considered, mixed salts, such as $NaNH_4HPO_4$, undoubtedly exist. But nothing is known in regard to the ionization of such salts in mixtures, and it seems not improbable that such un-ionized salts are produced at the expense of the simple salts, and that the ionization relations of the mixture are not greatly affected.

The final concentrations, which are given in the following tables, were

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[1] *Z. physik. Chem.*, 31, 218 (1899).

[2] For a discussion of the experimental evidence, see A. A. Noyes, *Z. physik. Chem.*, 52, 635-6 (1905); *Science*, 20, 583-4 (1904). For an example in which the application of this principle is carefully explained, see Sherrill, This Journal, 29, 1665 (1907).

obtained by the usual method of approximations,[1] which need not be explained here. The values given have been made to satisfy all possible requirements. Thus in Table XVI the total NH_4 and total Na are equal to C and 2 C respectively; the total PO_4 is equal to $C(1-h)$; the total HPO_4 and the sum $(NH_4OH) + (OH^-)$ are each equal to Ch; and the total equivalent concentrations of the positive and negative ions are equal. (By total ion concentration is always meant the sum of the equivalent concentrations of either all the positive or all the negative ions, *not* the sum of both these types of ions.) Similar relationships hold in the other tables. For the sake of convenience in testing these relationships numbers which are not significant have been retained. All concentrations (except the total ion-concentration, which is in equivalents) are in formula weights per liter.

TABLE XVI.

$Na_2NH_4PO_4$.

Salt	0.1	0.05	0.02
NH_4OH	0.09542	0.04755	0.01902
Total ion	0.1207	0.06825	0.03102
OH^-	0.000607	0.000502	0.000441
HPO_4^{--}	0.05705	0.03219	0.01475
PO_4^{---}	0.00201	0.001123	0.0003607
NH_4^+	0.00270	0.00163	0.000742
Na^+	0.1180	0.06662	0.03028
$(NH_4)_2HPO_4$	0.00088	0.000379	0.0001126
Na_2HPO_4	0.0381	0.01548	0.00461
$(NH_4)_3PO_4$	0.000044	0.0000196	0.0000043
Na_3PO_4	0.00192	0.000803	0.000174
K_3	3.42×10^{-13}	4.10×10^{-13}	3.27×10^{-13}
K_3 (mean)	3.6×10^{-13}		

TABLE XVII.

$NaNH_4HPO_4$.

Salt	0.1	0.05
NH_4OH	0.002945	0.001510
Total ion	0.1182	0.06648
OH^-	8.7×10^{-7}	7.9×10^{-7}
$H_2PO_4^-$	0.00214	0.001184
HPO_4^{--}	0.05803	0.03265
NH_4^+	0.0582	0.03273
Na^+	0.0600	0.03375
$NH_4H_2PO_4$	0.000396	0.000161
NaH_2PO_4	0.000408	0.000165
$(NH_4)_2HPO_4$	0.0192	0.00780
Na_2HPO_4	0.0198	0.00804
K_2	1.84×10^{-7}	2.06×10^{-7}
K_2 (mean)	1.95×10^{-7}	

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[1] Sherrill, *loc. cit.*

TABLE XVIII.

	$Na_3NH_4P_2O_7$			$Na_2(NH_4)_2P_2O_7$	
Salt	0.1	0.05	0.02	0.05	0.02
NH_4OH	0.01056	0.00657	0.00346	0.00892	0.004721
Total ion	0.1270	0.0753	0.03625	0.0757	0.0365
OH^-	6.2×10^{-6}	6.7×10^{-6}	7.6×10^{-6}	4.2×10^{-6}	4.2×10^{-6}
$HP_2O_7^{---}$	0.00526	0.00373	0.00225	0.00506	0.00307
$P_2O_7^{----}$	0.0278	0.01605	0.00738	0.01513	0.00682
NH_4^+	0.0292	0.0169	0.00785	0.0361	0.0171
Na^+	0.0978	0.0584	0.0284	0.0396	0.0194
$(NH_4)_3HP_2O_7$	0.00123	0.00064	0.000262	0.00184	0.000775
$Na_3HP_2O_7$	0.00408	0.0022	0.000948	0.00202	0.00088
$(NH_4)_4P_2O_7$	0.01415	0.00615	0.00198	0.01237	0.00396
$Na_4P_2O_7$	0.0475	0.02125	0.00718	0.01358	0.00450
K_4'	4.9×10^{-9}	3.8×10^{-9}	2.6×10^{-9}	4.1×10^{-9}	2.8×10^{-9}
K_1' (mean)	3.6×10^{-9}				

TABLE XIX.

	$Na_2NH_4HP_2O_7$	
Salt	0.05	0.02
NH_4OH	0.001167	0.0004941
Total ion	0.0830	0.0385
OH^-	7.4×10^{-7}	6.7×10^{-7}
$H_2P_2O_7^{--}$	0.000785	0.000372
$HP_2O_7^{---}$	0.02714	0.01258
NH_4^+	0.0272	0.01263
Na^+	0.0558	0.02587
$(NH_4)_2H_2P_2O_7$	0.000126	0.0000403
$Na_2H_2P_2O_7$	0.000257	0.0000825
$(NH_4)_3HP_2O_7$	0.00711	0.00227
$Na_3HP_2O_7$	0.01458	0.00466
K_3'	2.76×10^{-7}	2.98×10^{-7}
K_3' (mean)	2.9×10^{-7}	

These ionization constants are brought together in tabular form, compared with those of other common acids, and further discussed in the summary at the end of this article.

5. The Hydrolysis of Ammonium Di-sodium Phosphate Determined by Conductance Measurements.

The method employed involved the measurement of the change of conductance produced by the addition of varying amounts of ammonium hydroxide to solutions of di-sodium phosphate. If we consider the reaction to be expressed by the equation

$$2Na^+ + HPO_4^{--} + NH_4OH = 2Na^+ + PO_4^{---} + NH_4^+ + H_2O$$

it is evident that there should be an increase in the conductance of the solution, due to the change of undissociated ammonium hydroxide into ammonium ion, and also to the change of HPO_4^{--} ion into the (presumably more mobile) trivalent PO_4^{---} ion. It should therefore be possible to calculate the degree of hydrolysis of the ammonium salt from the measured increase in specific conductance and other known data.

The required solutions were prepared by weighing the proper amounts of the stock solution of di-sodium phosphate in a calibrated flask of 500 cc. capacity, adding the required volumes of standard ammonia from a burette, and finally making up to the mark with conductivity water, at 18°. The standard ammonia solution was titrated immediately before use with standard hydrochloric acid. The preparation of these standard solutions has been described above in Section. 2. During the measurements great care was taken to protect the ammonia solutions from the atmosphere. This was conveniently done by using compressed air to effect the transfer of the solutions from vessel to vessel. For this purpose the air was purified by passing through a series of vessels containing successively absorbent cotton, alkaline potassium permanganate solution, sodium hydroxide solution, and pure water.

TABLE XX.

The Conductance Data.

Mols. Na_2HPO_4 per liter.	Equiv. NH_4OH per mol. Na_2HPO_4.	Spec. conduct. × 10^6. I.	II.	Mean.	Increase of cond.	100 (1 — *h*) calculated.
0.05	0	....	....	6513[1]	...	....
0.05	1	6757	6754	6756	234	(3.90)
0.05	2	6859	6851	6855	342	5.48
0.05	3	6931	6927	6929	416	6.67
0.05	4	6967	6969	6968	455	7.30
0.02	0	....	....	2948[1]	...	0.0
0.02	1	3087	3086	3087	139	(2.70)
0.02	2	3182	....	3182	234	4.55 (?)
0.02	4	3224	3223	3224	276	5.36
0.02	16	3475	....	3475	527	10.27

The distribution experiments have given a measure of the degree of hydrolysis, *h*, of the solutions containing one equivalent of ammonia per formula weight of Na_2HPO_4; and the values of 1–*h* are 0.0390 and 0.0270 respectively for the solutions of concentrations 0.05 and 0.02 mol. The values of 1–*h* of the solutions containing more ammonia, which are given in the last column of the table, were obtained from the "increase of conductance" by assuming simple proportionality, since the unhydrolyzed part is directly proportional to the increase of conductance. In this manner additional data were obtained for calculating the values of the hydrolysis constant K_W/K_3K_B and the ionization constant K_3. Corrections were made for the influence of the un-ionized substances in the solution as in the calculations in Section 4.

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[1] This is the value of the specific conductance after making a slight correction for hydrolysis (cf. Table VII), and is therefore the conductance that the solution would have if the only ions present were Na^+ and HPO_4^{--}.

The results are given in Table XXI, expressed in milli-formula weights per liter (except the total ion concentration, which is in milli-equivalents). By comparing the ion concentrations and specific conductance of each solution with those of the corresponding solution containing no ammonia, and by making use of the mobilities of the ions given in Table V, values of the mobility of the PO_4^{---} ion were calculated, which are given in the table.

Table XXI.

Solutions Containing Na_2HPO_4 and Varying Amounts of NH_4OH.

Salt	50.0	50.0	50.0	50.0	50.0
Ammonia	0.0	50.0	100.0	150.0	200.0
Total ion	67.14	68.25	68.70	68.98	69.31
NH_4OH	0.0	47.55	96.54	145.77	195.27
OH	0.0	0.502	0.722	0.895	1.075
HPO_4^{--}	33.57	32.19	31.62	31.16	30.96
PO_4^{---}	0.0	1.123	1.58	1.924	2.103
NH_4^+	0.0	1.63	2.30	2.80	3.125
Na^+	67.14	66.62	66.40	66.18	66.19
$(NH_4)_2HPO_4$	0.0	0.379	0.520	0.630	0.695
Na_2HPO_4	16.43	15.485	15.13	14.88	14.69
$(NH_4)_3PO_4$	0.0	0.0196	0.0387	0.0573	0.070
Na_3PO_4	0.0	0.803	1.120	1.355	1.478
$\mu(PO_4^{---})$	.....	199	196	198	185
$K_3 \times 10^{13}$	.....	4.10	4.08	4.07	3.75

Salt	20.0	20.0	20.0	20.0
Ammonia	0.0	20.0	80.0	320.0
Total ion	30.40	31.02	31.66	32.93
NH_4OH	0.0	19.02	78.025	316.09
OH	0.0	0.441	0.901	1.853
HPO_4^{--}	15.20	14.75	14.31	13.50
PO_4^{---}	0.0	0.3607	0.7153	1.359
NH_4^+	0.0	0.742	1.490	2.930
Na^+	30.40	30.28	30.17	30.00
$(NH_4)_2HPO_4$	0.0	0.1126	0.217	0.396
Na_2HPO_4	4.80	4.60	4.40	4.05
$(NH_4)_3PO_4$	0.0	0.0043	0.0168	0.0620
Na_3PO_4	0.0	0.174	0.341	0.633
$\mu(PO_4^{---})$	.....	192	181	160
$K_3 \times 10^{13}$	.....	3.27	3.27	3.20

The values of K_3 are remarkably constant in each of the two series of experiments. The numerical values of the constant for the solutions containing more than one equivalent of ammonia are of course not independent of the value for the solution containing one equivalent, but the fact that K_3 is almost unchanged by a sixteenfold increase in the concentration of ammonia must be regarded as a confirmation of the accuracy of the value of K_3, 3.6×10^{-13}, as determined by the distribution experiments. These results also afford a striking illustration of the value of the empirical principle used in calculating the concentration of the different ions and undissociated substance. In this connection it may be mentioned that in each case the approximations were completed before the value of K_3 was calculated, and that no alterations have been subsequently made.

When the nature of the calculations is considered the results obtained for the formular conductance of the PO_4^{---} ion must also be regarded as satisfactory. For example, the change in the concentration of the HPO_4^{--} ion is the most important single item in the calculations, and this is a difference between two large numbers. Since the values in each series increase as the proportion of ammonia decreases, it has seemed better to assume the maximum limiting value of about 200 for μ/PO_4^{---} rather than an average value.

The small value of $\mu(PO_4^{---})$ in the last experiment of each series is due in part to the fact that the OH^- concentration is large and the undissociated NaOH no longer negligible. In the experiment with 200 milli-equivalents of ammonia, the concentration of undissociated NaOH was estimated to be 0.10 milli-mol, and on making the necessary corrections the chief change was a small decrease in the Na^+ and HPO_4^{--} ion concentrations, with a resulting increase of $\mu(PO_4^{---})$ from 185 to a value between 187 and 190. Similarly in the experiment with 320 milli-equivalents of ammonia, (NaOH) was 0.12 milli-mol, and $\mu(PO_4^{---})$ was increased from 160 to 165–170. The corresponding increases in $K_3 \times 10^{-13}$ were only 1 or 2 in the second decimal place.

There is still another factor to be considered: namely, the probability that the ionization of Na_3PO_4 is somewhat less than that of $Na_3HP_2O_7$, instead of being equal to it as has been assumed. This conclusion is based upon the fact that the uni-bivalent salt Na_2HPO_4 is less ionized than $Na_2H_2P_2O_7$. The necessary correction is probably not greater than 5 per cent., which would give a value of 200–210 for $\mu(PO_4^{---})$. The possible "error" is evidently very large, and can hardly be less than 30. The final (experimental) value is therefore

$$\mu(PO_4^{---}) = 205 \pm 30.$$

From an examination of the relationships between the conductances of the different phosphate ions (see Table XXIII below), one may conclude that the value of $\mu(PO_4^{---})$ is probably as high as 230.

6. Summary.

In this article, methods have been described for the preparation and analysis of pure solutions of ortho- and pyrophosphoric acids and of their sodium and ammonium salts. The results of conductance measurements of the sodium salts and of the acids have been presented (see Table I, page 737).

A convenient and accurate method of measuring the hydrolysis of ammonium salts has been developed, based upon the fact that when an aqueous solution of ammonia is shaken with chloroform, the ammonia distributes itself between the two non-miscible solvents, so that the ratio of its concentrations is constant at a given temperature. This ratio having been satisfactorily determined (Table II, page 739) the distribution was also measured for solutions of the hydrolyzed ammonium salts and therefrom the degrees of hydrolysis of the salts were calculated. The distribution data for the various salts is found in Table III, pages 740–1.

From the hydrolysis measurements preliminary values of the ionization-constants of the successive hydrogens of ortho- and pyrophosphoric acids were calculated (Table IV, page 743) on the assumption that all salts were competely dissociated.

The values of these ionization constants were then corrected for the effect of the un-ionized substances existing in the solutions, on the basis of the empirical principles which have been found to govern the ionization of salts alone and in mixtures (Tables XV–XIX, pages 752–6).

The so-obtained final values of the ionization constants of ortho- and pyrophosphoric acids are given in the following table, together with those of some other acids[1] which are included for the sake of comparison.

TABLE XXII.

Ionization = Constants at 18°.

Orthophosphoric..................	$H_2PO_4^-$	$+ H^+$[2]	1.1×10^{-2}
"	HPO_4^{--}	$+ H^+$	1.95×10^{-7}
"	PO_4^{---}	$+ H^+$	3.6×10^{-13}
Pyrophosphoric..................	$H_3P_2O_7^-$	$+ H^+$[2]	1.4×10^{-1}
"	$H_2P_2O_7^{--}$	$+ H^+$[2]	1.1×10^{-2}
"	$HP_2O_7^{---}$	$+ H^+$	2.9×10^{-7}
"	$P_2O_7^{----}$	$+ H^+$	3.6×10^{-9}
Hydrochloric..................	Cl^-	$+ H^+$[2]	6×10^{-1}
Hydrosulphate ion[3]..................	SO_4^{--}	$+ H^+$	1.9×10^{-2}
Acetic..................	$C_2H_3O_2^-$	$+ H^+$	1.8×10^{-5}
Carbonic..................	HCO_3^-	$+ H^+$	3.0×10^{-7}
Hydrocarbonate ion[4]..................	CO_3^{--}	$+ H^+$	6.0×10^{-11}
Hydrosulphic[5]..................	HS^-	$+ H^+$	9.1×10^{-8}
Hydrosulphide ion[6]..................	S^{--}	$+ H^+$	1.2×10^{-15}
Boric..................	$H_2BO_3^-$	$+ H^+$	1.7×10^{-9}

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[1] Walker, *Z. physik. Chem.*, 32, 137 (1900).

[2] Each of the "constants" K_1, K'_1, K'_2, and K_{HCl} decreases with decreasing ion-concentration. The numbers given in the table correspond to a total equivalent ion-concentration 0.026.

[3] Noyes and Eastman, Carnegie Institution Publications, No. 63, 276 (1907). The value 0.019 corresponds to an equivalent ion-concentration 0.016.

[4] McCoy, *Am. Chem. J.*, 29, 455 (1903).

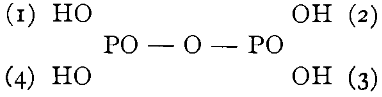
[5] Auerbach, *Z. physik. Chem.*, 49, 217 (1904).

Knox, *Trans. Faraday Soc.*, 1908, 43. This value is at 25°.

Orthophosphoric acid, with reference to the first equivalent of hydrogen, evidently behaves like a fairly strong acid; with reference to the second, like a weak acid intermediate between carbonic acid and hydrosulphic acid; and with reference to the third, like a remarkably weak acid intermediate between the acid radicals HCO_3^- and HS^- of these two acids. These facts are in harmony with the heats of neutralization, and with the well-known behavior of the acid towards indicators, for one equivalent of hydrogen may be titrated with methyl orange and two with phenolphthalein, while according to Salm[1] the third may be titrated with trinitrobenzene. It is convenient to use the term phosphoric acid with reference to the ionization of the first hydrogen only, and to use the names dihydrophosphate ion and monohydrophosphate ion respectively for the second and third acids.

Pyrophosphoric acid behaves in a similar manner. With reference to the first hydrogen it is a strong acid, though not quite so strong as hydrochloric or nitric acid. Trihydropyrophosphate ion $H_3P_2O_7^-$ is a somewhat weaker acid, and its "ionization constant" is almost identical with that of orthophosphoric acid at the same ion-concentration. Dihydropyrophosphate ion, $H_2P_2O_7^{--}$, is a weak acid, of almost the same strength as dihydrophosphate ion, $H_2PO_4^-$, while monohydropyrophosphate ion, $HP_2O_7^{---}$, is still weaker, but by no means as weak as monohydrophosphate ion, HPO_4^{--}. These facts are also in harmony with the behavior of pyrophosphoric acid toward indicators: two equivalents of hydrogen may be titrated with methyl orange, but the third cannot be determined with phenolphthalein, for the end-point is affected by the dissociation of the fourth hydrogen.

These results doubtless have a relation to the molecular structure of the acids in question. In the case of dibasic organic acids the ratio (K_1/K_2) of the constants for the two successive hydrogens is small when the second COOH group is remotely situated from the first, and becomes greater as the COOH groups approach each other. In other words, the presence of a negative charge tends to prevent the dissociation of the second H^+ ion, and its influence is greater, the nearer that charge is to the second COOH. It is therefore probable that the first and second hydrogens of pyrophosphoric acid dissociate from remote OH groups, and that the third and fourth arise from OH groups situated near the first and second. This is illustrated by the numbers in parentheses attached to the following structural symbol of pyrophosphoric acid:



$$\begin{array}{lcr} (1)\ \mathrm{HO} & & \mathrm{OH}\ (2) \\ & \mathrm{PO - O - PO} & \\ (4)\ \mathrm{HO} & & \mathrm{OH}\ (3) \end{array}$$

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[1] Salm, *Z. physik. Chem.*, **57**, 471 (1906).

This would explain why there is not a very great difference between the ionization tendencies of the first and second hydrogens or between those of the third and fourth hydrogens, while the difference between the former and latter pairs is enormous. It also explains the fact that the great difference between the second and third constants of the pyro acid corresponds to that between the first and second constants of the ortho acid, and the fact that the ratio of the third and fourth constants of the pyro acid is very much less than that of the second and third constants of the ortho acid.

These ionization constants were used for correcting the conductance measurements of the different salts for the effect of hydrolysis and of hydrogen-ion dissociation; and by graphical extrapolation, the limiting conductances (at zero concentration) were determined. Since, however, the calculations of the final values of these conductances and of the ionization constants are mutually dependent, it was necessary to use a method of approximation and to repeat the calculations till the value of each had no longer an appreciable influence on that of the other.

In Tables VII to XIII (pages 747-50) are given the corrected values of the formular conductances of the various salts. Each table also contains the limiting conductance at zero concentration and the percentage ionization at the different concentrations. The same data for ortho- and pyrophosphoric acid are given in Tables X and XIV.

The relation between the conductance of the different ions and their valence[1] is of great interest, since this seems to be the first case in which the values of three similar ions having three different valences have been determined. The following table contains the values of the formular and equivalent conductances at 18°. The numbers following the ± signs are the estimated values of the maximum error.

TABLE XXIII.

	Formular conductance.	Equivalent conductance.
HPO_4^-	26.4 ± 1.0	26.4 = 1 × 26.4
HPO_4^{--}	106.8 ± 2.0	53.4 = 2 × 26.7
PO_4^{---}	205.0 ± 30.0	69.0 = 3 × 23.0
$HP_2O_7^-$	(20.4 ± 1.0)[2]	(20.4 = 1 × 20.4)[2]
$H_2P_2O_7^{--}$	83.3 ± 1.0	41.6 = 2 × 20.8
$HP_2O_7^{---}$	179.2 ± 4.0	59.7 = 3 × 19.9
$P_2O_7.^{----}$	325.6 ± 10.0	81.4 = 4 × 20.3

The results for both acids show in a striking manner that the equivalent conductance of the ions is proportional to their valence or in other words to the charge upon them. This must be so in the case of ions which, because of their equal size, meet with an equal frictional resistance in

[1] Cf. A. A. Noyes, Carnegie Institution Publications, No. 63, page 336.

[2] Value derived by estimation from those of the other ions.

moving through the solution, since the electric force driving them is proportional to the charge upon them.

It has also been shown that the ionization values for the salts involved in this investigation, most of which are of multivalent types, conform to the principle that at the same concentration the ionization is roughly the same for all salts having the same valence product and to the principle that the un-ionized fraction is greater, the greater the value of the valence product (see Fig. 2, page 753).

In conclusion, the authors wish to express their thanks to Professor A. A. Noyes for suggesting this research and for his valuable advice and assistance freely given throughout its progress.

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THE RATE OF HYDRATION OF PYROPHOSPHORIC ACID IN AQUEOUS SOLUTION.

BY G. A. ABBOTT.

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It is well known that pyrophosphoric acid is unstable in aqueous solution, gradually changing through hydration into orthophosphoric acid. At the room temperature, in dilute solutions, the change is complete only after weeks, or even months, but the rate is enormously accelerated by rise of temperature. Thus, at 100°, in a 0.05 formular solution of pyrophosphoric acid, the hydration has been found to be practically complete after two hours. This hydration is attended by a marked decrease in the conductance of the solution; therefore the rate of the reaction may be easily determined by measuring the change of the conductance. By choosing a suitable temperature the velocity may be made to assume a value convenient for the measurements.

The measurements about to be described were made in one of the platinum-lined steel bombs used in this laboratory for investigating the conductance of aqueous solutions at high temperatures.[1] This apparatus proved admirably adapted to the work, for it enabled measurements to be made of the conductance of the acid solutions at temperatures up to 100°, without danger of contamination or change of concentration by evaporation.

A solution of pyrophosphoric acid containing 0.05 formular weights of $H_4P_2O_7$, prepared as described in the recent article of Abbott and Bray,[2] was put into the bomb, which was properly closed and then brought

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[1] See Carnegie Institution Publications, No. 63, p. 9 (1907). *Z. physik. Chem.*, 46, 325 (1903).

[2] See preceding paper.