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THE FIRST DISSOCIATION OF PHOSPHORIC ACID IN AQUEOUS SALT SOLUTIONS AT 18°

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In a previous paper¹ the author has employed conductivity data of pure phosphoric acid solutions in recalculations of the first dissociation constant. The present paper deals with an investigation of this important dissociation in aqueous solutions containing certain inorganic salts.

It is at present impossible to interpret correctly electrical conductivity measurements of solutions of high ionic concentration, and on this account the conductivity method is inapplicable to a study of the first dissociation of phosphoric acid in salt solutions. The method discussed in this paper has been used to determine the stoichiometric dissociation constant in solutions of sodium chloride, potassium chloride, magnesium chloride, and calcium chloride, of varying concentration. From what follows it will be seen that the method presented herein is somewhat similar to that evolved by Harned and Robinson² for studying the dissociations of weak electrolytes, but it seems to possess certain advantages over their method. Thus the assumption of complete dissociation of hydrochloric acid (which is later checked and proved experimentally) does not involve a possible error in the e. m. f. of a "chloride" as well as a "hydrogen" electrode, and there is no delay waiting for a "chloride" electrode to reach equilibrium. Furthermore, by replacing the hydrochloric acid with nitric acid the method could be extended to solutions containing nitrates, and corrections might be made if the nitric acid proved to dissociate incompletely.

Outline of the Method and the Principles Involved

Electrometric measurement of hydrogen-ion activity is ordinarily subject to junction potential and standardization errors, and these may influence the second decimal place so seriously that the result can safely be called " P_{H} value" only. A chain consisting of two half-cells in which are solutions of the same concentration with respect to some neutral foreign metal chloride, but of different concentration with respect to very small quantities of hydrochloric acid, has a negligible liquid junction potential, and may be used to find the relative hydrogen-ion activities in the two solutions with great exactitude. If the hydrochloric acid in one half-cell is replaced by a small quantity of phosphoric acid, the junction potential will still be negligibly small and the relative hydrogen-ion activities can

¹ Lugg, *THIS JOURNAL*, 53, 1 (1931).

² Harned and Robinson, *ibid.*, 50, 3157 (1928).

again be measured with accuracy. Secondary and tertiary dissociations of phosphoric acid are negligible under these acid conditions, and were the actual concentration of hydrogen ions in the hydrochloric acid solution known, the first stoichiometric dissociation constant, K_1 , of phosphoric acid could then be calculated, because the activity coefficients of hydrogen ions are the same in solutions whose thermodynamic environments are kept sensibly constant by a relatively high concentration of foreign salt.

Although it is an experimental fact that the measured hydrogen-ion activity is directly proportional to the small hydrochloric acid concentration when the ionic environment is kept sensibly constant, it cannot be concluded therefrom that the hydrochloric acid is completely dissociated, because it may be shown from the mass law that the same behavior would be observed even if hydrochloric acid were a typically weak acid. But if the provisional assumption of complete dissociation for the hydrochloric acid is made, and the phosphoric acid dissociation constant calculated on it, the validity of this assumption may be tested by repeating the measurement in the presence of a different quantity of phosphoric acid. Theory and experiment show that the activity coefficients of ions and un-ionized solutes in the presence of a preponderating amount of foreign salt are constant. The second determination of K_1 could be the same as the first only if the provisional assumption were valid. Such double determinations of K_1 in sodium, potassium, magnesium and calcium chloride solutions are recorded herein, and from their close agreement provide excellent confirmation for the Complete Dissociation Theory in the case of hydrochloric acid, a typical strong electrolyte.

Instead of employing a chain such as that described above, one might measure the e. m. f. between a calomel electrode and a quinhydrone electrode in the hydrochloric acid solution, and repeat the measurement with phosphoric acid replacing the hydrochloric acid. Provided that precautions are taken to ensure the junction potential being the same in both measurements, the difference in e. m. f. will be the same as that of the chain described earlier, and as the quinhydrone salt error will be the same in both cases, the difference in e. m. f. will be subject to no errors other than experimental ones.

This procedure was actually followed in obtaining the present data, in the hope that the hydrogen-ion activity coefficient could be obtained with fair accuracy in each case, after correcting for the quinhydrone salt error. Junction potentials were of such magnitude, however, and so variable, that this could not be done with any expectation that the results would have physical significance. To ensure that the changes in junction potential would not vitiate the measured difference in e. m. f. between phosphoric acid and hydrochloric acid solutions, the 0.1 *N* potassium chloride calomel electrode was connected by the same saturated agar bridge successively

with the two solutions; the order was then reversed and a mean value of the differences was taken. It was found that the difference could be reproduced by this method to within a few tenths of a millivolt. Stock solutions were standardized to within 0.1%. All measurements were made at 18.0°.

Where ΔE is the e. m. f. difference in volts, (H_3PO_4 solution)-(HCl solution), α_{H^+} represents hydrogen-ion activity, and p signifies negative common logarithm, we have

$$-\frac{\Delta E}{0.05773} = \Delta p\alpha_{\text{H}^+} = p\alpha_{\text{H}^+(\text{H}_3\text{PO}_4)} - p\alpha_{\text{H}^+(\text{HCl})} \quad (1)$$

Since γ_{H^+} , the hydrogen-ion activity coefficient, is the same in both solutions

$$\Delta p\alpha_{\text{H}^+} = p[\text{H}^+]_{(\text{H}_3\text{PO}_4)} - p[\text{H}^+]_{(\text{HCl})} \quad (2)$$

Assuming $[\text{H}^+]_{(\text{HCl})} = [\text{HCl}]$, $[\text{H}^+]_{(\text{H}_3\text{PO}_4)}$ in the phosphoric acid solution is given by

$$p[\text{H}^+]_{(\text{H}_3\text{PO}_4)} = p[\text{HCl}] - \frac{\Delta E}{0.05773} \quad (3)$$

$[\text{H}^+]_{(\text{H}_3\text{PO}_4)}$ must equal $[\text{H}_2\text{PO}_4^-]$ for electroneutrality, and where $[\text{H}_3\text{PO}_4]_0$ represents the initial phosphoric acid molarity, the mass law gives

$$K_1 = \frac{[\text{H}^+]^2}{[\text{H}_3\text{PO}_4]_0 - [\text{H}^+]_{(\text{H}_3\text{PO}_4)}} \text{ or } pK_1 = 2p[\text{H}^+]_{(\text{H}_3\text{PO}_4)} - p([\text{H}_3\text{PO}_4]_0 - [\text{H}^+]_{(\text{H}_3\text{PO}_4)}) \quad (4)$$

Results

The data are given in Table I, which contains in the order of the columns, foreign salt molarity, hydrochloric acid molarity, phosphoric acid molarity, ΔE , $[\text{H}^+]_{(\text{H}_3\text{PO}_4)}$, pK_1 , and $\sqrt{\mu}$. The ionic strength, μ , has been calculated for the phosphoric acid solutions from the definition, $\mu = \frac{1}{2}\sum(Cz^2)$, where C is the concentration of any ion in moles per liter, and z is its valence. In calculating μ , the metal chlorides were assumed to be completely dissociated.

TABLE I
EXPERIMENTAL DATA

[For. salt]	[HCl]	[H ₃ PO ₄]	ΔE	[H ⁺]	pK_1	$\sqrt{\mu}$
			Sodium Chloride			
0.020	0.0015	0.002	+0.00340	0.00172	1.977	0.147
.050	.0020	.002	-.00365	.00173	1.955	.227
.050	.0040	.005	-.00140	.00378	1.930	.232
.100	.0040	.005	-.00080	.00387	1.877	.322
.200	.0040	.005	-.00040	.00394	1.835	.452
.400	.0040	.005	-.00005	.00399	1.802	.636
.600	.0040	.005	+.00055	.00409	1.735	.777
.800	.0040	.005	+.00070	.00411	1.721	.897
1.600	.0040	.005	+.00085	.00414	1.700	1.267
1.600	.0040	.010	+.01505	.00729	1.707	1.268

TABLE I (Concluded)

[For. salt]	[HCl]	[H ₂ PO ₄]	ΔE	[H ⁺]	pK_1	$\sqrt{\mu}$
Potassium Chloride						
0.020	0.0015	0.002	+0.00330	0.00171	1.996	0.147
.050	.0020	.002	— .00350	.00174	1.933	.227
.100	.0040	.005	— .00095	.00385	1.891	.322
.100	.0060	.010	+ .00235	.00659	1.895	.327
.200	.0040	.005	— .00080	.00387	1.877	.452
.400	.0040	.005	— .00025	.00396	1.821	.636
.600	.0040	.005	— .00010	.00398	1.809	.777
.800	.0040	.005	± .00000	.00400	1.796	.897
1.400	.0040	.005	+ .00045	.00407	1.748	1.185
1.400	.0040	.010	+ .01480	.00723	1.724	1.186
Magnesium Chloride						
0.010	0.0020	0.002	—0.00360	0.00173	1.953	0.178
.025	.0040	.005	— .00080	.00387	1.877	.280
.050	.0040	.005	— .00045	.00393	1.841	.392
.100	.0040	.005	+ .00045	.00407	1.748	.552
.250	.0040	.005	+ .00120	.00420	1.657	.869
.250	.0040	.010	+ .01590	.00757	1.628	.870
Calcium Chloride						
0.010	0.0020	0.002	—0.00350	0.00174	1.935	0.178
.025	.0040	.005	— .00065	.00390	1.859	.280
.050	.0040	.005	— .00035	.00395	1.829	.392
.100	.0040	.005	+ .00035	.00406	1.757	.552
.200	.0040	.005	+ .00135	.00422	1.642	.778
.200	.0040	.010	+ .01600	.00757	1.628	.779
.350	.0060	.010	+ .00650	.00778	1.564	1.029

Discussion

By definition the stoichiometric constant, K_1 , becomes the activity constant, K_1' , at infinite dilution, where the activity coefficients of all ions and molecules concerned are unity. K_1' is a true constant, and its relation to K_1 is given in

$$pK_1 = pK_1' - p\gamma_{H^+} - p\gamma_{H_2PO_4^-} + p\gamma_{H_3PO_4} \quad (5)$$

The Hückel³ equation connecting the activity coefficient of a univalent ion of the r th kind with the ionic strength in aqueous solutions at 18° may be expressed

$$p\gamma_r = \frac{0.5 \sqrt{\mu}}{1 + r \sqrt{\mu}} - R\mu \quad (6)$$

where r and R are both positive, and constant for a particular type of ionic environment. r is proportional to the mean limit of approach of ions to ions of kind r .

The Debye-McAulay⁴ equation connects the activity coefficient of an un-ionized molecule of the s th kind with the ionic strength

³ Hückel, *Physik. Z.*, **26**, 93 (1925).

⁴ Debye and McAulay, *ibid.*, **26**, 22 (1925).

$$p\gamma_s = -\frac{S'}{\rho}\mu = -S\mu \quad (7)$$

where S' is constant for a particular un-ionized solute in a particular solvent and ρ is a mean diameter of the ions present. S is therefore constant for a particular type of ionic environment. The concentration of un-ionized molecules has been found experimentally to influence γ_s , relatively little. S' , and hence S , may be positive or negative.

Substituting (6) and (7) with appropriate coefficients in (5)

$$pK_1 = pK'_1 - \frac{0.5\sqrt{\mu}}{1+a\sqrt{\mu}} - \frac{0.5\sqrt{\mu}}{1+b\sqrt{\mu}} - (S-A-B)\mu \quad (8)$$

the r and R of equation (6) being replaced by a and A for H^+ ions, and by b and B for $H_2PO_4^-$ ions. If a and b are equal, or, for practical purposes, when they are not too dissimilar, equation (8) may be simplified to

$$pK_1 = pK'_1 - \frac{\sqrt{\mu}}{1+a\sqrt{\mu}} - C\mu \quad (9)$$

where a now has some mean value, and $(S-A-B)$ is replaced by C .

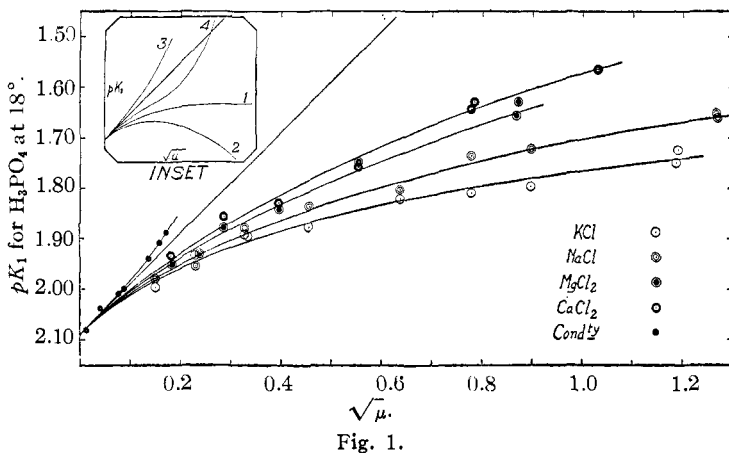


Fig. 1.

Whatever the values of the constants, equations (8) and (9) both reduce in the limit, as $\sqrt{\mu}$ approaches zero, to

$$pK_1 = pK'_1 - \sqrt{\mu} \quad (10)$$

An examination of successive differential coefficients reveals that equations (8) and (9) both give similar curve types when plotted with decreasing pK_1 values as ordinates and $\sqrt{\mu}$ values as abscissas. These types are shown in the inset to Fig. 1. If C is zero, both equations give type 1, the curve being asymptotically parallel to the $\sqrt{\mu}$ axis. If C is negative, type 2 (concave downward) results from both equations. If C is positive and greater than $(a+b)/2$ in equation (8) (or greater than a in equation (9)), type 3 (concave upward) results. If C is negative and less than

$(a + b)/2$ in equation (8) (or less than a in equation (9)), type 4 is obtained. This curve is first concave downward to a point of inflection, and then proceeds concave upward. A limiting straight line, representing equation (10), is also shown.

The data in Table I were plotted as shown in Fig. 1, and curves were drawn through the points. As pK_1' has been obtained with sufficient accuracy from conductivity data, the extension of the curves to $\sqrt{\mu} = 0$, $pK_1 = 2.09$, was a matter of interpolation rather than extrapolation. Points from the author's recalculations of conductivity data are reproduced in Fig. 1 and the theoretical limiting straight line, $pK_1 = 2.09 - \sqrt{\mu}$, is also shown. Work done at higher $\sqrt{\mu}$ values might eventually show that the sodium chloride and potassium chloride curves rightly belong together or separately to type 2 or type 4, but at present they seem to satisfy the conditions for type 1 (*i. e.*, $C = 0$). The first few points on the magnesium chloride and calcium chloride curves suggest curves of type 4, but at higher $\sqrt{\mu}$ values there is no suggestion of this. It is possible that these salts dissociate incompletely, perhaps yielding compound ions, and, if so, the $\sqrt{\mu}$ values would be incorrect and the equation constants upset. Both curves drawn are of type 1. In passing, it should be mentioned that Onsager⁵ has shown from conductivity data that salts such as sodium chloride, potassium chloride, magnesium chloride and calcium chloride, behave in dilute solution as if they were completely dissociated. Approximate equations of the form of (9) in which $C = 0$ may be applied to the four salt curves

$$\text{NaCl} \quad pK_1 = 2.09 - \frac{\sqrt{\mu}}{1 + 1.60 \sqrt{\mu}} \quad (11)$$

$$\text{KCl} \quad pK_1 = 2.09 - \frac{\sqrt{\mu}}{1 + 2.12 \sqrt{\mu}} \quad (12)$$

$$\text{MgCl}_2 \quad pK_1 = 2.09 - \frac{\sqrt{\mu}}{1 + 1.14 \sqrt{\mu}} \quad (13)$$

$$\text{CaCl}_2 \quad pK_1 = 2.09 - \frac{\sqrt{\mu}}{1 + 0.93 \sqrt{\mu}} \quad (14)$$

Since C is made zero here, it means that $S = A + B$ and is positive, but it is impossible to evaluate it. The smaller the value of a in equation (9), the smaller ρ should be in equation (7) and so S should be larger. The curve drawn from conductivity data belongs to type 3, and the author's equation to it is $pK_1 = 2.09 - \sqrt{\mu}/(1 + 1.0 \sqrt{\mu}) - 1.8$, S being positive and so large that A and B were assumed to be negligible in comparison and S was put equal to 1.8. The value 1.0 for a was assumed between discussed limits.

It will be observed in Table I that the higher the initial concentration of phosphoric acid in the presence of a fixed amount of salt, the lower, as a

⁵ Onsager, *Physik. Z.*, **28**, 277 (1927).

rule, is the value found for pK_1 . The reverse would be expected if hydrochloric acid were incompletely dissociated. It has been concluded therefore that small specific ion effects, and possibly those due to the small amounts of undissociated phosphoric acid, alone are responsible for the small decrease in pK_1 , that hydrochloric acid is completely dissociated even in presence of very much metal chloride, and that the pK_1 values are quite reliable to within the experimental limits of accuracy. In the absence of detailed knowledge concerning the second dissociation of sulfuric acid, the method cannot be applied to sulfate solutions containing phosphoric acid.

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Summary

A method is discussed for studying weak acid dissociations in salt solutions, particularly the first dissociation of phosphoric acid in chloride solutions. Using a less delicate modification of it, experimental work has been done with phosphoric acid in the presence of sodium, potassium, magnesium and calcium chlorides, and the results are given and discussed.

Evidence is adduced to show that hydrochloric acid must be considered to be completely dissociated in solution, even in presence of much metal chloride.

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