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RECALCULATIONS OF THE FIRST DISSOCIATION CONSTANT OF PHOSPHORIC ACID IN AQUEOUS SOLUTION AT 18°, AND INCIDENTAL DETERMINATION OF THE ACTIVITY COEFFICIENTS OF THE UNDISSOCIATED ACID MOLECULES

BY JOSEPH W. H. LUGG

In 1907 Noyes and Eastman[1] measured the formula conductivities of phosphoric acid in aqueous solutions of low concentration at 18°, and in 1909 Abbott and Bray[2] used these data in conjunction with their own determination of the equivalent conductivity at infinite dilution of $H^+ + H_2PO_4^-$ ions, in calculations of the first stoichiometric dissociation constant. It appears that no reliable conductivity measurements of dilute phosphoric acid solutions have been made since then.

Sherrill and Noyes[3] in 1926 recalculated the first constant from Noyes and Eastman's data and by way of correcting for inter-ionic electrical effects they made use of the fact noted by MacInnes,[4] namely, that mobilities of certain monatomic univalent ions (K^+, Na^+, Cl^-, etc.), up to about $0.1\ N$ concentration, are independent of the oppositely charged ions associated with them provided these latter are monatomic and univalent.

In their recalculations of the original data, Sendroy and Hastings[5] did not correct for inter-ionic attraction forces. They calculated the ionic strengths of the solutions from the original phosphoric acid molarities instead of from the equivalent ion concentrations.

Onsager's[6] admirable development of the Debye–Hückel theory[7] furnishes means for correcting the measured conductivities of the phosphoric acid solutions for inter-ionic attraction forces. For completely dissociated

[1] Noyes and Eastman, Carnegie Inst. Washington Publ. No. 63, 1907, p. 262.
[2] Abbott and Bray, THIS JOURNAL, 31, 729 (1909).
[3] Sherrill and Noyes, ibid., 48, 1861 (1926).
[4] MacInnes, ibid., 43, 1217 (1921).
[5] Sendroy and Hastings, J. Biol. Chem., 71, 783 (1927).
[6] Onsager, Physik. Z., 28, 277 (1927).
[7] Debye and Hückel, Physik. Z., 24, 305 (1923).

uni-univalent electrolytes in aqueous solution at 18°, Onsager's limiting equation is

$$\Lambda = \Lambda_\infty - (35.7 + 0.159\Lambda_\infty)\sqrt{2c} \qquad (1)$$

where Λ is the equivalent conductivity at concentration c and Λ_∞ is the equivalent conductivity at infinite dilution. Practically all modern evidence weighs in favor of the contention that strong electrolytes such as NaCl, KCl, LiCl, HCl, KOH, etc., and many of higher valence type, are completely dissociated in aqueous solution, even up to molar concentration. To conductivity data for the uni-univalent electrolytes, Debye and Hückel[8] have applied equations of the form

$$\Lambda = \Lambda_\infty - a\sqrt{2c} + b2c \qquad (2)$$

determining the constants a and b for each electrolyte by the method of least squares. It may be concluded from Onsager's paper that a negative value for b connotes incomplete dissociation.

The a values agree excellently with the Onsager theoretical coefficients, so the assumption that an equation of the form of (2) would apply to solutions containing only H^+ and $H_2PO_4^-$ ions necessarily in equal concentration is well founded. With the value of Λ_∞ at 18° known, a could be calculated from Equation 1, and b may be assigned the rough value $+40$, from a consideration of the positive Debye–Hückel coefficients.

Determination of Λ_∞ ($H^+ + H_2PO_4^-$) at 18°

The quantity μ which occurs frequently in this paper is not quite the same as the "ionic strength" as defined by Lewis and Randall,[9] but is defined in the identity, $\mu \equiv \frac{1}{2}\Sigma(Cz^2)$, where C is the concentration of an ion in moles per liter, and z is its valence. "μ" defined in this way has greater significance in the Onsager and Debye–Hückel equations.

In arriving at a value for Λ_∞ ($H^+ + H_2PO_4^-$), the conductivity data of Abbott and Bray[2] for the salt NaH_2PO_4 were employed, but were first corrected for dissociation of the $H_2PO_4^-$ ions. The corrections were considerably smaller than those calculated by Abbott and Bray. A generalized equation for the second stoichiometric dissociation constant of phosphoric acid and rough values for the mobilities of the ions H^+, $H_2PO_4^-$ and HPO_4^-, used in calculating the corrections to be applied to Λ NaH_2PO_4 as measured, appear below

$$pK_2 = 7.16 - \frac{2\sqrt{\mu}}{1 + 1.5\sqrt{\mu}} \qquad (3)$$

$\Lambda_\infty H^+ = 314$; $\Lambda_\infty H_2PO_4^- = 27$; $\Lambda_\infty \frac{1}{2}HPO_4^- = 53$. Decreases in these values with increase in μ are calculable from the Onsager equations.

Equation 3 has been deduced by the author from his own data for the

[8] Debye and Hückel, *Physik. Z.*, 24, 305 (1923).

[9] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923.

second constant[10] and from the data in W. Mansfield Clark's 1928 edition of "The Determination of Hydrogen Ions." From these sources it is found that in presence of most salts, $p\overline{K}_2$ (*i. e.*, $pK_2 + p\gamma_{H^+}$) = 7.16 − 1.5 $\sqrt{\bar{\mu}}/1 + a\sqrt{\bar{\mu}}$) at 18°, where p signifies negative common logarithm, γ_{H^+} is the activity coefficient of H^+ ion, and a is a constant determined by the ionic environment. Replacing $p\gamma_{H^+}$ from Equation 12 of this paper, one obtains for pK_2 at 18°, the approximate equation pK_2 = 7.16 − 2 $\sqrt{\bar{\mu}}/(1 + a\sqrt{\bar{\mu}})$. The most likely value for a in NaH_2PO_4 solutions seems to be about 1.5, but the uncertainty will not materially affect the calculations.

Where d is the degree of dissociation of the $H_2PO_4{}^-$ ion, calculated with the help of Equation 3, we have

$$\Lambda_{corr.}\ NaH_2PO_4 = \Lambda NaH_2PO_4 - d\Lambda H^+ - 2d\Lambda^{1/2}HPO_4{}^- + d\Lambda H_2PO_4{}^-$$

Table I contains the data of Abbott and Bray for NaH_2PO_4 conductivity; corrections to be applied for secondary dissociation of the H_2PO_4 ions; corrected values of ΛNaH_2PO_4; values of μ; and values of $\sqrt{\bar{\mu}}$.

TABLE I

EQUIVALENT CONDUCTIVITY OF NaH_2PO_4 AT 18°

Molarity of NaH₂PO₄	Approx. $\sqrt{\bar{\mu}}$	Molar conductivity (measured), ΛNaH₂PO₄	Corrn.	Corr. molar or equivalent conductivity, Λcorr. NaH₂PO₄
0	0			70.1[a]
0.001	0.032	71.68 ?	−3.8	67.9
.003	.055	69.23	−2.4	66.8
.005	.071	67.58	−1.8	65.8
.010	.100	65.53	−1.1	64.4
.020	.141	61.43 ?	−0.7	61.7
.050	.229	58.26	− .5	57.8
.100	.316	54.43	− .3	54.1
.200	.447	49.74	− .2	49.5

[a] Extrapolated.

Corrected values of Λ were plotted against corresponding values of $\sqrt{\bar{\mu}}$, and the curve drawn was extrapolated from the points for lowest concentrations almost linearly with $\sqrt{\bar{\mu}}$ to the point, $\sqrt{\bar{\mu}}$ = 0, $\Lambda_{corr.}$ = 70.1. Slopes of tangents to the curve at low $\sqrt{\bar{\mu}}$ values corresponded very well with the slope of the theoretical limiting straight line, Λ = 70.1 − (35.7 + 0.159 × 70.1)$\sqrt{2\mu}$, divergences being in the direction expected for a completely dissociated salt.

For $\Lambda_\infty NaCl$, the value 108.9 determined by Debye and Hückel[8] from the data of Kohlrausch and Maltby was accepted. A value 379.3 for $\Lambda_\infty HCl$ was obtained from the data of Goodwin and Haskell[11] by extra-

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[10] Not yet published.

[11] Goodwin and Haskell, *Phys. Rev.*, 19, 369 (1904).

polating to $\sqrt{\mu} = 0$ a curve connecting Λ with $\sqrt{\mu}$, just as in the case of NaH_2PO_4.

These values of Λ_∞ for the three electrolytes, NaH_2PO_4, NaCl and HCl, are for 18°, and Λ_∞ ($H^+ + H_2PO_4^-$) at 18° is readily obtained from $379.3 + 70.1 - 108.9$, giving 340.5.

Thus the equation one would expect to apply to aqueous solutions at 18° containing only H^+ and $H_2PO_4^-$ ions is

$$\Lambda = \Lambda_\infty - (35.7 + 0.159 \times 340.5) \sqrt{2e} + 40 \times 2e, \text{ that is}$$
$$\Lambda = \Lambda_\infty - 127.1 \sqrt{e} + 80e \tag{4}$$

where e is the equivalent ion concentration and Λ refers to a dilution $1/e$.

Although the second term ($80e$) is not negligible, it is obviously small compared with the first ($127.1 \sqrt{e}$) up to $e = 0.04$, so the uncertainty attached to the coefficient 80 will be found scarcely to affect the calculations below that value of e.

Calculation of the First Stoichiometric Dissociation Constant.—In aqueous solution phosphoric acid dissociates as follows

$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$; $\quad H_2PO_4^- \rightleftharpoons H^+ + HPO_4^-$; $\quad HPO_4^- \rightleftharpoons H^+ + PO_4^-$
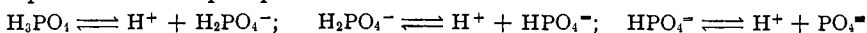
For any but almost infinitely dilute solutions of the free acid, the magnitudes of the three dissociation constants are such as to allow the production of only H^+ and $H_2PO_4^-$ ions in any appreciable quantity. OH^- ion concentrations, of course, are negligibly small in consequence of the hydrogen ionization of the acid. Thus the conductivity of phosphoric acid solutions down to a molarity of, say, 0.0001 may be considered due entirely to the presence of H^+ and $H_2PO_4^-$ ions in equal concentration. Hence where Λ is the molar conductivity at molarity c of a solution of phosphoric acid at 18°, and d is the degree of the first dissociation, we have, neglecting viscosity changes which are small enough at low concentrations

$$\Lambda/d = \Lambda_\infty (H^+ + H_2PO_4^-) - A \sqrt{dc} + Bdc \tag{5}$$

where A is 127.1 and B is 80. Transposition, squaring of both sides and subsequent rearrangement lead to

$$(B^2c^2)d^4 + (2B\Lambda_\infty - A^2c)d^3 - (2B\Lambda c - \Lambda_\infty^2)d^2 - (2\Lambda\Lambda_\infty)d + \Lambda^2 = 0 \tag{6}$$

Certain roots of this biquadratic in d would have to be excluded and it must be recalled that only the positive extraction of $\sqrt{dc}$ in Equation 5 is to be used.

Defining $\Lambda_{corr.}$ in the relation $\Lambda_{corr.}/\Lambda_\infty = d$, and substituting in Equation 5, one obtains

$$\Lambda_{corr.} = \Lambda + Ad \sqrt{dc} - Bd^2c \tag{7}$$

and $\Lambda_{corr.}$ is Λ corrected for inter-ionic attraction forces. From Equation 7 $\Lambda_{corr.}$ may be obtained by a series of successive approximations and then d may be calculated from the definition. Two such approximations were found sufficient to give values of $\Lambda_{corr.}$ unaltered in the first decimal place by successive approximations, and values of d appearing in

Table II were derived from these instead of from laborious solution of Equation 6.

By the law of mass action we have for the first stoichiometric dissociation constant, square brackets signifying molarities

$$K_1 = \frac{[\text{H}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} = \frac{dcdc}{(1-d)c} = \frac{d^2c}{(1-d)} \tag{8}$$

In logarithmic form, where p signifies negative common logarithm, Equation 8 becomes

$$pK_1 = p[\text{H}^+] + p[\text{H}_2\text{PO}_4] - p[\text{H}_3\text{PO}_4] = 2pd + pc - p(1-d) \tag{9}$$

Table II contains in the order of the columns, the data of Noyes and Eastman, corrections to Λ, $\Lambda_{\text{corr.}}$, d, μ, $\sqrt{\mu}$, K_1 and pK_1.

TABLE II

Original H₃PO₄ molarity, c	Λ	Corrn.	$\Lambda_{\text{corr.}}$	$d = \frac{\Lambda_{\text{corr.}}}{\Lambda_{\infty}}$	$\mu = e = dc$	$\sqrt{\mu}$	$K_1 = \frac{d^2c}{(1-d)}$	pK_1
0				1.0000	0	0	0	2.090ᵃ
0.0002	330.8	1.8	332.6	0.9769	0.0001954	0.0140	0.00826	2.083
.0020	283.1	4.3	287.4	.8441	.001688	.0411	.00915	2.039
.0100	203	5.9	208.9	.6136	.006136	.0783	.00974	2.011
.0125	191.2	6.0	197.2	.5791	.007239	.0851	.00997	2.001
.0500	122.7	6.0	128.7	.3780	.01890	.1375	.01149	1.940
.0800	104	6.0	110.0	.3231	.02585	.1608	.01234	1.909
.1000	96.5	5.9	102.4	.3008	.03008	.1734	.01294	1.888

ᵃ Extr.

The Constant at Infinite Dilution.   Activity Coefficients of H_3PO_4.—
By definition and the mass law, the first activity dissociation constant of phosphoric acid K_1' is given in Equation 10 and is an exact constant. α_{X} signifies activity of X, and $\alpha_{\text{X}} = \gamma_{\text{X}}[\text{X}]$, where γ_{X} is the activity coefficient, expresses its relation to the molarity. The chosen standard state in which $\gamma_{\text{X}} = 1$ (i. e., $\alpha_{\text{X}} = [\text{X}]$) for H^+, H_2PO_4^-, and H_3PO_4, is infinite dilution in each case.

$$K_1' = \frac{\alpha_{\text{H}^+} \times \alpha_{\text{H}_2\text{PO}_4^-}}{\alpha_{\text{H}_3\text{PO}_4}} \tag{10}$$

Hence replacing α_{X} by $\gamma_{\text{X}}[\text{X}]$ and expressing in logarithmic form

$$pK_1' = p[\text{H}^+] + p[\text{H}_2\text{PO}_4] - p[\text{H}_3\text{PO}_4] + p\gamma_{\text{H}^+} + p\gamma_{\text{H}_2\text{PO}_4} - p\gamma_{\text{H}_3\text{PO}_4}$$

Substitution from Equation 9 followed by rearrangement, gives

$$pK_1 = pK_1' - p\gamma_{\text{H}^+} - p\gamma_{\text{H}_2\text{PO}_4^-} + p\gamma_{\text{H}_3\text{PO}_4} \tag{11}$$

For variation of the activity coefficient of an ion with μ, the Debye-Hückel[12] equation has been found to apply admirably up to $\mu = 0.5$ or more

$$p\gamma_1 = \frac{0.5 \, z_1^2 \, \sqrt{\mu}}{1 + 3.3 \times 10^7 a_1 \sqrt{\mu}} \tag{12}$$

[12] Debye-Hückel, *Physik. Z.,* **24**, 185 (1923).

where z_i is the valence of the ion and a_i is the mean limit of approach of ions to ions of kind "i."[13]   In place of $3.3 \times 10^7 a_i$ one may use the coefficients a for H^+ and b for $H_2PO_4^-$ ions, in solutions containing H^+ and $H_2PO_4^-$ ions. Then $-p\gamma_{H^+} - p\gamma_{H_2PO_4^-}$ may be put in the form

$$\frac{-0.5 \sqrt{\mu}}{1 + a \sqrt{\mu}} + \frac{-0.5 \sqrt{\mu}}{1 + b \sqrt{\mu}}$$

and provided a and b be of the same order of magnitude the expression may be reduced for practical purposes to

$$- \frac{\sqrt{\mu}}{1 + a \sqrt{\mu}}$$

where a now has some mean value.   The expression approaches $-\sqrt{\mu}$ as $\sqrt{\mu} \longrightarrow 0$.

Debye and McAulay[14] have investigated variation of the activity coefficient of a non-electrolyte in presence of an electrolyte, and have deduced a theoretical equation which may be expressed

$$p\gamma_{\text{non-elect.}} = -S\mu \tag{13}$$

where S is a constant depending upon the mean effective ionic radius, among other things.   Experimentally, it has been shown by these authors and by Randall and Failey[15] that the variation depends almost entirely upon the concentration of electrolyte and scarcely at all upon the concentration of non-electrolyte up to moderate concentrations, and is, moreover, in agreement with the general equation.   One may therefore replace $p\gamma_{H_3PO_4}$ in Equation 11 by $-S\mu$, where S is a constant.   Equation 11 becomes

$$pK_1 = pK_1' - \frac{\sqrt{\mu}}{1 + a \sqrt{\mu}} - S\mu \tag{14}$$

$dpK_1/d \sqrt{\mu} = -1/(1 + a \sqrt{\mu})^2 - 2S \sqrt{\mu}$, giving slopes of tangents to the curve of Equation 14 and showing that the slope is -1 when $\sqrt{\mu} = 0$.

Values of pK_1 appearing in Table II were plotted against corresponding values of $\sqrt{\mu}$, but practically no weight was placed upon the point corresponding with lowest phosphoric acid concentration, because Λ_∞ and $\Lambda_{\text{corr.}}$ cannot be known exactly and for this point it requires an error of but ± 0.1 in either to effect an error of ± 0.01 in pK_1.   A smooth curve was drawn with tangential slopes continually approaching -1 as $\sqrt{\mu}$ decreased to zero.[16] pK_1 at $\sqrt{\mu} = 0$ (*i. e.*, pK_1') was found to be 2.09.   The values obtained by Sherrill and Noyes and by Sendroy and Hastings, are 2.08 and 2.11, respectively.

[13] The additional "salting out term," $(-C\mu)$, deduced by Hückel [*Physik. Z.*, **26**, 931 (1925)], where C is small and positive, may well be omitted here since its effects would be inappreciable up to $\sqrt{\mu} = 0.2$.   A very small increase in the value of a_i compensates for the omission up to much higher values of $\sqrt{\mu}$.

[14] Debye and McAulay, *ibid.*, **26**, 22 (1925).

[15] Randall and Failey, *Chem. Reviews*, **4**, 271 (1927).

[16] When S is positive, Equation 14 permits such a smooth extrapolation only provided that $S > a$.   The condition is satisfied in this case.

In Fig. 1 are shown the curve connecting pK_1 with $\sqrt{\mu}$ and passing through the point $pK_1 = 2.09$, $\sqrt{\mu} = 0$, the limiting straight line $pK_1 = 2.09 - \sqrt{\mu}$, and a curve $pK_1 = 2.09 - \sqrt{\mu}/(1 + 1.0\sqrt{\mu})$. The choice of a value 1.0 for a in Equation 14 is suggested from an examination of scattered data for different electrolytes, and it is considered unlikely to be in error by more than $+0.5$ or -0.3. From the divergence of the two curves in the figure, S in Equation 14 is readily calculated to be 1.8. An error
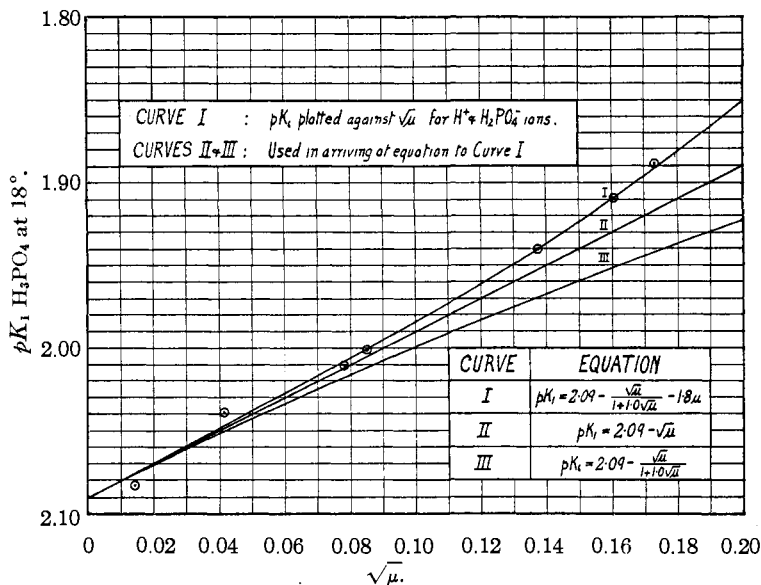

Fig. 1.

of ±0.3 in the chosen value for a, would result in an error of about ±0.2 in the calculated value of S. With the assumed value 1.0 for a, therefore, the equation connecting pK_1 for pure phosphoric acid in dilute aqueous solution at 18°, with μ calculated from the H^+ and $H_2PO_4^-$ ions, is

$$pK_1 = 2.09 - \frac{\sqrt{\mu}}{1 + 1.0\sqrt{\mu}} - 1.8\mu \qquad (15)$$

making the equation for the activity coefficient of undissociated phosphoric acid in presence of H^+ and $H_2PO_4^-$ ions in aqueous solution at 18°.

$$p\gamma_{H_3PO_4} = -1.8\mu \qquad (16)$$

In conclusion the author wishes to acknowledge his indebtedness to Dr. S. W. Pennycuick of the Adelaide University for reading the manuscript and suggesting alterations, and making the necessary arrangements for publication.

Summary

1.   From data in the literature it has been found that Λ_∞ NaH_2PO_4 is 70.1 at 18°, and from this and the values 108.9 and 379.3 for Λ_∞ NaCl and

Λ_∞ HCl, respectively, Λ_∞ (H$^+$ + H$_2$PO$_4^-$) has been calculated to be 340.5 at that same temperature.

2. Values for the first stoichiometric dissociation constant of phosphoric acid alone in aqueous solution at 18° have been calculated from the data of Noyes and Eastman. pK_1' (*i. e.*, pK_1 at infinite dilution) has been assigned the value 2.09. An equation well fitting the data is $pK_1 = 2.09 - \sqrt{\mu}/(1 + 1.0 \sqrt{\mu}) - 1.8\mu$.

3. An approximate equation for the activity coefficient of the undissociated fraction in pure dilute aqueous solutions of phosphoric acid at 18° is $p\gamma_{\text{H}_3\text{PO}_4} = - 1,8\mu$, where μ is calculated from th eequivalent ion concentration.
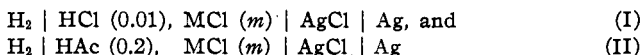

THE TEMPERATURE COEFFICIENT OF DISSOCIATION OF ACETIC ACID IN POTASSIUM AND SODIUM CHLORIDE SOLUTIONS[1]

BY HERBERT S. HARNED AND GEORGE M. MURPHY

It has been shown by Harned and Robinson, and Harned and Owen[2] that the ionization constant, hydrogen- or hydroxide-ion concentrations, and ionic activity coefficients of weak acids and bases may be determined from measurements of cells without liquid junction. Their measurements were all made at 25°. Since it is a matter of considerable importance to study the effect of temperature on the dissociation of a weak electrolyte both in a pure solvent and in salt solutions, the present study was undertaken. To this end accurate measurements of the cells

$$\text{H}_2 \mid \text{HCl (0.01), MCl } (m) \mid \text{AgCl} \mid \text{Ag, and} \qquad \text{(I)}$$
$$\text{H}_2 \mid \text{HAc (0.2), MCl } (m) \mid \text{AgCl} \mid \text{Ag} \qquad \text{(II)}$$

at 20, 25 and 30° have been made, in which HAc is acetic acid, and MCl sodium and potassium chlorides.

Experimental Procedure and Results

The cells employed were of the usual H-type, and were equipped with a three-way stopcock through which the hydrogen entered the cell. By the proper manipulation of this stopcock, the cell could easily be transferred from a thermostat maintained at one temperature to one at another temperature without danger of the hydrogen electrode coming into contact with air. Equilibrium in the cell was considered established when

[2] Harned and Robinson, THIS JOURNAL, **50**, 3157 (1928); Harned and Owen, *ibid.*, **52**, 5079 (1930).