ceeding layer (the adsorbing molecules all of the same species) partakes of the special state of the first layer in lessened degree until finally a layer is reached wherein the molecular state differs little from what may be imagined as a molecular "contact" arrangement.

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THE ACTIVITY COEFFICIENTS OF THE IONS IN CERTAIN PHOSPHATE SOLUTIONS

A CONTRIBUTION TO THE THEORY OF BUFFER ACTION[1]

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The behavior of weak electrolytes furnished one of the earliest and most complete confirmations of the theory of electrolytic dissociation. The degree of dissociation of such weak acids as acetic acid was shown to follow the law of mass action in 1888, and was calculated from measurements of conductivity by means of Ostwald's dilution law. The constants obtained from such studies of solutions of weakly dissociated electrolytes have remained the most useful that we possess for their quantitative characterization.

The characterization of strongly dissociated electrolytes in terms of the mass law remained difficult until the electrical forces resulting from the charges borne by ions were taken into account. The theory of inter-ionic forces deduced by Debye and Hückel[2] appears to be adequate for the quantitative description of behavior in even moderately concentrated solutions of strong electrolytes.

Systems containing both weak electrolytes and strong electrolytes are of general occurrence and of great significance both in chemistry and biology. The conditions that obtain when a weak acid is in the presence of its salts are, however, less easily analyzed than those that obtain in dilute solutions of the pure acid. The characterizations of such mixed electrolyte solutions have advanced in recent years, but the successive approximations, though they have made accurate investigation possible, have suffered from want of an underlying theory. The theory of inter-ionic forces renders it possible to apply the mass law to weak electrolytes in the presence of other ions.

The dissociation of a weak acid, HA, into a hydrogen ion, H^+, and its characteristic anion, A^-, may be described in terms of the mass law. In

[1] A preliminary account of this investigation was communicated to the Twelfth International Physiological Conference, Stockholm, 1926.

[2] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923). Debye and McAulay, *ibid.*, **26**, 22 (1925). Hückel, *Naturwissenschaften*, **3**, 199 (1924); *Physik. Z.*, **26**, 93 (1925).

the absence of any other ions save those into which the weak acid dissociated, it sufficed, in characterizing the conductivities of dilute solutions, to employ stoichiometric concentrations as the quantities in the mass-law equation. (Recently it has been suggested that the Ostwald dilution law yields better constants even in these cases, if account is taken of interionic forces.[3]) The form of the mass law may be retained in more concentrated solutions as well, and in those containing other ions. In such solutions the quantities in the mass law may be defined as activities,

$$a_{\mathrm{H}^+}.a_{\mathrm{A}^-}/a_{\mathrm{HA}} = Ka \qquad (1)$$

and related to stoichiometric concentrations by means of activity coefficients.

$$a_{\mathrm{A}^-}/(\mathrm{A}) = \gamma_{\mathrm{A}};\ a_{\mathrm{HA}}/(\mathrm{HA}) = \gamma_{\mathrm{HA}} \qquad (2)$$

The titration of a weak acid by a base may be defined by Equation 1 In electromotive-force studies of such titrations, the quantity measured is the negative logarithm of the hydrogen-ion activity, termed the *P*H. In general the activities of the other ion into which a weak acid dissociates have not been accurately known. As a first approximation it sufficed to substitute for the activity of this ion the stoichiometric concentration of the salt formed by neutralization of the acid. This approximation appeared justified since the acids themselves were so weakly dissociated. As a result, the anionic concentration derived from their dissociation could be neglected in comparison with that derived from the dissociation of their salts. The nature of the equilibrium in systems containing weak acids and their salts was simultaneously considered by L. J. Henderson[4] and E. W. Washburn[5] nearly twenty years ago. Not only did they introduce this approximation, but they noted that the weak acid prevented any great change in the activity of the hydrogen ion as long as the solution contained appreciable concentrations both of the weak acid and its salt. The role of partially neutralized weak acids in maintaining the constancy of the hydrogen-ion activity has been termed buffer action. The nature of buffer action, its chemical advantages and its biological significance have been considered often and adequately.

The substitution of the stoichiometric concentration of the salt of a weak acid for the activity of its ion may introduce a serious error, for when the salt is of even moderate concentration the activity coefficient, which measures deviation from the ideal condition in which there are no interionic forces, diverges widely from unity. By substituting for the activity of the ion in Equation 1 the product of its activity coefficient and its stoichi-

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[3] MacInnes, THIS JOURNAL, **48,** 2068 (1926). Sherrill and Noyes, *ibid.*, **48,** 1861 (1926).

[4] Henderson, *Am. J. Physiol.*, **15,** 257 (1906); **21,** 173 (1908); THIS JOURNAL, **30,** 954 (1908).

[5] Washburn, THIS JOURNAL, **30,** 31 (1908).

ometric concentration as defined in Equation 2, an expression is obtained which is identical with Equation 1 when γ is equal to 1, and susceptible of application even when the activity coefficient diverges widely from unity.

$$a_{\mathrm{H}^+}.(\mathrm{A})\gamma/a_{\mathrm{HA}} = Ka \qquad (3)$$

It appears from Equation 3 that the activity of the hydrogen ion can remain constant in the presence of a definite ratio of a weak acid to its salt only insofar as the activity coefficient remains constant. Moreover, only when the activity coefficient is equal to unity can such data reveal the dissociation constant of the acid. Investigations in which the activity coefficient is not unity, but in which it remains constant, may also be described in terms of Equation 3 by considering the ratio of the true dissociation constant to the activity coefficient as equal to a new constant $K'a$.

$$a_{\mathrm{H}^+}.(\mathrm{A})/a_{\mathrm{HA}} = Ka/\gamma = K'a \qquad (4)$$

Despite the fact that the activity coefficients of the ions into which certain of the weak acids dissociate have not been known, it has been possible to characterize experimentally many finite systems, and to employ buffer solutions of those concentrations, that have been thus standardized. Among these are the phosphate and borate solutions studied by Sørensen,[6] the acetate solutions studied by Walpole,[7] and the phthalate solutions studied by Clark.[8]

In certain of these systems the conditions of equilibrium have been somewhat complicated by the fact that the activity coefficients of the ions have not remained constant even though the concentration of the salt has. Under such circumstances Equation 4 cannot be employed even for a finite concentration of salt. Moreover, it is often desirable to employ other buffer concentrations than those which have been standardized. Accordingly, it seemed desirable to extend the investigations into the activity coefficients of buffer systems of Brönsted,[9] Michaelis,[10] Warburg[11] and Hastings and Sendroy,[12] and thus to test the validity of the fundamental notions and equations involved in buffer action.

The second dissociation constant of phosphoric acid is in the neighborhood of neutrality, and the buffer solutions studied by Sørensen[6] have, therefore, been particularly useful. These have consisted of mixtures of 0.0667 *M* solution of potassium dihydrogen phosphate and a 0.0667 *M* solution of disodium phosphate. The phosphate ion thus changes from a univalent

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[6] Sørensen, *Compt. rend. trav. Lab. Carlsberg*, **8**, 1 (1909); **8**, 396 (1910); *Biochem. Z.*, **21**, 131 (1909); **22**, 352 (1909).

[7] Walpole, *J. Chem. Soc.*, **105**, 2501 (1914).

[8] Clark and Lubs, *J. Biol. Chem.*, **25**, 479 (1916).

[9] Brönsted, *J. Chem. Soc.*, **119**, 574 (1921).

[10] (a) Michaelis and Kakinuma, *Biochem. Z.*, **141**, 394 (1923). (b) Michaelis and Krüger, *ibid.*, **119**, 307 (1921).

[11] Warburg, *Biochem. J.*, **16**, 153 (1922).

[12] Hastings and Sendroy, *J. Biol. Chem.*, **65**, 445 (1925).

to a bivalent ion in these systems. Since univalent and bivalent ions generally have quite different activity coefficients, and since their activity coefficients are differently affected by change in concentration, an approximation like Equation 4 is not adequate to characterize accurately such systems.

The mass-law equation for the second dissociation constant of phosphoric acid may be written

$$a_{\mathrm{H}^+}.a_{\mathrm{HPO}_4^=}/a_{\mathrm{H}_2\mathrm{PO}_4^-} = Ka_2 \qquad (5)$$

The activity of the univalent and the bivalent ions may be put equal to the products of their stoichiometric concentrations and activity coefficients, γ_1 and γ_2.

$$a_{\mathrm{H}_2\mathrm{PO}_4^-} = \gamma_1(\mathrm{H}_2\mathrm{PO}_4^-);\ a_{\mathrm{HPO}_4^=} = \gamma_2(\mathrm{HPO}_4^=) \qquad (6)$$

An equation comparable to Equation 3 results from the combination of 5 and 6.

$$a_{\mathrm{H}^+}(\mathrm{HPO}_4^=)\gamma_2/(\mathrm{H}_2\mathrm{PO}_4^-)\gamma_1 = Ka_2 \qquad (7)$$

Written in the following logarithmic form, this is often termed the Henderson-Hasselbalch equation.

$$P_{\mathrm{H}}^+ + \log\,[(\mathrm{H}_2\mathrm{PO}_4^-)/(\mathrm{HPO}_4^=)] = P_K - \log\,\gamma_1/\gamma_2 = P_K' \qquad (8)$$

The usefulness of this logarithmic form depends upon the fact that the quantity determined by electromotive-force measurements is the negative logarithm of the hydrogen-ion activity, P_{H}. The electromotive-force measurements made by Sørensen upon 0.0667 M phosphate mixtures of potassium dihydrogen phosphate and disodium phosphate are recorded in Table I. The first column gives the mole fraction of total phosphate as disodium phosphate. Both the monopotassium and the disodium

TABLE I

RECALCULATION OF SØRENSEN'S ELECTROMOTIVE-FORCE MEASUREMENTS ON MIXTURES OF 0.0667 M $\mathrm{KH_2PO_4}$ AND $\mathrm{Na_2HPO_4}$

Mole fraction of total phosphate as $\mathrm{Na_2HPO_4}$	Ionic strength, $(\mathrm{KH_2PO_4}) + 3(\mathrm{Na_2HPO_4})$ μ	Sq. root of ionic strength, $\sqrt{\mu}$	$\frac{(\mathrm{KH_2PO_4})}{(\mathrm{Na_2HPO_4})}$, R	P_{H}	P_K', $\log R + P_{\mathrm{H}}$	Log (γ_1/γ_2), calcd., $\frac{1.5\sqrt{\mu}}{1 + 1.5\sqrt{\mu}}$	P_K', + log (γ_1/γ_2)
0.025	0.07001	0.2645	39.00	5.288	6.879	0.284	7.163
.050	.07333	.2708	19.00	5.589	6.868	.289	7.157
.100	.07999	.2828	9.00	5.906	6.860	.298	7.158
.200	.09333	.3055	4.00	6.239	6.841	.314	7.155
.300	.10667	.3264	2.33	6.468	6.835	.329	7.164
.400	.11999	.3463	1.50	6.643	6.819	.342	7.161
.500	.13333	.3648	1.00	6.813	6.813	.354	7.167
.600	.14667	.3830	0.67	6.979	6.805	.365	7.170
.700	.15999	.4000	.428	7.168	6.799	.375	7.174
.800	.17333	.4163	.250	7.381	6.779	.384	7.163
.900	.18667	.4321	.111	7.731	6.776	.393	7.169
.950	.19333	.4397	.0526	8.043	6.764	.397	7.161
.975	.19667	.4436	.0256	(8.338)	(6.746)	.400	(7.146)
						Av.	7.164

salts may be considered strong electrolytes, and their concentrations equal to those of the univalent and bivalent phosphate ions, respectively. The ratio of these ions in the various solutions, as revealed by the concentrations of their salts, is recorded in Col. 4 of Table I, with their *P*H values in Col. 5. Over such a range that this ratio changed from 39:1 to 1:39, the *P*H changed from 5.288 to 8.338. The logarithm of the ratio plus the *P*H value is the left-hand side of Equation 8, and is recorded in the next column and designated as $P_{K'}$. Over the range in which the *P*H varied from 5.288 to 8.338, $P_{K'}$ varied only from 6.879 to 6.746. The difference between these limiting values, 0.133, is small in comparison with the change in *P*H, and fully justifies the conclusion that the mass law holds extremely well in dilute phosphate solutions, even when the activity coefficients are neglected. This difference is, however, ten times as great as the probable error, and represents changes in the activity coefficients of these dilute solutions.

Michaelis and Krüger[10b] have studied the change in *P*H with dilution of a solution containing equal parts of potassium dihydrogen phosphate and disodium phosphate. Their results are reported in Table II. The highest concentration studied by them was identical with Sørensen's, 0.0667 *M*. They confirmed his value for this solution of *P*H 6.813. Upon dilution the *P*H steadily increased until it reached the value 7.088 in a solution diluted fifty-fold. When the concentration of the univalent is equal to that of the bivalent phosphate ion, *P*H equals $P_{K'}$ (Equation 8). In

TABLE II

ELECTROMOTIVE-FORCE MEASUREMENTS UPON EQUIMOLECULAR MIXTURES OF KH_2PO_4 AND K_2HPO_4

Expt.	Total phosphate, (KH_2PO_4) + (K_2HPO_4), *M*	Ionic strength, (KH_2PO_4) + $3(K_2HPO_4)$, μ	Sq. root of ionic strength, $\sqrt{\mu}$	*P*H	Log (γ_1/γ_2). calcd., $\frac{1.5\sqrt{\mu}}{1 + 1.65\sqrt{\mu}}$	P_K'. + log (γ_1/γ_2)
Michaelis and Krüger	0.00133	0.00267	0.052	7.088	0.071	7.159
	.00266	.00532	.073	7.068	.098	7.166
	.00334	.00667	.082	7.069	.108	7.177
	.01333	.02667	.163	6.990	.193	7.183
	.03334	.06667	.258	6.904	.272	7.176
	.06667	.13333	.365	6.813	.342	7.155
Sørensen	.06667	.13333	.365	6.813	.342	7.155
51	.06667	.13333	.365	6.817	.342	7.159
135	.12000	.2400	.490	6.737	.406	7.143
68	.16667	.33333	.577	6.721	.433	7.154
67	.33334	.6668	.817	6.638	.522	7.160
66	.50000	1.0000	1.000	6.599	.566	7.165
134	.60000	1.2000	1.095	6.570	.585	7.155
65	.66667	1.33333	1.154	6.573	.596	7.169
133	1.2000	2.4000	1.549	6.520	.653	7.173
					Av.	7.164

these experiments $P_{K'}$ and, therefore, the logarithm of the activity coefficients, was changed by 0.275. At infinite dilution the activity coefficient should be equal to 1, and $P_{K'}$ to P_K. Michaelis and Krüger estimated that $P_{K'}$ for phosphoric acid was equal to 7.1 by extrapolation of their results.

In both of these investigations the phosphate solutions were relatively dilute. The measurements that we have made have been upon more concentrated phosphate mixtures. Certain of these measurements upon equimolecular mixtures are appended to Table II. The standard solutions used consisted of solutions of potassium dihydrogen phosphate and of potassium hydroxide. The acid salt, potassium dihydrogen phosphate, was used by Sørensen, and he has described adequate standards of purity.[6] Whereas potassium dihydrogen phosphate may be readily recrystallized and weighed out as the anhydride, the bivalent salt, $Na_2HPO_4.2H_2O$, employed by Sørensen has occasionally given trouble in this Laboratory by passing over to a higher hydrate. Moreover, it seemed desirable for this investigation to have but one cation present. Potassium hydroxide was employed as base, and any desired amount of the acid salt, KH_2PO_4, transformed into dipotassium phosphate according to the equation

$$KH_2PO_4 + KOH = K_2HPO_4 + H_2O \qquad (9)$$

In solutions whose hydrogen potentials are reported, the ratio of potassium dihydrogen phosphate to dipotassium phosphate was varied from 9:1 to 1:8, and the concentration of total phosphate from 0.06 to 1.20 *M*. The stock solutions were 1.5 *M* potassium dihydrogen phosphate and 4 *M* potassium hydroxide. Several solutions were used in the course of the investigations, and the hydrogen potentials of the same mixture made from different stock solutions were in good agreement. At least two, and often four different electrodes were employed in measuring the electromotive force of each buffer mixture. Both 0.1 *N* and saturated calomel electrodes were used, and were repeatedly checked against each other. A saturated potassium chloride salt bridge was employed without correction for the liquid-junction potential. The results have been calculated by means of the value 0.3380 for the 0.1 *N* calomel electrode at 18°. They are recorded in Table III.

The average hydrogen potential of each mixture studied is recorded in Table IV, and graphically represented in Fig. 1 in which the amount of the acid salt, KH_2PO_4, transformed into dipotassium phosphate is expressed as ordinate, and the P_H as abscissa. Curves are drawn through mixtures of the same concentration of total phosphate. This conventional method of representing the titration of a weak acid and a base reveals a family of curves. These are translated to more acid reactions in more concentrated solutions. Moreover, their shapes diverge more from that demanded by the simple form of the mass law, the more concentrated the

TABLE III

ELECTROMOTIVE-FORCE MEASUREMENTS UPON MIXTURES OF KH_2PO_4 AND K_2HPO_4

Total phosphate, (KH_2PO_4) + (K_2HPO_4), *M*	Mole fraction of total phosphate as K_2HPO_4						
	0.100	0.167	0.250	0.333	0.500	0.667	0.889
	Ratio of univalent to bivalent phosphate: $(KH_2PO_4)/(K_2HPO_4)$						
	9	5	3	2	1	$^1/_2$	$^1/_8$
	Hydrogen potentials of phosphate solutions						
0.0600	5.899	6.122	6.349	6.534	...	...	7.681
	5.898	6.153	6.351	6.511	...	...	7.713
	5.908	6.151	6.370	6.536	...	...	7.697
	...	6.142	6.359	6.520	...	...	7.703
	...	6.140	...	6.531	...	...	7.691
	5.902	6.142	6.357	6.526			7.697
.1200	5.797	6.030	...	6.453	6.740	7.036	7.633
	5.787	6.034	...	6.452	6.732	7.024	7.634
	5.810	6.041	...	6.460	6.735	7.033	...
	...	6.047	...	...	6.740	...	...
	...	...	...	...	6.740	...	...
	5.798	6.038		6.455	6.737	7.031	7.633
.3000	...	5.892	6.122	6.305	...	6.941	7.596
	...	5.892	6.125	6.311	...	6.938	7.594
	...	5.899	6.121	6.302	...	6.950	7.597
	...	...	...	...	...	...	7.583
	...	...	...	...	...	...	7.583
		5.894	6.123	6.306		6.943	7.591
.6000	5.445	5.709	5.989	6.206	6.567	6.907	7.617
	5.451	5.727	6.000	6.206	6.570	6.914	7.618
	5.469	5.725	5.995	...	6.572	6.926	...
	5.455	5.720	5.995	6.206	6.570	6.916	7.618
.9000	...	...	5.907	...	...	6.920	7.655
	...	...	5.898	...	...	6.912	7.656
	...	...	5.893	...	...	6.925	7.650
	...	...	...	...	...	...	7.658
			5.899			6.919	7.655
1.2000	5.220	5.514	5.838	6.104	6.519	6.935	...
	5.244	5.530	5.834	6.097	6.522	6.935	...
	5.237	5.522	5.819	6.086	...	...	...
	...	5.532	...	6.123	...	...	...
	...	5.520	...	6.072	...	...	...
	5.234	5.524	5.830	6.096	6.520	6.935	

phosphate solution. This divergence is greater in concentrated acid than in concentrated alkaline solutions. Mixtures consisting largely of dipotassium phosphate are changed but little in *P*H by dilution from a concentration of 1.2 to 0.06 *M*. This relative independence of the *P*H, in the neighborhood of 7.5 of relatively concentrated alkaline mixtures, is in marked contrast to the fan-like spread of the curves under such circumstances that the univalent salt predominates.

In order to analyze these data further the logarithms of the ratio of the concentrations of the univalent to the bivalent phosphate ions have been added to the *P*H of the respective mixtures. The result yields $P_{K'}$ (Table IV). This quantity varies from 6.188 to 6.856, indicating a change in ($\log \gamma_1/\gamma_2$) of 0.668. The activity coefficient of the one ion has therefore changed far more than the other. These data record both the influence of concentration and of valence upon the apparent dissociation constant. These influences may be conveniently expressed in terms of the change in activity coefficients, and considered in terms of the Debye-Hückel theory of inter-ionic forces.

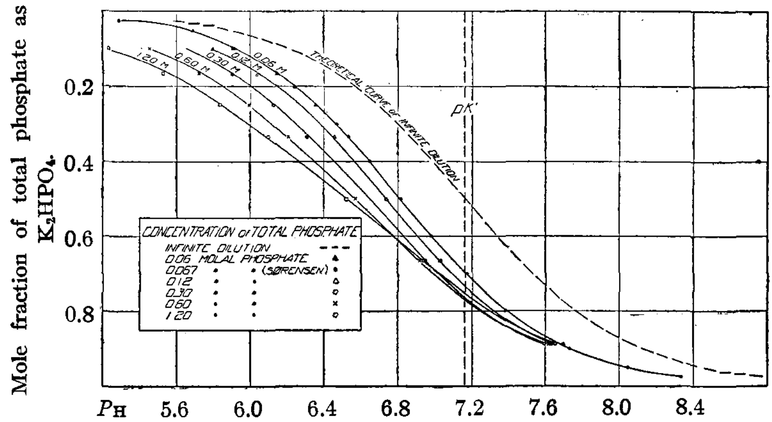

Fig. 1.—Titration curves of phosphate solutions of different concentrations.

The negative logarithm of the activity coefficient of an ion is proportional, in the Debye equation for very dilute solutions, to the square of its valence, *Z*, and the square root of the "ionic strength" of Lewis,[13] μ, expressed, however, as moles per liter, instead of moles per 1000 g. of water. The proportionality constant includes the absolute temperature, the Boltzmann constant and the dielectric constant of the solution. At ordinary temperatures these reduce to the value 0.5, and the equation becomes

$$-\log \gamma = 0.5\, Z^2\sqrt{\mu} \tag{10}$$

In the phosphate solutions studied, the ionic strength, μ, is equal to the concentration of the uni-univalent salt plus three times that of the uni-bivalent salt. Equation 10 holds only in such dilute solutions that μ is less than 0.01. None of Sørensen's solutions, and but three of those studied by Michaelis and Krüger, were as dilute as this. For more con-

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

centrated solutions the equations are extended by including a term for the mean effective diameter of the ions in solution, b, expressed as centimeters, and a term κ expressing the effective thickness of the ionic atmosphere, estimated by Debye as equal to $0.33 \times 10^{-8}\sqrt{\mu}$. The expanded equation becomes

$$-\log \gamma = 0.5\, Z^2\sqrt{\mu}/(1 + \kappa b) \tag{11}$$

In the phosphate mixtures under investigation there is always present a univalent and a bivalent ion. For the univalent ion Equation 11 becomes

$$-\log \gamma_1 = 0.5\sqrt{\mu}/(1 + \kappa b) \tag{12}$$

and for the bivalent

$$-\log \gamma_2 = 2.0\sqrt{\mu}/(1 + \kappa b) \tag{13}$$

Combining these equations yields

$$\log (\gamma_1/\gamma_2) = 1.5\sqrt{\mu}/(1 + \kappa b) \tag{14}$$

In this equation but one quantity is unknown, b, the mean effective diameter of the ions.

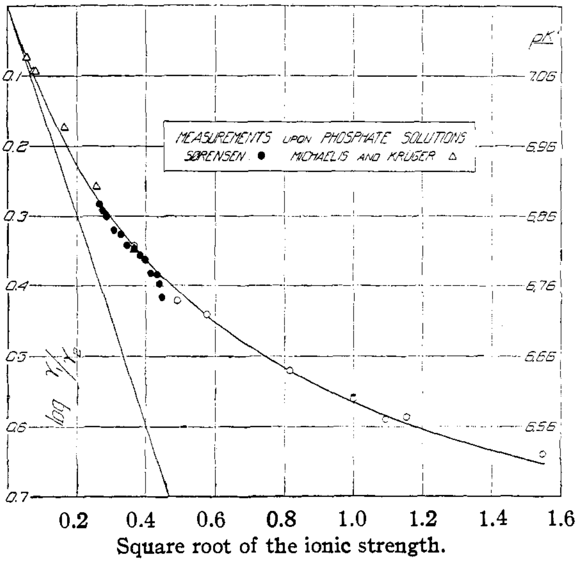

Fig. 2.

By substituting the above expression for the activity coefficients of the phosphate ions in Equation 8 we have

$$P_{H^+} + \log [(H_2PO_4^-)/(HPO_4^=)] = P_K - 1.5\sqrt{\mu}/(1 + \kappa b) = P_K' \tag{15}$$

All of the quantities upon the left side of this equation are known. In solutions containing equal concentrations of the univalent and the bivalent ions, such as are considered in Table II, the left side of the equation reduces to the experimentally determined electromotive-force measurement. These data are graphically represented in Fig. 2, the P_H or P_K' being plotted as ordinate, and the square root of the ionic strength as abscissa.

As $\sqrt{\mu}$ approaches 0, the activity coefficient approaches unity, and P_H approaches P_K. Graphical extrapolation of these data to infinitely dilute solution thus renders it possible to estimate P_K, and suggests a value of 7.16 for this constant.

Provided the term b in the above equations was negligible, all of the measurements would fall upon the straight line in Fig. 1 of slope 1.5. This term is negligible in few of the measurements considered, for divergence from the straight-line relationship occurs in very dilute solutions. Equation 15 may be solved for b by substituting the value for P_K determined by graphical extrapolation. This calculation yields 5×10^{-8} cm. for b, the apparent effective diameter of the ions in equimolecular mixtures of potassium dihydrogen phosphate and dipotassium phosphate.

If we substitute the value of b estimated above, Equation 15 becomes

$$P_{H^+} + \log\left[(H_2PO_4^-)/(HPO_4^=)\right] = P_K - 1.5\sqrt{\mu}/(1 + 1.65\sqrt{\mu}) \qquad (16)$$

The negative logarithms of the activity coefficients of equimolecular phosphate solutions have been calculated by means of this equation, and are recorded in next to the last column in Table II. These, added to the hydrogen potentials measured, yield constant values for P_K in solutions varying in molecular concentration from 0.00133 to 1.20.

The measurements made by Sørensen upon 0.0667 M phosphate solutions have also been graphically represented in Fig. 2, and have been calculated by means of Equation 15 in Table I. The values for P_K are in excellent agreement with each other and with those in Table II, despite the fact that b has being maintained constant, whereas the ratio of the univalent to the bivalent phosphate ion has varied widely. This greatly influenced the ionic strength, and this quantity dominates the Debye equation in moderately dilute solutions. The assumption of a slightly different value for b has but little influence upon P_K. Thus, reducing b from 5.0 to 4.5×10^{-8} cm., the average value of P_K is increased only from 7.152 to 7.164.

In the calculations to be made upon the more concentrated phosphate solutions which have been studied, the value 7.16 will be adopted. This is a new value for this constant. Michaelis and Krüger estimated P_K to be 7.10 by extrapolation of their electromotive-force measurements. The conductivity measurements of Abbott and Bray[14] yielded 1.95×10^{-7} as the second dissociation constant of phosphoric acid, P_K, equals 6.73. Our results suggest a value for Ka_2 of 0.69×10^{-7}.

From the results of the electromotive-force measurements upon more concentrated phosphate mixtures, values of log (γ_1/γ_2) have been computed. They are given in Table IV and graphically represented in Fig. 3. The change with concentration in log (γ_1/γ_2) was greatest in the mixtures containing the largest amounts of potassium dihydrogen phosphate. These much more nearly approach the straight-line relation which should

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[14] Abbott and Bray, THIS JOURNAL, **31**, 729 (1909).

TABLE IV

CALCULATION OF THE ACTIVITY COEFFICIENTS OF MIXTURES OF KH_2PO_4 AND K_2HPO_4

Total phosphate, (KH_2PO_4) + (K_2HPO_4) M	Mole fraction of total phosphate as K_2HPO_4						
	0.100	0.167	0.250	0.333	0.500	0.667	0.889
	Ratio of univalent to bivalent phosphate: $(KH_2PO_4)/(K_2HPO_4)$						
	9	5	3	2	1	$^1/_2$	$^1/_8$
	Hydrogen potentials of phosphate solutions						
0.0600	5.902	6.142	6.357	6.526	...	...	7.697
.1200	5.798	6.038	...	6.455	6.737	7.031	7.633
.3000	...	5.894	6.123	6.306	...	6.943	7.591
.6000	5.455	5.720	5.995	6.206	6.570	6.915	7.618
.9000	...	...	5.899	...	...	6.919	7.655
1.2000	5.234	5.524	5.830	6.096	6.520	6.935	...
	$P_H + \log [(KH_2PO_4)/(K_2HPO_4)] = P_{K'}$						
0.0600	6.856	6.841	6.834	6.827	...	...	6.794
.1200	6.752	6.737	...	6.756	6.737	6.730	6.730
.3000	...	6.593	6.600	6.607	...	6.642	6.693
.6000	6.409	6.419	6.472	6.507	6.570	6.614	6.715
.9000	...	...	6.376	...	...	6.618	6.752
1.2000	6.188	6.223	6.307	6.397	6.520	6.634	...
	$7.16 - P_{K'} = \log (\gamma_1/\gamma_2)$						
0.0600	0.304	0.319	0.326	0.333	...	...	0.366
.1200	.408	.423	...	.404	0.423	0.430	.430
.3000	...	.567	.560	.553	...	.518	.467
.6000	.751	.741	.688	.653	.590	.546	.445
.9000	...	...	.784	...	...	.542	.408
1.2000	.972	.937	.853	.763	.640	.526	...

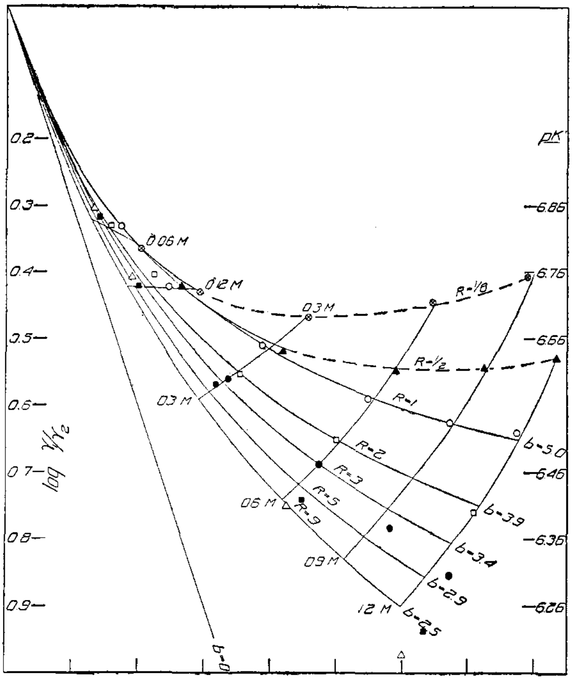
occur in dilute solutions than do equimolecular mixtures (Fig. 2, Table II), and suggest that a smaller value be ascribed to b in Equation 15. Values of b have been estimated by means of this equation for different mixtures of potassium dihydrogen phosphate and dipotassium phosphate. Values of $\log (\gamma_1/\gamma_2)$ have been calculated by means of these values of b, and are compared with those obtained experimentally in Table V. The curves in Fig. 3 are drawn on the basis of these values of b. They depart from the experimental points more in the more acid than in the neutral mixtures. Whether this is to be explained in terms of liquid-junction potentials in these relatively concentrated solutions cannot be decided at this time.

In more alkaline mixtures containing larger amounts of dipotassium phosphate, the activity coefficients again become larger—that is, their negative logarithms become smaller—in the concentrated solutions. No value of b can account for the form of these curves. Their change in direction suggests that the phenomenon known as "salting out" is involved, and demands that the salting-out term in the Debye-Hückel equation for concentrated solutions be taken into consideration.

An increase in the activity of many kinds of ions occurs in concentrated solutions, and is sometimes referred to as the "salting-out" effect. The negative logarithm of the activity coefficient accordingly diminishes, and it has been shown that this change is proportional to the molecular concentration, or to the ionic strength.[2] This component of inter-ionic action is thus accounted for by adding the terms proportional to the square root of the ionic strength, a term proportional to the molecular concentration, or the ionic strength in the expression for the activity coefficient of an ion (Equation 11).

$$-\log \gamma = 0.5\, Z^2\sqrt{\mu}/(1 + \kappa b) - Ks\mu \tag{17}$$

The proportionality constant, *Ks*, will, of course, have a different value if the salting-out effect is related to the molecular concentration, rather than to the ionic strength. The salting-out term becomes negligible in dilute solution since $\sqrt{\mu}$ is then great in comparison with μ. In concentrated solution μ becomes great in comparison with $\sqrt{\mu}$, and under these circumstances the salting-out term dominates the Debye-Hückel expression for the activity coefficient of an ion.



Square root of the ionic strength.

Fig. 3.—The activity coefficients of mixtures of KH_2PO_4 and K_2HPO_4.

Substituting this complete expression for the activity coefficient of an ion in the general form of the Henderson-Hasselbalch equation for buffer action yields

$$P_{H^+} - \log\,[(\text{salt})/(\text{acid})] = P_K - 0.5\, Z^2\sqrt{\mu}/(1 + \kappa b) + Ks\mu \tag{18}$$

The addition of a salting-out term renders it possible to calculate the activity coefficients of the most concentrated alkaline phosphate mixtures studied. The same value of *b* could be used that was deduced from the measurements upon equimolecular mixtures. There is no reason to suppose that a salting-out effect was not present in these mixtures, however, and somewhat closer agreement is obtained in the more alkaline mixtures, and future calculations simplified, if a somewhat smaller value of *b* is assumed; namely, 4.5 × 10^{-8} cm. The product κb then becomes $1.5\sqrt{\mu}$, and the complete equation

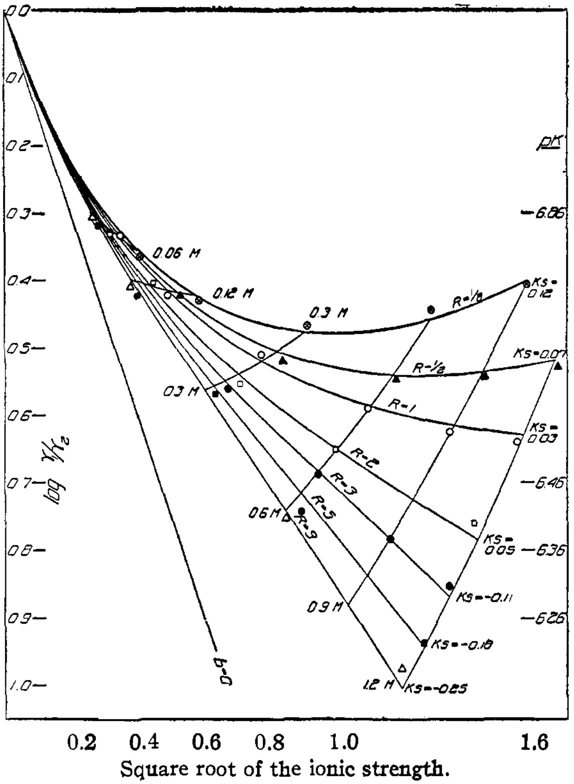


Fig. 4.—The activity coefficients of mixtures of KH_2PO_4 and K_2HPO_4.

$$P_{H^+} + \log\,[(H_2PO_4^-)/(HPO_4^{=})] = 7.16 - 1.5\sqrt{\mu}/(1 + 1.5\sqrt{\mu}) + Ks\mu \qquad (19)$$

The only unknown quantity in this equation is *Ks*, and this quantity has been evaluated for the different mixtures studied. *Ks* is a constant for different dilutions of the same mixture, but varies with the composition of the mixture (Fig. 5). Activity coefficients calculated by means of these values of *Ks* are reported in Table V, and are graphically represented by the curves in Fig. 4.

The agreement between the experimentally determined and the calculated activity coefficients is as satisfactory as the present constants and measurements warrant. Closer correspondence could, no doubt, be achieved if both b and Ks were allowed to vary, but this would render the calculations and the interpolations cumbersome. In the interest of further simplifying the estimation of the P_H of phosphate mixtures the suggestion was made[15] that b be retained constant in the acid mixtures as well, and the salting-out constant allowed to become negative in sign. Activity coefficients calculated on this basis are also recorded in Table V, and graphically represented in Fig. 4. Comparison of the three final columns in this table, one recording experimentally determined values of log (γ_1/γ_2), the other values calculated on the assumption either of a varying value of b, or of a constant value of b and a varying value of Ks, leaves little doubt that either procedure will suffice in dilute or in the more acid solutions. Both terms are necessary in the concentrated mixtures in which the bivalent ion predominates, and will suffice for all the systems studied. Figs. 3 and 4 represent the same comparison.

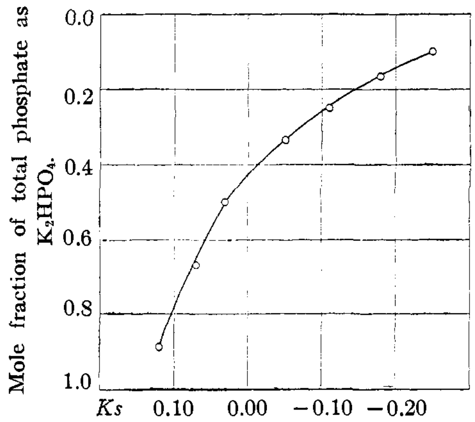


Fig. 5.

There is every reason to believe that the electrical size of the univalent may be smaller than that of the bivalent phosphate ion. The assumption that b is constant, and the explanation of the observed variation in log (γ_1/γ_2) by a term proportional to μ instead of to $\sqrt{\mu}$, must for the present be regarded as yielding an empirical interpolation formula. As such it is extremely useful. Of the terms on the right side of Equation 19 only one, Ks, changes with the ratio of potassium dihydrogen phosphate to dipotassium phosphate. The relation between the value of Ks and the mole fraction of dipotassium phosphate in the mixture is represented in Fig. 5. The remaining terms have been calculated for round values both of the molecular concentration and of the ionic strength and are recorded in Tables VI and VII. The interpolation tables give the apparent second dissociation constant, or rather its negative logarithm, $P_{K'}$, of the different phosphate mixtures. These tables make it possible to estimate the P_H

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[15] I am indebted to Dr. G. Scatchard for this suggestion, and further for calling my attention to the results of Åkerlöf [This Journal, **48**, 1160 (1926)] upon sulfate solutions which also yield negative salting-out terms.

TABLE V

A COMPARISON OF THE CALCULATION AND THE MEASUREMENT OF THE ACTIVITY COEFFICIENTS OF MIXTURES OF KH_2PO_4 AND K_2HPO_4

Mole fraction of total phosphate as K_2HPO_4	Total phosphate, $(KH_2PO_4) + (K_2HPO_4)$, M	Ionic strength of soln. $(KH_2PO_4) + 3(K_2HPO_4)$ μ	Log (γ_1/γ_2) calcd.[a] $\frac{1.5\sqrt{\mu}}{1+\kappa b\sqrt{\mu}}$	Log (γ_1/γ_2) calcd. $\frac{1.5\sqrt{\mu}}{1+1.5\sqrt{\mu}} - Ks\mu$[b]	Log (γ_1/γ_2) obs. $7.16 - P_K'$
0.100	0.0600	0.072	0.329	0.305	0.304
	.1200	.144	.433	.398	.408
	.6000	.720	.749	.740	.751
	1.2000	1.440	.904	1.003	.972
0.167	0.0600	0.080	.334	0.312	.319
	.1200	.160	.434	.404	.423
	.3000	.400	.591	.559	.567
	.6000	.800	.723	.717	.741
	1.2000	1.600	.858	.943	.937
0.250	0.0600	0.090	.337	.320	.326
	.3000	.450	.574	.552	.560
	.6000	.900	.689	.686	.688
	.9000	1.350	.756	.784	.784
	1.2000	1.800	.803	.866	.853
0.333	0.0600	0.100	.338	.327	.333
	.1200	.200	.426	.411	.404
	.3000	.500	.555	.540	.553
	.6000	1.000	.656	.650	.653
	1.2000	2.000	.752	.779	.763
0.500	0.0666	0.133	.342	.350	.343
	.1200	.240	.406	.417	.423
	.1666	.333	.443	.454	.439
	.3334	.667	.522	.531	.522
	.5000	1.000	.566	.570	.561
	.6000	1.200	.585	.586	.590
	.6666	1.333	.596	.594	.587
	1.2000	2.400	.653	.627	.640
0.667	0.1200	0.280	.415	.423	.430
	.3000	.700	.515	.508	.518
	.6000	1.400	.586	.542	.546
	.9000	2.100	.623	.538	.542
	1.2000	2.800	.649	.519	.526
0.889	0.0600	0.167	.358	.360	.366
	.1200	.334	.431	.424	.430
	.3000	.833	.528	.478	.467
	.6000	1.667	.594	.459	.445
	.9000	2.500	.630	.403	.408

[a] The following values of b have been employed for the phosphate mixtures varying from 0.1 to 0.889 in mole fraction of dipotassium phosphate: 2.5, 2.9, 3.4, 3.9, 5.0, 5.2 and 5.3 × 10^{-8} cm.

[b] The following values of Ks have been employed for the phosphate mixtures varying from 0.1 to 0.889 in mole fraction of dipotassium phosphate: −0.25, −0.18, −0.11, −0.05, +0.03, +0.07, +0.12.

of any buffer mixture of potassium dihydrogen phosphate and dipotassium phosphate of less than 1.2 *M*. They thus extend the tables given by Sørensen to more concentrated solutions. Solutions more dilute than those studied by Sørensen are accurately calculated by means of Equation 15 which contains no salting-out term.

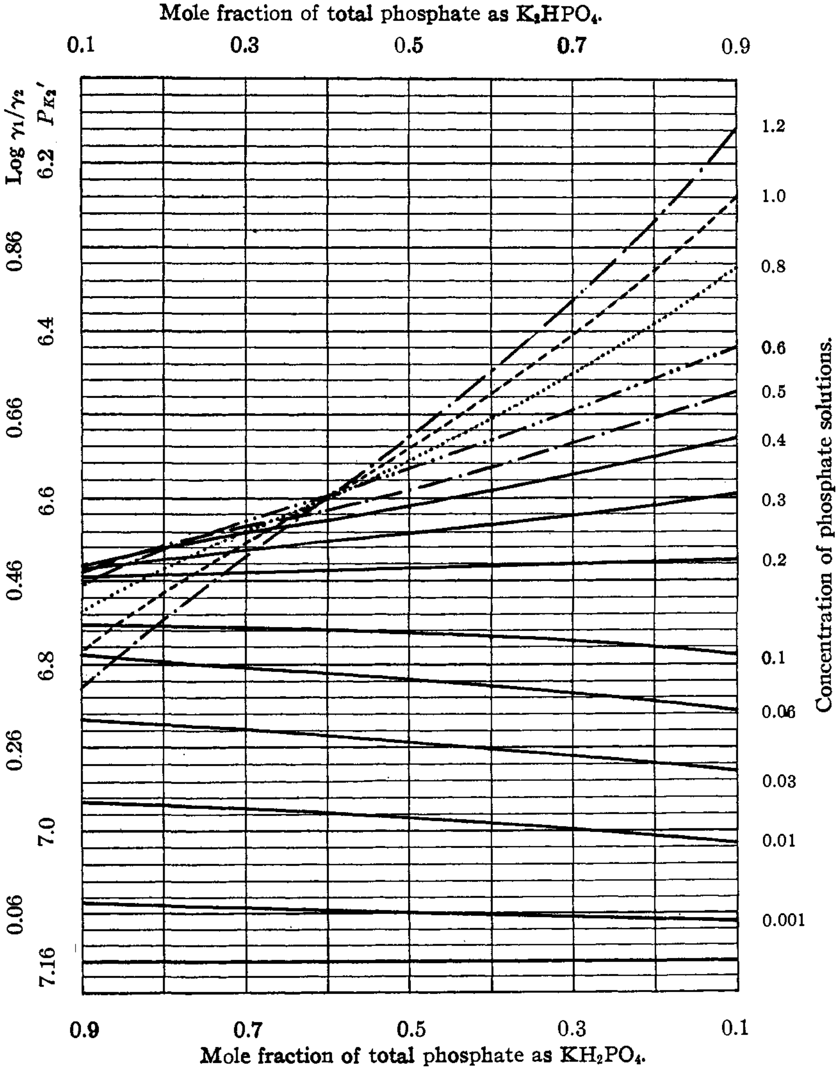

Fig. 6.

Graphical methods of estimating $P_{K'}$ are furnished by Figs. 6 and 7. The mole fraction of the total phosphate as potassium dihydrogen phosphate and as dipotassium phosphate is given as ordinates, and both log (γ_1/γ_2)

and $P_{K'}$ as abscissas. In Fig. 6 the curves represent the concentration of total phosphate. If a solution of potassium dihydrogen phosphate is employed so that (when partially neutralized with potassium hydroxide and brought to a given volume) its concentration corresponds to a curve in Fig. 6, then $P_{K'}$ is determined by the fraction of potassium dihydrogen phosphate transformed. If equivalent concentrations of potassium dihydrogen phosphate and potassium hydroxide are employed, the cc. of base per cc. of potassium dihydrogen phosphate give the mole fraction

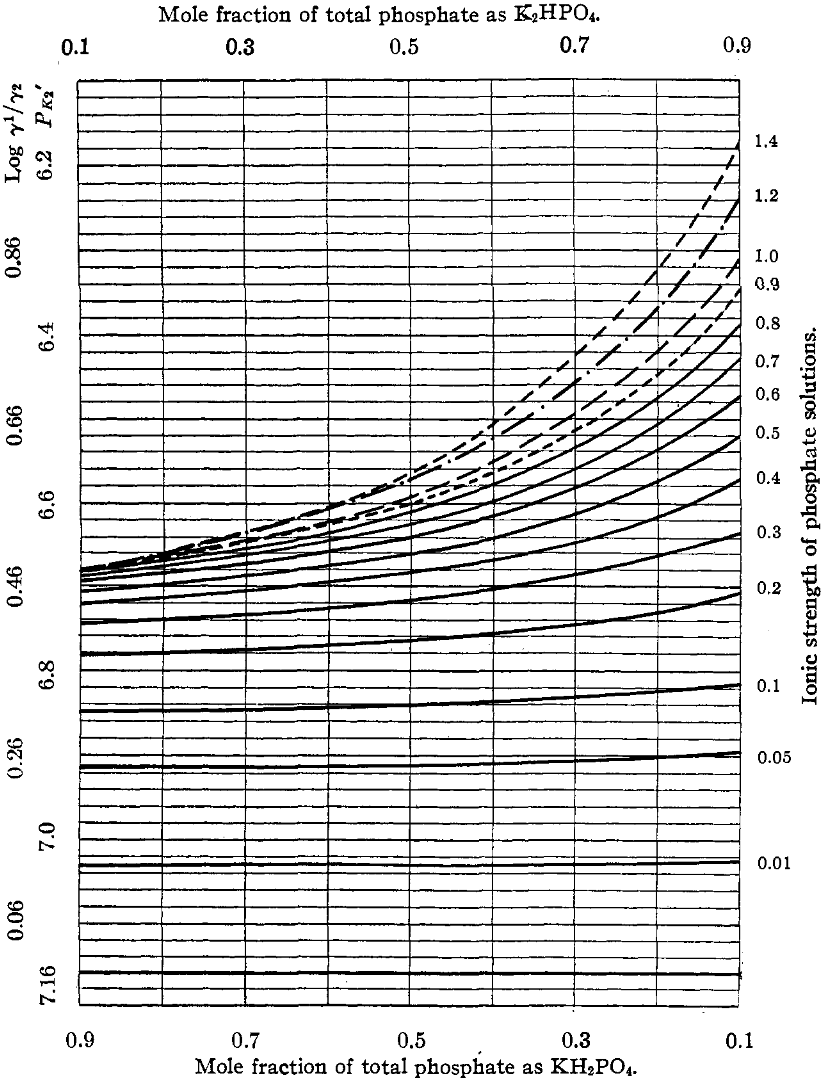

Fig. 7.

TABLE VI

INTERPOLATED VALUES OF THE ACTIVITY COEFFICIENTS OF MIXTURES OF KH_2PO_4 AND K_2HPO_4

Concn. of total phosphate, M	Mole fraction of total phosphate as K_2HPO_4								
	0.1 $Ks = -0.25$	0.2 $Ks = -0.14$	0.3 $Ks = -0.07$	0.4 $Ks = -0.01$	0.5 $Ks = +0.03$	0.6 $Ks = +0.06$	0.7 $Ks = +0.08$	0.8 $Ks = +0.10$	0.9 $Ks = +0.12$
	$\log (\gamma_1/\gamma_2) = 1.5\sqrt{\mu}/(1 + 1.5\sqrt{\mu}) - Ks\mu$								
0.1	0.372	0.379	0.386	0.391	0.395	0.400	0.405	0.407	0.408
.2	.484	.481	.481	.478	.475	.473	.472	.468	.462
.3	.564	.552	.544	.529	.520	.509	.502	.492	.478
.4	.630	.607	.590	.567	.549	.532	.518	.501	.479
.5	.688	.655	.629	.596	.570	.545	.526	.501	.472
.6	.740	.697	.662	.620	.586	.554	.528	.496	.458
.8	.835	.770	.719	.657	.607	.560	.521	.476	.423
1.0	.922	.836	.767	.686	.620	.558	.507	.448	.379
1.2	1.003	.895	.809	.710	.627	.551	.488	.414	.330
	$P_{K'} = 7.16 - \log (\gamma_1/\gamma_2)$								
0.1	6.788	6.781	6.774	6.769	6.765	6.760	6.755	6.753	6.752
.2	6.676	6.679	6.679	6.682	6.685	6.687	6.688	6.692	6.698
.3	6.596	6.608	6.616	6.631	6.640	6.651	6.658	6.668	6.682
.4	6.530	6.553	6.570	6.593	6.611	6.628	6.642	6.659	6.681
.5	6.472	6.505	6.531	6.564	6.590	6.615	6.634	6.659	6.688
.6	6.420	6.463	6.498	6.540	6.574	6.606	6.632	6.664	6.702
.8	6.325	6.390	6.441	6.503	6.553	6.600	6.639	6.684	6.737
1.0	6.238	6.324	6.393	6.474	6.540	6.602	6.653	6.712	6.781
1.2	6.157	6.265	6.351	6.450	6.533	6.609	6.672	6.746	6.830

of total phosphate as dipotassium phosphate. The corresponding abscissa is then read, and the P_H calculated by means of the mass law.

This figure illustrates how rapidly $P_{K'}$ departs from P_K in dilute solution. It also illustrates the change in the activity coefficient and therefore in the apparent dissociation constant brought about by change in valence. The direction of this change is different in dilute than in concentrated solution. At a concentration slightly less than 0.2 M, the activity coefficients of the ions in these solutions appear to be independent of the mole fraction of total phosphate as dipotassium phosphate. In more concentrated solutions, the phosphate ratio exerts the dominant influence. In mixtures consisting largely of potassium dihydrogen phosphate, $P_{K'}$ changes relatively little. The constancy of $P_{K'}$ under these circumstances as in those considered before, is related to the opposite sign and almost equal influence of the salting-out term, and of the term in the Debye-Hückel equation defining the decrease in activity with increasing ionic strength.

The curves in Fig. 7 represent solutions of equal ionic strength. This figure and Table VII supply a need felt in this Laboratory for a method of preparing buffer solutions of the same ionic strength and varying P_H, or of the same P_H and varying ionic strength. This need arose in the course

TABLE VII

INTERPOLATED VALUES OF THE ACTIVITY COEFFICIENTS OF MIXTURES OF KH_2PO_4 AND K_2HPO_4

$$\log (\gamma_1/\gamma_2) = 1.5\sqrt{\mu}/(1 + 1.5\sqrt{\mu}) - Ks\mu$$

Ionic strength of phosphate soln., μ	Mole fraction of total phosphate as K_2HPO_4								
	0.1 $Ks = -0.25$	0.2 $Ks = -0.14$	0.3 $Ks = -0.07$	0.4 $Ks = -0.01$	0.5 $Ks = +0.03$	0.6 $Ks = \pm 0.06$	0.7 $Ks = \pm 0.08$	0.8 $Ks = +0.10$	0.9 $Ks + +0.12$
0.1	0.347	0.336	0.329	0.323	0.319	0.316	0.314	0.312	0.310
.2	.451	.429	.415	.403	.395	.389	.385	.381	.377
.3	.526	.493	.472	.454	.442	.433	.427	.421	.415
.4	.587	.543	.515	.491	.475	.463	.455	.447	.439
.5	.640	.585	.550	.520	.500	.485	.475	.465	.455
.6	.688	.622	.580	.544	.520	.502	.490	.478	.466
.7	.732	.655	.606	.564	.536	.515	.501	.487	.473
.8	.773	.685	.629	.581	.549	.525	.509	.493	.477
.9	.812	.713	.650	.596	.560	.533	.515	.497	.479
1.0	.850	.740	.670	.610	.570	.540	.520	.500	.480
1.1	.886	.765	.688	.622	.578	.545	.523	.501	.479
1.2	.922	.790	.706	.634	.586	.550	.526	.502	.478
1.3	.956	.813	.722	.644	.592	.553	.527	.501	.475
1.4	.990	.836	.738	.654	.598	.556	.528	.500	.472
1.5	1.023	.858	.753	.663	.603	.558	.528	.498	.468
1.6	...	.879	.767	.671	.607	.559	.527	.495	.463
1.7	...	.900	.781	.679	.611	.560	.526	.492	.458
1.8	...	...	.794	.686	.614	.560	.524	.488	.452
1.9	...	...	.807	.693	.617	.560	.522	.484	.446
2.0	...	...	...	.700	.620	.560	.520	.480	.440
2.1	...	...	...	.706	.622	.559	.517	.475	.433
2.2	...	...	...	.712	.624	.558	.514	.470	.426
2.3	...	...	...	...	.626	.557	.511	.465	.419
2.4	...	...	...	...	.627	.555	.507	.459	.411
2.5	...	...	...	...	...	.553	.503	.453	.403
2.6	...	...	...	...	...	.552	.500	.448	.396
2.7	...	...	...	...	...	.549	.495	.441	.387
2.8	...	...	...	...	...	...	.491	.435	.379
2.9	...	...	...	...	...	...	.487	.429	.371
3.0	...	...	...	...	...	...	...	.422	.362

$$P_K = 7.16 - \log (\gamma_1/\gamma_2)$$

Ionic strength of phosphate soln., μ	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0.1	6.813	6.824	6.831	6.837	6.841	6.844	6.846	6.848	6.850
.2	6.709	6.731	6.745	6.757	6.765	6.771	6.775	6.779	6.783
.3	6.634	6.667	6.688	6.706	6.718	6.727	6.733	6.739	6.745
.4	6.573	6.617	6.645	6.669	6.685	6.697	6.705	6.713	6.721
.5	6.520	6.575	6.610	6.640	6.660	6.675	6.685	6.695	6.705
.6	6.472	6.538	6.580	6.616	6.640	6.658	6.670	6.682	6.694
.7	6.428	6.505	6.554	6.596	6.624	6.645	6.659	6.673	6.687
.8	6.387	6.475	6.531	6.579	6.611	6.635	6.651	6.667	6.683
.9	6.348	6.447	6.510	6.564	6.600	6.627	6.645	6.663	6.681
1.0	6.310	6.420	6.490	6.550	6.590	6.620	6.640	6.660	6.680
1.1	6.274	6.395	6.472	6.538	6.582	6.615	6.637	6.659	6.681
1.2	6.238	6.370	6.454	6.526	6.574	6.610	6.634	6.658	6.682

Table VII (*Concluded*)

Ionic strength of phosphate soln., μ	Mole fraction of total phosphate as K_2HPO_4								
	0.1 $Ks = -0.25$	0.2 $Ks = -0.14$	0.3 $Ks = -0.07$	0.4 $Ks = -0.01$	0.5 $Ks = +0.03$	0.6 $Ks = +0.06$	0.7 $Ks = +0.08$	0.8 $Ks = +0.10$	0.9 $Ks = +0.12$
1.3	6.204	6.347	6.438	6.516	6.568	6.607	6.633	6.659	6.685
1.4	6.170	6.324	6.422	6.506	6.562	6.604	6.632	6.660	6.688
1.5	6.137	6.302	6.407	6.497	6.557	6.602	6.632	6.662	6.692
1.6	...	6.281	6.393	6.489	6.553	6.601	6.633	6.665	6.697
1.7	...	6.260	6.379	6.481	6.549	6.600	6.634	6.668	6.702
1.8	...	...	6.366	6.474	6.546	6.600	6.636	6.672	6.708
1.9	...	...	6.353	6.467	6.543	6.600	6.638	6.676	6.714
2.0	...	...	...	6.460	6.540	6.600	6.640	6.680	6.720
2.1	...	...	...	6.454	6.538	6.601	6.643	6.685	6.727
2.2	...	...	...	6.448	6.536	6.602	6.646	6.690	6.734
2.3	...	...	...	...	6.534	6.603	6.649	6.695	6.741.
2.4	...	...	...	...	6.533	6.605	6.653	6.701	6.749
2.5	...	...	...	...	...	6.607	6.657	6.707	6.757
2.6	...	...	...	...	...	6.608	6.660	6.712	6.764
2.7	...	...	...	...	...	6.611	6.665	6.719	6.773
2.8	...	...	...	...	...	...	6.669	6.725	6.781
2.9	...	...	...	...	...	...	6.673	6.731	6.789
3.0	...	...	...	...	...	...	...	6.738	6.798

of a study of the solvent action of neutral salts upon certain proteins,[16] and led to the present investigation. The dependence of many chemical and biochemical phenomena upon electrical environment often renders it desirable, in studying the influence of reaction, to maintain constant the ionic strength of the solution.

Summary

1. The theory of buffer action has been extended by consideration of the activity coefficients of the ions into which the salts of weak acids dissociate.

2. Combination of the Henderson-Hasselbalch equation for buffer action with the Debye-Hückel equation for the activity coefficient of an ion yields $P_H - \log [(\text{salt})/(\text{acid})] = P_K - 0.5\sqrt{\mu}/(1 + \kappa b) + Ks\mu$.

3. The phosphate standards measured by Sørensen are described by the following form of this equation with an accuracy of ±0.01 P_H:

$$P_{H^+} + \log [(KH_2PO_4)/(K_2HPO_4)] = 7.16 - 1.5\sqrt{\mu}/(1 + 1.5\sqrt{\mu}).$$

4. The value of 7.16 for P_K is a new estimate of the second dissociation constant of phosphoric acid: $Ka_2 = 0.69 \times 10^{-7}$.

5. Electromotive-force measurements have been made upon mixtures of potassium dihydrogen phosphate and dipotassium phosphate of concentrations up to 1.2 *M*. These measurements upon concentrated buffer solutions may be characterized by the following equation, provided a "salting-out" term is added: $P_{H^+} + \log [(KH_2PO_4)/(K_2HPO_4)] = 7.16 - 1.5\sqrt{\mu}/(1 + 1.5\sqrt{\mu}) + Ks\mu$.

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[16] Cohn and Prentiss, *J. Gen. Physiol.*, Loeb Memorial Volume, **1926**.

6. Values of the salting-out constant, *Ks*, have been estimated for different mixtures of potassium dihydrogen phosphate and dipotassium phosphate.

7. Tables and graphs are given which facilitate the preparation of buffer solutions of the same ionic strength and varying *P*H or of the same *P*H and varying ionic strength.

BOSTON, MASSACHUSETTS

[CONTRIBUTION FROM THE PHYSICO-CHEMICAL LABORATORY OF THE POLYTECHNIC INSTITUTE OF COPENHAGEN]

THE DISSOCIATION CONSTANT OF NITRAMIDE

BY J. N. BRÖNSTED AND CECIL V. KING

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1. Introduction

In a kinetic study of the decomposition of nitramide into nitrous oxide and water,[1] $H_2N_2O_2 \longrightarrow N_2O + H_2O$, it was found that the reaction under ordinary conditions is divisible into two partial reactions, one of which is catalytic and the other "spontaneous" in nature. In sufficiently acid solution containing only strong acids, the spontaneous decomposition is the only measurable reaction independent of the concentration of the acid. In 0.01 and 0.001 *N* hydrochloric acid, for example, the velocities are practically identical. If the acidity is considerably lower the velocity increases, which may be due either to a spontaneous reaction of the nitramide anion, $HN_2O_2^- \longrightarrow N_2O + OH^-$, or to the catalytic effect of hydroxyl ions increasing in number as the acidity decreases.

For an exact interpretation of the phenomena of the catalytic and spontaneous decomposition of nitramide in solutions of small acidity—phenomena which are the subject of further study in this Laboratory—it would be valuable to know with some accuracy to what extent nitramide dissociates under the prevailing conditions. For that purpose we have carried out the present investigation to determine the dissociation constant of nitramide as an acid.

Immediately after the discovery of nitramide by Thiele and Lachman[2] in 1895, there arose some discussion on the strength of the compound as an acid. While Thiele and Lachman themselves, from consideration of the chemical properties of the substance, thought it a rather strong acid, Hantzsch and Kaufmann[3] concluded from conductivity measurements that it was only very weakly dissociated. They did not find it possible

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[1] (a) Brönsted and Pedersen, *Z. physik. Chem.*, **108**, 185 (1924). (b) Brönsted and Duus, *ibid.*, **117**, 299 (1925).

[2] Thiele and Lachman, *Ann.*, **288**, 267 (1895).

[3] Hantzsch and Kaufmann, *Ann.*, **292**, 317 (1896).