

# First Dissociation Constant of Phosphoric Acid From 0° to 60° C; Limitations of the Electromotive Force Method for Moderately Strong Acids

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An accurate determination by the electromotive-force method of the dissociation constant of an acid as strong as the first acidic group of phosphoric acid requires that the hydrogen-ion concentration be established with greater accuracy than is usually attainable. The uncertain quantity is the activity coefficient of hydrochloric acid in the particular mixture under study. It is shown that the calculation of this coefficient by the Debye-Hückel equation, which affords an adequate estimate of the small hydrogen-ion correction in buffer solutions composed of weak acids, fails to yield the desired accuracy for mixtures in which the acid is dissociated to an appreciable extent. In order to determine the common logarithm of the first dissociation constant of phosphoric acid with an accuracy believed to be  $\pm 0.005$  unit, the hydrogen-ion concentration of some of the buffer mixtures studied was kept at low levels by use of a large excess of potassium dihydrogen phosphate. Other solutions contained formic acid instead of hydrochloric acid, thereby lowering the hydrogen-ion concentration still further. In addition, particular attention was given to a choice of reasonable values for the activity coefficient used to estimate the hydrogen-ion correction.

By these means the first dissociation constant,  $K_1$ , of phosphoric acid was calculated from emf measurements of 71 phosphate buffer solutions, together with supplementary data from the literature for 18 additional solutions. The result from 0° to 60° C is given by

$$-\log K_1 = \frac{799.31}{T} - 4.5535 + 0.013486 T,$$

where  $T$  is the temperature in °K. The changes of heat content, entropy, and heat capacity for the dissociation of 1 mole of aqueous phosphoric acid in the standard state were found to be  $-7,650$  j,  $-66.8$  j deg $^{-1}$ , and  $-154$  j deg $^{-1}$ , respectively, at 25° C.

## 1. Introduction

Experience has proved that the electromotive-force method is well suited to the accurate determination of the dissociation constants of many weak acids and bases in aqueous solution. However, it is not generally recognized that the accuracy obtainable by this method diminishes with increasing strength of the acid or base. When approximately 10 percent or more of a weak acid is dissociated in solution, the uncertainty in establishing the true concentrations of the ionic and molecular species becomes so large that an exact determination of the dissociation constant is no longer possible.

Some years ago the author undertook to measure the electromotive force of a series of cells of the type



where  $m$  is molality, in an attempt to extend the investigation of Nims [1]<sup>1</sup> to other temperatures and buffer ratios. It was found to be impossible to obtain an accurate value for the first dissociation constant of phosphoric acid by analysis of the data for mixtures in which  $1 < x < 3$ . At the time it ap-

peared unlikely that the dissociation constant of an acid as strong as the first acidic group of phosphoric acid could be fixed with an accuracy of 0.01 in the common logarithm by this emf method, and the study was accordingly abandoned. The cause of the difficulty was readily apparent; the activity coefficient of hydrochloric acid in the buffer solutions must be known accurately in order to obtain the hydrogen-ion concentration and, consequently, the molalities of phosphoric acid and primary phosphate ion from which the buffer ratio is computed. This activity coefficient cannot readily be determined exactly, and use is usually made of estimated values, calculated perhaps by some form of the Debye-Hückel equation. This device is completely adequate for acids so weak that the total contribution of the hydrogen ion is small but is unsatisfactory, in general, when the pH of the buffer solution lies below 2.5 to 3.0.

It was realized later that two possibilities of reducing the hydrogen-ion concentration might be feasible, and the investigation was resumed. The first and simpler approach is to increase the value of  $x$  as greatly as is consistent with adequate buffer capacity and to estimate the activity coefficient from independent data. The second is to substitute a weak acid of known strength for the hydrochloric acid which, together with potassium dihydrogen phosphate, forms the buffer solutions, at the same

<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

time adding neutral chloride to furnish the desired concentration of that ion. This latter procedure complicates the analysis of the data, for the hydrogen-ion concentration is then fixed by two dissociative equilibria instead of one. However, it is possible to evaluate the constant for one of these equilibria when that for the other is known [2, 3, 4].

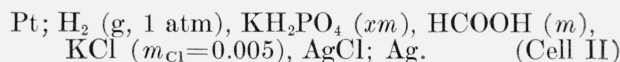
The results of both approaches are presented. Data for 46 mixtures of potassium dihydrogen phosphate and hydrochloric acid, in which  $x$  varied from 1.2 to 6, are reported. Twenty-five mixtures of potassium dihydrogen phosphate and formic acid (ratios 5:1 and 8:1) with added potassium chloride were also studied. The combined data, as well as those for 18 solutions studied by Nims [1], were used to evaluate  $K_1$  for phosphoric acid from 0° to 60° C with an estimated accuracy of  $\pm 0.005$  unit and to demonstrate the manner in which the accuracy of the electromotive-force method depends upon the strength of the acid studied.

## 2. Experimental Procedures and Results

Two different preparations of potassium dihydrogen phosphate were used. The first was prepared from reagent-grade salt by two recrystallizations from water. The salt was dried at 110° to 130°. A determination of the loss in weight suffered by weighed samples on ignition to metaphosphate indicated that the dried salt retained less than 0.02 percent of water. This portion of salt was used to prepare the 32 solutions grouped in series 1 through 4 (see table 1). The second preparation, from which the solutions of series 5 through 7 were made, was NBS Standard Sample 186-Ib.

The potassium chloride was a fused sample free of bromide [5]. Reagent-grade 90-percent formic acid was distilled twice in an all-glass still. Only the middle fraction was retained for redistillation or for use in the preparation of the solutions. Hydrochloric acid was diluted to a concentration of 6 molar and distilled in a similar fashion. An approximately 0.1-molar solution of the distilled acid was standardized gravimetrically by weighing silver chloride. The specific conductance of the water used in preparing the buffer solutions did not exceed  $1.0 \times 10^{-6}$  ohm<sup>-1</sup> cm<sup>-1</sup>. In view of the low pH of all of the buffer solutions, no special precautions were taken to exclude carbon dioxide, although dissolved air was removed by passage of nitrogen through the solutions before the cells were filled. In other respects, the experimental procedure was essentially the same as that followed in the determination of the second dissociation constant of phosphoric acid [6].

The solutions prepared from potassium dihydrogen phosphate and hydrochloric acid were grouped into five series according to the ratio of the molalities of the two components, that is,  $m_{\text{KH}_2\text{PO}_4} : m_{\text{HCl}}$ . This ratio was 1.2414:1 for series 1; 1.2683:1 for series 2; 1.5581:1 for series 3; 2.184:1 for series 4; and 6:1 for series 5. The cells containing the aqueous mixtures of potassium dihydrogen phosphate and formic acid can be represented as follows:



The molality of potassium chloride was 0.005 in each solution, but the ratio of the molality of potassium dihydrogen phosphate to that of formic acid was 5:1 in series 6 and 8:1 in series 7.

The measured electromotive force of each cell was corrected to a hydrogen partial pressure of 1 atm in the usual way. The pH value of each of the 71 buffer solutions at each temperature of measurement was computed by the defining equation<sup>2</sup>

$$\text{pH} \equiv -\log (f_{\text{H}} f_{\text{Cl}} m_{\text{H}}) = \frac{(E - E^\circ)F}{2.3026 RT} + \log m_{\text{Cl}}, \quad (1)$$

in which  $f$  represents a molal activity coefficient;  $E$  and  $E^\circ$  are the electromotive force and standard potential, respectively, of the cell at the appropriate absolute temperature,  $T$ ; and  $R$  and  $F$  are the gas constant and the faraday. Values of  $E^\circ$  and  $2.3026RT/F$  in absolute volts are summarized in an earlier publication [7]. The pH values are listed in table 1.

## 3. Calculation of the Dissociation Constant: Series 1 to 5.

### 3.1. The Conventional Electromotive-Force Method

Inasmuch as the hydrogen-ion concentration in the buffer solutions of series 1 to 5 can be expressed in terms of the first dissociation equilibrium of phosphoric acid, pH can be related directly through the mass law with  $K_1$ , the first dissociation constant, and the molalities and activity coefficients of phosphoric acid and primary phosphate ion. Making the substitution in eq 1 and rearranging gives the formal expression for  $\log K_1$ :

$$-\log K_1 = \text{pH} + \log \frac{m_{\text{H}_3\text{PO}_4}}{m_{\text{H}_2\text{PO}_4^-}} + \log \frac{f_{\text{H}_3\text{PO}_4} f_{\text{Cl}}}{f_{\text{H}_2\text{PO}_4^-}}, \quad (2)$$

This substitution is the basis of the method of determining the dissociation constant, as outlined by Roberts [8] and by Harned and Ehlers [9]. The solutions of series 1 to 5 (cell I) were composed of hydrochloric acid,  $m$  moles/1,000 g of water, and potassium dihydrogen phosphate,  $xm$  moles/1,000 g of water. Because of the appreciable dissociation of the phosphoric acid formed, the reaction between these two components is incomplete, and at equilibrium

$$m_{\text{H}_3\text{PO}_4} = m - m_{\text{H}}, \quad (3)$$

and

$$m_{\text{H}_2\text{PO}_4^-} = m(x-1) + m_{\text{H}}. \quad (4)$$

The hydrogen-ion concentration needed to compute the concentrations of the two phosphate species

<sup>2</sup> For convenience, the charges carried by hydrogen ( $\text{H}^+$ ) and chloride ( $\text{Cl}^-$ ) ions will not be indicated. Likewise,  $m_{\text{H}}$  will represent the total concentration of hydrogen ion, whether hydrated or not.

can be obtained, in principle, either from the mass law by successive arithmetical approximations with a provisional dissociation constant or from pwH. In both cases activity coefficients must be estimated, and simplicity favors the latter:

$$-\log m_{\text{H}} = \text{pwH} + \log f_{\text{H}} f_{\text{Cl}}. \quad (5)$$

Inasmuch as it is not possible to obtain the exact value of  $f_{\text{H}} f_{\text{Cl}}$ , it is convenient to define an "apparent"  $m_{\text{H}}$ , namely  $m'_{\text{H}}$ , that approaches the true  $m_{\text{H}}$  at low ionic strengths:

$$-\log m'_{\text{H}} = \text{pwH} - \frac{2A\sqrt{\mu}}{1 + Ba^*\sqrt{\mu}}. \quad (5a)$$

The Debye-Hückel equation has been substituted for  $\log f_{\text{H}} f_{\text{Cl}}$  on the right-hand side of eq 5a;  $A$  and  $B$  are constants at a particular temperature [10],

TABLE 1. pwH from 0° to 50° for aqueous mixtures of potassium dihydrogen phosphate and hydrochloric acid and for aqueous mixtures of potassium dihydrogen phosphate, formic acid, and potassium chloride

$m_{\text{KH}_2\text{PO}_4}$	pwH at (°C)—												
	0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°	55°	60°
Series 1. $\text{KH}_2\text{PO}_4:\text{HCl}=1.2414:1$													
0.13818	1.7960	1.8072	1.8180	1.8294	1.8418	1.8529	1.8729	1.8891	1.9050	1.9233	1.9415	1.9583	1.9772
.12289	1.8236	1.8337	1.8439	1.8556	1.8678	1.8784	1.8965	1.9119	1.9278	1.9462	1.9637	1.9825	2.0027
.08765	1.8899	1.8993	1.9091	1.9195	1.9309	1.9436	1.9557	1.9701	1.9835	1.9999	2.0186	2.0363	2.0544
.04705	2.0219	2.0307	2.0389	2.0484	2.0568	2.0683	2.0813	2.0945	2.1065	2.1219	2.1367	2.1521	2.1680
.02870	2.1331	2.1414	2.1491	2.1572	2.1665	2.1763	2.1880	2.1997	2.2123	2.2264	2.2402	2.2539	2.2682
.02427	2.1733	2.1815	2.1886	2.1967	2.2050	2.2143	2.2252	2.2367	2.2482	2.2619	2.2751	2.2884	2.3024
.010572	2.3877	2.3939	2.3996	2.4053	2.4121	2.4192	-----	-----	-----	-----	-----	-----	-----
Series 2. $\text{KH}_2\text{PO}_4:\text{HCl}=1.2683:1$													
0.14117	1.8099	1.8197	1.8303	1.8428	1.8552	1.8693	-----	-----	-----	-----	-----	-----	-----
.11333	1.8595	1.8690	1.8796	1.8915	1.9029	1.9155	-----	-----	-----	-----	-----	-----	-----
.08642	1.9113	1.9206	1.9296	1.9440	1.9502	1.9638	-----	-----	-----	-----	-----	-----	-----
.06759	1.9620	1.9709	1.9801	1.9907	2.0010	2.0123	2.0267	2.0425	2.0577	2.0743	2.0908	2.1079	2.1250
.05386	2.0102	2.0184	2.0270	2.0374	2.0470	2.0587	2.0714	2.0863	2.1001	2.1160	2.1325	2.1491	2.1661
.03196	2.1221	2.1295	2.1372	2.1461	2.1551	2.1662	2.1774	2.1902	2.2021	2.2179	2.2317	2.2468	2.2628
.015488	2.2978	2.3038	2.3097	2.3171	2.3236	2.3322	2.3417	2.3525	2.3632	2.3755	2.3880	2.4004	2.4128
.011046	2.3888	2.3926	2.3976	2.4037	2.4106	2.4189	2.4269	2.4356	2.4449	2.4562	2.4671	2.4779	2.4883
Series 3. $\text{KH}_2\text{PO}_4:\text{HCl}=1.5581:1$													
0.17343	-----	-----	-----	-----	-----	2.0139	2.0334	2.0532	2.0727	2.0945	2.1165	2.1382	2.1603
.13787	1.9825	1.9958	2.0066	2.0206	2.0351	2.0497	2.0696	2.0899	2.1084	2.1301	2.1500	2.1710	2.1934
.11447	2.0139	2.0256	2.0363	2.0498	2.0634	2.0771	2.0966	2.1148	2.1332	2.1545	2.1727	2.1938	2.2157
.09439	2.0437	2.0555	2.0667	2.0798	2.0916	2.1058	2.1259	2.1450	2.1621	2.1826	2.2009	2.2205	2.2417
.05590	2.1352	2.1463	2.1548	2.1664	2.1775	2.1892	2.2047	2.2218	2.2372	2.2551	2.2712	2.2895	2.3085
.04646	2.1685	2.1771	2.1871	2.1977	2.2089	2.2209	2.2382	2.2571	2.2724	2.2921	2.3023	2.3204	2.3394
.04230	2.1865	2.1974	2.2048	2.2161	2.2274	2.2385	2.2560	2.2733	2.2886	2.3059	2.3189	2.3369	2.3559
.019571	2.3437	2.3506	2.3602	2.3692	2.3790	2.3885	2.4013	2.4156	2.4276	2.4416	2.4536	2.4681	2.4834
Series 4. $\text{KH}_2\text{PO}_4:\text{HCl}=2.184:1$													
0.2437	2.1600	2.1758	2.1902	2.2079	2.2256	2.2451	2.2641	2.2855	2.3075	2.3331	2.3605	2.3865	2.4131
.18880	2.1875	2.2033	2.2164	2.2340	2.2516	2.2703	2.2896	2.3078	2.3263	2.3539	2.3804	2.4053	2.4314
.17753	2.1970	2.2107	2.2246	2.2412	2.2583	2.2764	2.2963	2.3171	2.3359	2.3636	2.3860	2.4127	2.4388
.11627	2.2450	2.2580	2.2700	2.2860	2.3031	2.3189	2.3384	2.3576	2.3741	2.3988	2.4252	2.4481	2.4732
.10961	2.2494	2.2622	2.2744	2.2898	2.3054	2.3233	2.3438	2.3599	2.3801	2.4045	2.4283	2.4524	2.4776
.07075	2.3048	2.3174	2.3286	2.3433	2.3577	2.3736	2.3908	2.4090	2.4275	2.4494	2.4712	2.4933	2.5163
.06118	2.3264	2.3366	2.3476	2.3614	2.3747	2.3898	2.4071	2.4259	2.4457	2.4662	2.4877	2.5075	2.5316
.04076	2.3857	2.3942	2.4043	2.4174	2.4305	2.4437	2.4592	2.4757	2.4923	2.5122	2.5328	2.5527	2.5734
.019761	-----	-----	-----	-----	-----	2.5649	-----	-----	-----	-----	-----	-----	-----
Series 5. $\text{KH}_2\text{PO}_4:\text{HCl}=6:1^a$													
0.3638	-----	-----	-----	-----	-----	2.8645	-----	-----	-----	-----	-----	-----	-----
.3008	2.7762	2.7921	2.8083	2.8259	2.8468	2.8685	2.8921	2.9168	2.9419	2.9693	2.9967	-----	-----
.2435	-----	-----	-----	-----	-----	2.8756	-----	-----	-----	-----	-----	-----	-----
.2403	2.7850	2.7966	2.8139	2.8331	2.8542	2.8757	2.8980	2.9220	2.9466	2.9746	3.0001	-----	-----
.19788	-----	-----	-----	-----	-----	2.8835	-----	-----	-----	-----	-----	-----	-----
.18084	2.7953	2.8094	2.8255	2.8442	2.8631	2.8839	2.9026	2.9267	2.9505	2.9780	3.0034	-----	-----
.13710	-----	-----	-----	-----	-----	2.8959	-----	-----	-----	-----	-----	-----	-----
.13590	-----	-----	-----	-----	-----	2.8980	-----	-----	-----	-----	-----	-----	-----
.11932	2.8157	2.8291	2.8438	2.8611	2.8793	2.8995	2.9169	2.9394	2.9626	2.9894	3.0135	-----	-----
.10348	-----	-----	-----	-----	-----	2.9104	-----	-----	-----	-----	-----	-----	-----
.09540	-----	-----	-----	-----	-----	2.9133	-----	-----	-----	-----	-----	-----	-----
.08354	-----	-----	-----	-----	-----	2.9219	-----	-----	-----	-----	-----	-----	-----
.05932	-----	-----	-----	-----	-----	2.9431	-----	-----	-----	-----	-----	-----	-----
.05927	2.8655	2.8778	2.8904	2.9053	2.9216	2.9404	2.9576	2.9789	2.9992	3.0234	3.0463	-----	-----

<sup>a</sup> The 5 solutions for which pwH from 0° to 50° is listed make up series 5a; the remainder are in series 5b;

TABLE 1. *pwH from 0° to 50° for aqueous mixtures of potassium dihydrogen phosphate and hydrochloric acid and for aqueous mixtures of potassium dihydrogen phosphate, formic acid, and potassium chloride—Continued*

$m_{\text{KH}_2\text{PO}_4}$	pwH at (°C)—													
	0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°	55°	60°	
Series 6. $\text{KH}_2\text{PO}_4:\text{HCOOH}=5:1$ ; $\text{KCl}=0.005m$														
0.3018	-----	-----	-----	-----	-----	3.3886	-----	-----	-----	-----	-----	-----	-----	-----
.2417	3.3526	-----	-----	-----	-----	3.3872	-----	-----	-----	-----	3.4542	-----	-----	-----
.19889	-----	-----	-----	-----	-----	3.3833	-----	-----	-----	-----	-----	-----	-----	-----
.19227	-----	-----	-----	-----	-----	3.3848	-----	-----	-----	-----	-----	-----	-----	-----
.16137	-----	-----	-----	-----	-----	3.3899	-----	-----	-----	-----	-----	-----	-----	-----
.14376	-----	-----	-----	-----	-----	3.3919	-----	-----	-----	-----	-----	-----	-----	-----
.12916	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	3.4617	-----	-----	-----
.12892	3.3561	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
.12694	-----	-----	-----	-----	-----	3.3896	-----	-----	-----	-----	-----	-----	-----	-----
.11013	-----	-----	-----	-----	-----	3.3938	-----	-----	-----	-----	-----	-----	-----	-----
.09661	-----	-----	-----	-----	-----	3.3946	-----	-----	-----	-----	-----	-----	-----	-----
.09320	-----	-----	-----	-----	-----	3.3945	-----	-----	-----	-----	-----	-----	-----	-----
.08812	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	3.4695	-----	-----	-----
.08791	3.3629	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
.08357	-----	-----	-----	-----	-----	3.3994	-----	-----	-----	-----	-----	-----	-----	-----
.06736	-----	-----	-----	-----	-----	3.4056	-----	-----	-----	-----	-----	-----	-----	-----
.06688	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	3.4764	-----	-----	-----
.06669	3.3714	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
.05390	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	3.4840	-----	-----	-----
.05371	3.3812	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
Series 7. $\text{KH}_2\text{PO}_4:\text{HCOOH}=8:1$ ; $\text{KCl}=0.005m$														
0.3867	-----	-----	-----	-----	-----	3.5121	-----	-----	-----	-----	-----	-----	-----	-----
.19331	-----	-----	-----	-----	-----	3.5121	-----	-----	-----	-----	-----	-----	-----	-----
.12885	-----	-----	-----	-----	-----	3.5148	-----	-----	-----	-----	-----	-----	-----	-----
.09664	-----	-----	-----	-----	-----	3.5197	-----	-----	-----	-----	-----	-----	-----	-----
.06442	-----	-----	-----	-----	-----	3.5338	-----	-----	-----	-----	-----	-----	-----	-----

and  $a^*$  is the ion-size parameter. The ionic strength,  $\mu$ , of these mixtures is given by <sup>3</sup>

$$\mu = xm + m_{\text{H}} \quad (6)$$

The Debye-Hückel equation suggests that the last term of eq 2 will be zero, or nearly so, in the region of low ionic strengths. Terms of this sort are indeed found to be small at low concentrations and to vary linearly with ionic strength in the region of moderate concentrations. The evaluation of  $\log K_1$  is accordingly made by extrapolation to infinite dilution of the apparent  $\log K_1$ , or  $\log K'_1$ , derived from the following equation:

$$-\log K'_1 = \text{pwH} + \log \frac{m - m'_{\text{H}}}{m(x-1) + m'_{\text{H}}} \quad (7)$$

### 3.2. Limitations of the Conventional Method as Applied to Moderately Strong Acids

The procedure outlined in the foregoing section may be termed "the conventional emf method." The choice of  $a^*$  in eq 5a is somewhat arbitrary, being guided only by our knowledge of what constitutes a "reasonable" ion size, for the magnitude of this parameter is often of the same order as the ionic diameter in angstrom units. If  $-\log K$  for the acid exceeds 3, the particular choice of  $a^*$ , within the

reasonable range 2 to 8, is of little concern, for  $m_{\text{H}}$  is small compared to  $m$ , and relatively large errors in  $m'_{\text{H}}$  alter the last term of eq 7 but slightly. However, when the acid is as strong as the first dissociation step of phosphoric acid, for which  $-\log K_1$  is about 2.12 [1],  $m'_{\text{H}}$  is quite large and the choice of  $a^*$  becomes an important consideration.

Figure 1 demonstrates the failure of the extrapolation lines computed with various values of  $a^*$  to converge at an ionic strength of zero. The open circles are the data at 25° for series 1, the most acidic solutions included in the study. The values of  $a^*$  (eq 5a) are indicated at the right of each line. When  $a^*=0$ , the last term of eq 5a reduces to the Debye-Hückel limiting law. The dots in figure 1 were computed from the data of series 5a at 25°. The ratio of phosphate to hydrochloric acid is considerably higher than in series 1. Accordingly  $m'_{\text{H}}$  is smaller, and the choice of  $a^*$  has less effect upon the result. It is unlikely that the difficulty could be resolved and the lines made to converge by obtaining data at lower ionic strengths, for the degree of dissociation of the phosphoric acid would be inevitably increased. Furthermore, still higher ratios of primary phosphate to hydrochloric acid might introduce uncertainties in the extrapolation, and it seems advisable to avoid them.

### 3.3. Estimation of the Activity Coefficient

Various possible means of choosing the correct extrapolation line were next considered. Up to this point the determination of the dissociation constant

<sup>3</sup>  $\mu = \frac{1}{2} \sum m_i z_i^2$ , where  $m_i$  and  $z_i$  are, respectively, the molality and charge of the ion of species  $i$ .

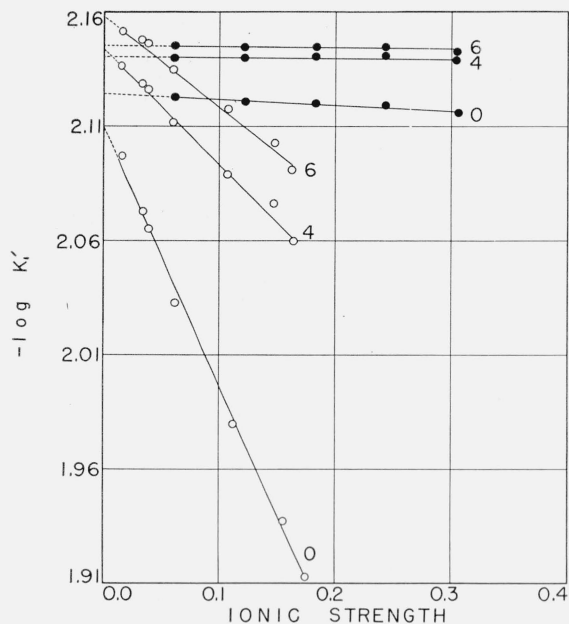


FIGURE 1. Effect of  $a^*$  on the extrapolation at two different ratios of potassium dihydrogen phosphate to hydrochloric acid.

The value of  $a^*$  used appears beside each line. Circles represent data of series 1; dots are for series 5a.

is completely rigorous, and it is unfortunate that a partially nonthermodynamic step need be introduced. As eq 5 suggests, different extrapolation lines with different intercepts exist because the correct value of  $f_{\text{H}}f_{\text{Cl}}$  in each buffer solution is unknown. Unfortunately, the required activity coefficients cannot readily be determined. Nevertheless, the most probable range of  $a^*$  (eq 5a) can be narrowed somewhat in the light of the values that have been found to describe the behavior of the activity coefficient of hydrochloric acid and  $f_{\text{H}}f_{\text{Cl}}$  in other mixtures of similar composition. Thus  $\log f_{\text{H}}f_{\text{Cl}}$  in aqueous solutions of hydrochloric acid with ionic strengths less than 0.2 is represented by the last term of eq 5a with  $a^*=6.0$ . If the hydrochloric acid is replaced partially or even completely by alkali chloride without altering the ionic strength, the activity coefficient term,  $f_{\text{H}}f_{\text{Cl}}$ , decreases [11].<sup>4</sup> To represent these new, lower activity coefficients, a lower value of  $a^*$  is necessary. Accordingly,  $a^*$  for  $f_{\text{H}}f_{\text{Cl}}$  is found to approach a limit of 4.6 to 5.4 in pure solutions of sodium chloride and potassium chloride with ionic strengths of 0.2 or less. The principles of ionic interaction lead us to expect, in this instance, a larger specific effect of cations than of anions. Hence, it is possible that the activity coefficient of hydrochloric acid in a mixture of the acid and primary potassium phosphate does not differ greatly from that in a pure solution of potassium chloride. The most probable range of  $a^*$  can be fixed at 4 to 6 and a value of 5 chosen as a first approximation.

<sup>4</sup> Except possibly with lithium chloride, for which some measurements show a small increase.

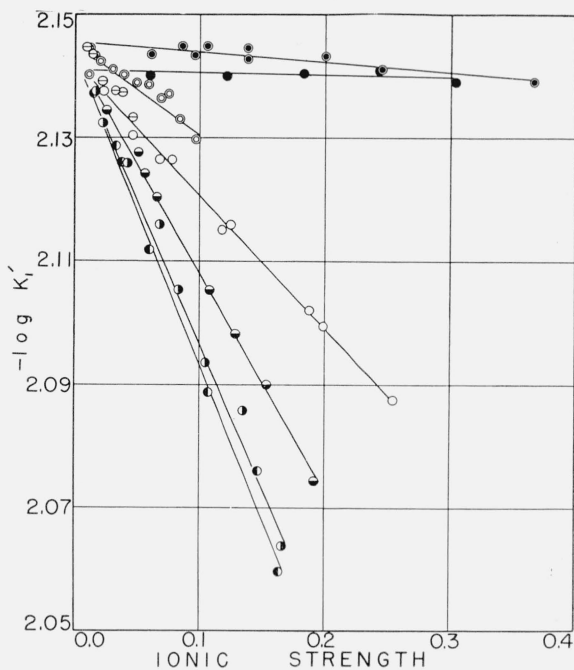


FIGURE 2. Plot of  $-\log K'_1$  at 25° as a function of ionic strength.

A value of 4 was used for  $a^*$  in equation 5a. ●=series 1; ○=series 2; ◐=series 3; ◑=series 4; ⊖=Nims series 1; ⊕=Nims series 2,3; ●=series 5a; ◑=series 5b.

Two separate calculations of  $-\log K'_1$  were made at 0°, 25°, and 50° by eq 7. A value of 4 for  $a^*$  (eq 5a) was used for the first and 6 for the second. The data of series 1 to 5 were supplemented by those of Nims [1], who studied three series of six solutions each. The ratios of the molalities of potassium dihydrogen phosphate to hydrochloric acid in the latter were, respectively, 2.071:1 (series N1); 3.102:1 (series N2); and 3.079:1 (series N3). Two or three approximations were necessary in computing  $\log K'_1$ , as the contribution of the hydrogen ion to the total ionic strength was considerable. The extrapolation lines for  $a^*=4$  are shown in figure 2.

#### 4. Calculation of the Dissociation Constant: Series 6 and 7

In order to reduce the hydrogen-ion concentration below the level in the mixtures containing 6 moles of potassium dihydrogen phosphate to 1 of hydrochloric acid (series 5), two series of solutions were prepared from potassium dihydrogen phosphate and formic acid. Each buffer solution was also 0.005 molal with respect to potassium chloride. The formal expression relating the product of the dissociation constants for the two acids to the emf or pH has been derived in another article [4]:

$$-1/2 \log K_1 K_F = \text{pWH} + 1/2 \log \frac{m_{\text{H}_3\text{PO}_4} m_{\text{HFO}}}{m_{\text{H}_2\text{PO}_4^-} m_{\text{FO}^-}} + 1/2 \log \frac{f_{\text{H}_3\text{PO}_4} f_{\text{HFO}} f_{\text{Cl}}^2}{f_{\text{H}_2\text{PO}_4^-} f_{\text{FO}^-}} \quad (8)$$

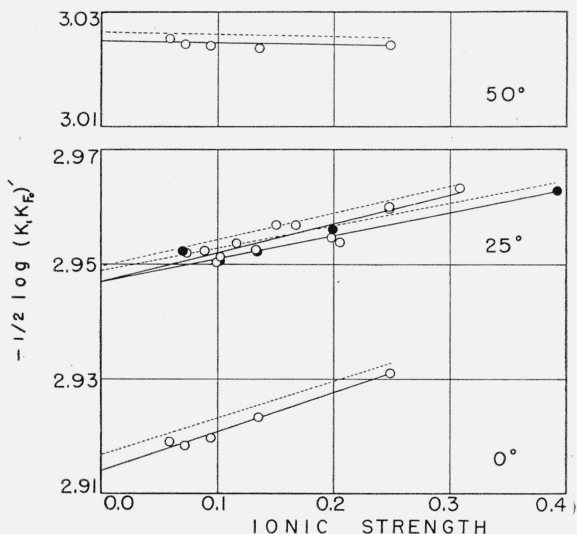


FIGURE 3. Plot of  $-\frac{1}{2} \log (K_1 K_F)'$  at  $0^\circ$ ,  $25^\circ$ , and  $50^\circ$  as a function of ionic strength.

Circles (series 6) and dots (series 7) were calculated from the experimental data, using  $a^*=4$ , and the solid lines were fitted to them. The broken lines indicate the shift that would result from using  $a^*=6$ .

Inasmuch as  $K_F$ , the dissociation constant of formic acid ( $\text{HFO}$ ), is well known from  $0^\circ$  to  $60^\circ$  [12, 13], the value of  $K_1$  can be derived from the product,  $K_1 K_F$ .

If  $m_1$  represents the molality of potassium dihydrogen phosphate and  $m_2$  that of formic acid,

$$m_{\text{H}_3\text{PO}_4} = m_{\text{F}_0^-} - m_{\text{H}}, \quad (9)$$

$$m_{\text{HF}_0} = m_2 - m_{\text{F}_0^-}, \quad (10)$$

and

$$m_{\text{H}_2\text{PO}_4^-} = m_1 + m_{\text{H}} - m_{\text{F}_0^-}. \quad (11)$$

Furthermore, the last term of eq 8, which becomes zero at infinite dilution, is a linear function of ionic strength at low and moderate concentrations. Hence,  $\log K_1 K_F$  can be evaluated conveniently by extrapolation to infinite dilution of the apparent quantity,  $\log (K_1 K_F)'$ , computed by the equation

$$-\log (K_1 K_F)' = \text{pWH} + \frac{1}{2} \log \frac{(m_2 + m_{\text{H}}' - m_{\text{F}_0^-}') - m_2 m_{\text{H}}' / m_{\text{F}_0^-}'}{m_1 + m_{\text{H}}' - m_{\text{F}_0^-}'} \quad (12)$$

The calculation of the formate molality rests on the assumed equality of  $f_{\text{H}} f_{\text{Cl}}$  and  $f_{\text{H}} f_{\text{F}_0^-} / f_{\text{HF}_0}$  at moderate concentrations and is hence given the prime mark denoting an apparent or inexact quantity:

$$m_{\text{F}_0^-}' = m_2 y / (1 + y), \quad (13a)$$

where

$$\log y = \text{pWH} + \log K_F. \quad (13b)$$

Equation 5a is used once more to compute  $m_{\text{H}}'$ , the

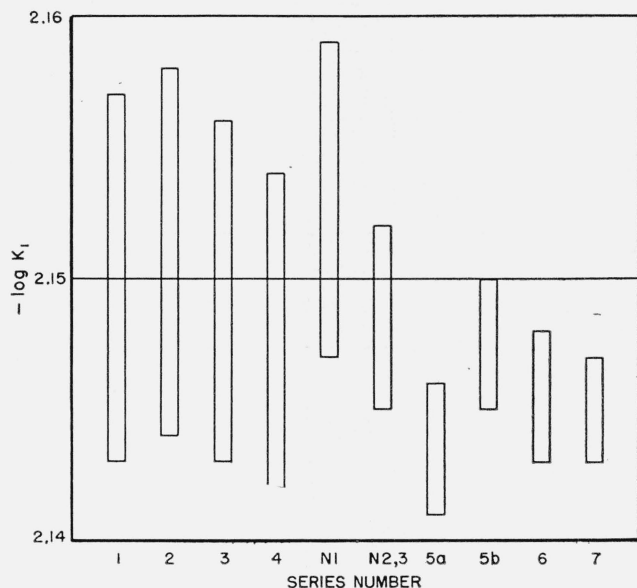


FIGURE 4. Effect of choice of  $a^*$  on the value of  $-\log K_1$  at  $25^\circ$  obtained from 10 groups of solutions.

apparent hydrogen-ion concentration, and the ionic strength is given by

$$\mu = m_1 + m_{\text{H}}' + m_{\text{Cl}} = m_1 + m_{\text{H}}' + 0.005. \quad (14)$$

It should be emphasized that  $m_{\text{H}}'$ ,  $m_{\text{F}_0^-}'$ , and  $\log (K_1 K_F)'$  approach the true  $m_{\text{H}}$ ,  $m_{\text{F}_0^-}$ , and  $\log K_1 K_F$  as the solution becomes more and more dilute.

The data of series 6 and 7 were used to calculate  $-\frac{1}{2} \log (K_1 K_F)'$  in the manner described above. As before, two different values of  $a^*$ , 4 and 6, were used to obtain  $m_{\text{H}}'$  by eq 5a. Two successive approximations were sufficient to establish consistent values of  $m_{\text{H}}'$  and  $\mu$ . The dissociation constant of formic acid,  $K_F$ , was taken to be  $1.638 \times 10^{-4}$  at  $0^\circ$ ,  $1.772 \times 10^{-4}$  at  $25^\circ$ , and  $1.650 \times 10^{-4}$  at  $50^\circ$  [13]. The results for series 6 are shown as open circles in figure 3 and those for series 7 as dots. The plotted points have been calculated from the experimental data, using  $a^*=4$ , and the solid lines fitted to them. The broken lines indicate the shift that would result from using  $a^*=6$ . The intercepts are listed in table 2. The difference is about 0.002 to 0.003 in  $-\frac{1}{2} \log K_1 K_F$ , or about 0.005 in  $\log K_1$ . The uncertainty in  $a^*$  is expected to have a smaller effect on the results of series 7 (8:1 ratio of primary phosphate to formic acid) than on series 6 (5:1 ratio).

TABLE 2. Summary of  $-\frac{1}{2} \log K_1 K_F$  for two values of the ion-size parameter

$t$	Series 6		Series 7	
	$a^*=4$	$a^*=6$	$a^*=4$	$a^*=6$
$^\circ\text{C}$				
0.....	2.914 <sub>2</sub>	2.916 <sub>8</sub>		
25.....	2.947 <sub>0</sub>	2.949 <sub>0</sub>	2.947 <sub>0</sub>	2.949 <sub>0</sub>
50.....	3.025 <sub>0</sub>	3.026 <sub>0</sub>		

## 5. The Dissociation Constant at 25°

Table 3 summarizes the values of the first dissociation constant computed from all seven series and the data of Nims [1], a total of 81 buffer solutions. The series are arranged in the table from top to bottom in the order of decreasing acidity, and it is evident, both in the table and in figure 4, that the uncertainty of the determination decreases in the same way. For  $a^*=4$ , the 10 groups of solutions furnish about the same value of  $-\log K_1$ . The mean of these is 2.144, and the mean deviation from this figure is only 0.0014. For  $a^*=6$ , the values of  $-\log K_1$  display a general downward trend with increasing ratio of phosphate salt to acid. It is not believed that the constancy indicates the correctness of a value of 4 for  $a^*$ , as the parameter usually changes somewhat with buffer ratio. The lower end of each bar in figure 4 corresponds to  $a^*=4$ , the upper end to  $a^*=6$ .

The mean of the 20 values of  $-\log K_1$  given in table 3 was chosen as the best estimate of  $-\log K_1$  that could be made. This average figure of  $2.148 \pm 0.005$  at 25° is considerably higher than 2.124 found by Nims [1] with  $a^*=0$ , that is, by computing  $f_{\text{H}}f_{\text{Cl}}$  in eq 5 from the Debye-Hückel limiting law. Noyes and Eastman [14] have reported the conductance of seven solutions of phosphoric acid of molalities ranging from 0.0002 to 0.1. From these data, Sherrill

and Noyes [15] derived a value of 2.081 for  $-\log K_1$  at 18°. In a later recalculation, Lugg [16] obtained 2.09. This figure is in good agreement with 2.096 given by Nims for 18° [1]. Mason and Culvern [17] have recently extended the conductance measurements at 25°. From their data for the dilute solutions, together with those of Noyes and Eastman, they obtained 2.126 for  $-\log K_1$  at 25°. However, there is some indication that their data, treated independently, would yield a value near 2.140.

Bjerrum and Unmack have calculated the first dissociation constant of phosphoric acid from measurements of the emf of hydrogen-calomel cells at 18°, 25°, and 37° [18]. Their results are compared in the following table with those of Nims [1] and those reported here.

	18°	25°	37.5°
Bjerrum and Unmack	2.120	2.161	2.235
Nims	2.096	2.124	2.185
Bates	2.119	2.148	2.209

The value given by Bjerrum and Unmack at 37° has been corrected to 37.5° by addition of 0.003. By the analysis of titration curves for phosphoric acid in the presence of alkali chlorides, Hentola obtained 2.172 for  $-\log K_1$  at 25° [19].

## 6. The Temperature Coefficient of $\log K_1$

Although the choice of the correct  $K_1$  at 25° was dependent upon a partly arbitrary selection of  $a^*$  (eq 5a), the temperature coefficient of  $\log K_1$  was found to be substantially unaffected by this selection. In other words, the difference between  $\log K_1$  at 0° and 50° was practically the same whether  $a^*$  were 4 or 6, as shown in table 4, where  $\log K_0 - \log K_t$  is tabulated for seven groups of solutions. The figures in parentheses are the values calculated with 6 for  $a^*$ , and the others were obtained with  $a^*=4$ . The values of  $\log K_1$  at each temperature were derived by the methods described earlier in this paper. The average difference at each temperature, given in the last column, was combined with 2.148, the value of

TABLE 3. Summary of  $-\log K_1$  at 25° for two values of the ion-size parameter

Series	$-\log K_1$ for—		$\Delta(\log K_1)$
	$a^*=4$	$a^*=6$	
1	2.143	2.157	0.014
2	2.144	2.158	.014
3	2.143	2.156	.013
4	2.142	2.154	.012
Nims 1	2.147	2.159	.012
Nims 2, 3	2.145	2.152	.007
5a	2.141	2.146	.005
5b	2.145	2.150	.005
6	2.143	2.148	.005
7	2.143	2.147	.004
Mean	2.148		

TABLE 4. Change of the first dissociation constant of phosphoric acid with temperature calculated with  $a^*=4$ ; values for  $a^*=6$  appear in parentheses

$t$	$\log K_0 - \log K_t$ from series—							Average $\log K_0 - \log K_t$
	1	2	3	4	Nims 2, 3	5a	6	
°C								
0	0(0)	0(0)	0(0)	0(0)	0(0)	0(0)	0(0)	0(0)
5	0.018	0.018	0.015	0.016	0.016	0.016	0.016	0.0166
10	.033	.033	.031	.032	-----	.031	-----	.0320
15	.051	.050	.051	.051	-----	.050	-----	.0506
20	.071	.070	.071	.071	-----	.070	-----	.0706
25	.091(0.090)	.091(0.090)	.091(0.090)	.092(0.092)	0.088(0.087)	.094(0.093)	0.100(0.100)	.0924(0.0917)
30	.116	.113	.118	.117	-----	.111	-----	.1150
35	.138	.139	.147	.141	-----	.136	-----	.1402
40	.169	.168	.171	.168	-----	.162	-----	.1676
45	.196	.193	.198	.195	-----	.191	-----	.1946
50	.225(0.222)	.222(0.222)	.223(0.222)	.224(0.221)	.220(0.218)	.218(0.216)	.225(0.223)	.2223(0.2205)
55	.253	.252	.252	.252	-----	-----	-----	.2522
60	.282	.282	.281	.282	-----	-----	-----	.2816

$-\log K_1$  at  $25^\circ$ , to obtain  $-\log K_1$  at the other 12 temperatures. The following equation, the constants of which were determined by the method of least squares, represents the "observed"  $\log K_1$  from  $0^\circ$  to  $60^\circ$  with an average deviation of  $\pm 0.0005$ :

$$-\log K_1 = \frac{799.31}{T} - 4.5535 + 0.013486T. \quad (15)$$

The observed and calculated values are summarized in the second and third columns of table 5, and  $K_1$  is given in the last column.

TABLE 5. Summary of  $-\log K_1$  and  $K_1$  from  $0^\circ$  to  $60^\circ$

$t$	$-\log K_1$ (observed)	$-\log K_1$ (calculated eq 15)	$K_1 \times 10^3$
$^\circ C$			
0	2.056	2.0565	8.79
5	2.073	2.0713	8.45
10	2.088	2.0880	8.17
15	2.107	2.1064	7.82
20	2.127	2.1266	7.46
25	2.148	2.1483	7.11
30	2.171	2.1714	6.75
35	2.196	2.1961	6.37
40	2.224	2.2222	5.97
45	2.251	2.2494	5.61
50	2.277	2.2780	5.28
55	2.308	2.3078	4.92
60	2.338	2.3386	4.59

## 7. Thermodynamic Quantities

The changes of free energy,  $\Delta F^\circ$ , of heat content,  $\Delta H^\circ$ , of entropy,  $\Delta S^\circ$ , and of heat capacity,  $\Delta C_p^\circ$ , for the first dissociation process in the standard state were calculated from eq 15 and the usual formulas [20]. The results are given in table 6. In view of the relatively large uncertainty in the value of  $-\log K_1$ , the accuracy of  $\Delta F^\circ$  is estimated to

TABLE 6. Thermodynamic quantities for the process:  $H_3PO_4 = H^+ + H_2PO_4^-$  in aqueous solution

$t$	$\Delta F^\circ$	$\Delta H^\circ$	$\Delta S^\circ$	$\Delta C_p^\circ$
$^\circ C$	$j \text{ mole}^{-1}$	$j \text{ mole}^{-1}$	$j \text{ deg}^{-1} \text{ mole}^{-1}$	$j \text{ deg}^{-1} \text{ mole}^{-1}$
0	10,752			
5	11,034			
10	11,319			
15	11,618	-6,136	-61.6	-149
20	11,932	-6,886	-64.2	-151
25	12,261	-7,650	-66.8	-154
30	12,600	-8,426	-69.4	-157
35	12,956	-9,216	-72.0	-159
40	13,328	-10,018	-74.5	-162
45	13,705	-10,832	-77.1	-164
50	14,087			
55	14,500			
60	14,906			

be about  $\pm 30 \text{ j mole}^{-1}$ . On the other hand, the temperature coefficient at  $25^\circ$  seems rather well established, and accordingly  $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta C_p^\circ$  are believed accurate within  $150 \text{ j mole}^{-1}$ ,  $0.5 \text{ j deg}^{-1} \text{ mole}^{-1}$ , and  $5 \text{ j deg}^{-1} \text{ mole}^{-1}$ , respectively, at  $25^\circ$ . The uncertainty in the temperature coefficient of  $\log K_1$  is considerably larger near the ends of the temperature range covered by the measurements than in the middle. Hence, these three thermodynamic quantities are given only for temperatures from  $15^\circ$  to  $45^\circ$ .

The value of  $\Delta H^\circ$  at  $25^\circ$ ,  $-7,650 \text{ j mole}^{-1}$ , is to be compared with  $-7,420 \text{ j mole}^{-1}$  derived from the emf data of Nims [1, 13] and with  $-8,160 \text{ j mole}^{-1}$  from the calorimetric data of Pitzer [21]. Pitzer chose  $-7,870 \text{ j mole}^{-1}$  as a "best value." For the entropy change on dissociation, the measurements of Nims lead to  $\Delta S^\circ = -65.7 \text{ j deg}^{-1} \text{ mole}^{-1}$  at  $25^\circ$  and those of Pitzer to  $-66.9$ . The latter figure is in excellent agreement with  $-66.8 \text{ j deg}^{-1} \text{ mole}^{-1}$  obtained in this investigation.

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