

bility in that their product is equal to the coefficient of thermal expansion<sup>8</sup>

$$\left(\frac{\partial P}{\partial T}\right)_V \cdot \frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \quad (3)$$

Values for  $(\partial P/\partial T)_V$  computed from this equation are listed in Table I, which shows that  $\text{SiCl}_4$  has the lowest and  $\text{AsCl}_3$  the highest. Comparison with the thermal pressure coefficients previously obtained by direct measurement<sup>9</sup> for four of these liquids indicates fairly good agreement; uncertainty in the specific heats probably accounts for much of whatever differences exist.

A thermodynamic equation of state applicable to all substances is

$$(\partial E/\partial V)_T = T(\partial P/\partial T)_V - P \quad (4)$$

which makes it possible to calculate the important coefficient for the variation of energy with volume,  $(\partial E/\partial V)_T$ . For a liquid, this quantity is also called the internal pressure (dimensions of energy/volume are equivalent to pressure) because it is a measure of the attractions and repulsions of the molecules. These energy-volume coefficients obtained from equation (4), taking  $P$  as atmospheric pressure ( $1.013 \times 10^6$  dynes/cm.<sup>2</sup>), are given in Table I. Again there is no monotonic variation with molecular weight.

(8) Westwater, Frantz and Hildebrand, *Phys. Rev.*, **31**, 135 (1928).

(9) Hildebrand and Carter, *THIS JOURNAL*, **54**, 3592 (1932).

**Estimation of Heat Capacity.**—The heat capacity  $c_P$  may be estimated by means of equation (2), if the other quantities are known. This may be illustrated in the case of  $\text{PBr}_3$ . Assuming as an approximation that  $\gamma$  for this compound is 1.45, the same as for  $\text{PCl}_3$  and  $\text{AsCl}_3$ , we find that the heat capacity at  $30^\circ$  is 0.417 joule/gram, with a presumable accuracy of a few per cent.

TABLE II

BOND INCREMENTS FOR MOLAR SOUND VELOCITY			
Bond	Increment	Bond	Increment
C-Cl	236	P-Cl	277
Si-Cl	266	P-Br	307
Ti-Cl	276	P=O	85
Ge-Cl	265	As-Cl	295
Sn-Cl	273	Sb-Cl	249

**Acknowledgment.**—It is a pleasure to acknowledge the many helpful suggestions made by Dr. G. R. Ringo during the course of this work.

### Summary

The velocity of sound at  $30^\circ$  in ten inorganic halides has been determined; on the average, it is lower than in the organic halides. Such properties as compressibility, ratio of specific heats, and the energy-volume coefficient have been computed from the sound velocities. There is no systematic variation with molecular weight in any of these properties.

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[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS]

## Resolution of the Dissociation Constants of Citric Acid at 0 to $50^\circ$ , and Determination of Certain Related Thermodynamic Functions<sup>1</sup>

BY ROGER G. BATES AND GLADYS D. PINCHING

The development of exact electromotive-force methods<sup>2,3</sup> has brought about a considerable extension of our knowledge of the thermodynamics of weak electrolytes in recent years. In general, these experimental procedures, based upon electromotive-force measurements of cells without liquid junction, have been applied only to systems the composition of which can be completely expressed in terms of stoichiometric concentrations, the water equilibrium, and a single step in the dissociation of the weak electrolyte. If two or more acids or acidic groups are partially neutralized in the same range of hydrogen-ion concentrations, as is often the case with organic polybasic acids, the composition of the mixture may be quite difficult to establish. For this reason little attention has been directed to the

resolution, by thermodynamic methods, of the dissociation constants of dibasic acids for which  $K_1/K_2$  is less than 1000.

Separation of the constants for three overlapping equilibria is even more laborious. For citric acid,  $K_1/K_2$  and  $K_2/K_3$  are both about 44 at  $25^\circ$ . Existing values<sup>4,5,6</sup> of the thermodynamic constants for this acid were derived from electromotive-force measurements of cells with liquid junction. The analysis of the data rests in each instance upon a computation of the hydrogen-ion concentration or activity. Consequently, an assumption regarding the potential at the liquid junction must be introduced.

In spite of the interest that attaches to the thermodynamics of such a three-step dissociation process, no determination of the constants of a tribasic acid, with or without overlapping, has

(1) Presented before the Physical and Inorganic Division at the September, 1947, meeting of the American Chemical Society at New York City.

(2) H. S. Harned and B. B. Owen, *THIS JOURNAL*, **52**, 5079 (1930).

(3) H. S. Harned and R. W. Ehlers, *ibid.*, **54**, 1350 (1932).

(4) H. S. Simms, *J. Phys. Chem.*, **32**, 1121 (1928).

(5) I. M. Kolthoff and W. Bosch, *Rec. trav. chim.*, **47**, 558 (1928).

(6) N. Bjerrum and A. Unmack, *Kgl. Danske Videnskab. Selskab., Math.-fys. Medd.*, **9**, No. 1 (1929).

heretofore been made by methods free of the uncertainties of a liquid junction. The changes of entropy and of heat capacity accompanying dissociation are computed from the first and second derivatives, respectively, of electromotive force (or  $\log K$ ) with temperature. Hence, these functions can be established accurately only from a multifarious series of measurements over a range of temperatures.

The three dissociation constants of citric acid have therefore been determined at intervals of 5° from 0 to 50° by measurement of the electromotive force of hydrogen-silver chloride cells without liquid junction. The changes of free energy, heat content, entropy and heat capacity accompanying the acidic dissociation of one mole of citric acid or one gram ion of primary or secondary citrate ion in the standard state at 0 to 50° have been calculated.

### Method of Resolution

All of the cells are represented by the following scheme

Pt; H<sub>2</sub>(g), citrate buffer solution, KCl, AgCl(s); Ag

Each value of the electromotive force of this cell for a solution of known chloride concentration furnishes a measure of  $-\log(f_{\text{H}}f_{\text{Cl}}m_{\text{H}})$ , where  $m$  is molality and  $f$  is the activity coefficient on the molal scale. For convenience, this experimental quantity has been termed  $p\text{wH}$ .<sup>7</sup> The

$$p\text{wH} \equiv -\log(f_{\text{H}}f_{\text{Cl}}m_{\text{H}}) = \frac{(E - E^0)\text{F}}{2.3026 RT} + \log m_{\text{Cl}} \quad (1)$$

value of  $E^0$  in int. v. has been determined by Harned and Ehlers,<sup>8</sup> and  $2.3026 RT/\text{F}$  in the same units has been tabulated in an earlier publication from this Bureau.<sup>9</sup>

The buffer solutions in the range of  $p\text{H}$  governed principally by the third dissociation equilibrium were prepared from tertiary potassium citrate and secondary potassium citrate. In order to minimize corrections for the second dissociation step, the salts were combined in the molal ratio 3:1. The advantage of a similar preponderance of free citric acid over primary potassium citrate for the determination of the first constant is offset by the enhanced correction for hydrogen ion, and for this reason a molal ratio of unity was selected. The  $K_2$  correction is therefore more important in the determination of  $K_1$  than of  $K_3$ , although only two equilibria need be considered in each instance.

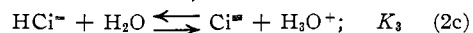
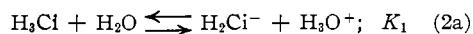
The compositions of mixtures of primary and secondary citrates, on the other hand, can be

(7) R. G. Bates, *Chem. Rev.*, **42**, 1 (1948).

(8) H. S. Harned and R. W. Ehlers, *THIS JOURNAL*, **55**, 2179 (1933). The determination of  $E^0$  from these data has also been examined by H. S. Harned and D. D. Wright, *ibid.*, **55**, 4849 (1933), and by W. J. Hamer, J. O. Burton and S. F. Acree, *J. Research Natl. Bur. Standards*, **24**, 269 (1940).

(9) G. G. Manov, R. G. Bates, W. J. Hamer and S. F. Acree, *THIS JOURNAL*, **65**, 1765 (1943).

expressed completely only in terms of all three steps in the dissociation of the acid, namely<sup>10</sup>



Hence, no pair of constants can be evaluated by simple simultaneous solution of two formal equations derived exclusively from data corresponding to the three regions where the buffer capacity is highest. One of the authors has recently shown,<sup>11</sup> however, that the resolution of the constants for overlapping equilibria can be materially simplified with the aid of electromotive-force data for buffer solutions composed simply of a single acid salt (with added chloride). In this way a second equation can be written in terms of  $K_1$  and  $K_2$  (or  $K_2$  and  $K_3$ ) with at most a relatively minor correction for a third equilibrium.

It is therefore possible to obtain the first and second constants from an analysis of only two sets of data and, by a similar procedure, also the second and third constants. In practice, the equations are most conveniently solved by the method of approximations. The concentrations of secondary and tertiary citrates were so chosen that the influence of  $K_2$  on the third constant was kept relatively small. It was found by trial that  $pK_2$  need be known only within 0.03 to yield a value of  $pK_3$  accurate to 0.001 unit. For the same accuracy in  $pK_1$ , it is necessary to know  $pK_2$  to the nearest 0.01 unit. Somewhat larger errors are inherent in the value of  $pK_2$  derived in this way, however, for the electromotive force of the cells containing the acid salt depends upon the product of two constants.<sup>11</sup> It follows, then, that the equations for overlapping are of limited usefulness in determining  $K_2$  accurately, although they are a material aid in resolving the constants, for they permit the first and third equilibria readily to be freed of the influence of the second. With a knowledge of  $K_1$  and  $K_3$ , however,  $K_2$  can be determined by conventional methods.

The buffer solutions studied are conveniently grouped into five series: (1) mixtures of citric acid and potassium dihydrogen citrate, (2) potassium dihydrogen citrate, (3) mixtures of potassium dihydrogen citrate and dipotassium hydrogen citrate, (4) dipotassium hydrogen citrate, and (5) mixtures of dipotassium hydrogen citrate and tripotassium citrate. Potassium chloride was added to each solution. The number of solutions studied in each of these five series was respectively, 19, 25, 10, 5 and 25.

**Series 1.**—For systems governed principally by the first dissociation equilibrium, such as

(10) In these equations, Ci is written for citrate, and  $K$  is the thermodynamic dissociation constant. For simplicity, H will be written for hydronium ion, and the charges will be omitted from the symbols for this ion and for chloride ion. The activity of water does not depart greatly from unity in the dilute solutions, and it will therefore be omitted from the equations. As usual,  $pK \equiv -\log K$ .

(11) R. G. Bates, *THIS JOURNAL*, **70**, 1579 (1948).

those of series 1, it is convenient to write the relationship between  $p\text{wH}$  and  $pK_1$  in the form

$$pK_1 = p\text{wH} + \log \frac{m_{\text{H}_3\text{Cl}}}{m_{\text{H}_2\text{Cl}^-}} + \log \frac{f_{\text{H}_3\text{Cl}} f_{\text{Cl}^-}}{f_{\text{H}_2\text{Cl}^-}} \quad (3)$$

The concentration term,  $m_{\text{H}_3\text{Cl}}/m_{\text{H}_2\text{Cl}^-}$ , can be expressed in terms of  $m$  (the stoichiometric molality of citric acid and of primary potassium citrate),  $m_{\text{H}}$ , and  $m_{\text{HCl}^-}$  by consideration of the equilibria that fix the compositions of the solutions of series 1. If the Debye-Hückel equation<sup>12</sup> is assumed, the last term of equation (3) disappears at low ionic strengths. Hence, the "apparent" first constant,  $K_1'$ , which becomes equal to the thermodynamic  $K_1$  at zero ionic strength, is given by

$$pK_1' = p\text{wH} + \log \frac{m - m_{\text{H}} + m_{\text{HCl}^-}}{m + m_{\text{H}} - 2m_{\text{HCl}^-}} \quad (4)$$

The apparent hydrogen-ion concentration,  $m_{\text{H}}$ , which approaches the true hydrogen-ion concentration at low ionic strengths, was obtained from  $p\text{wH}$  by substitution of the Debye-Hückel equation for the activity coefficients of hydrogen and chloride ions

$$-\log m_{\text{H}} = p\text{wH} + \log f_{\text{H}} f_{\text{Cl}^-} = p\text{wH} - \frac{2A\sqrt{\mu}}{1 + Ba^*\sqrt{\mu}} \quad (5)$$

The constants  $A$  and  $B$  depend upon the temperature<sup>9</sup>;  $a^*$  is the ion-size parameter. The ionic strength,  $\mu$ , of the mixtures of series 1 is

$$\mu = m + m_{\text{H}} + m_{\text{HCl}^-} + m_{\text{KCl}} \quad (6)$$

The necessary correction for the molality of secondary citrate ion,  $m_{\text{HCl}^-}$ , is made only with an estimate of  $K_2$

$$m_{\text{HCl}^-} = m_{\text{H}_2\text{Cl}^-} (\text{antilog } p\text{wH}) K_2 / f^2 \quad (7)$$

The activity coefficient,  $f^a$ , was computed here and in other steps of the calculations by the Debye-Hückel equation<sup>12</sup>

$$\log f^a = \frac{-nA\sqrt{\mu}}{1 + Ba^*\sqrt{\mu}} \quad (8)$$

**Series 2.**—The value of  $(K_1 K_2)'$ , the apparent product of  $K_1$  and  $K_2$ , is related to the electromotive force of the cells containing primary potassium citrate and potassium chloride by the following equation<sup>13</sup>

$$-1/2 \log (K_1 K_2)' = p\text{wH} - 1/2 \log \frac{m_{\text{H}_3\text{Cl}} + m_{\text{H}} - m_{\text{Cl}^-}}{m_{\text{H}_3\text{Cl}}} + \frac{A\sqrt{\mu}}{1 + Ba^*\sqrt{\mu}} \quad (9)$$

The true  $K_1 K_2$  is obtained by extrapolation of apparent values to zero ionic strength, where the last term of the equation is zero. In writing equation (9), the activity coefficient of the molecular acid has been assumed to be unity, and that of each ionic species has been represented by the Debye-Hückel formula.

The second term on the right of equation (9) changes but slightly with relatively large altera-

(12) P. Debye and E. Hückel, *Physik. Z.*, **24**, 185 (1923).

(13) Compare Case IV of ref. 11.

tions in the estimated molality of free citric acid. Consequently it can be obtained readily with sufficient accuracy by the approximation<sup>11</sup>

$$\frac{m_{\text{H}_3\text{Cl}} + m_{\text{H}} - m_{\text{Cl}^-}}{m_{\text{H}_3\text{Cl}}} \approx \frac{mx + m_{\text{H}} - 2m_{\text{Cl}^-}}{mx - m_{\text{H}}} \quad (10)$$

where  $m$  is the molality of potassium dihydrogen citrate and  $x$  is a function of the concentration dissociation constants,  $k_n$

$$x \equiv \frac{2(k_2/k_1)^{1/2}}{1 + 2(k_2/k_1)^{1/2}} \quad (11)$$

These concentration constants are related to the thermodynamic constants,  $K_n$ , by the following expression

$$k_n = K_n / f^{2n} \quad (12)$$

The activity coefficient,  $f^n$ , is obtained by equation (8).

The concentration of hydrogen ion in equation (10) is small compared with  $m_{\text{H}_3\text{Cl}}$ . Its approximate value is derived from  $p\text{wH}$  by equation (5). The concentration of citrate ion,  $m_{\text{Cl}^-}$ , in primary citrate solutions of molality,  $m$ , not exceeding 0.1 is less than 1% of  $m_{\text{H}_3\text{Cl}}$ . Hence, this molality is a correction of secondary importance in equation (10) and can be estimated with sufficient accuracy if the approximate magnitude of  $K_3$  is known

$$m_{\text{Cl}^-} = \frac{K_3 m_{\text{HCl}^-}}{f^6 m_{\text{H}}} \approx \frac{K_3 (mx + m_{\text{H}})}{2f^6 m_{\text{H}}} \quad (13)$$

In order to estimate  $m_{\text{H}}$  and  $m_{\text{HCl}^-}$ , as well as to perform the extrapolation, the ionic strength was calculated by

$$\mu = m (1 + 0.5x) + 1.5m_{\text{H}} + 2.5m_{\text{Cl}^-} + m_{\text{KCl}} \quad (14)$$

It has been shown<sup>11</sup> that the choice of  $a^*$  in equations (5) and (8) has a negligible influence upon  $K_1 K_2$  in the limit of zero ionic strength, provided the same value is used in both equations.

**Series 3.**—In a buffer mixture composed of primary and secondary potassium citrates and potassium chloride, each at a molality  $m$ , the second dissociation constant is given by

$$pK_2 = p\text{wH} + \log \frac{m_{\text{H}_2\text{Cl}^-}}{m_{\text{HCl}^-}} + \log \frac{f_{\text{H}_2\text{Cl}^-} f_{\text{Cl}^-}}{f_{\text{HCl}^-}} \quad (15)$$

The second term on the right can be written in terms of  $m$  and the actual concentrations of free citric acid and of tertiary ion in the buffer solutions. Likewise, the activity-coefficient term can be expressed by the Debye-Hückel equation, and the second constant can be obtained in the usual manner by extrapolation to zero ionic strength of apparent values,  $pK_2'$ , defined by

$$pK_2' = p\text{wH} + \log \frac{m - 2m_{\text{H}_3\text{Cl}} + m_{\text{Cl}^-}}{m + m_{\text{H}_3\text{Cl}} - 2m_{\text{Cl}^-}} + \frac{2A\sqrt{\mu}}{1 + Ba^*\sqrt{\mu}} \quad (16)$$

The ionic strengths of the buffer solutions of series 3 are given by

$$\mu = 5m + 0.5m_{\text{H}} + m_{\text{H}_3\text{Cl}} + m_{\text{Cl}^-} \quad (17)$$

The values of  $m_{\text{H}_3\text{Cl}}$  and of  $m_{\text{Cl}^-}$  are readily obtained, when  $K_1$  and  $K_3$  have been determined,

with sufficient accuracy by a short series of approximations

$$m_{\text{H}_2\text{Cl}} = f^2 m_{\text{H}}(m - 2m_{\text{H}_2\text{Cl}} + m_{\text{Cl}^{\ominus}})/K_1 \quad (18)$$

$$m_{\text{Cl}^{\ominus}} = K_2(m + m_{\text{H}_2\text{Cl}} - 2m_{\text{Cl}^{\ominus}})/(f^2 m_{\text{H}}) \quad (19)$$

The concentration of hydrogen ion is obtained as before by equation (5).

**Series 4.**—The electromotive force of the cells containing mixtures of secondary potassium citrate and potassium chloride, each at molality  $m$ , is related to  $(K_2K_3)'$ , the apparent value of  $K_2K_3$ , by the equation<sup>14</sup>

$$-\frac{1}{2} \log (K_2K_3)' = pH - \frac{1}{2} \log \frac{m_{\text{H}_2\text{Cl}^-} + m_{\text{H}} + 2m_{\text{H}_2\text{Cl}}}{m_{\text{H}_2\text{Cl}^-}} + \frac{3A\sqrt{\mu}}{1 + Ba^*\sqrt{\mu}} \quad (20)$$

The second term on the right of equation (20) is readily obtained by

$$\frac{m_{\text{H}_2\text{Cl}^-} + m_{\text{H}} + 2m_{\text{H}_2\text{Cl}}}{m_{\text{H}_2\text{Cl}^-}} \approx \frac{my + m_{\text{H}} + 2m_{\text{H}_2\text{Cl}}}{my - m_{\text{H}} - 2m_{\text{H}_2\text{Cl}}} \quad (21)$$

where

$$y \equiv \frac{2(k_3/k_2)^{1/2}}{1 + 2(k_3/k_2)^{1/2}} \quad (22)$$

The concentration constants,  $k_n$ , are obtained by equations (8) and (12), and  $m_{\text{H}}$  by equation (5). The choice of  $a^*$  in equations (5) and (8) has a negligible effect upon the second term on the right of formula (20). The molality of citric acid,  $m_{\text{H}_2\text{Cl}}$ , amounts to only 4% of  $my$ . It is calculated with sufficient accuracy by the approximate formula

$$m_{\text{H}_2\text{Cl}} \approx \frac{f^2 m_{\text{H}}(my - m_{\text{H}})}{2K_1} \quad (23)$$

Finally, the ionic strengths of the solutions of series 4 are given by

$$\mu = m(4 + 0.5y) + 2.5m_{\text{H}} + 2m_{\text{H}_2\text{Cl}} \quad (24)$$

**Series 5.**—The principal equilibrium in mixtures of secondary potassium citrate ( $m_1$ ), tertiary potassium citrate ( $m_2$ ), and potassium chloride is (2c). The third constant is given by

$$pK_3 = pH - \log \frac{m_{\text{Cl}^{\ominus}}}{m_{\text{HCl}^{\ominus}}} + \log \frac{f_{\text{Cl}^{\ominus}} f_{\text{HCl}^{\ominus}}}{f_{\text{Cl}^{\ominus}}} \quad (25)$$

The concentration of hydrogen ion in these solutions is so small that it can be neglected entirely. Consideration of the second and third dissociation steps, equilibria (2b) and (2c), leads to the equality

$$\frac{m_{\text{Cl}^{\ominus}}}{m_{\text{HCl}^{\ominus}}} = \frac{m_2 + m_{\text{H}_2\text{Cl}^-}}{m_1 - 2m_{\text{H}_2\text{Cl}^-}} \quad (26)$$

Hence, when the activity coefficients are expressed by the Debye-Hückel equation, the following extrapolation formula is obtained.

$$pK_3' = pH - \log \frac{m_2 + m_{\text{H}_2\text{Cl}^-}}{m_1 - 2m_{\text{H}_2\text{Cl}^-}} + \frac{4A\sqrt{\mu}}{1 + Ba^*\sqrt{\mu}} \quad (27)$$

The molality of the primary anion,  $m_{\text{H}_2\text{Cl}^-}$ , is but 1.5% of  $m_1$  for mixtures of series 5, in which  $= 3m_1$ . It was evaluated by equation (7)

(14) Compare Case V of ref. 11.

with substitution of  $m_1$  for  $m_{\text{CH}^-}$ . The ionic strength is given by

$$\mu = 3m_1 + 6m_2 + m_{\text{H}_2\text{Cl}^-} + m_{\text{KCl}} \quad (28)$$

The problem of resolving the three constants was approached in the following manner. Inasmuch as the precise determination of any one of the constants requires a knowledge of at least one of the others, it was first necessary to ascertain the accuracy with which these other constants must necessarily be estimated to allow  $pK$  to be established with an accuracy of 0.001. As indicated earlier in this paper,  $pK_2$  need be known to 0.01 unit for the accurate determination of  $pK_1$  and to 0.03 unit for the calculation of  $pK_3$  from the measurements of series 5. As a point of departure,  $pK_2$  was taken as 4.76, the value at 25° found by Bjerrum and Unmack.<sup>6</sup> Values for the first and third constants were then obtained by analysis of the data for solutions of series 1 and series 5. With these, values of  $K_1K_2$  and of  $K_2K_3$ , from which a new  $K_2$  could be derived, were obtained from the measurements of series 2 and series 4 and the calculation of  $pK_1$  and  $pK_3$  repeated. A third approximation was usually unnecessary. Finally, with  $pK_1$  and  $pK_3$  already established, the values of  $pK_2$  derived from series 2 and series 4 were supplemented by a calculation of  $pK_2$  from the measurements with solutions of series 3. Approximation methods were used in establishing the ionic and molecular concentrations and the ionic strength for each solution.

## Experimental

**Anhydrous Citric Acid.**—Anhydrous citric acid of special purity was obtained through the courtesy of Chas. Pfizer & Co., Inc. Samples of the acid were titrated with a carbonate-free solution of sodium hydroxide to the blue color of thymol blue. The acid was found to have a neutralization value of 100.03  $\pm$  0.05%.

**Tripotassium citrate monohydrate** of reagent grade was crystallized twice from water. Before the first crystallization, the saturated solution of the salt was adjusted to pH 8.8 to 9.0 by the addition of small amounts of a solution of potassium hydroxide. The salt was dried at 110°. The weight of ash obtained when three 5-g. samples were heated in a muffle furnace at 800° averaged 100.04% of the theoretical, with a mean deviation of 0.06.

**Potassium dihydrogen citrate** was prepared by mixing aqueous solutions of citric acid and tripotassium citrate monohydrate in the correct proportions and crystallizing. The salt was dried in a vacuum at a temperature below 80°<sup>16</sup> and was analyzed by titration with standard alkali to the thymol blue end-point and by differential electro-metric titration. Some difficulty was experienced in obtaining primary salt of the correct composition by repeated crystallization from water or by precipitation from an aqueous solution with ethanol. One sample of salt used appeared to contain about 0.3 mole % of citric acid. Corrections for this amount of free acid were applied to the experimental data.

**Dipotassium hydrogen citrate** could not conveniently be crystallized from water. Solutions of this salt were therefore prepared as required from solutions of citric acid and of the tertiary salt.

**Potassium chloride** was purified and fused in an atmos-

(15) I. M. Kolthoff and J. J. Vleschhouwer, *Biochem. Z.* **179**, 410 (1928); **183**, 444 (1927).

TABLE I

E.M.F. OF THE CELL Pt; H<sub>2</sub>, CITRATE BUFFER SOLUTION, KCl, AgCl; Ag FROM 0 TO 50°, IN INTERNATIONAL VOLTS

<i>m</i>	<i>E</i> <sub>0</sub>	<i>E</i> <sub>5</sub>	<i>E</i> <sub>10</sub>	<i>E</i> <sub>15</sub>	<i>E</i> <sub>20</sub>	<i>E</i> <sub>25</sub>	<i>E</i> <sub>30</sub>	<i>E</i> <sub>35</sub>	<i>E</i> <sub>40</sub>	<i>E</i> <sub>45</sub>	<i>E</i> <sub>50</sub>
Series 1. H <sub>3</sub> Cl ( <i>m</i> ), KH <sub>2</sub> Cl ( <i>m</i> ), KCl ( <i>m</i> )											
0.07936	0.46670	0.46722	0.46761	0.46794	0.46828	0.46861	0.46854	0.46866	0.46913	.....	0.46952
.07368 <sup>a</sup>	.46884	.....	.46976	.....	.47058	.47096	.47119	.....	.47166	.....	.47196
.06068	.47376	.47435	.47493	.47544	.47593	.47637	.47685	.47717	.47747	.47771	.47794
.05971	.47410	.47457	.47521	.47558	.47594	.47661	.47694	.47725	.47763	.....	.47802
.05700	.47539	.....	.47659	.....	.47754	.47807	.47842	.....	.47909	.....	.47959
.05093 <sup>a</sup>	.47835	.....	.47969	.....	.48074	.48120	.48175	.....	.48264	.....	.48337
.04957	.....	.....	.....	.....	.....	.48210	.....	.....	.....	.....	.....
.04145	.48345	.....	.48492	.....	.48617	.48701	.48743	.....	.48852	.....	.48938
.04062	.48386	.48470	.48552	.48626	.48697	.48763	.48814	.48869	.48922	.48969	.49014
.03978	.....	.....	.....	.....	.....	.48802	.....	.....	.....	.....	.....
.03592	.48700	.....	.48884	.....	.49032	.49105	.49166	.....	.49280	.....	.49359
.03212 <sup>a</sup>	.49020	.....	.49186	.....	.49342	.49406	.49482	.....	.49610	.....	.49720
.02488 <sup>a</sup>	.49672	.....	.49868	.....	.50048	.50136	.50216	.....	.50370	.....	.50500
.02163	.49997	.50126	.50227	.50332	.50432	.50538	.50609	.50694	.50778	.50854	.50927
.019524	.50279	.50402	.50507	.50614	.50714	.50811	.50904	.50993	.51076	.....	.51235
.014646 <sup>a</sup>	.....	.....	.51294	.....	.51526	.51640	.51747	.....	.51953	.....	.52146
.010042	.....	.....	.....	.....	.....	.52751	.....	.....	.....	.....	.....
.009788	.52108	.52271	.52419	.52564	.52705	.52844	.52958	.53081	.53200	.53316	.53425
.005074	.53879	.54080	.54263	.54448	.54622	.54793	.54948	.55107	.55259	.55411	.55553
Series 3. KH <sub>2</sub> Cl ( <i>m</i> ), K <sub>2</sub> HCl ( <i>m</i> ), KCl ( <i>m</i> )											
.08126 <sup>a</sup>	.54246	.54424	.54602	.54776	.54944	.55122	.55293	.55460	.55636	.55806	.55978
.07708	.54383	.54562	.54724	.54896	.55067	.55233	.55451	.55625	.55806	.55979	.56142
.06109 <sup>a</sup>	.54998	.55192	.55386	.55574	.55760	.55964	.56140	.56327	.56525	.56700	.56884
.05322	.55364	.55561	.55756	.55962	.56160	.56373	.56559	.56757	.56963	.57154	.57352
.04516	.55804	.56017	.56221	.56438	.56649	.56866	.57058	.57271	.57483	.57684	.57892
.04039 <sup>a</sup>	.56107	.56319	.56541	.56756	.56964	.57192	.57402	.57610	.58816	.58030	.58217
.02577	.57314	.57562	.57799	.58040	.58276	.58532	.58759	.58994	.59236	.59469	.59707
.02085 <sup>a</sup>	.57884	.58139	.58399	.58640	.58886	.59146	.59376	.59614	.59865	.60115	.60362
.017848	.58301	.58569	.58827	.59083	.59343	.59612	.59857	.60116	.60371	.60620	.60888
.010551 <sup>a</sup>	.....	.59969	.60278	.60572	.60854	.61134	.61413	.61675	.61972	.62268	.62540
Series 5a. K <sub>2</sub> HCl ( <i>m</i> ), K <sub>3</sub> Cl (3 <i>m</i> ), KCl ( <i>m</i> )											
.02087 <sup>a</sup>	.66986	.67448	.67910	.68374	.68842	.69336	.69818	.70320	.70817	.71317	.71834
.017807 <sup>a</sup>	.67457	.67928	.68400	.68888	.69372	.69871	.70367	.70870	.71374	.71888	.72420
.016687 <sup>a</sup>	.67648	.68128	.68604	.69092	.69580	.70092	.70558	.71092	.71606	.72117	.72639
.014133 <sup>a</sup>	.68153	.68639	.69130	.69626	.70128	.70650	.71166	.71677	.72195	.72726	.73260
.012517	.68518	.69017	.69506	.70018	.70542	.71062	.71579	.72109	.72645	.73180	.73731
.012489	.68535	.69038	.69519	.70029	.70549	.71074 <sup>a</sup>	.71594	.72132	.72659	.73197	.73750
.010578 <sup>a</sup>	.69016	.69526	.70048	.70566	.71088	.71615	.72146	.72687	.73236	.73790	.74345
.010045	.69196	.69715	.70234	.70749	.71282	.71807	.72353	.....	.....	.....	.....
.008453	.69691	.70195	.70720	.71263	.71817	.72373	.72917	.73471	.74023	.74563	.75132
.008183 <sup>a</sup>	.69804	.70332	.70860	.71398	.71938	.72489	.73023	.73588	.74158	.74729	.75306
.007056 <sup>a</sup>	.70246	.70784	.71325	.71876	.72426	.72980	.73544	.74109	.74684	.75265	.75847
.005823	.70797	.71346	.71903	.72454	.73026	.73596	.74169	.....	.....	.....	.....
.004739 <sup>a</sup>	.71447	.72008	.72574	.73147	.73728	.74316	.74905	.75497	.76096	.76702	.77329
.004117 <sup>a</sup>	.71848	.72426	.73006	.73589	.74178	.74766	.75351	.75960	.76566	.77186	.77809
.003524 <sup>a</sup>	.72326	.72908	.73494	.74086	.74686	.75288	.75896	.76508	.77133	.77758	.78383
.002194 <sup>a</sup>	.73739	.74345	.74956	.75574	.76206	.76839	.77476	.78122	.78773	.79428	.80102
.0013717 <sup>a</sup>	.75103	.75736	.76374	.77022	.77685	.78342	.79010	.79671	.80357	.81038	.81731
Series 5b. K <sub>2</sub> HCl ( <i>m</i> ), K <sub>3</sub> Cl (2.9795 <i>m</i> ), KCl (2.7478 <i>m</i> )											
.03128 <sup>a</sup>	.....	.....	.....	.....	.....	.65292	.....	.....	.....	.....	.....
.02520	.....	.....	.....	.....	.....	.65992	.....	.....	.....	.....	.....
.02241	.....	.....	.....	.....	.....	.66387	.....	.....	.....	.....	.....
.02077 <sup>a</sup>	.....	.....	.....	.....	.....	.66644	.....	.....	.....	.....	.....
.017473	.....	.....	.....	.....	.....	.67209	.....	.....	.....	.....	.....
.013757	.....	.....	.....	.....	.....	.68026	.....	.....	.....	.....	.....
.010626	.....	.....	.....	.....	.....	.68899	.....	.....	.....	.....	.....
.005883	.....	.....	.....	.....	.....	.70880	.....	.....	.....	.....	.....

<sup>a</sup> Each e. m. f. value is the average result of 2 cells (4 pairs of electrodes). Of 193 such measurements, 128 differed by 0.1 mv. or less, 46 by 0.1 to 0.2 mv. and 19 by more than 0.2 mv.

phere of nitrogen as described by the authors in an earlier publication.<sup>16</sup>

Air was removed from each cell solution by bubbling nitrogen through each solution flask for at least two hours. An air-free technique was used in filling the cells. Measurements at the 11 temperatures extended over a period of three days. The cells showed remarkable stability, however, and often resumed their initial values of electromotive force within a few hundredths of a millivolt at the conclusion of the series. The average change during this time was about 0.1 mv.

Two constant-temperature water-baths and two potentiometers were used. Temperatures were measured with a platinum resistance thermometer and with a calibrated mercury thermometer. The standards of electromotive force were two saturated Weston cells maintained in a temperature-controlled box of the type described by Mueller and Stimson.<sup>17</sup> The cells had been calibrated recently by this Bureau. Other details concerning the experimental methods are described elsewhere.<sup>18</sup>

**Results**

The electromotive force of the cells containing solutions of series 1, 3 and 5, corrected as usual to 1 atm. partial pressure of hydrogen, is listed in Table I. The electromotive force of cells containing 25 solutions of potassium dihydrogen citrate of molality *m* in 0.01 *m* potassium chloride (series 2) was found to be a linear function of log *m* at each temperature

$$E_t = a + b \log m \quad (29)$$

The constants of equation (29) are given in Table II, together with the mean difference, Δ, between observed and calculated values of the electromotive force. Five solutions were studied in series 4 to demonstrate, by comparison with the results from series 2, the internal consistency of the equations for overlapping. The data obtained at 25° are listed in Table III.

TABLE II

CONSTANTS OF EQUATION (29) FOR DATA OF SERIES 2			
<i>t</i> , °C.	<i>a</i>	<i>b</i> × 10 <sup>3</sup>	Δ, mv.
0	0.55279	-4.15	0.08
5	.55488	-4.22	.07
10	.55669	-4.43	.07
15	.55863	-4.52	.09
20	.56050	-4.63	.10
25	.56226	-4.80	.07
30	.56409	-4.92	.08
35	.56591	-5.04	.12
40	.56754	-5.22	.11
45	.56942	-5.32	.12
50	.57127	-5.34	.12

TABLE III

ELECTROMOTIVE FORCE OF THE CELL Pt; H <sub>2</sub> , K <sub>2</sub> HCl ( <i>m</i> ), KCl ( <i>m</i> ), AgCl; Ag AT 25° (SERIES 4)	
<i>m</i>	<i>E</i> , int. v.
0.08063	0.59149
.06031	.60053
.04007	.61352
.02036	.63490
.01000	.65700

(16) G. D. Pinching and R. G. Bates, *J. Research Natl. Bur. Standards*, **57**, 311 (1946).

(17) E. F. Mueller and H. F. Stimson, *ibid.*, **13**, 699 (1934).

(18) R. G. Bates and S. F. Acree, *ibid.*, **30**, 129 (1943).

The determination of *pK*<sub>1</sub> is portrayed in Fig. 1, where *pK*<sub>1</sub>' at 25° computed from the measurements of series 1 is plotted as a function of the ionic strength. The curve at the bottom represents the value of *pK*<sub>1</sub>' obtained by equation (4) when *m*<sub>HCl</sub><sup>-</sup>, which embodies the correction for the second dissociation step, is omitted.

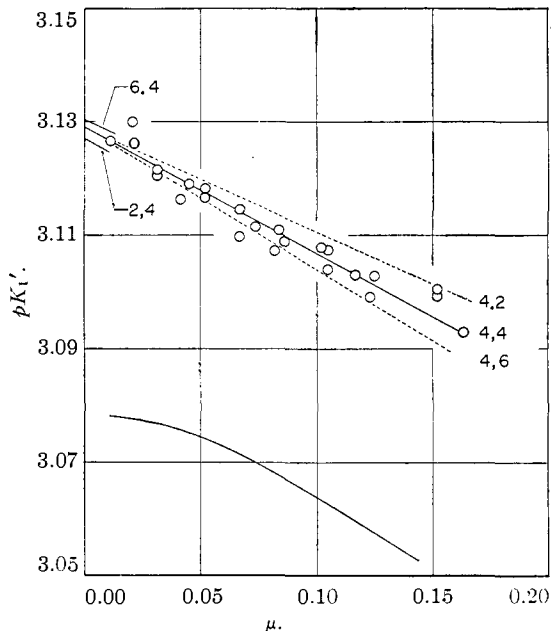


Fig. 1.—Determination of *pK*<sub>1</sub> from data of series 1.

Two numbers appear beside each of the upper curves of Fig. 1. The first of these represents the value of *a*\* chosen for the computation of *m*<sub>H</sub> by equation (5), and the second is the value used to obtain *m*<sub>HCl</sub><sup>-</sup> by equations (7) and (8). Unfortunately, the first acidic dissociation is so strong that some uncertainty is introduced in the final *pK*<sub>1</sub> by the arbitrary choice of *a*\* for the computation of the hydrogen-ion concentration by equation (5). Nevertheless, the value of *a*\* used to compute the *K*<sub>2</sub> correction by equations (7) and (8) is of little concern, for the lines converge satisfactorily when the correction for the second dissociation step is made with different values of *a*\*, provided that *a*\* of equation (5) does not vary. The three different intercepts at zero ionic strength show, however, that the value of *pK*<sub>1</sub> determined by extrapolation is dependent upon the value of *a*\* chosen to compute the hydrogen-ion correction. When *a*\* is changed from 4 to 6 or 2, *pK*<sub>1</sub> is, respectively, raised or lowered by 0.001 to 0.002. A value of 4 was used in the calculation at each temperature. It is therefore impossible to consider *pK*<sub>1</sub> more accurate than ±0.003. Inasmuch as the estimation of *m*<sub>H</sub> or *m*<sub>OH</sub> in a buffer solution from the electromotive force necessarily requires an assumption regarding activity coefficients, the accuracy of this electromotive-force method diminishes some-

what when  $pK$  is less than 3 or greater than 11.<sup>19</sup>

The extrapolation of data obtained with the solutions in series 2 (mixtures of primary potassium citrate and potassium chloride) is shown in Fig. 2. The choice of  $a^*$  in formulas (5) and (8) has, within reasonable limits, a negligible effect on the second term on the right of equation (9). The value of  $a^*$  in equation (9) is chosen to yield a straight-line extrapolation. A value of 3 was found best suited to this purpose at each temperature, and, for convenience, this value was also used in equations (5) and (8).

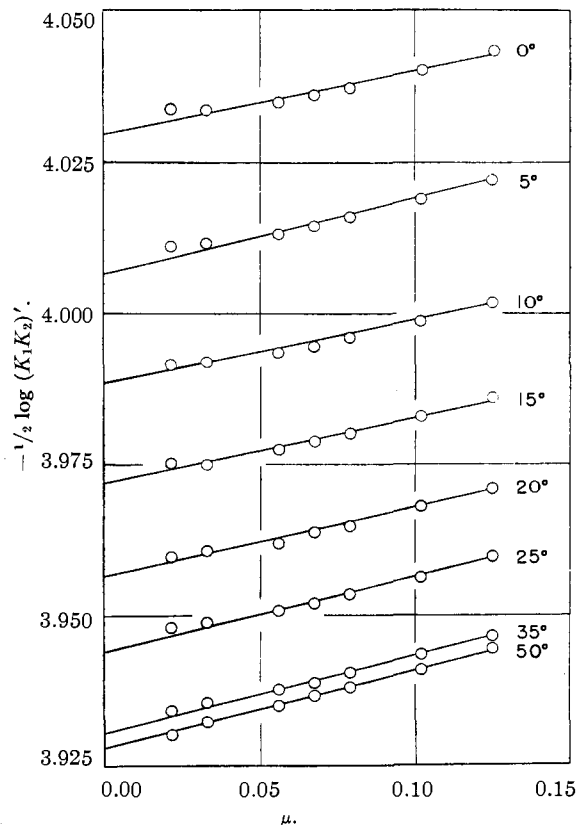


Fig. 2.—Determination of  $K_1K_2$  from data of series 2.

Figure 3 is a plot of  $pK_2'$ , derived from the measurements of series 3 by equation (16), as a function of ionic strength at 25°. The extrapolation was made most conveniently, as the figure shows, with the use of  $a^* = 6$  in equation (16). Inasmuch as the curves converged satisfactorily at zero ionic strength when different values of  $a^*$  were used in equation (8) to compute the activity coefficients of formulas (18) and (19),  $a^*$  was taken as 6 also in equation (8).

(19) In the analysis of some unpublished data, the senior author has found the extrapolated value of  $pK$  for the first step in the dissociation of phosphoric acid to be altered by nearly 0.03 when  $a^*$  used to compute  $mH$  is changed from 2 to 6.  $pK_1$  is 2.12: L. F. Nims, *THIS JOURNAL*, **56**, 1110 (1934). A similar but much less pronounced effect has been reported by W. J. Hamer, G. D. Pinching, and S. F. Acree, *J. Research Natl. Bur. Standards*, **35**, 539 (1945), for *o*-phthalic acid, a weaker acid than phosphoric.

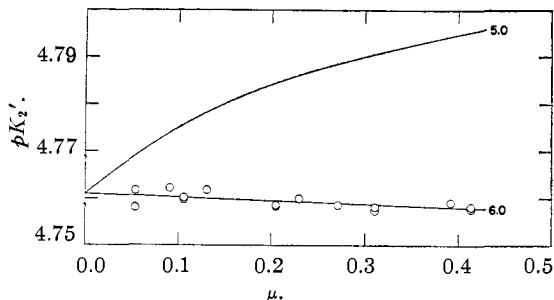


Fig. 3.—Determination of  $pK_2$  from data of series 3. Number beside each curve indicates the value of  $a^*$  used.

The essential agreement of  $pK_2$  values calculated by the equations for overlapping from the measurements of series 8 and of series 4 is demonstrated in Fig. 4. These curves show, as well, the consistency of the results for  $pK_1$  and  $pK_3$  at this temperature, for the open circles were derived from  $-1/2 \log (K_1K_2)'$  of equation (9) together with  $pK_1$ , whereas the dots were obtained from  $-1/2 \log (K_2K_3)'$  of equation (20), together with  $pK_3$ . Curves a, b, and c correspond to 4.2, 4.7, and 5.2, respectively, for  $a^*$  in formula (20), and d, e, and f were calculated by formula (9) with the use of 2, 3, and 4, respectively, for  $a^*$ . The value of  $a^*$  in equations (5) and (8) is without appreciable effect on the concentration term of formula (20). Hence 4.7, the value yielding the best extrapolation of the data of series 4, was employed.

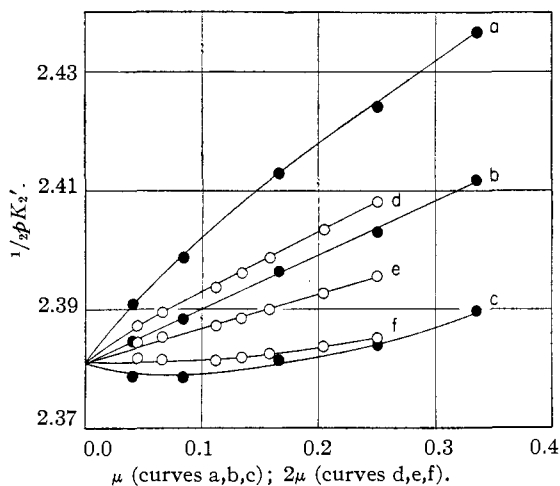


Fig. 4.—Determination of  $pK_2$  from data of series 2 (curves d, e, and f) and of series 4 (curves a, b, and c).

The determination of  $pK_3$  at 25° from an analysis of the results for buffer solutions of series 5 is illustrated in Fig. 5. The effect of a change of  $a^*$  in equation (27) upon the extrapolation is indicated by the positions of the three solid lines labeled 5.6, 6.0 and 6.4. These were calculated from the data of series 5a, whereas series 5b yielded  $pK_3'$  values represented by the dots, for

TABLE IV  
VALUES OF  $pK_1$ ,  $pK_2$  AND  $pK_3$

$t, ^\circ\text{C.}$	$pK_1$	$pK_2$		Average	$pK_3$
		Series 2	Series 3		
0	3.220 $\pm$ 0.0033	4.837	4.836 $\pm$ 0.0012	4.837	6.393 $\pm$ 0.0015
5	3.200 $\pm$ .0020	4.813	4.813 $\pm$ .0015	4.813	6.386 $\pm$ .0019
10	3.176 $\pm$ .0022	4.799	4.795 $\pm$ .0012	4.797	6.383 $\pm$ .0016
15	3.160 $\pm$ .0021	4.783	4.782 $\pm$ .0013	4.782	6.384 $\pm$ .0016
20	3.142 $\pm$ .0020	4.769	4.768 $\pm$ .0012	4.769	6.388 $\pm$ .0013
25	3.128 $\pm$ .0018	4.761	4.761 $\pm$ .0009	4.761 <sup>a</sup>	6.396 $\pm$ .0011
30	3.116 $\pm$ .0017	4.757	4.753 $\pm$ .0015	4.755	6.406 $\pm$ .0020
35	3.109 $\pm$ .0024	4.752	4.750 $\pm$ .0013	4.751	6.423 $\pm$ .0020
40	3.099 $\pm$ .0018	4.753	4.748 $\pm$ .0014	4.750	6.439 $\pm$ .0018
45	3.097 $\pm$ .0013	4.757	4.752 $\pm$ .0011	4.754	6.462 $\pm$ .0019
50	3.095 $\pm$ .0022	4.760	4.755 $\pm$ .0013	4.757	6.484 $\pm$ .0024

<sup>a</sup> 4.761 was also obtained from Series 4.

$a^* = 6.0$ . The dashed line shows the course of the extrapolation of series 5a solutions when the correction for  $K_2$  ( $m_{\text{H}_2\text{C}_1^-}$  in formula (27)) is ignored. It is apparent that employment of a three-fold excess of tertiary salt over secondary salt has effectively reduced the magnitude of the correction. If  $a^*$  in equation (8) is changed from 4 to 6, the second term on the right of formula (27) undergoes a change amounting to 0.0023 for an ionic strength of 0.45. Nevertheless, the differences disappear in the extrapolation to zero ionic strength.

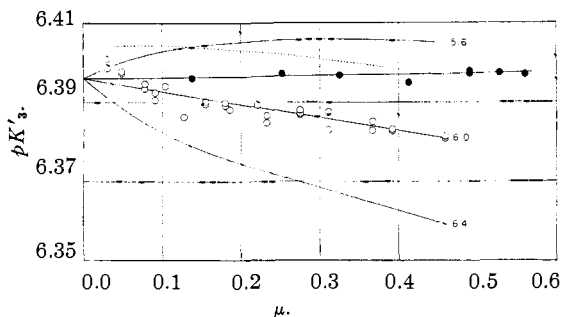


Fig. 5.—Determination of  $pK_3$  from data of series 5a (open circles and curved lines) and of series 5b (dots).

The experimental points at the two lowest ionic strengths are seen to lie somewhat above the curves used for extrapolation. The departures correspond to 0.16, 0.20, 0.22, and 0.36 mv. and are, with one exception, only slightly larger than the estimated experimental error. If these data in dilute solutions are correct, the plots of  $pK_3'$  with respect to ionic strength would have to depart from the paths predicted by the Hückel equation<sup>20</sup> and followed at the higher concentrations. For  $a^*$  less than 5.8, these curves would have points of inflection at ionic strengths near 0.05 that cannot be justified in terms of the Hückel equation alone. The influence of the higher terms of the Debye-Hückel theory<sup>21</sup> upon

(20) E. Hückel, *Physik. Z.*, **26**, 93 (1925). This equation differs from (8) by inclusion of a term linear in ionic strength.

(21) T. H. Gronwall, V. K. LaMer and K. Sandved, *ibid.*, **29**, 358 (1928); V. K. LaMer, T. H. Gronwall and L. J. Greiff, *J. Phys. Chem.*, **35**, 2245 (1931).

the last term of equation (25) is large and could cause a rapid change in slope at concentrations below the lowest studied in this investigation. Unfortunately, the effect of higher terms at ionic strengths above 0.1 cannot readily be ascertained, and it is impossible to say whether the linearity of the plot between 0.05 and 0.57 $\mu$  is consistent with a pronounced change of slope below  $\mu = 0.05$ .

The negative logarithms of the constants for the three steps in the dissociation of citric acid at the 11 temperatures are summarized in Table IV and plotted as a function of temperature in Fig. 6. The characteristic minimum in  $pK$  is shifted to lower temperatures as the strength of the acidic group decreases. The values of  $pK$  at 18, 25 and 37° are compared in Table V with earlier determinations based upon electromotive-force measurements of cells with liquid junction. The agreement among the values of

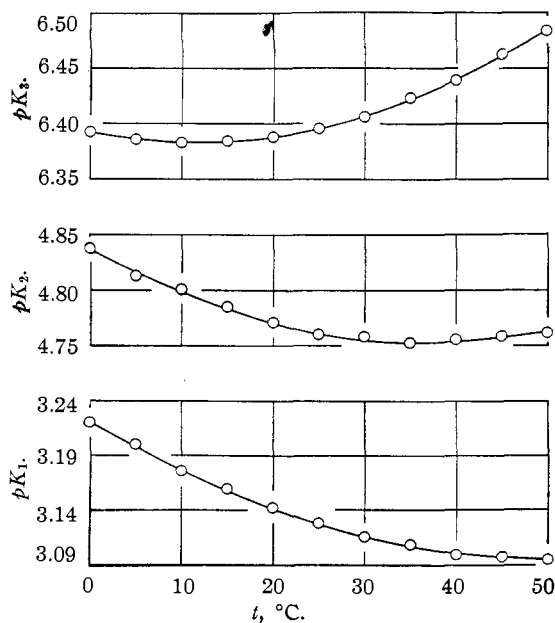


Fig. 6.— $pK_1$ ,  $pK_2$  and  $pK_3$  plotted as a function of temperature.



$pK_2$  and among three of the four values of  $pK_3$  is satisfactory, but  $pK_1$  obtained from cells with liquid junction is lower by 0.05 to 0.07 than that found in this investigation.

TABLE V

COMPARISON OF  $pK$  WITH THAT DERIVED FROM THE E. M. F. OF CELLS WITH LIQUID JUNCTION

	Method	$t_j$ °C.	$pK_1$	$pK_2$	$pK_3$
Simms <sup>4</sup>	Cells with l. j.	25	3.08	4.74	6.26
Kolthoff and Bosch <sup>5</sup>	Cells with l. j.	18	3.075	4.752	6.407
Bjerrum and Unmack <sup>6</sup>	Cells with l. j.	18	3.087	4.769	6.398
		25	3.057	4.759	6.400
		37	3.042	4.747	6.424
This investigation	Cells without l. j.	18	3.149	4.774	6.386
		25	3.128	4.761	6.396
		37	3.105	4.750	6.429

### Thermodynamic Functions

The values of  $pK_1$ ,  $pK_2$  and  $pK_3$  listed in Table IV were fitted by the method of least squares to an equation of the form<sup>22</sup>

$$-\log K_n = A/T + B + CT \quad (30)$$

where  $T$  is the temperature on the Kelvin scale ( $^{\circ}\text{C.} + 273.16$ ). The constants of equation (30) are given in Table VI. The average difference between the "observed"  $pK_1$  at the 11 temperatures and the corresponding values calculated by equation (30) is 0.0010. For  $pK_2$  and  $pK_3$  the differences are, respectively, 0.0009 and 0.0007.<sup>23</sup>

TABLE VI

CONSTANTS OF EQUATION (30)

Dissociation step	A	B	C
1	1255.6	-4.5635	0.011673
2	1585.2	-5.4460	.016399
3	1814.9	-6.3664	.022389

The molal changes of free energy,  $\Delta F^0$ , of heat content,  $\Delta H^0$ , of entropy,  $\Delta S^0$ , and of heat capacity,  $\Delta C_p^0$  that accompany each of the dissociation processes in the standard state are readily derived from the constants of equation (30).

$$\Delta F^0 = 2.3026 R(A + BT + CT^2) \quad (31)$$

$$\Delta H^0 = 2.3026 R(A - CT^2) \quad (32)$$

$$\Delta S^0 = 2.3026 R(-B - 2CT) \quad (33)$$

$$\Delta C_p^0 = 2.3026 R(-2CT) \quad (34)$$

where  $R$ , the gas constant, is 8.3127 int. j. deg.<sup>-1</sup> mole<sup>-1</sup>. These thermodynamic quantities are summarized in Table VII.

The molal entropy change at 25° for the first step in the dissociation is -11.0 cal. deg.<sup>-1</sup>, -19.8 for the second step, and -32.0 for the third.

(22) H. S. Harned and R. A. Robinson, *Trans. Faraday Soc.*, **36**, 973 (1940).

(23) The first and third constants can be represented by the equation  $-\log K_n = A/T + B + C \log T$  with average differences of 0.0018 and 0.0012, respectively, between "observed" and calculated  $-\log K_n$ . Inasmuch as equation (30) gave a better fit of the dissociation constants, it was used to calculate the thermodynamic functions. The differences between the thermodynamic quantities derived from the two equations are not large at 25° but are considerably greater at the extremes of the temperature range.

TABLE VII

THERMODYNAMIC QUANTITIES FOR THE DISSOCIATION OF CITRIC ACID AND OF THE PRIMARY AND SECONDARY CITRATE IONS

°C.	$\Delta F^0$ , int. j. mole <sup>-1</sup>	$\Delta H^0$ , int. j. mole <sup>-1</sup>	$\Delta S^0$ , int. j. deg. <sup>-1</sup> mole <sup>-1</sup>	$\Delta C_p^0$ , int. j. deg. <sup>-1</sup> mole <sup>-1</sup>
Process: $\text{H}_3\text{Ci} = \text{H}^+ + \text{H}_2\text{Ci}^-$				
0	16,843	7,362	-34.7	-122
5	17,023	6,746	-37.0	-124
10	17,214	6,118	-39.2	-127
15	17,415	5,480	-41.4	-129
20	17,627	4,831	-43.6	-131
25	17,852	4,170	-45.9	-133
30	18,087	3,498	-48.1	-135
35	18,333	2,815	-50.4	-138
40	18,590	2,121	-52.6	-140
45	18,859	1,416	-54.8	-142
50	19,138	700	-57.1	-144
Process: $\text{H}_2\text{Ci}^- = \text{H}^+ + \text{HCi}^-$				
0	25,284	6,921	-67.2	-171
5	25,634	6,055	-70.4	-175
10	25,993	5,174	-73.5	-178
15	26,368	4,278	-76.7	-181
20	26,760	3,365	-79.8	-184
25	27,153	2,437	-82.9	-187
30	27,589	1,494	-86.1	-190
35	28,027	534	-89.2	-193
40	28,481	-441	-92.4	-197
45	28,951	-1,432	-95.5	-200
50	29,437	-2,438	-98.6	-203
Process: $\text{HCi}^- = \text{H}^+ + \text{Ci}^-$				
0	33,429	2,762	-112.3	-234
5	34,000	1,581	-116.6	-238
10	34,594	378	-120.8	-243
15	35,209	-846	-125.2	-247
20	35,846	-2,092	-129.4	-251
25	36,503	-3,359	-133.7	-256
30	37,182	-4,647	-138.0	-260
35	37,883	-5,957	-142.3	-264
40	38,604	-7,288	-146.6	-268
45	39,348	-8,641	-150.8	-273
50	40,114	-10,015	-155.1	-277

The values for the first two steps are somewhat smaller than those found for other weak acids of the same electric type.<sup>24</sup> These functions have not heretofore been determined for a third dissociation step by methods free of the uncertainties of the liquid junction. However,  $\Delta F^0$ ,  $\Delta H^0$  and  $\Delta S^0$  for all three steps in the dissociation of phosphoric and citric acids can be derived from the data for hydrogen-calomel cells with liquid junction at 18, 25 and 37° reported by Bjerrum and Unmack.<sup>6</sup> For the third group of phosphoric acid,  $\Delta S^0$  is found to be approximately -35 cal. deg.<sup>-1</sup> mole<sup>-1</sup> at 27.5°, or about the same as for the third group of citric acid. The thermodynamic functions for the dissociation of citric acid were computed from the data of Bjerrum and Unmack and are compared in Table

(24) H. S. Harned and B. B. Owen, *Chem. Rev.*, **25**, 31 (1939).

VIII with those found in this investigation. The two sets of values are in good agreement. For these purposes, values in calories were obtained by dividing the number of int. j. by the conversion factor 4.1833.

TABLE VIII  
COMPARISON OF THERMODYNAMIC FUNCTIONS AT 25°

	$\Delta F^0$ , cal. mole <sup>-1</sup>	$\Delta H^0$ , cal. mole <sup>-1</sup>	$\Delta S^0$ , cal. deg. <sup>-1</sup> mole <sup>-1</sup>
Bjerrum and Unmack, Step 1	4170	940 <sup>a</sup>	-11
Step 2	6492	408 <sup>a</sup>	-20
Step 3	8731	-754 <sup>a</sup>	-32
This investigation, Step 1	4268	997	-11.0
Step 2	6491	583	-19.8
Step 3	8726	-803	-32.0

<sup>a</sup> Calculated from values at 27.5° with the use of  $\Delta C_p^0$  found in this investigation.

It is possible to compare  $\Delta C_p^0$  given in Table VII with that derived from the temperature coefficients of heats of dilution determined by Richards and Mair<sup>25</sup> and from the heat capacity measurements of Richards and Gucker<sup>26</sup> at 18°. From these data, Rossini<sup>27</sup> has evaluated the partial molal heat capacities of citric acid and of the three sodium citrates at infinite dilution. By combination of these with the partial molal heat capacities of hydrochloric acid and sodium chloride, also at infinite dilution,<sup>28</sup>  $\Delta C_p^0$  for each dissociation step can be computed. The results are summarized in Table IX. The sum of  $\Delta C_p^0$  for the three steps, given in the last line, repre-

TABLE IX

$\Delta C_p^0$  FOR THE DISSOCIATION OF CITRIC ACID AT 18°, IN CAL. DEG.<sup>-1</sup>

	Calorimetric	E. m. f., mv.
Step 1	-41	-31
Step 2	-37	-44
Step 3	-54	-60
Process: $H_3Ci = 3H^+ + Ci^{\equiv}$	-132	-135

(25) T. W. Richards and B. J. Mair, *THIS JOURNAL*, **51**, 740 (1929).

(26) T. W. Richards and F. T. Gucker, Jr., *ibid.*, **47**, 1876 (1925).

(27) F. D. Rossini, *Bur. Standards J. Research*, **4**, 313 (1930).

(28) F. D. Rossini, *ibid.*, **7**, 47 (1931).

sents  $\Delta C_p^0$  for the process:  $H_3Ci = 3H^+ + Ci^{\equiv}$ . The agreement can be considered satisfactory, inasmuch as the calorimetric results may be in error by 5 cal.<sup>27</sup> and the E.m.f. determination by an amount at least as large.

Coulombic forces are probably responsible for a considerable part of the change of  $\Delta C_p^0$  from step 1 to step 3, for there is no marked change in chemical type. Consequently, the apparent irregularity of the results given in the second column of Table IX seems of doubtful significance. The calorimetric data for citric acid used in computing these results have not been corrected for acidic dissociation, nor have the detailed compositions of the citrate salt solutions been considered in obtaining the heat capacities at infinite dilution. However, these corrections have only a small effect upon the partial molal heat capacities of the salts at infinite dilution. On the other hand, the correction for acidic dissociation alters the value for citric acid itself by 5 to 10 cal., but the magnitude and direction of the change are such as to make more pronounced the irregularity in  $\Delta C_p^0$  for the three dissociation steps, although the sum remains in good agreement with the results of the present investigation.

### Summary

The three dissociation constants of citric acid have been determined at intervals of 5° from 0 to 50° from measurements of the electromotive force of hydrogen-silver chloride cells without liquid junction. The resolution was accomplished by analysis of data for 84 buffer solutions grouped into five series, as follows: (1) mixtures of citric acid and primary potassium citrate, (2) primary potassium citrate, (3) mixtures of primary and secondary potassium citrates, (4) secondary potassium citrate, and (5) mixtures of secondary and tertiary potassium citrates. The changes of free energy, heat content, entropy, and heat capacity associated with the dissociation reactions in the standard state have been calculated from the dissociation constants at the eleven temperatures.

WASHINGTON, D. C.

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