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SECOND DISSOCIATION CONSTANT OF *o*-PHTHALIC ACID AND RELATED pH VALUES OF PHTHALATE BUFFERS FROM 0° TO 60° C

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ABSTRACT

Measurements were made of the potential difference between hydrogen electrodes and silver–silver-chloride electrodes in aqueous solutions of 72 different phthalate-chloride mixtures at 13 temperatures from 0° to 60° C. By described experimental and mathematical procedures, the second dissociation constant of *o*-phthalic acid and related thermodynamic quantities were evaluated, and pH values were assigned to 217 solutions, including some containing no potassium chloride. The addition of the chloride lowers the pH of the solutions principally because of an increase in the ionic strength.

The second dissociation constant may be computed at each temperature by the equation

$$\log K_2 = -2175.83/T + 9.55095 - 0.025694T,$$

where $T = t\ °\mathrm{C} + 273.16$.

The pH values of the solutions may be computed for ratios of dipotassium phthalate to acid potassium phthalate from 1 to 2, and for ionic strengths, μ, from 0. to 0.5, by the equation

$$\mathrm{pH} = -\log K_2 + \log \frac{\text{dipotassium phthalate}}{\text{acid potassium phthalate}} - 3A\sqrt{\mu}/(1+3.76B\sqrt{\mu}) + \beta\mu,$$

in which A and B are constants dependent upon the temperature, and β is a constant dependent upon the temperature, salt concentration, and buffer ratio.

The addition of potassium chloride lowers the pH of the solutions in accordance with the equation

$$\mathrm{pH} = (\mathrm{pH})_0 + \alpha_1 m_{\mathrm{KCl}} + \alpha_2 m^2_{\mathrm{KCl}} + \alpha_3 m^3_{\mathrm{KCl}},$$

where $(\mathrm{pH})_0$ is the value at any temperature for a solution containing no potassium chloride and α_1, α_2, and α_3 are constants.

These solutions with or without potassium chloride are useful as pH standards from 4.87 to 5.72 and vary only slightly with changes in temperature. They have good buffer capacity and may be readily prepared from pure materials. The NBS Standard Samples 84a and 84b of acid potassium phthalate or Standard Samples of comparable purity are recommended for preparation of the solutions, together with carbonate-free potassium hydroxide of high grade and distilled water of pH 6.7 to 7.3.

CONTENTS

I. INTRODUCTION

Precision pH standards may be defined as buffer solutions whose compositions can be accurately reproduced and the pH values accurately obtained by hydrogen-electrode measurements. The pH standards commonly used are prepared from a weak acid and its salt, such as acetic acid and sodium acetate, or by the neutralization of an acid with alkali. The ideal ones can be prepared directly from a single salt, preferably a salt that is easily purified and is neither hygroscopic nor deliquescent, such as acid potassium phthalate. This salt is now issued by the National Bureau of Standards for acidimetric work and may be used equally well as a pH standard.

Mixtures of acid potassium phthalate with hydrochloric acid or with sodium hydroxide were included in a list of standards for hydrogen-ion determination prepared by Clark and Lubs [1] [1] in 1916. They determined the pH of the solutions by a galvanic cell comprised of a hydrogen electrode, a salt bridge of saturated potassium chloride, and a decinormal calomel half-cell. For many years after their measurements, the reproducibility of hydrogen electrodes in solutions of acid potassium phthalate was questioned. Many experimenters found drifting potentials with hydrogen electrodes. However, it has been recently found that hydrogen electrodes prepared with palladium function well and that precise values of the pH of phthalate solutions can be obtained with their use [2]. Clark and Lubs chose 0.3379 v for the potential of their calomel half-cell at 20° C and assumed that the potentials at the junctions of the saturated potassium chloride bridge with the phthalate solution and the 0.1-*N* potassium chloride were zero. By this procedure, they obtained 3.974 for the pH of a 0.05-*M* solution of acid potassium phthalate. However, the liquid-junction potentials are not zero. For instance, the potential for the junction between 0.1-*N* and saturated potassium chloride is 0.00187 v at 25° C [3]. A value of 0.00251 v may be calculated by the Henderson equation [4] for the potential of the junction between saturated potassium chloride and 0.05-*M* acid potassium phthalate, if 50.5 is used for the mobility of the acid phthalate ion. These values with 0.3337 v [3] for the potential of the 0.1-*N* calomel half-cell excluding liquid-junction potentials give 0.3343 v for the value of the total calomel half-cell and bridge. Many other values for this half-cell, and, therefore, for the pH of 0.05-*M* acid potassium phthalate, have been suggested from time to time.

The problem of determining pH values from the emf of cells with liquid junction becomes more perplexing when it is realized that the potential of a liquid junction cannot be determined on a thermodynamic basis without assumptions regarding the magnitude of the activity coefficients of the individual ions involved at the liquid junction, and that the potential of a liquid junction depends upon the manner in which it is constructed. Clark and Lubs assumed that the hydrogen electrode gives a measure of hydrogen-ion concentration,

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[1] Figures in brackets indicate the literature references at the end of this paper.

whereas in reality it gives a measure of hydrogen-ion activity. In order to establish a pH scale on the basis of hydrogen-ion activity, Hitchcock and Taylor [5] and MacInnes, Belcher, and Shedlovsky [6] calibrated the calomel half-cell with solutions whose properties had been determined by cells without liquid junction.[2] The former obtained 0.2441 v for the saturated calomel half-cell and the latter 0.3360 v for the decinormal calomel half-cell. With the use of these values, they calculated 4.008 and 4.000, respectively, for the pH of 0.05-*M* acid potassium phthalate at 25° C. Recently, Hamer and Acree [9] obtained a value 4.008 for this solution by an abbreviated method based upon the measurements of galvanic cells without liquid junction.

A more precise method of approach to this problem is to make a comprehensive study of the thermodynamics of acid potassium phthalate or of mixtures of *o*-phthalic acid and potassium hydroxide. From the known equilibria of the two ionization steps in the dissociation of *o*-phthalic acid, designated as H_2Ph, and the concentration of the acid (a) and added base (b), it may be shown that the hydrogen-ion concentration of acid potassium phthalate of any strength ($a=b$ in this case) is given by eq 1:

$$H^3+[a+(K_1f_{H_2Ph})/(f_Hf_{HPh})]H^2+[(K_1K_2f_{H_2Ph})/(f^2_Hf_{Ph})]H-(aK_1K_2f_{H_2Ph})/(f^2_Hf_{Ph})=0, \qquad (1)$$

on the reasonable assumption that the effects of hydrolysis are small. Therefore, in order to obtain the true value of the hydrogen-ion concentration of acid potassium phthalate of any concentration, it is necessary to obtain precise values of the dissociation constants, K_1 and K_2, and of the activity coefficients, f, of the various ionic species.[3]

This paper gives the results of measurements of galvanic cells without liquid junctions and with hydrogen and silver-silver-chloride electrodes for the determination of K_2, the related activity coefficients, and the pH values of the solutions used in the determination of K_2. Measurements were made at 5-degree intervals from 0° to 60° C, inclusive, in order to determine the pH values over this range of temperature and to determine several thermodynamic quantities for the process $HPh^-=H^++Ph^=$. By comparison of these quantities with similar ones for other and similar types of dissociation, a critical estimate may be made of the reliability of the values of K_2. Determinations of K_2 were made prior to K_1 because the low solubility of *o*-phthalic acid prevents an accurate evaluation of the ionic sizes and "salting-out" coefficients of phthalate ions.

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[2] It is well known that an exact differentiation between hydrogen-ion concentration and activity cannot be made, as the value of the activity coefficient of the hydrogen ion cannot be determined without some assumption. Hitchcock and Taylor, and MacInnes, Belcher, and Shedlovsky in their method obtain a quantity that approximates the value of the hydrogen-ion activity. In this paper the assumption is made that the activity coefficients of ions are given by the Hückel equation and that the "salting-out" terms of the chloride and hydrogen ions are equal. See references [3, 7, 8] for discussions of assumptions used in connection with work on measurements of acidity.

[3] In this paper, the symbol f is used for the activity coefficient of an ion or molecule for any scale of concentration. In this work, molality is used as the concentration unit. The symbol γ is often used for activity coefficients on this scale of concentration.

II. METHOD FOR THE DETERMINATION OF THE SECOND DISSOCIATION CONSTANT OF *o*-PHTHALIC ACID

1. APPROXIMATE METHOD[4]

In the determination of the second dissociation constant of *o*-phthalic acid by the electromotive-force method, measurements are made of the emf of the galvanic cell

$$\text{Pd, } H_2(g)|KHPh(m_1),\ K_2Ph(m_2),\ KCl(m_3)|AgCl(s)|Ag(s) \qquad (1)$$

for a series of solutions of different molalities, m_1, m_2, and m_3, and of various buffer ratios, $K_2Ph/KHPh$, wherein the hydrogen and silver–silver-chloride electrodes are reversible, respectively, to hydrogen and chloride ions. The addition of the chloride is therefore a prerequisite for the use of silver–silver-chloride electrodes in such solutions. The calculations of the constant depend upon the equation[5]

$$E=E^\circ-(RT/F)\ln(a_{\mathrm{H}}a_{\mathrm{Cl}})=E^\circ-(RT/F)\ln a_{\mathrm{H}}-(RT/F)\ln(f_{\mathrm{Cl}}m_{\mathrm{Cl}}), \qquad (2)$$

relating the emf of the cell, E, with the activities of the hydrogen and chloride ions, and upon the mass-action expression

$$K_2=(a_{\mathrm{H}}a_{\mathrm{Ph}})/a_{\mathrm{HPh}}=(a_{\mathrm{H}}f_{\mathrm{Ph}}m_{\mathrm{Ph}})/(f_{\mathrm{HPh}}m_{\mathrm{HPh}}), \qquad (3)$$

which defines the dynamic equilibrium between the ions for the process $HPh^-=H^++Ph^=$. E° is the potential of the silver–silver-chloride electrode for unit activity of hydrochloric acid; a, f, and m are the activity, activity coefficient, and molality of the ions denoted by subscripts; and R, T, and F have their usual significance. In eq 2 and 3, E, E°, m_{Ph}, m_{HPh}, m_{Cl}, R, T, and F are known quantities, whereas a_{H} and the activity coefficient terms (f) are unknown quantities. The former unknown may be eliminated by combining eq 2 and 3 to give

$$\begin{aligned}&[(E-E^\circ)/(2.3026RT/F)+\log(m_3m_1/m_2)]+\\&\log(f_{\mathrm{Cl}}f_{\mathrm{HPh}}/f_{\mathrm{Ph}})=-\log K_2=\mathrm{p}K_2,\end{aligned} \qquad (4)$$

upon substitution of m_1, m_2, and m_3, respectively, for HPh^-, $Ph^=$ and Cl^-.

The last term on the left side of eq 4 is an unknown quantity. The values of the activity coefficients in this term give the magnitude of the deviations of the ions or molecules from the perfect state. If the ions in solution conformed to the laws of perfect solutes having unit activity coefficients, this term would be zero. Only at infinite dilution do ions possess the characteristics of ideal solutes. Hence if values of the term in brackets for decreasing values of (m_3m_1/m_2) are plotted against the ionic strength, values of $\mathrm{p}K_2$ are obtained by

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[4] A review of the development of the method and its application to a large number of acids and bases is given by Harned and Owen [10]. Heretofore, a successful application of the method to dibasic acids for which the ratio of the second to the first dissociation constant is greater than 10^{-3} has not been made (see Glasstone, Introduction to electrochemistry, p. 322, D. Van Nostrand Co., Inc., New York, N. Y., 1942), and involves successive approximations, which are tedious. The ratio of the constants for *o*-phthalic acid is about 3×10^{-3}, and hence the present paper presents the application of the method to a more involved system. For a review of earlier emf studies of the ionization of weak electrolytes, see references [11, 12].

[5] For simplicity, the ionic charges are omitted in the formulas and equations.

extrapolation to zero ionic strength. This extrapolation is usually difficult, owing to a marked curvature in the plots in the range of concentration accessible to experimental measurements [8]. However, this difficulty may be overcome by the use in eq 4 of the Debye-Hückel equations [13, 14] for the activity coefficients of the ions. From theoretical considerations Debye and Hückel obtained eq 5,

$$-\log f_i = Az_i^2\sqrt{\mu}/(1+Ba_i\sqrt{\mu})+\beta m_i, \tag{5}$$

for the activity coefficient of an ion in terms of the general constants A and B, the constants a_i and β characteristic of the electrolyte under consideration, the ionic charge, z_i, the ionic strength of the solution, μ, expressed in moles of solute per liter of solution, and the concentration of ions (or salt).[6] For the HPh^-, $Ph^=$, and Cl^- ions, this equation gives

$$-\log f_{HPh} = A\sqrt{\mu}/(1+Ba_i\sqrt{\mu})+\beta_{HPh}m_{HPh}, \tag{6}$$

$$-\log f_{Ph} = 4A\sqrt{\mu}/(1+Ba_i\sqrt{\mu})+\beta_{Ph}m_{Ph}, \tag{7}$$

$$-\log f_{Cl} = A\sqrt{\mu}/(1+Ba_i\sqrt{\mu})+\beta_{Cl}m_{Cl}. \tag{8}$$

Substitution of these expressions in eq 4 for the respective activity coefficients gives eq 9,

$$\begin{aligned}&(E-E^\circ)/(2.3026RT/F)+\log\,(m_3m_1/m_2)+2A\sqrt{\mu}/(1+Ba_i\sqrt{\mu})\\&-\beta_{HPh}m_{HPh}+\beta_{Ph}m_{Ph}-\beta_{Cl}m_{Cl}=-\log K_2=\mathrm{p}K_2.\end{aligned} \tag{9}$$

The term $(-\beta_{HPh}m_{HPh}+\beta_{Ph}m_{Ph}-\beta_{Cl}m_{Cl})$ may be replaced by $\beta\mu$. Justification of this may be shown as follows. If the properties of each ionic specie present in the mixture are additive functions of those of the individual ions composing the mixture, then $\beta_{Ph}m_{Ph}-\beta_{HPh}m_{HPh}-\beta_{Cl}m_{Cl}$ would equal $1/2(\beta_{Ph})\mu_{Ph}-\beta_{HPh}\mu_{HPh}-\beta_{Cl}\mu_{Cl}$ as $\mu_{Ph}=2m_{Ph}$, $\mu_{HPh}=m_{HPh}$, and $\mu_{Cl}=m_{Cl}$, and $\mu=\mu_{Ph}+\mu_{HPh}+\mu_{Cl}$. Now, if the ionic strength due to each ion is some fraction of the total ionic strength, namely, $\mu_{Ph}=p\mu$, $\mu_{HPh}=q\mu$, and $\mu_{Cl}=r\mu$ where p, q, and r are constants for a specified ratio of salts, we have $1/2(p\beta_{Ph})\mu-(q\beta_{HPh})\mu-(r\beta_{Cl})\mu=1/2(p\beta_{Ph}-2q\beta_{HPh}-2r\beta_{Cl})\mu=\beta\mu$. Hence the substitution of $\beta\mu$ for the term $(-\beta_{HPh}m_{HPh}+\beta_{Ph}m_{Ph}-\beta_{Cl}m_{Cl})$ is justified. With this substitution, eq 9 becomes

$$\begin{aligned}&[(E-E^\circ)/(2.3026\;RT/F)+\log\,(m_3m_1/m_2)+2A\sqrt{\mu}/(1+Ba_i\sqrt{\mu})]+\\&\beta\mu=-\log K_2=\mathrm{p}K_2\end{aligned} \tag{10}$$

$$\mathrm{p}K_2'+\beta\mu=\mathrm{p}K_2 \tag{10a}$$

where $\mathrm{p}K_2'$ is used to designate the terms in the brackets of eq 10. Values of $\mathrm{p}K_2$ are then obtained by extrapolation to infinite dilution of the values of $\mathrm{p}K_2'$ as a function of μ. The negative of the slopes of these plots gives the values of β for the various ratios of salts used in the experiments.

As values of p, q, and r are known for each ratio of salts, the values of β_{Ph}, β_{HPh}, and β_{Cl} may be determined from the observed values of β as the ratio of salts is altered. It should be noted that when all three salts are kept in constant ratio, values of p, q, and r remain the same

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[6] Scatchard [15] recommends the use of molality, or moles of solute per 1,000 g of solvent, in the Debye-Hückel equation. This recommendation has been followed in this laboratory.

even if the concentration of each salt varies considerably. However, values of p, q, and r vary if the ratio of only two salts is kept constant. Hence, it is simpler to use the molalities of each ionic species than values of p, q, and r in the calculations. When the molalities of each ionic species are used, a series of simultaneous equations of the type $(\beta_{Ph}m_{Ph}-\beta_{HPh}m_{HPh}-\beta_{Cl}m_{Cl}=\beta\mu)$ are obtained, from which the values of β_{HPh}, β_{HPh}, and β_{Cl} may be evaluated. In the present case the simultaneous equations were solved by the method of least squares.

It is then possible by using these individual β values to calculate the pH values of the different solutions by means of eq 2 or the expanded form of eq 3, namely,[7]

$$(E-E^{\circ})/(2.3026\,RT/F)+\log m_{Cl}-A\sqrt{\mu}/(1+Ba_i\sqrt{\mu})+\beta_{Cl}m_{Cl}= -\log a_H=\mathrm{pH}; \tag{11}$$

$$pK_2-\log(m_1/m_2)-3A\sqrt{\mu}/(1+Ba_i\sqrt{\mu})+\beta_{Ph}m_{Ph}-\beta_{HPh}m_{HPh}= -\log a_H=pH. \tag{12}$$

Frequently the hydrogen-ion concentration is also desired (see footnote 2). If it is assumed that $\beta_H=\beta_{Cl}$, the hydrogen-ion concentration may be computed [16] from the emf by the equation

$$(E-E^{\circ})/(2.3026\,RT/F)+\log m_{Cl}-2A\sqrt{\mu}/(1+Ba_i\sqrt{\mu})+\beta_{Cl}m_{Cl}+ \beta_H m_H=-\log m_H. \tag{13}$$

This equation is used in the calculation of m_H, needed for the more rigorous evaluation of K_2 described below.

In the above procedure, the terms involving β for the various ions were considered to be additive. This procedure may be justified as follows, from considerations of the activity coefficients of hydrochloric acid in acid-salt mixtures. Güntelberg [17] and Harned [18] have shown that the activity coefficient of hydrochloric acid in acid-salt mixtures of a constant total molality is given by the relationship

$$\log(f_H f_{Cl})_{\text{mixture}}=\log(f_H f_{Cl})_{\text{pure}}-k_1 m_{\text{salt}}, \tag{14}$$

where k_1 is a constant dependent upon the total molality of the mixture, and $(f_H f_{Cl})_{\text{pure}}$ is that for the total molality of the mixture. For mixtures of hydrochloric acid and potassium chloride at 25°C $k_1=0.080$ and 0.0624 for a total molality, respectively, of 0.1 and 0.5. For aqueous solutions of pure hydrochloric acid, Harned and Ehlers [19] obtained the expression[8] (eq 15) for the activity coefficient as a function of

$$\log(f_H f_{Cl})_{\text{pure}}=-A\sqrt{\mu}/(1+Ba_i\sqrt{\mu})+0.133\mu \tag{15}$$

the molality at 25° C. Hence, for an ionic strength of 0.1,

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[7] In the above treatment, a_i is considered to be the same for each ion. This constant has the dimensions of reciprocal centimeters and represents the so-called closest distance of approach of the ions in solution. On the other hand, the value of a_i could be considered an average of different values for the various ions. If this were the case, a different value of a_i would be required in eq 9 for different buffer ratios. The individual values of the closest distance of approach of each ion could then be determined by the method of simultaneous equations, using the relationship $a_i\mu=a_1m_1+a_2m_2+a_3m_3$ or some other more complex function, where a_i is the observed value for different buffer ratios and a_1, a_2, and a_3 represent, respectively, the closest distance of approach of the acid phthalate, phthalate, and chloride ions. It will be shown later in this paper that the same value of a_i represents the experimental data for different buffer ratios, and therefore within the experimental accuracy $a_i=a_1=a_2=a_3$ in phthalate-chloride mixtures.

[8] Harned and Ehlers in their paper used γ for the activity coefficient of hydrochloric acid. The symbol f used in this paper refers to the same numerical values as they give in their paper. It is now the procedure in the National Bureau of Standards to employ the symbol f for activity coefficients on any scale and use the symbols f_c, f_m, and f_x, respectively, for concentrations expressed in moles per liter of solution, moles per 1,000 g of solvent, and in mole fractions.

$$\log (f_{\mathrm{H}} f_{\mathrm{Cl}})_{\mathrm{mixture}} = -A\sqrt{\mu}/(1+Ba_i\sqrt{\mu}) + 0.133\mu - 0.080\ m_{\mathrm{salt}}, \quad (16)$$

and for an ionic strength of 0.5,

$$\log (f_{\mathrm{H}} f_{\mathrm{Cl}})_{\mathrm{mixture}} = -A\sqrt{\mu}/(1+Ba_i\sqrt{\mu}) + 0.133\mu - 0.0624\ m_{\mathrm{salt}}. \quad (17)$$

However, it has been found that the values of $\log (f_{\mathrm{H}} f_{\mathrm{Cl}})_{\mathrm{mixture}}$ may be represented equally well for both ionic strengths by the single equation

$$\log (f_{\mathrm{H}} f_{\mathrm{Cl}})_{\mathrm{mixture}} = -A\sqrt{\mu}/(1+Ba_i\sqrt{\mu}) + 0.0635\ m_{\mathrm{H}} + 0.0695 m_{\mathrm{Cl}}, \quad (18)$$

with an accuracy of ±0.0011 in the activity coefficient. Thus, the activity coefficients of hydrochloric acid in acid-salt mixtures may be calculated for different ionic strengths by an equation in which the terms involving β for H^+ and Cl^- ions are considered to be additive. In this treatment the value of a_i for acid-salt mixtures is about the same as for pure hydrochloric acid. Harned and Ehlers [19] obtained a value of 4.3 A. In all buffer mixtures studied by the method in which hydrogen and silver-silver-chloride electrodes are used, a_i should therefore have a value very close to that of hydrochloric acid or 4.3. The value of 3.76 A found in this investigation is considered to be a close approximation. As the addition of potassium salts lowers the activity coefficients of hydrochloric acid, the value of a_i for such mixtures could be somewhat lower than 4.3 A, and the value of 3.76 A obtained here is in accord with this fact.

2. COMPLETE METHOD

In the foregoing it was assumed that the buffer ratio, m_1/m_2, may be determined from the stoichiometrical molalities of acid potassium phthalate and dipotassium phthalate. However, owing to various ionic equilibria this is not strictly true and corrections must therefore be made accordingly.

In a mixture of *o*-phthalic acid with its acid salt, or a mixture of the latter with the completely neutralized salt, the essential equilibria are

$$H_2Ph = H^+ + HPh^-, \quad (19)$$

$$HPh^- = H^+ + Ph^=, \quad (20)$$

which upon subtraction give

$$2HPh^- = H_2Ph + Ph^=, \quad (21)$$

In each case, the ions and molecules are in dynamic equilibrium defined by the mass-action expressions. These give, respectively, for processes 19 and 21

$$K_1 = (a_{\mathrm{H}} f_{\mathrm{HPh}} m_{\mathrm{HPh}})/(f_{\mathrm{H_2Ph}} m_{\mathrm{H_2Ph}}), \quad (22)$$

and

$$K_2/K_1 = (a_{\mathrm{Ph}} a_{\mathrm{H_2Ph}})/a^2_{\mathrm{HPh}} = (f_{\mathrm{Ph}} f_{\mathrm{H_2Ph}} m_{\mathrm{Ph}} m_{\mathrm{H_2Ph}})/(f_{\mathrm{HPh}} m_{\mathrm{HPh}})^2, \quad (23)$$

where the terms have the same significance as above. The expression for process 20 is given by eq 3.

As a result of these equilibria, in a solution composed of KHPh of molality of m_1 and of K_2Ph of a molality of m_2

$$m_{HPh}=m_1-m_H-2m_{H_2Ph}, \tag{24}$$

as HPh^- is removed in process 20 to form H^+ ions and in process 21 to form H_2Ph. Also

$$m_{Ph}=m_2+m_H+m_{H_2Ph}, \tag{25}$$

as HPh^- is removed in process 20 in an amount equivalent to H^+ ions and in process 21 in an amount equivalent to H_2Ph. Consequently, the stoichiometrical molalities of KHPh and K_2Ph will be altered and a quantity of H_2Ph formed as a result of the above processes. However, if K_2/K_1 is less than about 10^{-3}, the tendency of reaction 21 to take place from left to right will be small and m_{H_2Ph} can be neglected in eq 24 and 25, leaving only the corrections for m_H. This was shown in a previous paper to be true for malonic acid for which K_2/K_1 is about 1.4×10^{-3} [8]. The values for m_H are obtained from the emf by eq 13 given above. This entails the method of successive approximations as $\mu=m_1+3m_2+m_3+2m_H$[9]. A preliminary value of m_H is first obtained from the emf, by the use of the stoichiometrical ionic strength. This value of m_H is then used to calculate a new ionic strength, and the process is repeated until self-consistent values of μ and m_H are obtained. Hence two equations, eq 13 and the equation $\mu=m_1+3m_2+m_3+2m_H$ are used in the method of successive approximations.

From data reported in the literature [20] for *o*-phthalic acid, K_2/K_1 is about 3×10^{-3} which exceeds the condition postulated for the neglect of m_{H_2Ph} in eq 24 and 25. Therefore corrections for H_2Ph, sometimes called "overlapping" corrections because H_2Ph and HPh^- are titrated simultaneously, become necessary even though they are small. They may be obtained as follows. If *a* equals the molality of the acid and *b* the molality of added alkali, then for any mixture of the two

$$a=m_{H_2Ph}+m_{HPh}+m_{Ph}, \tag{26}$$

and for electrical neutrality

$$b+m_H=m_{HPh}+2\ m_{Ph}. \tag{27}$$

By means of these equations and eq 3 and 22

$$m_{H_2Ph}=[2\ am_H-m_H(b+m_H)]/[2\ m_H+(K_1f_{H2Ph})/(f_Hf_{HPh})], \tag{28}$$

with the condition [10] that eq 29,

$$m_H{}^3+[a+(K_1f_{H_2Ph})/(f_Hf_{HPh})]m_H{}^2+[(K_1K_2f_{H_2Ph})/(f_Hf_{Ph})+(bK_1f_{H_2Ph})/(f_Hf_{HPh})-(aK_1f_{H_2Ph})/(f_Hf_{HPh})]\ m_H+[(K_1K_2f_{H_2Ph})/(f_H{}^2f_{Ph})](b-2a)=0, \tag{29}$$

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[9] The ionic strength actually is given by $\mu=m_1+3m_2+m_3+2m_H+m_{H_2Ph}$, where value of m_{H_2Ph} is given by eq 28. As values of m_{H_2Ph} are so small, the term m_{H_2Ph} may be neglected in determining the ionic strength.

[10] This condition must be imposed. In the four eq 3, 22, 26 and 27 there are 5 unknowns, namely K_1, K_2, m_{H_2Ph}, m_{HPh}, and m_{Ph}, provided m_H is determined experimentally. Hence an unequivocal solution is not possible without the introduction of a restriction or condition. Frequently, a solution of the equations is obtained in titration experiments by selecting 2 widely separated values for m_H on the titration curve and substituting them in eq 29 and solving the two equations simultaneously for K_1 and K_2. This procedure is the same as imposing a condition.

obtained by the elimination of $m_{\mathrm{H_2Ph}}$, m_{HPh}, and m_{Ph} in eq 3, 22, 26, and 27 is satisfied for the solutions of any composition and concentration. However, solution of eq 28 required a knowledge of m_{H}, the activity coefficients, K_1, and K_2. Values of m_{H} can be obtained from the emf by eq 13 described above. Values of K_2 used first are those obtained by the simplified method described above. A value of 1.3×10^{-3} was used for K_1[20].[11] The Debye-Hückel equations were employed to calculate the activity coefficients of the ions and the activity coefficient of H_2Ph was taken equal to unity, as is customary. After values of $m_{\mathrm{H_2Ph}}$ are calculated by use of eq 28 they are used in eq 24 and 25 to calculate new values of the molality for the HPh^- and $Ph^=$ ions. These latter values are then used to calculate new values of K_2 and this arithmetical procedure is repeated until self-consistent values of K_2 and $m_{\mathrm{H_2Ph}}$ are obtained.

The corrections for both m_{H} and $m_{\mathrm{H_2Ph}}$ become less significant as the ionic strength of the solutions increases. It was found that the total corrections, Δ, may be expressed as a function of the ionic strength by the eq

$$\Delta=(\omega+\lambda\sqrt{\mu})/\mu, \tag{30}$$

where ω and λ are constants independent of the temperature. With these corrections eq 10, 11, and 12 become

$$(E-E^\circ)/(2.3026RT/F)+\log\,(m_3m_1/m_2)-(\omega+\lambda\sqrt{\mu})/\mu+2A\sqrt{\mu}/(1+Ba_i\sqrt{\mu})+\beta\mu=\mathrm{p}K_2, \tag{31}$$

$$(E-E^\circ)/(2.3026RT/F)+\log\,m_{\mathrm{Cl}}-A\sqrt{\mu}/(1+Ba_i\sqrt{\mu})-(\omega+\lambda\sqrt{\mu})/\mu+\beta_{\mathrm{Cl}}m_{\mathrm{Cl}}=\mathrm{pH}, \tag{32}$$

and

$$\mathrm{p}K_2-\log\,(m_1/m_2)-3A\sqrt{\mu}/(1+Ba_i\sqrt{\mu})+(\omega+\lambda\sqrt{\mu})/\mu+\beta_{\mathrm{Ph}}m_{\mathrm{Ph}}-\beta_{\mathrm{HPh}}m_{\mathrm{HPh}}=\mathrm{pH}, \tag{33}$$

by which precise values of pH and $\mathrm{p}K_2$ (or K_2) can be computed.

Sometimes the β values are considered to be equal for all the ions involved, or $\beta_1=\beta_2=\beta_3=\beta$. Then eq 33 reduces to

$$\mathrm{p}K_2-\log\,(m_1/m_2)-3A\sqrt{\mu}/(1+Ba_i\sqrt{\mu})+(\omega+\lambda\sqrt{\mu})/\mu=\mathrm{pH}, \tag{34}$$

containing no β term,[12] and is therefore different from the Henderson-Debye-Hückel equation [21] generally used to express pH as a function of the ionic strength of the solution. In this case, the pH value of the solution could be calculated solely from the values of $\mathrm{p}K_2$ and the concentration of the buffer without regard to salt effects. In eq 34, $-3A\sqrt{\mu}/(1+Ba_i\sqrt{\mu})$ represents the value of $\log(f_{\mathrm{Ph}}/f_{\mathrm{HPh}})$. However, the logarithm of the ratio of any two activity coefficients does not vary with the ionic strength in accordance solely with the first term of the Debye-Hückel equation. Furthermore, differentiation of eq 34 with respect to μ or $\sqrt{\mu}$ does not give a minimum in the plots of

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[11] The calculations are insensitive to the value of K_1. A value of $1.0\mathrm{x}10^{-3}$ or $1.5\mathrm{x}10^{-3}$ will yield substantially the same value of $m_{\mathrm{H_2Ph}}$.

[12] This equation has been shown to be applicable to buffers composed of disodium malonate, acid sodium malonate, and sodium chloride for which β is zero [8]. When β is zero, it is not possible to determine the β values for the individual ions.

(pH vs μ) or (pH vs $\sqrt{\mu}$), a result contrary to observed facts for the pH of several weak buffers [22] and of water in the presence of neutral salts [23]. Eq 34 also requires, for example, that a solution containing 0.1 *M* K_2Ph, 0.1 *M* KHPh, and 0.1 *M* KCl would have the same pH value as one composed of 0.07 *M* K_2Ph, 0.07 *M* KHPh, and 0.22 *M* KCl, or of 0.02 *M* K_2Ph, 0.02 *M* KHPh, and 0.42 *M* KCl, because of the identity in the ionic strength of these three solutions. In short, no "specific salt effects" would be observed and the change in the pH of a solution upon addition of salts could be calculated solely by the theory of Debye and Hückel. It is therefore necessary, in order to explain observed results with phthalates, to use eq 33, which includes the β term.

III. EXPERIMENTAL PROCEDURES

1. MATERIALS AND SOLUTIONS

The solutions used in this investigation were prepared in a CO_2-free atmosphere from known weights of stock solutions containing acid potassium phthalate, dipotassium phthalate, and potassium chloride by dilution with known weights of conductivity water having a specific conductance of 0.6 to 1.0×10^{-6} mho. The stock solutions were prepared by the addition of a calculated amount of dry acid potassium phthalate and dry potassium chloride to a standardized solution of potassium hydroxide, previously freed of carbonate by the addition dropwise of a saturated solution of barium hydroxide until no more precipitate of barium carbonate is formed. The potassium hydroxide solution was prepared from high-grade material, which exceeded the ACS specifications for analytical reagents. It was standardized against benzoic acid, National Bureau of Standards Standard Sample 39 e, in a CO_2-free atmosphere by using phenolphthalein solution as the indicator. Results of five titrations agreed to 0.02 percent. Acid potassium phthalate, NBS Standard Sample 84a, having a certified purity of 100 percent determined by titration, was dried according to the directions given in the Bureau certificate and was allowed to cool in a desiccator containing concentrated sulfuric acid. The potassium chloride was recrystallized twice from conductivity water and then thrice from 95-percent ethanol to remove the last traces of bromide. It was dried for at least 10 hours at 110° C and allowed to cool in a desiccator containing concentrated sulfuric acid. After the solutions were prepared, they were deaerated by hydrogen gas, corrections being made for loss of water from the solutions. All weights were corrected to vacuum. In determining the amount of water lost during the deaeration, corrections were made for the volume of air in the flasks displaced by hydrogen gas by using the density of each gas.

2. ELECTRODES AND APPARATUS

The hydrogen electrodes were platinum foil covered with palladium, according to the directions of Hamer and Acree [2]. Electrodes of this type do not catalyze the reduction of phthalates and they function reversibly for well over 100 hours.

Silver–silver-chloride electrodes of the thermal-electrolytic type were prepared from pure materials by the method described in a previous paper [7]. They were sufficiently aged to bring them to a stable state.

The details of the apparatus employed in these studies, including the cells, bubble tubes, thermostat, and the emf recording instruments have been described by Hamer and Acree [7]. The cells and bubble tubes were filled under reduced pressure, the temperature of the thermostat was controlled within 0.01° C at all the temperatures, and the emf was measured with a calibrated potentiometer and with a galvanometer and a standard cell. The electromotive forces were corrected in the usual manner to 1 atmosphere of hydrogen pressure.

IV. CALCULATION OF THE SECOND DISSOCIATION CONSTANT OF *o*-PHTHALIC ACID

The electromotive forces obtained at 13 temperatures from 0° to 60° C in 4 series of experiments on 4 different buffer ratios, K_2Ph/$KHPh$, designated as series A to D, are given in tables 1 to 4 for the different solutions whose compositions are defined in terms of the concentration of acid potassium phthalate given in column 2 and the buffer ratio given at the top of each table. Table 5 gives the electromotive forces recorded for the same temperature range for seven less complete series of measurements on seven other buffer ratios, designated as series E to K. A number of dilutions were made in series A to D, whereas only two dilutions were made in the other seven series. Hence, only the first four series were used for the determination of pK_2 (or K_2) and the last seven together with the first four were used to determine the β values of the various ions of the mixtures. In series A to D the solutions had a buffer ratio, respectively, of 1.0057, 1.5070, 2.0005, and 2.0223; and a chloride-acid phthalate ratio, KCl/$KHPh$, respectively, of 1.0014, 1.0035, 1.0006, and 0.1858. Measurements of the emf were made for two slightly different ratios (see footnotes of tables 1 and 2). In the other series of experiments, the buffer ratio ranged from approximately 1 to 2, but the chloride-acid phthalate ratio varied considerably from approximately 0.09 to 0.70.

TABLE 1.—*Electromotive forces of galvanic cells with hydrogen and silver–silver-chloride electrodes and containing mixtures of phthalates and chlorides*

[Series A, Molality of dipotassium phthalate=1.0057×molality of acid potassium phthalate. Molality of potassium chloride=1.0014×molality of acid potassium phthalate]

Solution number	Molality of KHPh	Temperature in degrees centigrade					
		0	5	10	15	20	25
	Moles of solute per 1,000 g of water	*v*	*v*	*v*	*v*	*v*	*v*
A1	0.0007661	0.69696	0.70191	0.70723	0.71243	0.71781	0.72333
A2	.0014530	.68072	.68542	.69032	.69526	.70033	.70560
A3	.0016690	.67744	.68200	.68683	.69171	.69665	.70180
A4	.0023505	.66826	.67305	.67771	.68248	.68725	.69223
A5	.0031721	.66054	.66504	.66956	.67411	.67886	.68368
A6	.0034678	.65817	.66256	.66709	.67161	.67624	.68102
A7	.0036275	.65701	.66142	.66594	.67043	.67498	.67980
A8	.0048224	.64961	.65378	.65820	.66244	.66701	.67162
A9	.0049454	.64894	.65326	.65745	.66184	.66635	.67082
A10	.0069349	.63997	.64396	.64814	.65230	.65658	.66100
A11	.0095161	.63147	.63534	.63935	.64335	.64746	.65171
A12	.011319	.62675	.63059	.63451	.63830	.64231	.64664
A13	.014671	.61968	.62327	.62705	.63081	.63474	.63876
A14	.018381	.61345	.61702	.62068	.62432	.62813	.63190
A15	.023770	.60643	.60986	.61341	.61670	.62036	.62416
A16	.026358	.60357	.60688	.61027	.61376	.61731	.62093
A17	.027847	.60212	.60535	.60889	.61213	.61559	.61940
A18	.041527	.59098	.59407	.59718	.60042	.60376	.60705
A19	.062963	.57950	.58223	.58522	.58808	.59118	.59428
A20	.10781	.56477	.56726	.56990	.57244	.57514	.57800
A′1 [a]	.10803	.56468	.56716	.56979	.57237	.57508	.57789

Solution number	Temperature in degrees centigrade						
	30	35	40	45	50	55	60
	v	*v*	*v*	*v*	*v*	*v*	*v*
A1	0.72886	0.73339	0.74020	0.74595	0.75194	0.75802	0.76444
A2	.71077	.71598	.72148	.72685	.73259	.73836	.74454
A3	.70701	.71216	.71759	.72296	.72851	.73441	.74031
A4	.69725	.70225	.70751	.71271	.71809	.72380	.72934
A5	.68845	.69334	.69845	.70349	.70871	.71429	.71992
A6	.68581	.69063	.69565	.70065	.70589	.71141	.71689
A7	.68456	.68938	.69436	.69934	.70456	.71005	.71556
A8	.67612	.68085	.68575	.69058	.69551	.70099	.70622
A9	.67556	.68016	.68503	.68965	.69467	.70004	.70532
A10	.66543	.66981	.67455	.67918	.68406	.68921	.69437
A11	.65591	.66022	.66469	.66912	.67391	.67876	.68387
A12	.65057	.65478	.65934	.66371	.66825	.67306	.67795
A13	.64278	.64684	.65101	.65530	.65975	.66436	.66923
A14	.63585	.63986	.64390	.64799	.65233	.65693	.66161
A15	.62791	.63165	.63560	.63961	.64366	.64811	.65269
A16	.62468	.62842	.63237	.63614	.64026	.64470	.64917
A17	.62306	.62658	.63057	.63448	.63837	.64287	.64716
A18	.61054	.61395	.61757	.62119	.62509	.62917	.63331
A19	.59745	.60072	.60415	.60732	.61096	.61480	.61865
A20	.58081	.58370	.58672	.58940	.59281	.59633	.59985
A′1 [a]	.58072	.58358	.58666	.58960	.59282	.59630	.59972

[a] Molality of dipotassium phthalate=1.0074×molality of acid potassium phthalate. Molality of potassium chloride=1.0037×molality of acid potassium phthalate.

TABLE 2.—*Electromotive forces of galvanic cells with hydrogen and silver–silver-chloride electrodes and containing mixtures of phthalates and chlorides*

[Series B, Molality of dipotassium phthalate=1.5070×molality of acid potassium phthalate. Molality of potassium chloride=1.0035×molality of acid potassium phthalate]

Solution number	Molality of KHPh	Temperature in degrees centigrade					
		0	5	10	15	20	25
	Moles of solute per 1,000 g of water	*v*	*v*	*v*	*v*	*v*	*v*
B1	0.0004400	0.71979	0.72528	0.73096	0.73663	0.74248	0.74838
B2	.0006264	.71109	.71642	.72200	.72744	.73303	.73886
B3	.0011836	.69480	.69987	.70508	.71028	.71566	.72108
B4	.0018128	.68392	.68884	.69385	.69884	.70401	.70922
B5	.0023519	.67719	.68190	.68676	.69165	.69668	.70176
B6	.0030064	.67085	.67546	.68022	.68495	.68986	.69482
B7	.0034327	.66730	.67190	.67653	.68120	.68600	.69093
B8	.0035250	.66654	.67113	.67581	.68046	.68530	.69018
B9	.0048817	.65805	.66242	.66687	.67136	.67603	.68073
B10	.0069713	.64850	.65263	.65694	.66125	.66573	.67023
B11	.0087820	.64227	.64643	.65042	.65459	.65895	.66334
B12	.0088235	.64201	.64616	.65025	.65443	.65878	.66317
B13	.0089534	.64166	.64572	.64991	.65408	.65842	.66284
B14	.013470	.63057	.63445	.63832	.64236	.64644	.65054
B15	.017045	.62417	.62782	.63166	.63547	.63946	.64348
B16	.034937	.60433	.60767	.61093	.61445	.61802	.62163
B17	.051843	.59353	.59662	.59974	.60292	.60628	.60962
B18	.071943	.58472	.58761	.59060	.59355	.59671	.59986
B′1 [a]	.071886	.58473	.58761	.59068	.59360	.59668	.59988

Solution number	Temperature in degrees centigrade						
	30	35	40	45	50	55	60
	v	*v*	*v*	*v*	*v*	*v*	*v*
B1	0.75433	0.76034	0.76651	0.77269	0.77910	0.78576	0.79240
B2	.74464	.75049	.75649	.76250	.76874	.77523	.78149
B3	.72656	.73210	.73779	.74349	.74942	.75560	.76175
B4	.71449	.71981	.72530	.73078	.73650	.74246	.74834
B5	.70690	.71209	.71745	.72280	.72839	.73421	.74001
B6	.69984	.70490	.71013	.71535	.72082	.72651	.73219
B7	.69587	.70087	.70603	.71120	.71659	.72222	.72782
B8	.69511	.70009	.70523	.71038	.71575	.72137	.72696
B9	.68549	.69031	.69528	.70025	.70546	.71089	.71631
B10	.67482	.67945	.68422	.68900	.69401	.69926	.70461
B11	.66785	.67240	.67694	.68159	.68648	.69168	.69668
B12	.66761	.67211	.67676	.68141	.68629	.69150	.69659
B13	.66724	.67173	.67637	.68101	.68589	.69109	.69617
B14	.65475	.65901	.66342	.66784	.67248	.67735	.68226
B15	.64756	.65168	.65596	.66025	.66474	.66948	.67403
B16	.62524	.62896	.63286	.63674	.64079	.64511	.64936
B17	.61304	.61650	.62011	.62372	.62755	.63163	.63561
B18	.60307	.60632	.60972	.61312	.61673	.62058	.62427
B′1 [a]	.60309	.60636	.60975	.61316	.61678	.62065	.62450

[a] Molality of dipotassium phthalate=1.5139×molality of acid potassium phthalate. Molality of potassium chloride=1.0056×molality of acid potassium phthalate.

TABLE 3.—*Electromotive forces of galvanic cells with hydrogen and silver–silver-chloride electrodes and containing mixtures of phthalates and chlorides*

[Series C, Molality of dipotassium phthalate=2.0005×molality of acid potassium phthalate. Molality of potassium chloride=1.0006×molality of acid potassium phthalate]

Solution number	Molality of KHPh	Temperature in degrees centigrade					
		0	5	10	15	20	25
	Moles of solute per 1,000 g of water	*v*	*v*	*v*	*v*	*v*	*v*
C1	0.0012203	0.70038	0.70554	0.71085	0.71616	0.72158	0.72615
C2	.0026363	.68043	.68518	.69008	.69504	.70003	.70531
C3	.0044644	.66459	.67098	.67565	.68023	.68508	.68997
C4	.0087742	.64833	.65250	.65671	.66106	.66544	.67002
C5	.010675	.64287	.64696	.65125	.65543	.65960	.66411
C6	.016461	.63111	.63491	.63880	.64273	.64685	.65104
C7	.022447	.62254	.62621	.63000	.63377	.63773	.64159
C8	.030548	.61408	.61755	.62113	.62485	.62844	.63235
C9	.036014	.60964	.61296	.61645	.61993	.62350	.62724
C10	.042177	.60532	.60855	.61202	.61549	.61896	.62263
C11	.054400	.59848	.60161	.60488	.60811	.61147	.61491

Solution number	Temperature in degrees centigrade						
	30	35	40	45	50	55	60
	v	*v*	*v*	*v*	*v*	*v*	*v*
C1	0.73273	0.73835	0.74414	0.74993	0.75595	0.76228	0.76854
C2	.71059	.71578	.72110	.72656	.73216	.73813	.74395
C3	.69502	.69988	.70504	.71008	.71537	.72112	.72666
C4	.67458	.67924	.68383	.68860	.69365	.69895	.70413
C5	.66851	.67305	.67768	.68221	.68716	.69232	.69744
C6	.65535	.65944	.66393	.66826	.67290	.67777	.68256
C7	.64561	.64983	.65389	.65811	.66267	.66747	.67189
C8	.63612	.63994	.64399	.64800	.65223	.65681	.66125
C9	.63104	.63481	.63870	.64267	.64698	.65122	.65559
C10	.62614	.62995	.63363	.63756	.64158	.64604	.65007
C11	.61838	.62200	.62557	.62926	.63334	.63716	.64142

TABLE 4.—*Electromotive forces of galvanic cells with hydrogen and silver–silver-chloride electrodes and containing mixtures of phthalates and chlorides*

[Series D, Molality of dipotassium phthalate=2.0223×molality of acid potassium phthalate. Molality of potassium chloride=0.1858×molality of acid potassium phthalate]

Solution number	Molality of KHPh	Temperature in degrees centigrade					
		0	5	10	15	20	25
	Moles of solute per 1,000 g of water	*v*	*v*	*v*	*v*	*v*	*v*
D1	0.014013	0.67591	0.68055	0.68537	0.69022	0.69502	0.70002
D2	.023409	.66180	.66620	.67070	.67522	.67986	.68454
D3	.024878	.66019	.66450	.66895	.67341	.67796	.68279
D4	.030089	.65416	.65840	.66273	.66697	.67149	.67606
D5	.042383	.64569	.64978	.65395	.65815	.66234	.66672
D6	.043083	.64531	.64934	.65358	.65772	.66189	.66634
D7	.053814	.63940	.64335	.64741	.65128	.65548	.65965

TABLE 4.—*Electomotive forces of galvanic cells with hydrogen and silver–silver-chloride electrodes and containing mixture of phthalates and chlorides*—Con.

Solution number	Temperature in degrees centigrade						
	30	35	40	45	50	55	60
	v	*v*	*v*	*v*	*v*	*v*	*v*
D1	0.70445	0.71011	0.71535	0.72064	0.72606	0.73190	0.73754
D2	.68927	.69397	.69892	.70396	.70905	.71454	.71987
D3	.68743	.69221	.69711	.70194	.70690	.71264	.71784
D4	.68062	.68516	.68980	.69481	.69969	.70506	.71020
D5	.67110	.67558	.68012	.68470	.68953	.69467	.69958
D6	.67068	.67510	.67965	.68425	.68897	.69411	.69906
D7	.66388	.66818	.67255	.67510	.68168	.68665	.69145

TABLE 5.—*Electromotive forces of galvanic cells with hydrogen and silver–silver-chloride electrodes and containing mixtures of phthalates and chlorides*

Solution number	Molality of KHPh	Molality of K_2Ph / Molality of KHPh	Molality of KCl / Molality of KHPh	Temperature in degrees centigrade				
				0	5	10	15	20
	Moles of solute per 1,000 g of water			*v*	*v*	*v*	*v*	*v*
E1	0.055730	1.0074	0.6479	0.59356	0.59672	0.59989	0.60312	0.60644
E2	.10803	1.0074	.6479	.57556	.57831	.58109	.58388	.58678
F1	.053194	1.0074	.2777	.61530	.61879	.62243	.62610	.62980
F2	.10803	1.0074	.2777	.59613	.59920	.60242	.60561	.60891
G1	.075592	1.0074	.09257	.63196	.63563	.63959	.64237	.64742
G2	.10803	1.0074	.09257	.62230	.62590	.62957	.63325	.63705
H1	.036174	1.5139	.6956	.61234	.61586	.61946	.62304	.62660
H2	.071886	1.5139	.6956	.59378	.59685	.60006	.60321	.60641
I1	.024728	1.5139	.4143	.63525	.63917	.64380	.64724	.65184
I2	.071886	1.5139	.4143	.59620	.60954	.61296	.61636	.61990
J1	.054840	1.5139	.1392	.63952	.64349	.64757	.65143	.65569
J2	.071886	1.5139	.1392	.63219	.63604	.63997	.64383	.64776
K1	.026688	2.0223	.5575	.63214	.63595	.63992	.64388	.64790
K2	.053814	2.0223	.5575	.61319	.61661	.62014	.62371	.62731

Solution number	Temperature in degrees centigrade							
	25	30	35	40	45	50	55	60
	v	*v*	*v*	*v*	*v*	*v*	*v*	*v*
E1	0.60987	0.61329	0.61683	0.62047	0.62408	0.62795	0.63207	0.63617
E2	.58982	.59284	.59592	.59914	.60231	.60587	.60950	.61313
F1	.63360	.63747	.64144	.64544	.64940	.65375	.65831	.66285
F2	.61230	.61574	.61918	.62288	.62643	.63025	.63434	.63840
G1	.65153	.65565	.65990	.66422	.66849	.67306	.67784	.68259
G2	.64197	.64489	.64882	.65288	.65697	.66132	.66587	.67039
H1	.63048	.63428	.63813	.64218	.64614	.65037	.65491	.66031
H2	.60979	.61319	.61662	.62021	.62377	.62751	.63098	.63556
I1	.65561	.65986	.66419	.66870	.67311	.67780	.68279	.68775
I2	.62350	.62713	.63086	.63462	.63846	.64258	.64680	.65110
J1	.65995	.66422	.66854	.67305	.67748	.68222	.68716	.69204
J2	.65196	.65604	.66020	.66450	.66888	.67343	.67818	.68291
K1	.65202	.65619	.66050	.66484	.66918	.67379	.67866	.68345
K2	.63103	.63478	.63863	.64255	.64652	.65062	.65501	.66006

The emf was used in eq 9 and 31 to calculate pK'_2 by the use of data for $E°$ determined by Harned and Ehlers [19] and values of R, T, and F given by Hamer, Burton and Acree [8]. It was found that a_i must be assigned a value of 3.76±0.07A at all the temperatures in order for pK'_2 to vary linearly with the ionic strength. In figure 1, values of pK'_2 for the more dilute solutions are shown plotted against the ionic strength for series A to C at 25° C. The dotted line corresponds to the values of pK'_2 calculated on the basis of stoichiometrical molalities alone (eq 9), and the solid line to values corrected for the various processes depicted above, that is, for the hydrogen-ion and o-phthalic acid (or overlapping) corrections (eq 30). These corrections become less as the buffer ratio becomes larger, or the higher the pH of the solution is from that corresponding to the first equivalence point, as is indicated in the graph. These corrections vary with the ionic strength, becoming less as the ionic strength increases, and may be computed for the 13 temperatures by eq 30 given above. Numerical values of these constants are given in table 6 for the various buffer and chloride ratios. In figure 2, values of pK'_2, calculated by eq 31 with a value of 3.76 A for a_i, are shown

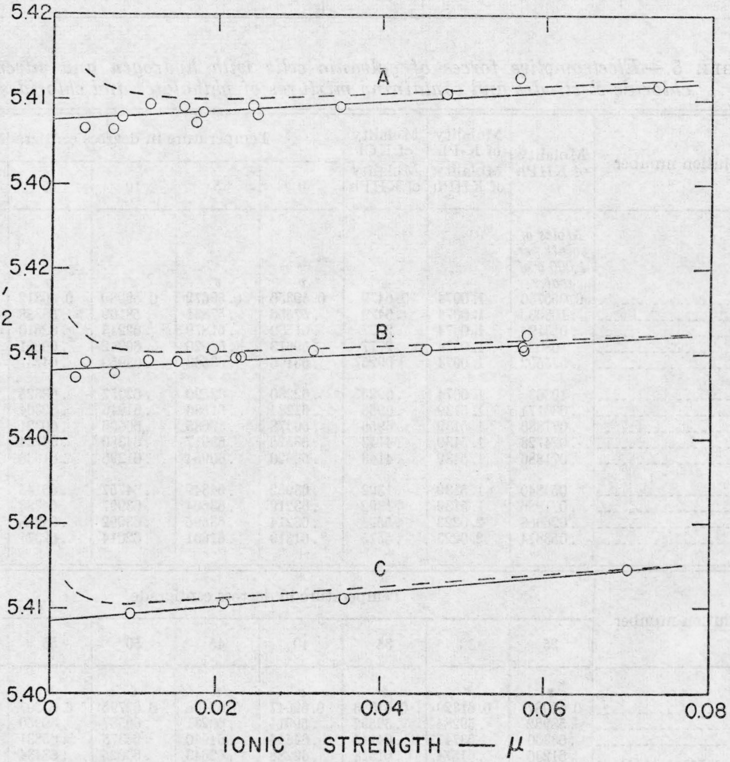

FIGURE 1.—*Plots of* pK'_2 *as a function of the ionic strength for dilute solutions of phthalate-chloride mixtures.*

Dotted line corresponds to stoichiometrical molalities. Solid line corresponds to ionic molalities. **A, B,** and C refer to the series of experiments designated by the same letters.

plotted against the ionic strength for series A to D at temperatures of 0°, 25°, 45°, and 60° C. Plots for the other temperatures are similar. The slopes of the lines give the magnitudes of the constant—β of eq 31, and the extrapolated value at zero ionic strength gives the value of pK_2, free of disturbing effects of the salts, the medium, or ionic association. Any value of a_i, different from 3.76 A, would give a curved line; neglect of the last term on the left side of eq 31 would give much lower values of pK'_2, which when plotted against the ionic strength would give a very marked curvature, concave to the axis of the abscissa; and the use of a value of zero for a_i (Debye-Hückel limiting law) would give much higher values of pK'_2, which when plotted against the ionic strength would give a curve convex to the axis of the abscissa.[13] In figure 3, values of pK'_2, calculated by eq 31 with an a_i value of 3.76 A, are shown plotted as ordinates against the ionic strength as abscissas for the other buffer and chloride ratios at 25° C. Graphs for the other temperatures are similar to these plots. The negative of the slopes of the lines again gives the

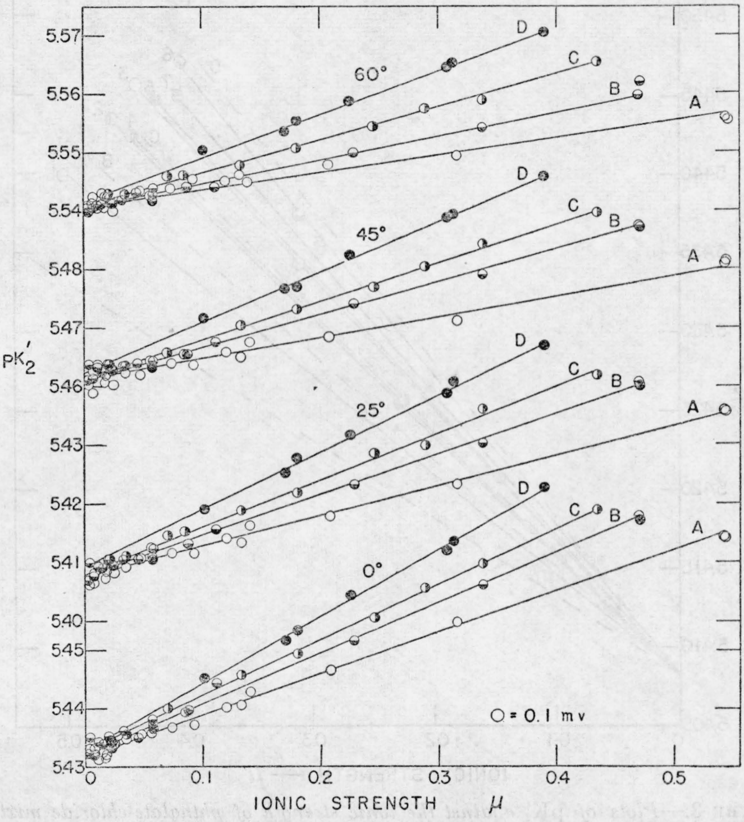

FIGURE 2.—*Extrapolation plots of pK'_2 against the ionic strength.*

A, B, C, and D refer to the series of experiments designated by the same letters.

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[13] See references [7, 8, and 24] for more details concerning the proper choice of values for a_i.

magnitude of the constant β of eq 31. Numerical values of β are given in table 7 for the different temperatures and various buffer and chloride ratios. The β values are a function of the buffer and chloride ratios, being higher for larger buffer ratios and lower chloride ratios. The β values in all cases decrease with respect to temperature. The data given in the table are smooth values, which were read from a large-scale plot of β against temperature and buffer and chloride ratios and are accurate on the average to 0.004 unit. It may be assumed that the values of β are independent of the ionic species in the solutions or that they apply to each ion, which would then concentrate all the effects of the salts, medium, or ionic associations at finite concentrations on the activity coefficient of the hydrogen ion and would lead to eq 34, given above. However, it has

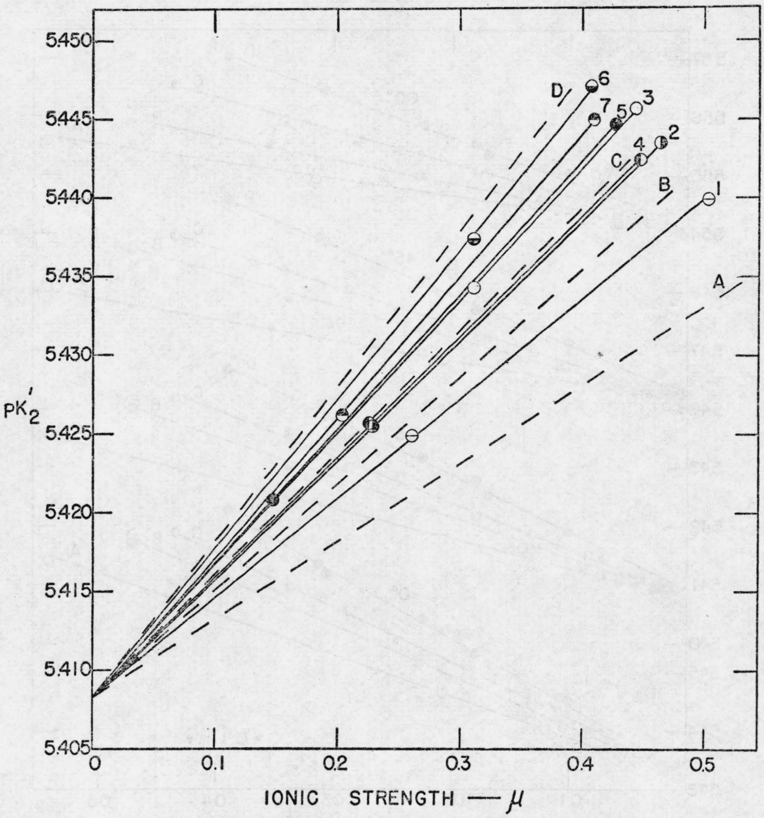

FIGURE 3.—*Plots of* pK_2' *against the ionic strength of phthalate-chloride mixtures, for a temperature of 25° C.*

Dotted lines correspond to values of pK_2' for series A, B, C, and D shown plotted in figure 2.

1, $K_2Ph=1.0074\times KHPh$ and $KCl=0.6479\times KHPh$ (series E)
2, $K_2Ph=1.0074\times KHPh$ and $KCl=0.2777\times KHPh$ (series F)
3, $K_2Ph=1.0074\times KHPh$ and $KCl=0.09257\times KHPh$ (series G)
4, $K^2Ph=1.5139\times KHPh$ and $KCl=0.6956\times KHPh$ (series H)
5, $K^2Ph=1.5139\times KHPh$ and $KCl=0.4143\times KHPh$ (series I)
6, $K^2Ph=1.5139\times KHPh$ and $KCl=0.1392\times KHPh$ (series J)
7, $K^2Ph=2.0223\times KHPh$ and $KCl=0.5575\times KHPh$ (series K)

been shown that this equation is inadequate. Therefore, the β values were considered to be dependent upon the kind and amount of the ionic species present in the solutions and to be given by $(-\beta_{\mathrm{Cl}}m_{\mathrm{Cl}}-\beta_{\mathrm{HPh}}m_{\mathrm{HPh}}+\beta_{\mathrm{Ph}}m_{\mathrm{Ph}})/\mu$ for each buffer and chloride ratio. By using the β values for each of the 11 ratios studied in 11 simultaneous equations, β_{Cl}, β_{HPh}, and β_{Ph} were evaluated by the method of least squares for each of the 13 temperatures.[14] The values are given in the last three rows of table 7. These values make possible the calculation of the values of pK'_2 and pH for any buffer ratio between 1 and 2 and for any chloride ratio from 0 to 1. It should be emphasized here that the values of β_{HPh}, β_{Cl}, and β_{Ph} are least-squared values. Values of these constants determined by solving any three simultaneous equations may show wide variations from the values obtained by the method of least squares and given in table 7. The values of β_{Ph} are much higher than the values of the other two, owing to its bivalent charge, and decrease with temperature whereas the other two increase.

TABLE 6.—*Numerical values of* ω *and* λ *for use in equation 30 for calculations of hydrogen-ion and overlapping corrections necessary in the determination of* pK_2 *and* pH

Ratio K_2Ph/KHPh	Ratio KCl/KHPh	$\omega\times10^6$	$\lambda\times10^5$
1.0057	1.0014	15	11
1.0074	1.0037	15	11
1.0074	0.6480	14	11
1.0074	.2777	12	11
1.0074	.09257	12	11
1.0074	.0000	11	11
1.5070	1.0035	10	9
1.5139	1.0056	10	9
1.5139	0.6955	9	9
1.5139	.4143	8	9
1.5139	.1392	7	9
1.5139	.0000	6	9
2.0005	1.0006	5	8.5
2.0223	.5575	3.5	8.5
2.0223	.1858	2	8.5
2.0223	.0000	1.2	8.5
1.00	1.00	15	11
1.50	1.00	10	9
2.00	1.00	5	8.5
1.00	0.00	11	11
1.50	.00	6	9
2.00	.00	1.2	8.5

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[14] See Kilpatrick [25] and Hitchcock [26] for a discussion of this subject. See also Morton [27] for a discussion of salt effects and Scatchard [15] for a treatment of concentrated solutions.

TABLE 7.—*Numerical values of the constant β in the Debye-Hückel equation for activity coefficients for various mixtures of acid potassium phthalate, dipotassium phthalate, and potassium chloride*

Series number	Temperature in degrees centigrade												
	0	5	10	15	20	25	30	35	40	45	50	55	60
A	−0.068	−0.064	−0.061	−0.057	−0.054	−0.050	−0.047	−0.044	−0.040	−0.037	−0.033	−0.030	−0.026
B	−.085	−.082	−.078	−.075	−.071	−.068	−.064	−.061	−.057	−.054	−.050	−.047	−.044
C	−.096	−.092	−.089	−.085	−.082	−.078	−.075	−.072	−.068	−.065	−.061	−.058	−.054
D	−.116	−.113	−.110	−.106	−.103	−.099	−.096	−.092	−.089	−.085	−.082	−.077	−.075
E	−.080	−.076	−.073	−.069	−.065	−.062	−.059	−.055	−.052	−.048	−.045	−.041	−.038
F	−.094	−.090	−.087	−.083	−.080	−.076	−.073	−.070	−.066	−.063	−.059	−.056	−.052
G	−.102	−.098	−.095	−.091	−.088	−.084	−.081	−.078	−.074	−.071	−.067	−.064	−.060
H	−.093	−.089	−.087	−.083	−.080	−.076	−.073	−.070	−.066	−.063	−.060	−.057	−.053
I	−.100	−.097	−.094	−.090	−.088	−.085	−.082	−.079	−.076	−.073	−.070	−.067	−.064
J	−.109	−.106	−.103	−.100	−.097	−.094	−.091	−.088	−.085	−.082	−.079	−.075	−.072
K	−.107	−.103	−.100	−.096	−.093	−.089	−.082	−.082	−.079	−.075	−.072	−.068	−.065
Ionic species [a]													
Ph$^=$	−.42	−.41	−.41	−.40	−.39	−.38	−.37	−.36	−.35	−.34	−.33	−.32	−.31
HPh$^-$	−.002	−.006	−.011	−.015	−.018	−.023	−.026	−.029	−.033	−.036	−.040	−.041	−.048
Cl$^-$	−.082	−.086	−.090	−.094	−.099	−.10	−.11	−.11	−.12	−.12	−.12	−.13	−.13

[a] Ph$^=$, HPh$^-$, and Cl$^-$ denote the diphthalate, acid phthalate, and chloride ions, respectively.

Values of pK_2 were then determined for the series of experiments A to D, the corresponding values of β being used. They are shown in figure 4 plotted as a function of the ionic strength. This figure is in reality a deviation plot. The average value of pK_2 with the mean deviation for each series is given in table 8. The average value of the four determinations with the total mean deviation is given in column 6 for each temperature. The deviations range from 0.0004 to 0.0011, which correspond to 0.02 to 0.07 mv in the emf. Values of the second dissociation constant of *o*-phthalic acid are given in the last column of this table.

TABLE 8.—*Summary of numerical values of* pK_2 *and* K_2 *calculated from measurements of four different buffer ratios at temperatures of 0° to 60° C*

Temperature	pK_2					$K_2\times10^6$
	Series A	Series B	Series C	Series D	Average	Average
°*C*						
0	[a]5.4319 ±0.0007	5.4326 ±0.0008	5.4324 ±0.0005	5.4323 ±0.0008	5.4323 ±0.0007	3.696
5	5.4177 ± .0010	5.4182 ± .0007	5.4178 ± .0004	5.4184 ± .0006	5.4180 ± .0008	3.820
10	5.4091 ± .0009	5.4093 ± .0008	5.4095 ± .0005	5.4103 ± .0008	5.4096 ± .0009	3.894
15	5.4043 ± .0008	5.4050 ± .0007	5.4053 ± .0008	5.4060 ± .0012	5.4052 ± .0009	3.934
20	5.4041 ± .0009	5.4051 ± .0008	5.4047 ± .0006	5.4053 ± .0006	5.4048 ± .0008	3.937
25	5.4077 ± .0008	5.4079 ± .0007	5.4085 ±.0006	5.4090 ± .0010	5.4083 ± .0008	3.906
30	5.4150 ± .0008	5.4154 ± .0007	5.4165 ±.0011	5.4160 ± .0006	5.4157 ± .0009	3.840
35	5.4259 ± .0010	5.4269 ± .0008	5.4278 ±.0008	5.4276 ± .0007	5.4271 ± .0010	3.740
40	5.5522 ± .0009	5.4423 ± .0007	5.4426 ±.0007	5.4423 ± .0009	5.4424 ± .0008	3.611
45	5.4613 ± .0010	5.4615 ± .0006	5.4616 ±.0006	5.4625 ± .0005	5.4617 ± .0008	3.454
50	5.4840 ± .0008	5.4848 ± .0007	5.4857 ±.0011	5.4849 ± .0005	5,4849 ± .0009	3.274
55	5.5108 ± .0011	5.5116 ± .0006	5.5128 ±.0008	5.5137 ± .0007	5.5122 ± .0011	3.075
60	5.5416 ± .0009	5.5403 ± .0005	5.5414 ±.0005	5.5418 ± .0007	5.5413 ± .0009	2.875

[a] Arithmetical mean deviations.

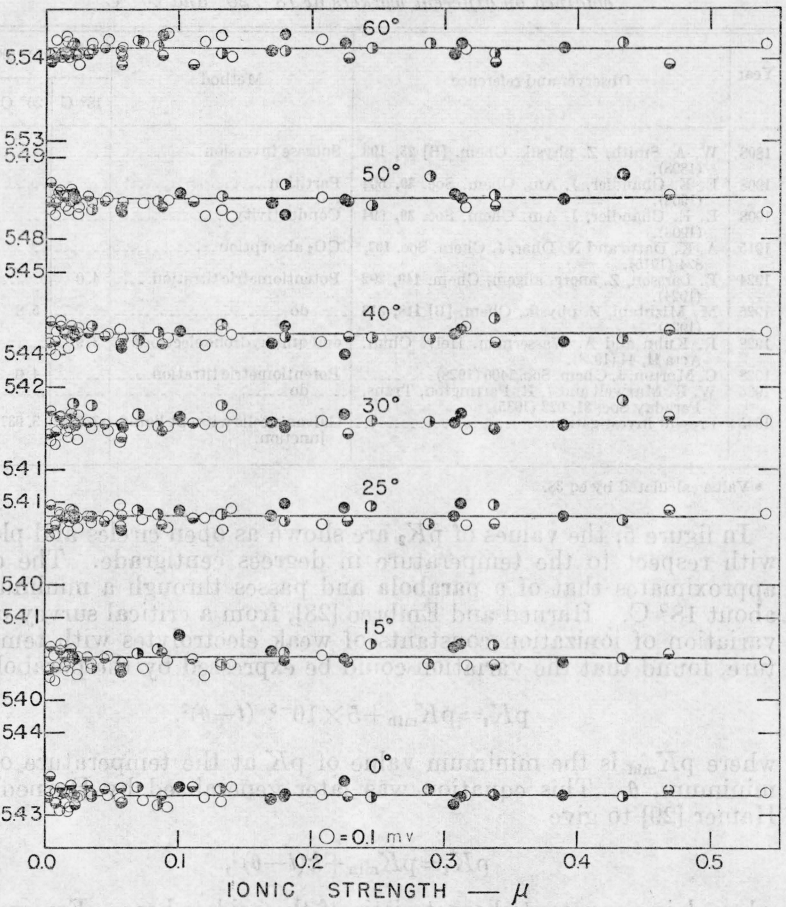

FIGURE 4.—*Plots of all values of* pK'_2 *for series A, B, C, and D at* 0°, 15°, 25°, 30°, 40°, 50°, and 60° *C as a function of the ionic strength.*

This plot represents a deviation plot.

(The symbols represent the same series of experiments given in figure 2.)

In table 9, the values of K_2 are compared with those obtained by other investigators at 18°, 20°, and 25° C. A critical comparison is not possible as previous investigations were limited to a single temperature and involved a number of uncertainties.

TABLE 9.—*Numerical values of the second ionization constant of orthophthalic acid obtained by different workers at 18°, 20° and 25° C*

Year	Observer and reference	Method	$K_2 \times 10^6$		
			18° C	20° C	25° C
1898	W. A. Smith, Z. physik. Chem. [B] **25,** 193 (1898).	Sucrose inversion			1.7
1908	E. E. Chandler, J. Am. Chem. Soc. **30,** 694 (1908).	Partition			3.1
1908	E. E. Chandler, J. Am. Chem. Soc. **30,** 694 (1908).	Conductivity			3.9
1915	A. K. Datta and N. Dhar, J. Chem. Soc. **107,** 824 (1915).	CO_2 absorption			1.82
1924	E. Larsson, Z. anorg. allgem, Chem. **140,** 292 (1924).	Potentiometric titration	4.0		
1925	M. Mizutani, Z. physik, Chem. [B] **118,** 318 (1925).	do		5.8	
1928	R. Kuhn and A. Wasserman, Helv. Chim. Acta **11,** 44 (1928).	emf quinhydrone electrode	3.9		
1928	C. Morton, J. Chem. Soc. 1406 (1928)	Potentiometric titration		4.6	
1935	W. R. Maxwell and J. R. Partington, Trans. Faraday Soc. **31,** 922 (1935).	do			5.2
1945	Present investigation	Galvanic cells without liquid junction.	[a]3.936	3.937	3.906

[a] Value calculated by eq 38.

In figure 5, the values of pK_2 are shown as open circles and plotted with respect to the temperature in degrees centigrade. The curve approximates that of a parabola and passes through a minimum at about 18° C. Harned and Embree [28], from a critical survey of the variation of ionization constants of weak electrolytes with temperature, found that the variation could be expressed by the parabolic eq

$$\mathrm{p}K_t = \mathrm{p}K_{\min} + 5\times 10^{-5}\ (t-\theta)^2, \tag{35}$$

where p$K_{\min}$ is the minimum value of pK at the temperature of the minimum, θ. This equation was later generalized by Harned and Hamer [29] to give

$$\mathrm{p}K_t = \mathrm{p}K_{\min} + k(t-\theta)^2, \tag{36}$$

where k is a constant characteristic of the acid or base. For example k is 8×10^{-5} for the bisulfate ion [16] and 6.4×10^{-5} for the bimalonate ion [8]. It was found that eq 35 only approximately reproduces the experimental values, the mean deviation being 0.014, which greatly exceeds the experimental error. Equation 36, with $\mathrm{p}K_{\min}=5.4049$, $k=8\times 10^{-5}$, and $\theta=18.5$, reproduces the experimental data very well except at 60° C, where a deviation of 0.0014 is found. An equation expressing the relation between pK_2 and the temperature may be obtained from eq 31. Both the emf obtained in this investigation and E° obtained by Harned and Ehlers vary quadratically with the temperature, and can be expressed by an equation of the form, $(E-E^\circ=a+bt+ct^2)$. Therefore,

$$\mathrm{p}K_2 = A^*/T + B + CT, \tag{37}$$

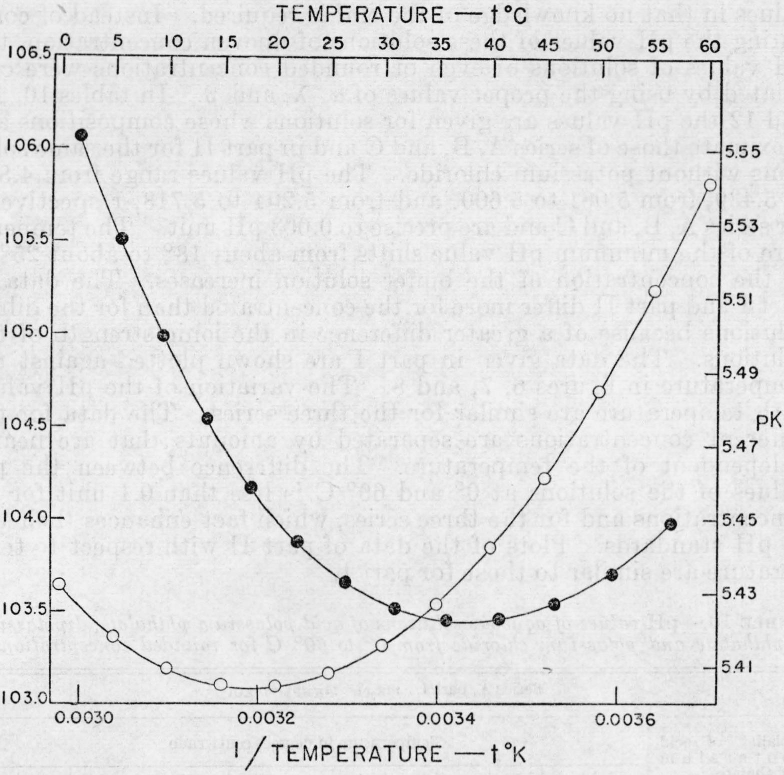

FIGURE 5.—*Plots of the values of* pK_2 *against the temperature in degrees centigrade (open circles) and of* $-R$ *in* K_2 *against the reciprocal of the absolute temperature (dark circles).*

The latter plot may be used to evaluate the heat of dissociation of the acid-phthalate ion.

as log m_{Cl}, log m_{HPh}, log m_{Ph}, ω and λ do not vary with respect to temperature and $2A\sqrt{\mu}/(1+Ba_i\sqrt{\mu})$ is equal to zero at infinite dilution for which pK_2 applies. A^*, B, and C differ from a, b, and c by the factor 2.3026 RT/F. This is the equation proposed by Harned and Robinson [30] for those acids and bases for which ω and λ are negligible. The constants of this equation were obtained by the method of least squares and the use of the average values of pK_2 given in table 8. The values of pK_2 are given with a mean deviation of 0.0008 by the equation

$$\mathrm{p}K_2 = 2175.83/T - 9.55075 + 0.025694T, \tag{38}$$

where $T = t$ °C$+273.16$.

V. pH VALUES OF PHTHALATE-CHLORIDE SOLUTIONS

The pH value of each solution of the four main series of experiments and of the seven less complete series used in the evaluation of K_2 may be computed either by eq 32 or 33 by using 3.76 A for a_i, the values of ω and λ given in table 6 and the values of β given in table 7. For synthetic solutions, eq 33 is preferable for the calculation of the pH values in that no knowledge of the emf is required. Instead of computing the pH values of these solutions of uneven concentration, the pH values of solutions of even or rounded concentrations were calculated by using the proper values of ω, λ, and β. In tables 10, 11, and 12 the pH values are given for solutions whose compositions approximate those of series A, B, and C and in part II for the same solutions without potassium chloride. The pH values range from 4.868 to 5.439, from 5.061 to 5.600, and from 5.204 to 5.713, respectively, for series A, B, and C and are precise to 0.003 pH unit. The temperature of the minimum pH value shifts from about 18° to about 25° C as the concentration of the buffer solution increases. The data of part I and part II differ more for the concentrated than for the dilute solutions because of a greater difference in the ionic strength of the solutions. The data given in part I are shown plotted against the temperature in figures 6, 7, and 8. The variation of the pH values with temperature are similar for the three series. The data for the different concentrations are separated by amounts that are nearly independent of the temperature. The difference between the pH values of the solutions at 0° and 60° C is less than 0.1 unit for all concentrations and for the three series, which fact enhances their use as pH standards. Plots of the data of part II with respect to temperature are similar to those for part I.

TABLE 10.—pH *values of aqueous solutions of acid potassium phthalate, dipotassium phthalate and potassium chloride from 0° to 60° C for rounded concentrations*

Molality of acid potassium phthalate	Temperature in degrees centigrade												
	0	5	10	15	20	25	30	35	40	45	50	55	60
	Series A, part 1. $m_{K_2Ph}=m_{KHPh}=m_{KCl}$												
Moles of solute/1,000 g of water													
0.10	4.918	4.899	4.886	4.874	4.870	4.868	4.869	4.875	4.883	4.896	4.913	4.933	4.955
0.07	4.958	4.940	4.928	4.917	4.913	4.912	4.914	4.920	4.929	4.943	4.961	4.982	5.004
0.05	4.998	4.980	4.969	4.958	4.955	4.955	4.957	4.963	4.974	4.989	5.006	5.028	5.052
0.03	5.059	5.042	5.031	5.022	5.019	5.019	5.023	5.030	5.041	5.057	5.075	5.098	5.123
0.02	5.106	5.090	5.079	5.070	5.068	5.068	5.072	5.080	5.092	5.108	5.127	5.151	5.176
0.01	5.180	5.163	5.153	5.146	5.144	5.144	5.149	5.158	5.171	5.188	5.207	5.233	5.259
0.007	5.213	5.197	5.187	5.180	5.178	5.179	5.184	5.193	5.207	5.224	5.244	5.269	5.296
0.005	5.241	5.225	5.216	5.209	5.208	5.209	5.214	5.224	5.238	5.255	5.275	5.300	5.327
0.003	5.279	5.263	5.254	5.248	5.246	5.249	5.255	5.264	5.278	5.296	5.317	5.343	5.370
0.002	5.305	5.290	5.281	5.275	5.273	5.276	5.282	5.292	5.306	5.325	5.346	5.372	5.399
0.001	5.341	5.326	5.317	5.312	5.311	5.313	5.320	5.330	5.345	5.363	5.385	5.410	5.439
	Series A, part 2. $m_{K_2Ph}=m_{KHPh}$ (no KCl)												
0.10	4.951	4.933	4.919	4.908	4.904	4.902	4.903	4.909	4.918	4.931	4.949	4.969	4.991
0.07	4.991	4.972	4.960	4.950	4.946	4.944	4.947	4.953	4.963	4.977	4.995	5.017	5.040
0.05	5.029	5.011	4.999	4.990	4.987	4.987	4.989	4.996	5.007	5.022	5.040	5.062	5.086
0.03	5.089	5.071	5.059	5.051	5.048	5.048	5.052	5.060	5.071	5.087	5.107	5.129	5.154
0.02	5.133	5.116	5.105	5.098	5.095	5.096	5.099	5.109	5.120	5.136	5.156	5.179	5.205
0.01	5.201	5.185	5.175	5.169	5.167	5.168	5.172	5.181	5.194	5.211	5.232	5.257	5.283
0.007	5.233	5.217	5.207	5.201	5.198	5.199	5.204	5.214	5.228	5.244	5.266	5.291	5.318
0.005	5.259	5.243	5.233	5.227	5.226	5.228	5.233	5.243	5.257	5.274	5.294	5.320	5.347
0.003	5.294	5.278	5.269	5.263	5.261	5.264	5.270	5.280	5.294	5.311	5.333	5.359	5.386
0.002	5.318	5.302	5.293	5.288	5.286	5.289	5.295	5.305	5.319	5.337	5.359	5.385	5.413
0.001	5.346	5.331	5.327	5.322	5.320	5.323	5.330	5.340	5.355	5.373	5.395	5.422	5.450

TABLE 11.—pH *values of aqueous solutions of acid potassium phthalate, dipotassium phthalate and potassium chloride from 0° to 60° C for rounded concentrations*

Series B, part 1. $m_{\mathrm{K_2Ph}} = 1.5\, m_{\mathrm{KHPh}} = 1.5\, m_{\mathrm{KCl}}$

Molality of acid potassium phthalate	Temperature in degrees centigrade												
	0	5	10	15	20	25	30	35	40	45	50	55	60
Moles of solute per 1,000 g of water													
0.07	5.110	5.091	5.078	5.069	5.063	5.061	5.063	5.068	5.077	5.090	5.107	5.127	5.150
0.05	5.147	5.129	5.117	5.107	5.102	5.101	5.103	5.109	5.119	5.133	5.151	5.172	5.195
0.04	5.173	5.155	5.143	5.134	5.129	5.128	5.131	5.138	5.149	5.163	5.180	5.202	5.225
0.02	5.255	5.237	5.226	5.219	5.214	5.215	5.218	5.226	5.238	5.252	5.272	5.295	5.319
0.01	5.330	5.313	5.303	5.296	5.294	5.294	5.298	5.307	5.318	5.335	5.355	5.379	5.405
0.008	5.352	5.336	5.326	5.318	5.316	5.317	5.322	5.331	5.344	5.360	5.381	5.404	5.430
0.005	5.396	5.380	5.370	5.363	5.361	5.361	5.368	5.378	5.390	5.407	5.428	5.452	5.479
0.004	5.415	5.398	5.388	5.383	5.380	5.382	5.387	5.397	5.410	5.427	5.449	5.474	5.500
0.002	5.464	5.449	5.439	5.434	5.432	5.434	5.440	5.450	5.464	5.482	5.503	5.529	5.556
0.001	5.504	5.489	5.480	5.475	5.473	5.476	5.482	5.493	5.507	5.524	5.546	5.572	5.600
Series B, part 2. $m_{\mathrm{K_2Ph}} = 1.5\, m_{\mathrm{KHPh}}$ (no KCl)													
0.07	5.135	5.116	5.103	5.094	5.088	5.086	5.088	5.093	5.103	5.116	5.133	5.154	5.176
0.05	5.171	5.153	5.141	5.132	5.127	5.126	5.128	5.134	5.144	5.158	5.176	5.198	5.221
0.04	5.196	5.178	5.167	5.158	5.153	5.153	5.156	5.162	5.173	5.188	5.206	5.227	5.251
0.02	5.275	5.258	5.246	5.239	5.236	5.236	5.241	5.248	5.260	5.275	5.294	5.317	5.342
0.01	5.348	5.331	5.321	5.312	5.311	5.312	5.317	5.326	5.338	5.354	5.376	5.399	5.425
0.008	5.369	5.353	5.343	5.329	5.333	5.334	5.340	5.349	5.361	5.377	5.398	5.422	5.449
0.005	5.410	5.394	5.384	5.381	5.376	5.376	5.382	5.393	5.405	5.422	5.443	5.468	5.495
0.004	5.428	5.411	5.402	5.396	5.394	5.396	5.401	5.411	5.424	5.442	5.463	5.488	5.505
0.002	5.474	5.459	5.450	5.444	5.443	5.445	5.451	5.461	5.475	5.493	5.515	5.540	5.568
0.001	5.512	5.497	5.488	5.481	5.481	5.484	5.490	5.502	5.515	5.533	5.555	5.580	5.608

TABLE 12.—pH *values of aqueous solutions of acid potassium phthalate, dipotassium phthalate and potassium chloride from 0° to 60° C for rounded concentrations*

Series C, part 1. $m_{\mathrm{K_2Ph}} = 2.0\, m_{\mathrm{KHPh}} = 2.0\, m_{\mathrm{KCl}}$

Molality of acid potassium phthalate	Temperature in degrees centigrade												
	0	5	10	15	20	25	30	35	40	45	50	55	60
Moles of solute per 1,000 g of water													
0.05	5.252	5.233	5.221	5.211	5.206	5.204	5.206	5.211	5.221	5.234	5.252	5.272	5.294
0.04	5.277	5.258	5.246	5.237	5.231	5.230	5.232	5.239	5.248	5.262	5.280	5.301	5.325
0.03	5.309	5.291	5.279	5.271	5.266	5.265	5.268	5.275	5.285	5.300	5.318	5.339	5.363
0.02	5.356	5.339	5.327	5.319	5.315	5.316	5.319	5.326	5.337	5.353	5.371	5.393	5.418
0.01	5.431	5.417	5.406	5.399	5.396	5.396	5.401	5.410	5.422	5.437	5.457	5.481	5.507
0.005	5.502	5.486	5.476	5.470	5.467	5.469	5.474	5.482	5.495	5.512	5.533	5.557	5.584
0.004	5.522	5.506	5.496	5.490	5.487	5.489	5.494	5.504	5.517	5.534	5.554	5.579	5.605
0.003	5.546	5.529	5.519	5.514	5.511	5.513	5.519	5.528	5.542	5.559	5.580	5.605	5.631
0.002	5.576	5.560	5.551	5.545	5.542	5.544	5.550	5.560	5.574	5.591	5.613	5.638	5.665
0.001	5.618	5.602	5.592	5.588	5.584	5.589	5.595	5.605	5.619	5.637	5.659	5.685	5.713
Series C, part 2. $m_{\mathrm{K_2Ph}} = 2.0\, m_{\mathrm{KHPh}}$ (no KCl)													
0.05	5.272	5.253	5.241	5.231	5.226	5.225	5.226	5.232	5.241	5.255	5.273	5.293	5.316
0.04	5.296	5.277	5.265	5.256	5.251	5.250	5.252	5.259	5.269	5.283	5.301	5.322	5.345
0.03	5.328	5.310	5.298	5.290	5.286	5.285	5.287	5.294	5.305	5.319	5.338	5.360	5.383
0.02	5.374	5.351	5.345	5.337	5.333	5.334	5.337	5.345	5.355	5.371	5.390	5.412	5.437
0.01	5.449	5.432	5.422	5.415	5.411	5.412	5.417	5.425	5.438	5.453	5.473	5.497	5.523
0.005	5.515	5.499	5.488	5.482	5.479	5.482	5.487	5.495	5.508	5.525	5.546	5.570	5.597
0.004	5.533	5.517	5.507	5.501	5.499	5.501	5.506	5.516	5.528	5.545	5.566	5.591	5.618
0.003	5.555	5.540	5.530	5.524	5.522	5.524	5.530	5.539	5.553	5.570	5.592	5.616	5.644
0.002	5.585	5.569	5.560	5.554	5.552	5.553	5.559	5.569	5.583	5.601	5.622	5.647	5.675
0.001	5.624	5.609	5.600	5.594	5.593	5.596	5.602	5.612	5.626	5.644	5.672	5.691	5.720

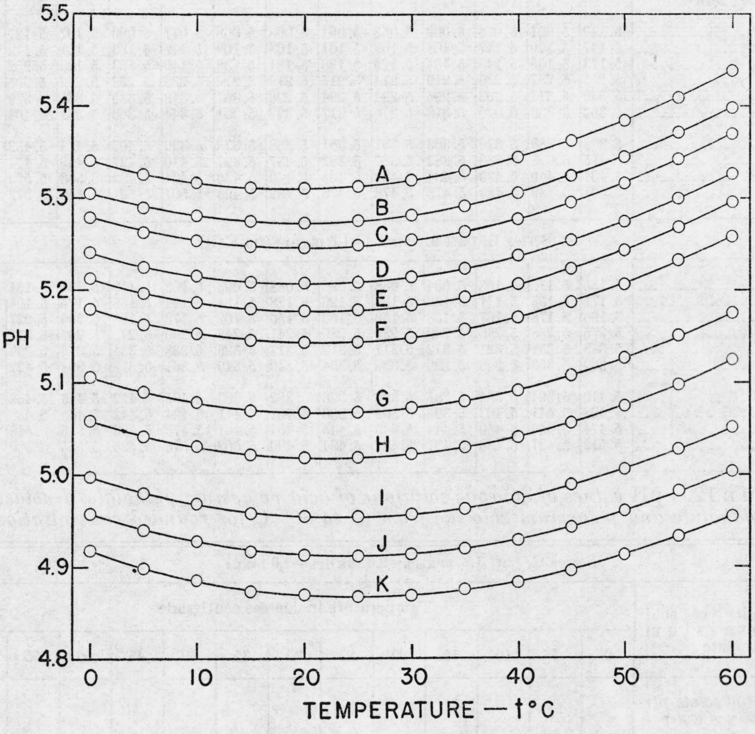

FIGURE 6.—*Plots of the* pH *values of phthalate-chloride solutions whose compositions correspond to those of series A against the temperature in degrees centigrade.*

A, 0.001 *M* KHPh; *B*, 0.002 *M* KHPh; *C*, 0.003 *M* KHPh; *D*, 0.005 *M* KHPh; *E*, 0.007 *M* KHPh; *F*, 0.01 *M* KHPh; *G*, 0.02 *M* KHPh; H, 0.03 *M* KHPh; *I*, 0.05 *M* KHPh; *J*, 0.07 *M* KHPh; *K*, 0.10 *M* KHPh.

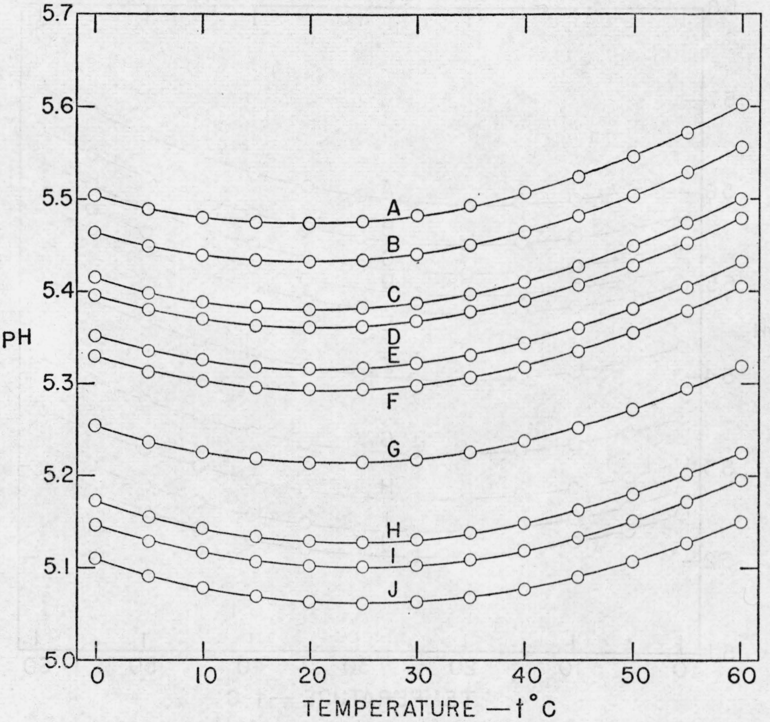

FIGURE 7.—*Plots of the* pH *values of phthalate-chloride solutions whose compositions correspond to those of series B against the temperature in degrees centigrade.*

A, 0.001 *M* KHPh; *B*, 0.002 *M* KHPh; *C*, 0.004 *M* KHPh; *D*, 0.005 *M* KHPh; *E*, 0.008 *M* KHPh; *F*, 0.01 *M* KHPh; *G*, 0.02 *M* KHPh; *H*, 0.04 *M* KHPh; *I*, 0.05 *M* KHPh; *J*, 0.0 *M* KHPh.

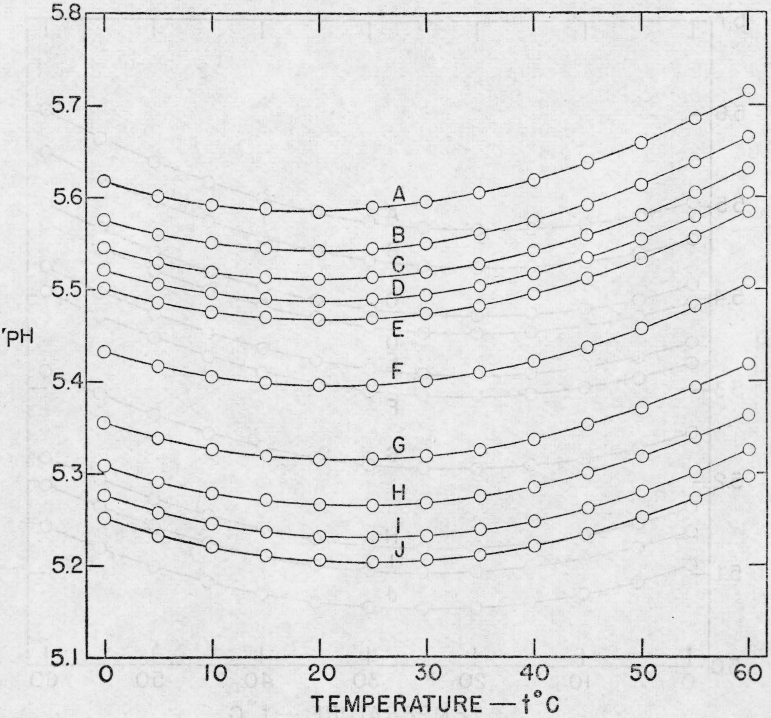

FIGURE 8.—*Plots of the* pH *values of phthalate-chloride solutions whose compositions correspond to those of series C against the temperature in degreees centigrade.*

A, 0.001 *M* KHPh; *B*, 0.002 *M* KHPh; *C*, 0.003 *M* KHPh; *D*, 0.004 *M* KHPh; *E*, 0.005 *M* KHPh; *F*, 0.01 *M* KHPh; *G*, 0.02 *M* KHPh; *H*, 0.03 *M* KHPh; *I*, 0.04 *M* KHPh· *J*, 0.05 *M* KHPh.

In table 13, the pH values at 25° C are given for solutions of different buffer ratios containing various amounts of potassium chloride. The data are shown plotted against the molality of potassium chloride in figures 9, 10, and 11. The addition of potassium chloride has a similar effect on the pH values for the three different buffer ratios and is more marked for dilute than for concentrated solutions. The pH of these solutions may be computed as a function of the molality of potassium chloride by the equation.

$$\mathrm{pH} = (\mathrm{pH})_0 + \alpha_1 m_{\mathrm{KCl}} + \alpha_2 m^2_{\mathrm{KCl}} + \alpha_3 m^3_{\mathrm{KCl}}, \qquad (39)$$

where $(\mathrm{pH})_0$ is the pH of a solution containing no potassium chloride and α_1, α_2, and α_3 are constants whose numerical values are practically independent of the temperature. Numerical values of $(\mathrm{pH})_0$, α_1, α_2, and α_3 are given in table 14. Values of the pH for any intermediate buffer ratio, concentration of acid potassium phthalate, or concentration of potassium chloride may be obtained conveniently by interpolation of the data of table 14.

TABLE 13.—pH *values of aqueous solutions of acid potassium phthalate and dipotassium phthalate containing various amounts of potassium chloride at 25° C*

Series A. Molality of dipotassium phthalate = molality of acid potassium phthalate

Molality of potassium chloride	Molality of acid potassim phthalate										
	0.10	0.07	0.05	0.03	0.02	0.01	0.007	0.005	0.003	0.002	0.001
Moles of solute per 1,000 g of water											
0.10	4.868	4.899	4.927	4.956	4.990	5.021	5.031	5.040	5.048	5.052	5.056
0.05	4.884	4.920	4.955	5.002	5.034	5.078	5.093	5.106	5.118	5.126	5.132
0.02	4.895	4.934	4.973	5.029	5.068	5.125	5.147	5.166	5.185	5.197	5.208
0.01	4.899	4.939	4.980	5.039	5.081	5.144	5.170	5.192	5.219	5.235	5.252
0.00	4.902	4.945	4.987	5.049	5.096	5.168	5.199	5.228	5.265	5.291	5.326

Series B. Molality of dipotassium phthalate = 1.5×molality of acid potassium phthalate

Molality of potassium chloride	Molality of acid potassium phthalate									
	0.07	0.05	0.04	0.02	0.01	0.008	0.005	0.004	0.002	0.001
Moles of solute per 1,000 g of water										
0.10	5.051	5.079	5.098	5.149	5.185	5.198	5.209	5.213	5.225	5.231
0.05	5.068	5.101	5.123	5.186	5.236	5.249	5.271	5.278	5.296	5.307
0.02	5.079	5.115	5.140	5.215	5.277	5.294	5.325	5.336	5.364	5.382
0.01	5.082	5.120	5.147	5.225	5.294	5.313	5.349	5.362	5.398	5.420
0.00	5.086	5.126	5.153	5.236	5.312	5.334	5.378	5.396	5.445	5.485

Series C. Molality of dipotassium phthalate = 2.0×molality of acid potassium phthalate

Molality of potassium chloride	Molality of acid potassium phthalate									
	0.05	0.04	0.03	0.02	0.01	0.005	0.004	0.003	0.002	0.001
Moles of solute per 1,000 g of water										
0.10	5.186	5.204	5.228	5.258	5.299	5.322	5.333	5.340	5.347	5.354
0.05	5.204	5.225	5.254	5.292	5.346	5.379	5.395	5.405	5.417	5.429
0.02	5.216	5.240	5.271	5.316	5.382	5.426	5.449	5.464	5.482	5.502
0.01	5.220	5.245	5.278	5.324	5.396	5.446	5.472	5.490	5.513	5.539
0.00	5.225	5.250	5.285	5.334	5.412	5.481	5.501	5.524	5.554	5.596

TABLE 14.—*Values of the constants* $(\mathrm{pH})_0, \alpha_1, \alpha_2$, *and* α_3 *in the equation* $\mathrm{pH} = (\mathrm{pH})_0 + \alpha_1 m_{\mathrm{KCl}} + \alpha_2 m^2_{\mathrm{KCL}} + \alpha_3 m^3_{\mathrm{KCL}}$ *which gives the* pH *of phthalate solutions as a function of the molality of potassium chloride*

Series A, Molality of dipotassium phthalate = molality of acid potassium phthalate				
Molality of acid potassium phthalate	$(\mathrm{pH})_0$	$-\alpha_1$	α_2	$-\alpha_3$
Moles of solute /1,000 g of water				
0.001	5.326	8.107	115.39	613.2
.002	5.291	6.116	75.43	381.8
.003	5.265	5.064	56.20	273.0
.005	5.228	3.792	35.09	159.7
.007	5.199	3.064	23.97	101.4
.01	5.168	2.499	17.72	74.3
.02	5.096	1.55	7.46	25.8
.03	5.049	1.05	3.11	19.3
.05	4.987	0.742	2.63	12.2
.07	4.945	.609	0.61	8.0
.10	4.902	.461	−1.00	3.5
Series B, Molality of dipotassium phthalate=1.5×molality of acid potassium phthalate				
0.001	5.485	6.956	92.10	479.4
.002	5.445	5.114	56.33	271.9
.004	5.396	3.629	32.87	148.7
.005	5.378	3.111	24.64	123.2
.008	5.334	2.232	12.54	38.2
.01	5.312	1.916	9.36	29.0
.02	5.236	1.170	3.30	12.2
.04	5.153	0.656	1.12	5.13
.05	5.126	.550	0.502	4.20
.07	5.086	.366	.101	2.73
Series C, Molality of dipotassium phthalate=2.0×molality of acid potassium phthalate				
0.001	5.596	6.156	75.53	383.0
.002	5.554	4.435	44.23	205.8
.003	5.524	3.611	31.62	139.1
.004	5.501	3.064	23.97	101.4
.005	5.481	2.680	19.01	83.0
.01	5.412	1.662	8.39	30.7
.02	5.334	0.985	3.61	13.5
.03	5.285	.756	2.50	6.5
.04	5.250	.635	2.10	2.7
.05	5.225	.576	1.96	0.9

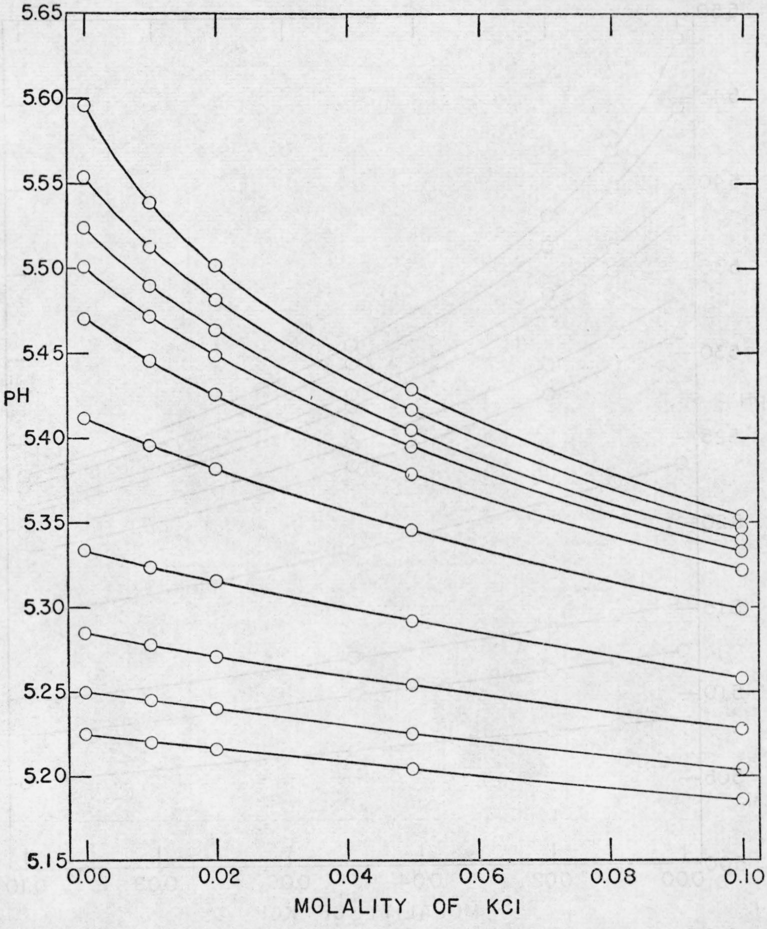

FIGURE 9.—*Plots of the* pH *values of solutions containing dipotassium phthalate and acid potassium phthalate in unit ratio at 25° C as a function of the molality of potassium chloride.*

The curves reading from the top correspond to 0.001, 0.002, 0.003, 0.005, 0.007, 0.01, 0.02, 0.03, 0.05, 0.07, and 0.10 molal acid potassium phthalate.

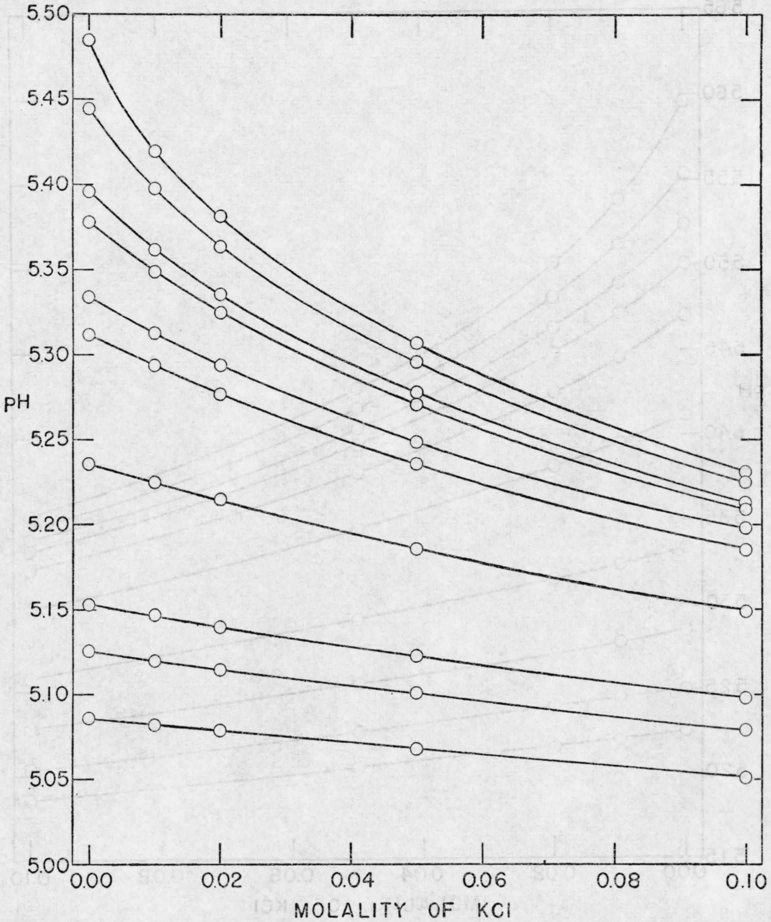

Figure 10.—*Plots of the* pH *values of solutions containing dipotassium phthalate and acid potassium phthalate in the ratio of 1.5 at 25° C as a function of the molality of potassium chloride.*

The curves reading from the top correspond to 0.001, 0.002, 0.004, 0.005, 0.01, 0.02, 0.04, 0.05, and 0.07 molal acid potassium phthalate.

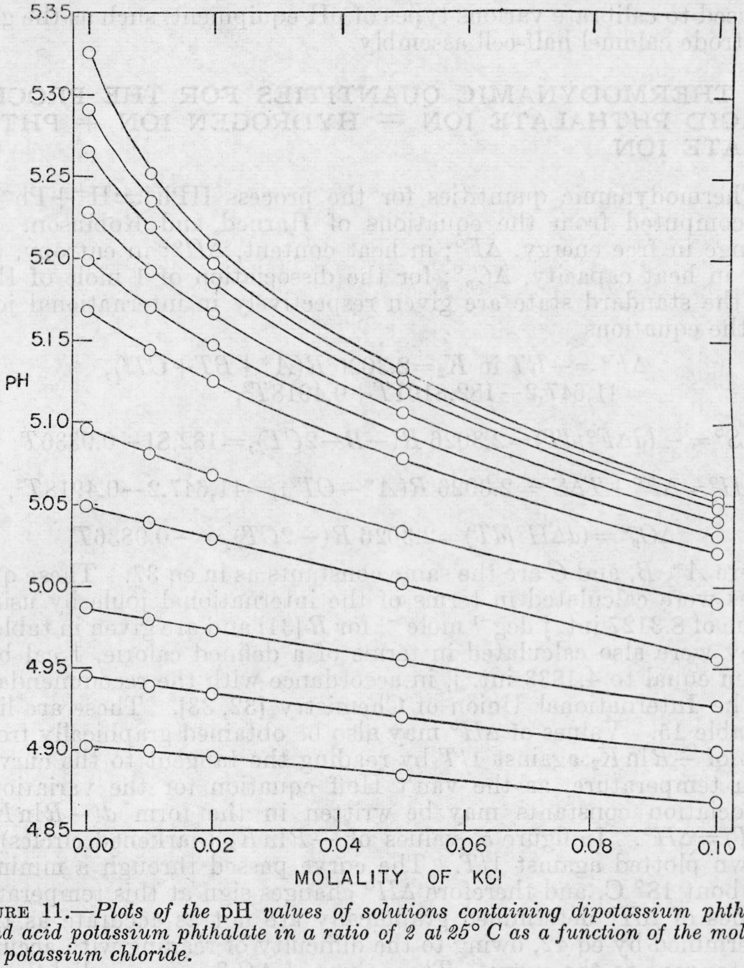

FIGURE 11.—*Plots of the* pH *values of solutions containing dipotassium phthalate and acid potassium phthalate in a ratio of 2 at 25° C as a function of the molality of potassium chloride.*

The curves reading from the top correspond to 0.001, 0.002, 0.003, 0.004, 0.005, 0.01, 0.02, 0.03, 0.04, and 0.05 molal acid potassium phthalate.

Each solution may be used as a standard for pH. It is proposed that they be prepared from the NBS Standard Sample 84a, of acid potassium phthalate, carbonate-free potassium hydroxide, and potassium chloride which meet the specifications of the American Chemical Society, and distilled water of pH 6.7 to 7.3 having a specific conductance of not over 1.0×10^{-6} mho. The solutions may be used to calibrate various types of pH equipment, such as the glass-electrode calomel half-cell assembly.

VI. THERMODYNAMIC QUANTITIES FOR THE PROCESS: ACID PHTHALATE ION ⇌ HYDROGEN ION + PHTHALATE ION

Thermodynamic quantities for the process $HPh^- \rightleftharpoons H^+ + Ph^=$ can be computed from the equations of Harned and Robinson. The change in free energy, $\Delta F°$; in heat content, $\Delta H°$; in entropy, $\Delta S°$; and in heat capacity, $\Delta C_p°$; for the dissociation of 1 mole of HPh^- for the standard state are given respectively in international joules by the equations

$$\begin{aligned}\Delta F° &= -RT \text{ in } K_2 = 2.3026\, R(A^* + BT + CT^2),\\ &= 41{,}647.2 - 182.8101T + 0.4918T^2, \end{aligned} \qquad (40)$$

$$\Delta S° = -(d\Delta F°/dT) = 2.3026\, R(-B - 2CT), = 182.81 - 0.9836T \qquad (41)$$

$$\Delta H° = \Delta F° + T\Delta S° = 2.3026\, R(A^* - CT^2), = 41{,}647.2 - 0.4918T^2, \qquad (42)$$

$$\Delta C_p° = (d\Delta H°/dT) = 2.3026\, R(-2CT), = -0.9836T, \qquad (43)$$

where A^*, B, and C are the same constants as in eq 37. These quantities were calculated in terms of the international joule by using a value of 8.3127 int. j deg^{-1} mole^{-1} for R [31] and are given in table 15. They were also calculated in terms of a defined calorie, 1 cal being taken equal to 4.1833 int. j, in accordance with the recommendation of the International Union of Chemistry [32, 33]. These are listed in table 15. Values of $\Delta H°$ may also be obtained graphically from a plot of $-R\ln K_2$ against $1/T$ by reading the tangent to the curve at each temperature, as the van't Hoff equation for the variation of dissociation constants may be written in the form $d(-R\ln K_2)/d(1/T) = \Delta H°$. In figure 5, values of $-R\ln K_2$ (darkened circles) are shown plotted against $1/T$. The curve passed through a minimum at about 18° C, and therefore $\Delta H°$ changes sign at this temperature. Values of $\Delta H°$ determined graphically are not as accurate as those determined by eq 42, owing to the difficulty of reading with accuracy the tangent to the curve. The values of $\Delta C_p°$ increase slightly with the temperature, as predicted by a semiempirical equation derived by Moelwyn-Hughes [34]. Values of $\Delta F°$ and $\Delta S°$ also increase with respect to temperature.

TABLE 15.—*Thermodynamic data from 0° to 60° C for the dissociation of the acid phthalate ion into hydrogen and phthalate ions*

Temperature	$\Delta F°$		$\Delta H°$		$\Delta S°$		$\Delta C_p°$	
°*C*	*Int. j*	*cal*	*Int. j*	*cal*	*Int. j*	*cal*	*Int. j*	*cal*
0	28, 407	6, 791	4, 951	1, 183	−85. 9	−20. 5	−268. 7	−64. 2
5	28, 849	6, 896	3, 595	859	−90. 8	−21. 7	−273. 6	−65. 4
10	29, 315	7, 008	2, 215	529	−95. 7	−22. 9	−278. 5	−66. 6
15	29, 806	7, 125	810	194	−100. 6	−24. 1	−283. 4	−67. 8
20	30, 321	7, 248	−620	−148	105. 5	−25. 2	−288. 4	−68. 9
25	30, 861	7, 377	−2, 074	−496	110. 5	−26. 4	−293. 3	−70. 1
30	31, 426	7, 512	−3, 552	−849	115. 4	−27. 6	−298. 2	−71. 3
35	32, 015	7, 653	−5, 055	−1, 208	120. 3	−28. 8	−303. 1	−72. 5
40	32, 629	7, 800	−6, 583	−1, 574	125. 2	−29. 9	−308. 0	−73. 6
45	33, 267	7, 952	−8, 136	−1, 945	130. 1	−31. 1	−312. 9	−74. 8
50	33, 930	8, 111	−9, 713	−2, 322	135. 1	−32. 3	−317. 9	−76. 0
55	34, 618	8, 275	−11, 314	−2, 705	140. 0	−33. 5	−322. 8	−77. 2
60	35, 330	8, 445	−12, 940	−3, 093	144. 9	−34. 6	−327. 7	−78. 3

The values of $\Delta F°$ are obtained directly from those for K_2. The errors in K_2 introduce uncertainties in the values of $\Delta F°$ of only 0.1 percent, or about 35 int. j or 7.5 calories. The values of $\Delta H°$ and $\Delta C_p°$ are subject to large error, estimated to be of the order of 100 calories in $\Delta H°$ and 3 calories in $\Delta C_p°$. The error in $\Delta S°$ is determined by the uncertainties in $\Delta H°$ and $\Delta C_p°$ and is approximately 0.3 calorie. Unfortunately no calorimetric measurements have been made of the heat of dissociation of the acid phthalate ion, or of the heat capacities of the ions involved in the dissociation of this ion, with which comparisons may be made. However, data are available for two other second dissociation of dibasic acids, namely for oxalic [35] and malonic acids [8], with which comparisons may be made. Values of $\Delta C_p°$ at 25° C for oxalic and malonic acids are, respectively, −59 and −61.3 calories, which are of the same order of magnitude as −70.1 found in this investigation and quite different from the average of about −40 calories found for monobasic acids [10, 36]. For the same acids, $\Delta S°$ is, respectively, −24.4 and −30.0 which is likewise of the same order of magnitude as −26.4 found in this investigation and some higher than an average value of about −20 calories found for monobasic acids [10, 36].

The similarity in the values of $\Delta C_p°$ and $\Delta S°$ for these three acids offers indirect confirmation of the reliability of the data obtained in this investigation.

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