sine, time of exposure and cooling, by the use of radioactive arsenic. The distribution curves show a marked accelerating effect of small amounts of water and an inhibiting effect of larger

amounts. A constant saturation value for arsine at the influent end of the bed is apparently not reached even after long exposure.

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Determination of the Product of the Constants for the Overlapping Dissociation of Weak Acids by Electromotive Force Methods

BY ROGER G. BATES

The exact determination of the thermodynamic dissociation constants of many weak dibasic and tribasic acids is complicated by the "overlapping" of the successive ionization steps. When the ratio of the thermodynamic constants for the primary and secondary steps, K_1/K_2, is less than 500 to 1000, as it is for most of the common aliphatic dicarboxylic acids[1] and many substituted benzoic acids,[2] the ionic and molecular concentrations cannot be established with sufficient accuracy by consideration of a single equilibrium. Hence, a determination of the constants often requires laborious arithmetical approximations.[3,4,5,6]

The constant for the second overlapping step in the dissociation of a dibasic acid can often be determined by the thermodynamic method of Harned and Ehlers[7] from measurements of cells without liquid junction. The determination is facilitated through choice of buffer solutions on the alkaline side of the midpoint of the neutralization curve for the second group, with a decrease in the correction for the first dissociation equilibrium. A buffer ratio of 5:1 appears not to be excessive.[8] However, the advantage of a similar procedure is sometimes offset in the evaluation of the first constant by the enhanced correction for hydrogen ion, the concentration of which must be established by successive approximations or, at a sacrifice of accuracy, derived from a pH measurement.[9]

When conditions cannot readily be chosen to isolate each of the individual equilibria in turn, solutions of the acid salt, where overlapping of the two equilibria is at a maximum, can be used to

advantage in establishing the product of the constants for two overlapping equilibria. A thermodynamic method for the determination of this product from measurements of the electromotive force of cells without liquid junction is described. If one dissociation constant of an overlapping pair is known, this procedure usually permits the other to be determined accurately.

Method

The electromotive force, E, of the cell

$$\text{Pt; H}_2\text{, acid salt } (m), \text{ MCl } (m_2), \text{ AgCl; Ag} \qquad \text{I}$$

where M represents an alkali metal and the acid salt is of one of the three types: MHA, MH₂A, or M₂HA, is given by

$$\frac{F(E - E^0)}{2.3026\,RT} + \log m_{\text{Cl}} = -\log(f_H f_{\text{Cl}} m_H) \equiv pw\text{H} \qquad (1)$$

For convenience, this experimental quantity will be termed pwH. In equation (1), f is an activity coefficient on the scale of molality (m), F is the faraday, and the other symbols have their usual significance. The hydrogen-ion concentration, m_H, is readily expressed in terms of dissociation constants, molalities, and activity coefficients. The product of the thermodynamic constants for the two overlapping steps is obtained by extrapolation of an appropriate function of E, with the aid of the Debye–Hückel formula,[10] to infinite dilution, where the estimated activity coefficients are exact. To simplify the treatment, the following discussion is restricted to solutions of acid salts with pH < 8, in which the concentration of hydroxyl ion can be ignored.

Case I. Acid Salt of a Dibasic Acid, K_1/K_2 <500.—The molecular and ionic species participating in the equilibria are H⁺, H₂A, HA⁻, and A⁼. The concentration of hydrogen ion, m_H, in solutions of the acid salt is given by

$$m_H^2 = \frac{K_1 K_2 m_{H_2A}}{m_A} \times \frac{f_{H_2A}}{f_H^2 f_A} \qquad (2)$$

Inasmuch as

$$m_A = m_{H_2A} + m_H \qquad (3)$$

we obtain, by combination of equations (1) and (2)

(1) R. Gane and C. K. Ingold, *J. Chem. Soc.*, 2153 (1931).

(2) W. R. Maxwell and J. R. Partington, *Trans. Faraday Soc.*, **33**, 670 (1937).

(3) F. Auerbach and E. Smolczyk, *Z. physik. Chem.*, **110**, 65 (1924); H. T. S. Britton, *J. Chem. Soc.*, 1896 (1925); N. Bjerrum and A. Unmack, *Kgl. Danske Videnskab. Selskab., Math.-fys. Medd.*, **9**, No. 1 (1929).

(4) H. S. Simms, THIS JOURNAL, **48**, 1239 (1926).

(5) W. J. Hamer and S. F. Acree, *J. Research Natl. Bur. Standards*, **35**, 381 (1945).

(6) W. J. Hamer, G. D. Pinching and S. F. Acree, *ibid.*, **35**, 539 (1945).

(7) H. S. Harned and R. W. Ehlers, THIS JOURNAL, **54**, 1350 (1932).

(8) G. D. Pinching and R. G. Bates, *J. Research Natl. Bur. Standards*, in press (data for oxalic acid).

(9) The simultaneous evaluation of overlapping K_1 and K_2 from pH-titration data obtained from cells with liquid junction has been described by J. C. Speakman, *J. Chem. Soc.*, 855 (1940).

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

$$-\frac{1}{2}\log(K_1K_2) = pwH - \frac{1}{2}\log\frac{m_{H_2A} + m_H}{m_{H_2A}} - \frac{1}{2}\log$$
$$\frac{f_A}{f_{H_3A}f_{Cl}^2} \quad (4)$$

To aid in the extrapolation, the Debye–Hückel equation may be employed for the ionic activity coefficients and unity assumed for the activity coefficient of the uncharged molecule. In this way an expression for the "apparent" value of the product of K_1 and K_2, namely $(K_1K_2)'$, is obtained

$$-\frac{1}{2}\log(K_1K_2)' = pwH - \frac{1}{2}\log\frac{m_{H_2A} + m_H}{m_{H_2A}} + \frac{A\sqrt{\mu}}{1 + Ba^*\sqrt{\mu}} \quad (5)$$

where A and B are constants of the Debye–Hückel theory,[11] μ is the ionic strength, and a^* is the so-called ion-size parameter. The limiting value of $(K_1K_2)'$ at zero ionic strength is K_1K_2.

Case II. Primary Acid Salt of a Tribasic Acid, $K_1/K_2 < 500$, $K_2/K_3 > 1000$.—The ionic and molecular species concerned are H^+, H_3A, H_2A^-, and HA^-. The molality of hydrogen ion is given by

$$m_H^2 = \frac{K_1K_2 m_{H_3A}}{m_{HA}} \times \frac{f_{H_3A}}{f_H^2 f_{HA}} \quad (6)$$

Inasmuch as the third dissociation step need not be considered

$$m_{HA} = m_{H_3A} + m_H \quad (7)$$

By combination of equations (1), (6) and (7), an expression is obtained that differs from equation (4) only in substitution of H_3A for H_2A and of HA for A in the subscripts of m and f. This expression can be written in a form suitable for extrapolation as follows

$$-\frac{1}{2}\log(K_1K_2)' = pwH - \frac{1}{2}\log\frac{m_{H_3A} + m_H}{m_{H_3A}} + \frac{A\sqrt{\mu}}{1 + Ba^*\sqrt{\mu}} \quad (8)$$

Case III. Secondary Acid Salt of a Tribasic Acid, $K_1/K_2 > 1000$, $K_2/K_3 < 500$.—The ionic species are H^+, H_2A^-, HA^-, and $A^=$. The square of the concentration of hydrogen ion is

$$m_H^2 = \frac{K_2K_3 m_{H_2A}}{m_A} \times \frac{f_{H_2A}}{f_H^2 f_A} \quad (9)$$

Equations (3) and (4) are valid for Case III as well as for Case I, with the substitution of the product K_2K_3 for K_1K_2. The charges of H_2A and A are, of course, now -1 and -3 instead of 0 and -2 as in Case I. By combination with the Debye–Hückel equation, an expression suitable for extrapolation is obtained

$$-\frac{1}{2}\log(K_2K_3)' = pwH - \frac{1}{2}\log\frac{m_{H_2A^-} + m_H}{m_{H_2A^-}} + \frac{3A\sqrt{\mu}}{1 + Ba^*\sqrt{\mu}} \quad (10)$$

(11) G. G. Manov, R. G. Bates, W. J. Hamer and S. F. Acree, This Journal, **65**, 1765 (1943).

Case IV. Primary Acid Salt of a Tribasic Acid, $K_1/K_2 < 500$ and $K_2/K_3 < 500$.[12]—The ionic and molecular species of concern in Case IV are H^+, H_3A, H_2A^-, HA^-, and $A^=$. All three steps in the dissociation of the acid must be considered, and

$$m_{HA} = m_{H_3A} + m_H - m_A \quad (11)$$

Formula (6) applies here, and equation (8) of Case II accordingly takes the form

$$-\frac{1}{2}\log(K_1K_2)' = pwH - \frac{1}{2}\log\frac{m_{H_3A} + m_H - m_{A^=}}{m_{H_3A}} + \frac{A\sqrt{\mu}}{1 + Ba^*\sqrt{\mu}} \quad (12)$$

Case V. Secondary Acid Salt of a Tribasic Acid, $K_1/K_2 < 500$ and $K_2/K_3 < 500$.—The molalities of the molecular acid and of the primary and tertiary ions in a solution of the secondary salt are related by

$$m_A = m_{H_2A} + m_H + 2m_{H_3A} \quad (13)$$

The hydrogen-ion concentration is given by equation (9). Hence, an expression analogous to equation (10) is obtained:

$$-\frac{1}{2}\log(K_2K_3)' = pwH - \frac{1}{2}\log$$
$$\frac{m_{H_2A^-} + m_H + 2m_{H_3A}}{m_{H_2A^-}} + \frac{3A\sqrt{\mu}}{1 + Ba^*\sqrt{\mu}} \quad (14)$$

Compositions of the Solutions

Only two overlapping dissociation steps are involved in Cases I, II and III. The evaluation of the second terms on the right of equations (5), (8) and (10) requires that the concentration of only one ionic or molecular species in addition to that of hydrogen ion be established. In equations (12) and (14) of Cases IV and V, the concentration of a second species, fortunately considerably smaller than that of the first, must be estimated. In each instance the hydrogen-ion concentration, m_H, can be computed from the equation

$$-\log m_H = pwH + \log f_H f_{Cl} = pwH - \frac{2A\sqrt{\mu}}{1 + Ba^*\sqrt{\mu}} \quad (15)$$

In the following discussion of the exact and approximate methods of computing these concentration terms, it will be convenient to employ the classical dissociation constants, k_n, for the three steps. For a weak tribasic acid

$$k_1 m_{H_3A} = m_H m_{H_2A}; \quad k_2 m_{H_2A} = m_H m_{HA}; \quad k_3 m_{HA} = m_H m_A \quad (16)$$

If, further, it is assumed that each activity coefficient is given by the Debye–Hückel equation, we may write

$$k_n = K_n/f^{2n} \quad (17)$$

(12) The formulas of Cases IV and V have been applied successfully to the resolution of the three overlapping constants of citric acid by Miss Gladys D. Pinching and the author (unpublished work). For citric acid, each ratio is about 44, and K_1/K_3 is about 1900. If K_1/K_3 were less than 1000, the separation would doubtless be more difficult.
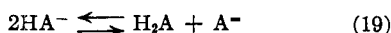
where

$$- \log f^n = nA\sqrt{\mu}/(1 + Ba^*\sqrt{\mu}) \quad (18)$$

and n is 1, 2, or 3. The symbol K_n represents the thermodynamic dissociation constant.

Complete or Exact Treatment, Cases I, II, and III.—When the acid salt of a dibasic acid with overlapping constants (Case I) is dissolved in water the interaction

$$2HA^- \underset{}{\overset{}{\rightleftharpoons}} H_2A + A^- \quad (19)$$

may proceed rather extensively. This reaction is usually considerably more important than the normal acidic dissociation of the intermediate ion. When K_1/K_2 is 4 (the theoretical lower limit for a symmetrical dibasic acid[13]), as much as half of the acid anion may be converted into H_2A and A^-.[13,14]

From the mass law and equations (3), (17) and (19) we have

$$\frac{k_2}{k_1} = \frac{K_2}{K_1 f^2} = \frac{m_{H_2A}(m_{H_2A} + m_H)}{(m - m_H - 2m_{H_2A})^2} \quad (20)$$

Even though m_H is obtained by equation (15) and the ratio of constants is known, equation (20) cannot readily be solved for m_{H_2A}. The desired quantity can, however, be obtained graphically or by trial.

Two features of this method are noteworthy. First, the second terms on the right of equations (5), (8), (10), (12) and (14) are of the form $1/2 \log [(a + b)/a]$, where a is large relative to b. Hence, the values of these terms are rather insensitive to small changes in a. The higher the pH of the solution of the acid salt the smaller is b, and the larger is the permissible error in a. Secondly, although the evaluation of both m_H and k_2/k_1 rests upon an assumed value of a^*, the ion-size parameter, the second terms on the right of these five extrapolation formulas are but little influenced by the choice of a^*, when the same value is used in both equation (15) and equation (18). This point will be illustrated later in this paper. The value of a^* used in the extrapolation equations themselves is immaterial, so long as the plots of $-1/2 \log (K_1K_2)'$ as a function of ionic strength display the convergence at infinite dilution demanded by theory.

The treatment of Cases II and III is entirely analogous to Case I. For Case II the principal equilibrium is

$$2H_2A^- \underset{}{\overset{}{\rightleftharpoons}} H_3A + HA^- \quad (21)$$
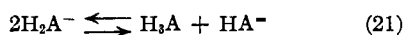
In equation (20), m_{H_2A} is replaced by m_{H_3A}. The extrapolation is performed with the aid of formula (8) instead of with (5). For Case III the principal ionic equilibrium is

$$2HA^- \underset{}{\overset{}{\rightleftharpoons}} H_2A^- + A^- \quad (22)$$
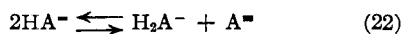
Hence, equation (20) becomes

$$\frac{k_3}{k_2} = \frac{K_3}{K_2 f^2} = \frac{m_{H_2A^-}(m_{H_2A^-} + m_H)}{(m - m_H - 2m_{H_2A^-})^2} \quad (23)$$

(13) R. Wegscheider, *Monatsh.*, **16**, 153 (1895); E. Q. Adams, THIS JOURNAL, **38**, 1503 (1916); N. Bjerrum, *Z. physik. Chem.*, **106**, 219 (1923).

(14) C. W. Davies. *J. Chem. Soc.*, 1850 (1939).

The extrapolation is made, of course, with equation (10)

Complete Treatment, Cases IV and V.—Formula (21) represents the principal equilibrium in solutions of the primary salt of a tribasic acid with three overlapping constants (Case IV). The secondary anion, HA^-, formed in this reaction is capable of further acidic dissociation, as is the primary anion. Contrary to the situation in Case II, where K_3 was too small to require consideration, three equilibria are involved here. Inasmuch as

$$m_{H_2A} = m - m_{H_3A} - m_{HA} - m_A \quad (24)$$

we have, from equation (11) and the mass-law expression for equilibrium (21)

$$\frac{k_2}{k_1} = \frac{m_{H_3A}(m_{H_3A} + m_H - m_A)}{(m - m_H - 2m_{H_3A})^2} \quad (20a)$$

The analogy with equation (20) is evident. The molality of A^- appearing in the numerator of (20a) is small (slightly less than 1% of m_{H_3A} in solutions of potassium dihydrogen citrate[12]). It is readily computed with an accuracy exceeding the experimental error in the electromotive force by

$$m_A = k_3 m_{HA}/m_H = K_3 m_{HA}/(m_H f^6) \quad (25)$$

from a first estimate of m_{HA} and a value of pK_3 accurate to ± 0.1. Otherwise, the evaluation of K_1K_2 parallels Case I.

The principal equilibrium in solutions of the secondary salt of a tribasic acid with three overlapping constants (Case V) is (22). Acidic dissociation of the secondary anion must be considered as well as the reaction of the primary anion formed in (22) with a part of the hydrogen ion liberated by dissociation of HA^-

$$H_2A^- + H^+ \underset{}{\overset{}{\rightleftharpoons}} H_3A \quad (26)$$
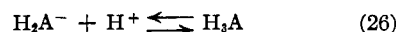
From equations (13), (24), and the mass law

$$\frac{k_3}{k_2} = \frac{m_{H_2A}(m_{H_2A} + m_H + 2m_{H_3A})}{(m - m_H - 2m_{H_2A} - 3m_{H_3A})^2} \quad (23a)$$

The molality of H_3A, like m_A in Case IV, is a correction of secondary importance. It is obtained with sufficient accuracy from the approximate K_1 and m_{H_2A} by

$$m_{H_3A} = m_H m_{H_2A}/k_1 = m_H m_{H_2A} f^2/K_1 \quad (27)$$

Approximate Treatment.—If the pH of the solution of acid salt is higher than 3.5 to 4.0, m_H is usually small with respect to m_{H_2A} and m_{H_3A} in equations (5), (8), (10), (12) and (14), and the treatment can be simplified. Fortunately, the acid salts of most dicarboxylic acids with overlapping fall in this category.

If m_H in equation (3) approaches zero, it is easy to show that the molality of molecular acid produced by reaction (19) is approximately

$$m_{H_2A} \approx \frac{1}{2}(mx - m_H) \quad (28)$$

where

$$x \equiv \frac{2(k_2/k_1)^{1/2}}{1 + 2(k_2/k_1)^{1/2}} \quad (29)$$

Hence, the concentration term of equation (5) is readily obtained and, by a similar procedure, also that of equation (8)

Cases I and II.—

$$\frac{m_{H_2A} + m_H}{m_{H_2A}} \approx \frac{mx + m_H}{mx - m_H}$$

$$\frac{m_{H_3A} + m_H}{m_{H_3A}} \approx \frac{mx + m_H}{mx - m_H} \quad (30)$$

Similarly, from equation (23), we have

$$m_{H_2A^-} \approx \frac{1}{2}(my - m_H) \quad (31)$$

where

$$y \equiv \frac{2(k_3/k_2)^{1/2}}{1 + 2(k_3/k_2)^{1/2}} \quad (32)$$

Hence, the concentration term of formula (10) is given by

Case III.—

$$\frac{m_{H_2A^-} + m_H}{m_{H_2A^-}} \approx \frac{my + m_H}{my - m_H} \quad (33)$$

By the same reasoning, the second term on the right of formula (12) can be expressed in terms of x

Case IV.—

$$\frac{m_{H_3A} + m_H - m_{A^-}}{m_{H_3A}} \approx \frac{mx + m_H - 2m_A}{mx - m_H} \quad (34)$$

In Case V the situation is slightly different, for a part of the primary anion, H_2A^-, produced by (22) is converted into H_3A. Hence

$$m_{H_3A} \approx \frac{1}{2}(my - m_H) - m_{H_2A} \quad (35)$$

The second term on the right of equation (14) is thus given by

Case V.—

$$\frac{m_{H_2A^-} + m_H + 2m_{H_3A}}{m_{H_2A^-}} \approx \frac{my + m_H + 2m_{H_3A}}{my - m_H - 2m_{H_3A}} \quad (36)$$

Ionic Strength.—Whether the complete or approximate treatment is used, sufficiently accurate values of the ionic strength can ordinarily be obtained with the aid of x and y

Case	Mixture	Ionic Strength	
I	MHA (m), MCl (m_2)	$m (1 + 0.5x) + 1.5m_H + m_2$	(37a)
II	MH₂A (m), MCl (m_2)	$m (1 + 0.5x) + 1.5m_H + m_2$	(37b)
III	M₂HA (m), MCl (m_2)	$m (3 + 0.5y) + 2.5m_H + m_2$	(37c)
IV	MH₂A (m), MCl (m_2)	$m (1 + 0.5x) + 1.5m_H + 2.5m_A + m_2$	(37d)
V	M₂HA (m), MCl (m_2)	$m (3 + 0.5y) + 2.5m_H + 2m_{H_3A} + m_2$	(37e)

Evaluation of K_1K_2 and K_2K_3

The determination of K_1K_2 for a dibasic acid is made as follows. Values of x are computed by equation (29) from a reasonable estimate of k_2/k_1, and a first estimate of the ionic strength is obtained by equation (37a). The hydrogen-ion concentration can be ignored or estimated from the approximate pH of the solution. Equation (15) yields a value of m_H when the ionic strength has been estimated, and the second term on the

right of equation (5) is computed with the aid of equation (20) or the approximation, equation (28). It is suggested that a value of 4.0 be assigned to a^* in equations (15) and (18). A first approximation of K_1K_2 is obtained by extrapolation of the right-hand side of equation (5) to infinite dilution. The plots of $-\frac{1}{2} \log (K_1K_2)'$ as a function of ionic strength will dictate the value of a^* in equation (5) necessary to provide an accurate extrapolation, although 4.0 is a reasonable first choice.

A value of K_2/K_1 results from combining K_1K_2 with K_1 or K_2, whichever is available from independent determinations, and a new k_2/k_1 is obtained with the assistance of equations (17) and (18). The process is then repeated. Inasmuch as m_{H_2A} need not be known accurately, a third approximation is usually unnecessary.

For the solution of Cases IV and V an approximate value of m_A or m_{H_3A} is calculated as described in an earlier section. In other respects, K_1K_2 and K_2K_3 are evaluated in Cases II, III, IV, and V exactly as is K_1K_2 in Case I.

The extrapolation of the right side of equations (12) and (14) to infinite dilution is illustrated in Fig. 1 with data for the acid salts of citric acid. The two sets of curves were computed from the electromotive force of cells of type I. The upper lines represent mixtures of secondary potassium citrate and potassium chloride, whereas the lower set was derived from studies of mixtures of primary potassium citrate and potassium chloride.[12,15] The approximate formulas (34) and (36) were used in evaluating the second terms on the right of equations (12) and (14). Curves a, b, c, d, e, and f were computed with a^* values of 5.0, 5.5, 6.0, 2.0, 3.0 and 4.0, respectively. As mentioned earlier, altering a^* in formulas (15) and (18) has little effect on the plotted points.

Limitations of the Approximation.—In Figure 2, the differences between the true $\frac{1}{2} \log [(m_{H_3A} + m_H)/m_{H_3A}]$ of formula (5) and approximate values computed by equation (30) are plotted as a function of the molality of the acid salt. To enhance the accuracy of the determination of the constants for the overlapping steps, the concentration of acid salt should preferably not be lower than 0.01 molal. The lower limit of $-\log m_H$ (pcH), below which the error of the approximation exceeds 0.0005 in $\frac{1}{2} \log (K_1K_2)'$ (0.03 mv. in the electromotive force), is a function of the magnitude of k_1/k_2, that is, of the extent of overlapping. The approximate treatment is adequate above pcH 3.25 when k_1/k_2 is 10, above 3.70 when k_1/k_2 is 100, and above 3.95 when k_1/k_2 is 215.

K_1K_2 for o-Phthalic Acid

The two dissociation constants of o-phthalic acid have been determined accurately by electromotive-force methods.[5,6] These constants can be employed to illustrate the application of the equa-

(15) These curves were plotted from preliminary data. They serve, nevertheless, to illustrate the nature of the extrapolation.
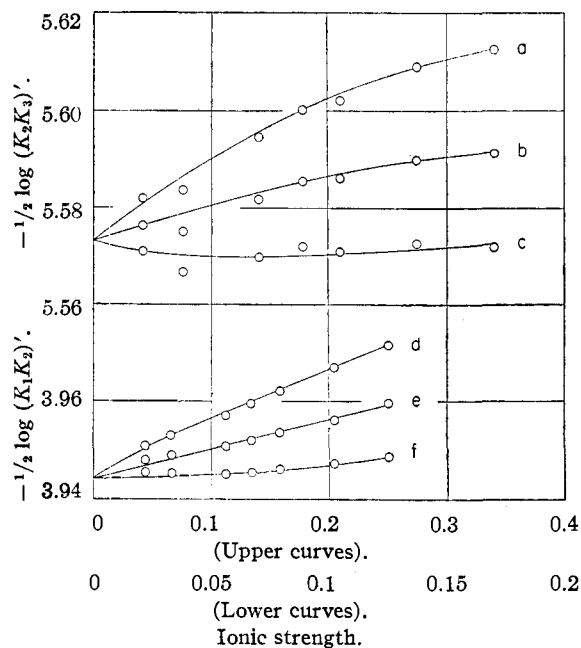
Fig. 1.—Determination of K_1K_2 and K_2K_3 for citric acid from the electromotive force of cell I at 25°.

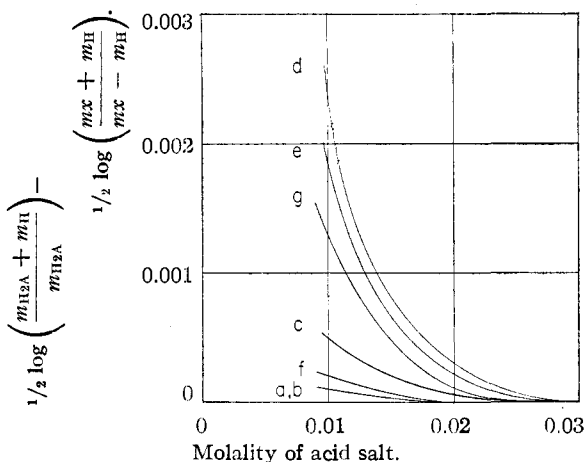tions of the foregoing sections and to test this method of determining K_1K_2.

Fig. 2.—Error of the approximation plotted as a function of the molality of the acid salt:

Curve	k_1/k_2	$-\log m_H$
a	7	3.43
b	10	3.50
c	10	3.25
d	10	3.00
e	20	3.15
f	100	3.80
g	100	3.50

The electromotive force of 19 cells of type I was measured at 25° with mixtures of acid potassium phthalate[16] and potassium chloride ($m_2 = 0.01$).

(16) National Bureau of Standards Standard Samples 84a and 84c.

Palladium electrodes were substituted for platinum.[17] The molality of acid salt varied from 0.01 to 0.07. The electromotive force in int. v. appeared to be a linear function of log m in this range

$$E_{25} = 0.57662 - 0.00476 \log m \qquad (38)$$

The reproducibility and stability of the cells with 0.01 m to 0.02 m acid potassium phthalate were not good, and an uncertainty of nearly 0.2 mv. must be assigned to the electromotive force at 0.01 m. The uncertainty is indicated in Fig. 3 by the varying sizes of the circles which represent the values of $-\frac{1}{2} \log (K_1K_2)'$. The approximate treatment was employed throughout. The error of the approximation is only 0.0002 in $-\frac{1}{2} \log (K_1K_2)'$ for the 0.01 m solution, the most dilute studied.
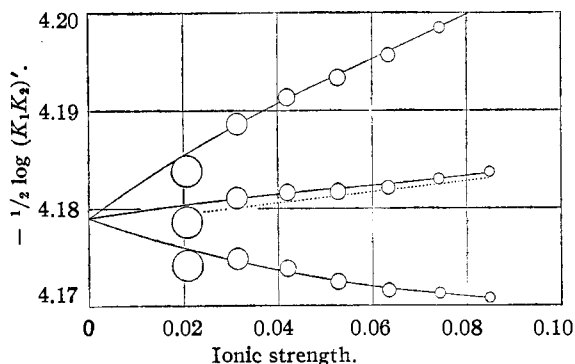

Fig. 3.—Determination of K_1K_2 for phthalic acid from the electromotive force of cell I at 25°: from top to bottom, the lines represent a^* values of 2.0, 4.0, and 6.0, equation (5). The curves are drawn to intersect at 4.179, the known value of $-\frac{1}{2} \log (K_1K_2)$.[5,6]

From top to bottom of Fig. 3, the three lines represent a^* values of 2.0, 4.0, and 6.0 in the last term of formula (5). In each instance, 4.0 was used for a^* in equations (15) and (18). When a^* was set equal to zero in these two equations, the middle curve in Fig. 3 took the position indicated by the dotted line. It is evident, therefore, that the final result is altered by only 0.001 if the Debye–Hückel limiting law ($a^* = 0$) is used in these two formulas. The three lines are drawn to intersect at 4.179, the value of $-\frac{1}{2} \log (K_1K_2)$ at 25°.[5,6]

It should be noted that the electromotive force of cell I containing a solution of primary or secondary acid salt is rather sensitive to variations in the composition of the salt. For example, the change in the electromotive force of the cell containing 0.05 m acid potassium phthalate and 0.01 m potassium chloride that results from a change of 0.1% in the titration value of the acid salt is about 0.17 mv. For phthalic acid, K_1/K_2 is 288.[5,6] The electromotive force is somewhat less sensitive to the purity of the salt when the extent of overlapping is greater. A change of 0.03 mv. in

(17) W. J. Hamer and S. F. Acree, J. Research Natl. Bur. Standards, 33, 87 (1944).

E corresponds to 0.001 in $pK_1 + pK_2$. Hence, the uncertainty in pK caused by experimental errors is twice that of the conventional method where a single dissociation step is involved.

Summary

The use of electromotive-force measurements of hydrogen–silver chloride cells without liquid junction in resolving the constants for the overlapping dissociation steps of weak dibasic and tribasic acids is discussed. When one constant of an overlapping pair is known, the second can be derived from studies of solutions of the appropriate primary or secondary acid salt with added alkali chloride. The equations for the five possible cases of overlapping have been developed. A simple means of estimating the molalities needed in the computation is described. The method has been applied to a determination of the product of the constants of phthalic acid at 25°. The result is consistent with earlier determinations of the two constants.

Synthesis of Products Related to Vitamin A. IV. The Application of the Darzens Reaction to β-Ionone[1a]

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One of the key intermediates in the synthesis of several biologically active vitamin A products[8] was produced by the application of the Darzens synthesis to β-ionone.[9] The structure of this product presented a special problem in view of the anomalous results obtained in the early stages of our investigation. When β-ionone was condensed with ethyl chloroacetate at low temperatures (−30 to −60°) in anhydrous ether or toluene using alcohol-free sodium ethoxide or methoxide as the condensing agents, the glycidic ester I was produced which upon hydrolysis presumably gave a glycidic acid of similar structure. When the crude glycidic ester was hydrolyzed and the crude glycidic acid decarboxylated in the presence or absence of powdered glass or by passing it under a reduced pressure downwards through a hot tube

(140–160°) packed with freshly reduced copper powder on pumice, the decarboxylation product had slightly different properties from that obtained by the decarboxylation of the pyridine salt of the same glycidic acid. Furthermore, decarboxylation under similar conditions of the two glycidic acids, one crystalline and the other highly viscous liquid both derived from pure glycidic ester, yielded products still different in physical and chemical properties. Table I shows the main fractions of decarboxylation products obtained by various methods from crude as well as from crystalline glycidic acids. Upon careful fractionation of a large sample of the decarboxylation product obtained from the crude glycidic acid using a four-foot packed fractionation column, three fractions were obtained: a small low-boiling fraction with a high index of refraction; a large fraction with an intermediate b. p. and an index of refraction ranging from 1.5133 (20°) to 1.5155 (25°); and a small high-boiling fraction with a high index of refraction. It may be seen from the table that the low-boiling fraction resembles in properties the main product obtained from the decarboxylation of the crystalline glycidic acid. The high-boiling fraction, on the other hand, has several properties in common with the main product resulting from the crude glycidic acid, except that it exhibits a secondary absorption maximum at 3000 Å.

The results shown in Table I raise the question whether the purified glycidic ester and the glycidic acids derived from it have the same structure as the corresponding crude compounds. The purified glycidic ester was found to have one active hydrogen (Zer.), while the crystalline glycidic acid showed the presence of two active hydrogens. Both the ester and the acid gave a strong ferric chloride reaction, and upon catalytic hydrogenation showed the presence of approximately three double bonds. Furthermore, the ultraviolet spec-

(1) (a) Since this and other work related to the synthesis of vitamin A was under confidential classification during the War, we wish to point out for purposes of priority the existence of two documents deposited in the Office of the Committee on Medical Research of the O. S. R. D. and describing the synthesis of biologically active vitamin A products using the Darzens aldehyde made from β-ionone as the key intermediate. These documents were dated March 6, 1942; (b) Paper No. 3, *Science*, **103**, 581 (1946). For paper No. 2, THIS JOURNAL, **63**, 752 (1941). First presented in part before the North Jersey Section of the A. C. S., April 9, 1945.

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(8) Milas, U. S. Patents 2,369,156–2,369,168, inclusive, excepting 2,369,158. Feb. 13 (1945); 2,382,085–086, Aug. 14 (1945).

(9) (a) Ishikawa and Matsuura, *Sci. Rep. Tokyo Bunrika Daigaku*, **3A**, 173 (1937); (b) Heilbron, Johnson, Jones and Spinks, *J. Chem. Soc.*, 727 (1942); Cymerman, Heilbron, Jones and Lacey, *ibid.*, 500 (1946).