Molecular Weight.—The molecular weights of the color-forming polyvinyl acetals are of the same order as the molecular weight of the starting polyvinyl alcohol. No appreciable scission or cross-linking resulting from the process of acetalization has been detected, and the number average molecular weight of the cyan color-forming polyvinyl acetal (V) lies in the same range as that of the parent polyvinyl alcohol from which it was prepared (Table III). From its composition, the calculated number average molecular weight of the acetal is about 13% higher than that of the parent polyvinyl alcohol. The measurements also indicate that the polymer has a molecular weight in the same range as that of photographic gelatin. An interesting point brought out by these measurements is the relatively small effect of changing *p*H in the alkaline region on the polyvinyl alcohol as compared with gelatin.

TABLE IV

PHYSICAL PROPERTIES OF FILMS[a] OF CYAN COLOR-FORMING POLYVINYL ACETAL V

Physical property	Polyvinyl acetal V	Gelatin
Tensile strength (lb./sq. in.)[b]		
50% R. H.	9800	13,600
Wet	590	Dissolves
Elongation (%)		
50% R. H.	4.2	6
Wet	60	Dissolves
Flexibility[c] 50% R. H.	1723	190
Tear strength[d] 50% R. H.	9.1	3.0

[a] Films were approximately 0.005 inch thick. [b] Measured on "Tinius-Olson Electromatic Tensile Tester." [c] M.I.T. Fold Test; A.S.T.M. Designation: D643-43 Method B (A.S.T.M. Standards, part 4, p. 907, 1949). [d] Relative values obtained with a pendulum-type tear tester.

Film Properties.—Transparent, colorless films of the color-forming polyvinyl acetals can be cast from aqueous alcohol solutions. These films are strong and relatively flexible and can be handled without a support. A comparison of the physical properties of films of the cyan color-forming polymer (V) with those of gelatin is given in Table IV. Of particular significance is the appreciable strength of the polyvinyl acetal films when wet. This is related to their ability to withstand relatively severe handling in the wet state.

Acknowledgment.—We wish to acknowledge our indebtedness to many of our colleagues without whose creative assistance this work could not have been done. We are particularly indebted to Drs. J. O. Corner, E. L. Martin, M. S. Raasch, and C. Weaver. We also wish to thank Dr. J. B. Nichols and Miss Beverly Price for molecular weight characterizations of the polymer, and members of the Analytical Division of the Chemical Department for analytical determinations and measurements of film properties.

In addition, we wish to acknowledge the continued support of the Photo Products Department in this work as well as the excellent coöperation and assistance of many members of the Photo Products Technical Division.

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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, COLUMBIA UNIVERSITY AND THE FLORIDA STATE UNIVERSITY]

A Differential Potentiometric Method of Measuring Acid and Base Dissociation Constants[1a]

BY ERNEST GRUNWALD[1b]

A potentiometric method for acid and base dissociation constants and autoprotolysis constants is presented which does not require knowledge of electrode or liquid junction potentials. Acid and base dissociation constants are derived from the rate of change of *p*H with added strong reagent at the equivalence point in the titration of weak bases or weak acids under conditions where the uncertain potentials are constant. A mathematical analysis is given, and the calculation of dissociation constants by rapidly converging successive approximations is discussed. Simple apparatus and experimental procedures are described. The computation of accurate rates of change at the equivalence point from potentiometric data near the equivalence point is outlined. The method has been found practical for the measurement of dissociation constants greater than 10^{-7}. Using the simple apparatus described, dissociation constants have been accurate to 2-3%. Autoprotolysis constants accurate to about 10% have been obtained from the measurement of both acid and base dissociation constants in conjugate acid-base systems.

Thermodynamic acid dissociation constants have been measured by potentiometric methods using cells without liquid junctions,[2a] usually of the type H_2/HA, MA, MX/AgX-Ag, but accurate values of the standard electrode potentials which are required are not generally available, particularly for organic solvents; furthermore, work with the silver-silver halide or hydrogen electrode is difficult in some solvents.[3,4] By using suitable cells with liquid junctions, experimental difficulties may often be overcome,[3] but again either the electrode potentials and junction potentials must be known, or calibration against a standard resorted to.[2b]

A potentiometric method avoiding these limitations measures the rate of change of *p*H with added reagent at the equivalence point of an acid-base titration, under conditions where the uncertain potentials are constant. This derivative is a sensitive function of the dissociation constants of the species present at the equivalence point.[5]

While the measurement of a rate of change of *p*H removes the limitations of the classical potentiometric methods for dissociation constants,[2] it introduces new difficulties. Prominent among these are the solution of the relevant equations, the development of convenient experimental techniques, and the accurate measurement of the derivatives involved.

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(1) (a) Presented at the Meeting of the American Chemical Society in San Francisco, Calif., March, 1949; (b) Frank B. Jewett Fellow, 1948-1949.

(2) (a) Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943, Chapter 15; (b) *ibid.*, p. 316-325.

(3) (a) Buckley and Hartley, *Phil. Mag.*, [7] **8**, 320 (1929); (b) Goodhue and Hixon, THIS JOURNAL, **56**, 1329 (1934); **57**, 1688 (1935).

(4) Moore and Felsing, *ibid.*, **69**, 1076 (1947).

(5) Kilpi, *Z. physik. Chem.*, **A177**, 116, 427 (1936).

The present article reports a version of the differential potentiometric method that has been used successfully in these Laboratories for a number of years. The experimental procedures are simple, and highly specialized apparatus is not required. The solution of the rigorous equations by successive approximations and the accurate measurement of derivatives has been accomplished. The method has proved especially valuable in obtaining acid dissociation constants in organic solvents with an accuracy of 2–3%.

Mathematical Analysis

For convenience, the symbols used in this article are summarized below.[6a]

$a_{\mathrm{H}}, a_{\mathrm{Cl}}, a_{\mathrm{HA}}$	activities of solutes indicated
$c_{\mathrm{H}}, c_{\mathrm{Cl}}, c_{\mathrm{HA}}$	molar (or gram-ionic) concentrations of solutes indicated
c	$(= c_{\mathrm{HA}} + c_{\mathrm{A}})$
c_0	$(= c$ at equivalence point)
D	dielectric constant
$\mathbf{E}$	e.m.f.
$\mathbf{E}'$	$(= \mathbf{FE}/2.3026RT)$
f_c	correction factor
$\mathbf{F}$	Faraday charge
H^+, OS^-	lyonium, lyate ion[6b]
K_{A}	thermodynamic acid dissociation constant
K_{A}'	$\left(= K_{\mathrm{A}} \frac{y_{\mathrm{HA}}}{y_{\mathrm{H}} y_{\mathrm{A}}}\right)$ concentration dissociation constant
K_{B}	thermodynamic base dissociation constant
K_{B}'	$\left(= K_{\mathrm{B}} \frac{y_{\mathrm{A}}}{y_{\mathrm{HA}} y_{\mathrm{OS}}}\right)$ concentration dissociation constant
K_{S}	autoprotolysis constant of the solvent[6b]
N	normality of strong titrating reagent
$p\mathrm{X}$	$(= -\log a_{\mathrm{X}})$
R	gas constant per mole
s	empirical slope
T	absolute temperature
$y_{\mathrm{H}}, y_{\mathrm{Cl}}, y_{\mathrm{HA}}$	molar activity coefficients of solutes indicated
ϵ	degree of neutralization[7]
μ	ionic strength
τ	$(= \sqrt{K'/c_0})$ titration function (K' is K_{A}' or K_{B}')

In the titration of weak bases with strong acid according to

$$\mathrm{A}^- + \mathrm{H}^+ = \mathrm{HA}$$

the lyonium ion concentration is given as a function of the degree of neutralization[7] by the implicit function

$$c_{\mathrm{H}} \frac{(c_{\mathrm{H}} - [\epsilon - 1]c)}{c - c_{\mathrm{H}} + [\epsilon - 1]c} = K_{\mathrm{A}} \frac{y_{\mathrm{HA}}}{y_{\mathrm{H}} y_{\mathrm{A}}} = K_{\mathrm{A}}' \qquad (1)$$

In the present analysis, we are interested in relating $\mathrm{d}p\mathrm{H}/\mathrm{d}\epsilon$ (equation 2) at the equivalence point ($\epsilon = 1$) to the dissociation constant of the weakly

$$\frac{\mathrm{d}pH}{\mathrm{d}\epsilon} = y_{\mathrm{H}} \left(\frac{\partial c_{\mathrm{H}}}{\partial \epsilon} + \frac{\partial c_{\mathrm{H}}}{\partial c} \frac{\mathrm{d}c}{\mathrm{d}\epsilon} + \frac{\partial c_{\mathrm{H}}}{\partial K_{\mathrm{A}}'} \frac{\mathrm{d}K_{\mathrm{A}}'}{\mathrm{d}\epsilon}\right) + c_{\mathrm{H}} \frac{\mathrm{d}y_{\mathrm{H}}}{\mathrm{d}\epsilon} \qquad (2)$$

ionized species (HA) produced in the titration. The partial derivatives $\partial c_{\mathrm{H}}/\partial \epsilon$, $\partial c_{\mathrm{H}}/\partial c$, $\partial c_{\mathrm{H}}/\partial K_{\mathrm{A}'}$, are obtained from (1), and $\mathrm{d}c/\mathrm{d}\epsilon$ from (3) where the choice of the plus or minus sign depends on whether

$$c = c_0 \Big/ \left(1 \pm [\epsilon - 1] \frac{c_0}{N}\right) \qquad (3)$$

the experiment is one of direct titration or back titration. Although the rigorous solution of $\mathrm{d}K_{\mathrm{A}}'/\mathrm{d}\epsilon$ and of $\mathrm{d}y_{\mathrm{H}}/\mathrm{d}\epsilon$ at the equivalence point is not possible without additional data, fortunately the term $y_{\mathrm{H}} \frac{\partial c_{\mathrm{H}}}{\partial K_{\mathrm{A}}'} \frac{\mathrm{d}K_{\mathrm{A}}'}{\mathrm{d}\epsilon} + c_{\mathrm{H}} \frac{\mathrm{d}y_{\mathrm{H}}}{\mathrm{d}\epsilon}$ is negligible compared with $\frac{\mathrm{d}p_{\mathrm{H}}}{\mathrm{d}\epsilon}$ for many practical cases. A conservative upper limit for the per cent. error due to neglecting this term, based on the Debye–Hückel limiting law for activity coefficients,[2] is $1 \times 10^8\ K_{\mathrm{A}}\ \mu^{1/2} c_0^{-1} \cdot (DT)^{-3/2}$. Thus in the example of 0.01 *vf.* formic acid in water at 25° at an ionic strength of 0.005, the error is less than 0.03%.

$\mathrm{d}p\mathrm{H}/\mathrm{d}\epsilon$ at the equivalence point is given[8] to an excellent approximation by equation 4, where c_0, N and $\mathrm{d}p\mathrm{H}/\mathrm{d}\epsilon$ can be obtained experimentally, the

$$-\left(\frac{\mathrm{d}p\mathrm{H}}{\mathrm{d}\epsilon}\right)_{\epsilon=1} = \frac{c_0(c_{\mathrm{H}} + K_{\mathrm{A}}'\ [1 \mp c_0/N])}{2.3026\ c_{\mathrm{H}}\ (2c_{\mathrm{H}} + K_{\mathrm{A}}')} \qquad (4)$$

latter from measurements involving cells with or without liquid junctions even in situations where the accurate determination of $p\mathrm{H}$ is prevented by uncertainties in electrode or junction potentials, provided the uncertain potentials are constant over the range of measurement. Since c_{H} is a function of K_{A}' (equation 5), the latter may be calculated. However the direct solution for K_{A}' is difficult, and

$$(c_{\mathrm{H}})_{\epsilon=1} = (K_{\mathrm{A}}'\ c_0)^{1/2} \left(\left[1 + \frac{1}{4} \frac{K_{\mathrm{A}}'}{c_0}\right]^{1/2} - \frac{1}{2}\left(\frac{K_{\mathrm{A}}'}{c_0}\right)^{1/2}\right) \qquad (5)$$

a more convenient method of solution by successive approximations is here developed.

The method utilizes the fact that the coefficient of $(K_{\mathrm{A}}'\ c_0)^{1/2}$ on the right in equation 5 is usually a second-order term of magnitude 0.9–1.0 and is a function of the single variable $\tau = (K_{\mathrm{A}}'/c_0)^{1/2}$. Equation 6 defines a function $D(\tau)$ such that c_{H} is given by equation 7. Values of the function $D(\tau)$ for the range $0.000 \leqq \tau \leqq 0.399$ have been computed,[9] and some of these are given in Table I.

$$D\ (\tau) = ([1 + \tfrac{1}{4}\tau^2]^{1/2} - \tfrac{1}{2}\tau) \qquad (6)$$

$$(c_{\mathrm{H}})_{\epsilon=1} = (K_{\mathrm{A}}'\ c_0)^{1/2}\ D(\tau) \qquad (7)$$

Equation 8 expresses τ as a function of experimental quantities and $D(\tau)$. It is well suited to solution by successive approximations since a first estimate of τ, usually accurate to better than 0.5%, is derived[8] from equation 9. This enables a first estimate of

$$-4.605\tau = \left(D(\tau) + \left[1 \mp \frac{c_0}{N}\right]\tau\right) \Big/ \left(\frac{\mathrm{d}p\mathrm{H}}{\mathrm{d}\epsilon}\right)_{\epsilon=1} D(\tau)\ (D(\tau) + \tfrac{1}{2}\tau) \qquad (8)$$

$$\tau^{-1} = -4.605 \left(\frac{\mathrm{d}p\mathrm{H}}{\mathrm{d}\epsilon}\right)_{\epsilon=1} \pm \frac{c_0}{N} - 1 \qquad (9)$$

$D(\tau)$, and, using equation 8, successive estimates of τ. In practice, the estimates converge rapidly, and the second estimate is usually acceptable.

Base dissociation constants may similarly be derived from the rate of change of $p\mathrm{H}$ with degree of

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(6) (a) The symbols conform as far as possible to the symbols used by Harned and Owen.[2] (b) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., p. 255.

(7) In titrations with strong acid to produce HA, $\epsilon_{\mathrm{HA}} = (c_{\mathrm{H}} + c_{\mathrm{HA}} - c_{\mathrm{OS}})/c$; in titrations with strong alkali to produce A, $\epsilon_{\mathrm{A}} = (c_{\mathrm{OS}} + c_{\mathrm{A}} - c_{\mathrm{H}})/c$. By defining ϵ in this manner, ϵ is continuous and equal to unity at the equivalence point; the terms c_{OH} in the expression for ϵ_{HA} and c_{H} in the expression for ϵ_{A} are due to the autoprotolysis of the solvent and are neglected in the derivation of equations 1, 8 and 10.

(8) For choice of plus or minus sign in equations 4, 8, 9, and 10, see equation 3.

(9) For the complete sets of values of $D(\tau)$ and of the correction factors f_c order Document 3258 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting \$1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or \$1.00 for photocopies (6 × 8 inches) readable without optical aid.

TABLE I

VALUES OF $D(\tau)$

τ	0.0	0.1	0.2	0.3
0.00	1.0000	0.9512	0.9050	0.8612
.01	0.9950	.9465	.9005	.8569
.02	.9901	.9418	.8960	.8527
.03	.9851	.9371	.8916	.8485
.04	.9802	.9324	.8872	.8444
.05	.9753	.9278	.8828	.8402
.06	.9705	.9232	.8784	.8361
.07	.9656	.9186	.8741	.8320
.08	.9608	.9140	.8698	.8279
.09	.9560	.9095	.8654	.8238

neutralization[7] of weak acids by strong alkali, according to

$$\mathrm{HA} + \mathrm{SO}^- = \mathrm{A}^- + \mathrm{SOH}$$

The equation applicable in this case is analogous to (8); pOS is substituted for pH and K_B' for K_A'.

It is clear from the preceding that the determination of dpH/dϵ at the equivalence point leads to values of K_A' and K_B'. Thermodynamic acid and base dissociation constants, K_A and K_B, are derivable from these by the usual methods[2] of extrapolation to infinite dilution. Whenever measurement of dpH/dϵ is feasible at both equivalence points in the conjugate acid–base system HA–A, the autoprotolysis constant of the solvent, $K_S = a_H a_{OS} = K_A K_B$, may be obtained.

It is of interest to note that the rate of change of hydrogen ion activity with degree of neutralization at the equivalence point is a function only of the *titration variable* τ. It also turns out the variation of pH with the quantity $(\epsilon - 1)/\tau$ near the equivalence point is roughly identical for all systems over considerable ranges of τ.

Experimental

Apparatus.—The e.m.f. of the cells was measured with a Beckman Model G pH meter.[10a] The pH scale of the instrument was used, so that e.m.f. was read in units of **E**′.

The cells were stoppered flat-bottoms of *ca.* 100-ml. capacity and 35 mm. diameter. The hard-rubber stopper, 2 cm. thick, was fitted with thermometer, glass electrode, calomel or silver–silver chloride electrode, gas inlet tube (which allowed slow passage of carbon dioxide-free, solvent-saturated air over the cell contents), and a hole for the loose insertion of a buret tip.

The glass and calomel electrodes were Beckman models[10a] 1190 and 1170 × 6, respectively. The silver–silver chloride electrode was prepared by electrolysis in the usual manner from 25 cm. of coiled, C.P. silver wire, gage #18, and was silver-soldered onto 80 cm. of shielded lead wire with terminal for plug-in connection to the model G pH meter.

The cell contents were stirred by means of a Mag-Mix magnetic stirring assembly.[10b] The driving magnet was enclosed in a flat-top case on the top of which was mounted a water-filled crystallizing dish which served as a thermostat for the cells. The cells, containing glass-enclosed $^1/_2$″ × $^1/_4$″ Alnico 5 magnetic stirring rods, were carefully centered with respect to the driving magnet and clamped into position.

The water in the crystallizing dish was stirred and maintained at 24.95 ± 0.05° by means of a 6 ft. coil of $^1/_4$″ copper tubing through which water was pumped rapidly from a nearby thermostat of conventional design.

Burets were 2- and 5-ml. Koch microburets, graduated in 0.01-ml. intervals, with standard taper joints and exchangeable tips. When positioned in the cell, the buret tips were immersed in the test solutions.

Materials.—Distilled water was redistilled from alkaline permanganate in an all-glass still protected by an Ascarite tube. J. T. Baker C.P. glacial acetic acid, General Chemical Co. reagent grade formic acid and potassium chloride, and Bureau of Standards benzoic acid were used without further purification.

o-Nitrophenol.—Eastman Kodak Co. "white label" material was recrystallized twice from methanol–petroleum ether (b.p. 70–90); m.p. 44.8–45.4°.

p-Benzoylphenol.—Eastman Kodak Co. technical material was twice treated with decolorizing carbon in hot ethanol, recrystallized once from ethanol–water, and twice from benzene; m.p. 133.4–134.8°.

Eimer and Amend "reagent grade" 60% perchloric acid was carefully standardized by comparison with Bureau of Standards benzoic acid and potassium acid phthalate. 0.05 N perchloric acid was prepared by dilution of weighed amounts of the 60% acid.

Carbonate-free 0.05 N sodium hydroxide and potassium hydroxide were prepared by throwing J. T. Baker sodium or potassium metal, 20–40 mg. at a time, into 100 ml. of water contained in a 250-ml. erlenmeyer flask covered with a watch glass. The resulting solutions were standardized against standard 0.05 N perchloric acid. They usually gave no detectable precipitate with barium hydroxide solution, although in some experiments reagent containing 0.25% carbonate (estimated by the barium hydroxide test) was used.

Procedure for Measuring Dissociation Constants.—The following two cells and procedures were used.

Cell I: Glass electrode/HA, NaA, $NaClO_4$, $HClO_4$/KCl (satd.)/Hg_2Cl_2–Hg.

Cell II: Glass electrode/HA, NaA, $NaClO_4$, $HClO_4$, KCl/AgCl–Ag.

Procedure for Cell II.—Aliquot portions of solutions of the acid, potassium chloride and of pure solvent were added to the cell, such that the final volume was 40–50 ml., the acid concentration 0.5–20 × 10^{-3} M, and the potassium chloride 0.7–3.0 × 10^{-3} M. The cell was mounted and equilibrated in the thermostat, and 0.05 N perchloric acid was added until **E**′ exceeded the initial value by 0.3–0.4 unit. This solution was then back-titrated with 0.05 N alkali, added in approximately equal amounts such that successive changes in **E**′ were 0.06–0.10, until the equivalence point had been passed by 0.3 **E**′ unit. Back-titration with 0.05 N alkali was usually continued, values of **E**′ for ϵ = $^2/_3$, $^1/_2$ and $^1/_3$ being recorded.

Procedures for Cell I and for the measurement of base dissociation constants were quite analogous; the regions within ±0.3 **E**′ unit of the equivalence points were covered, and values of **E**′ were spaced by 0.06–0.10 unit.

A slow stream of solvent-saturated carbon dioxide-free air (about 100 bubbles/min.) was passed over the cell contents throughout the measurements. This was necessary and sufficient to prevent the absorption of acidic constituents from the laboratory air by the test solutions at the higher pH's.

After the addition of an aliquot portion of titrating reagent, the solutions were stirred for 15–30 sec. followed by a waiting period of at least 30 sec. before **E**′ was read. Values of **E**′ did not change within the error of measurement upon repetition of the stirring, or upon extension of the waiting period up to several hours.

The increments in titrating reagents were usually such that $\Delta\epsilon \doteq \tau/3$. (See also next section; a sufficiently accurate estimate of τ was available or obtained in a preliminary run.) The increments in titrating reagent varied from 0.5–0.02 ml. and were precise to ±0.002 ml. Readings of **E**′ were precise to 0.005–0.01 unit (0.3–0.6 mv.). The 0.05 N titrating reagents were diluted whenever necessary in order that $\tau/3$ corresponded to more than 0.02 ml. of reagent. For cell I, $-\mathbf{E}' = p\mathrm{H} + \text{constant}$, provided that liquid junction potentials are constant over the range of measurement. To effect this constancy a carrying electrolyte, sodium or potassium perchlorate, was added at concentrations of at least five times the maximum hydrogen ion concentration. It was not investigated whether this precaution which seemed sufficient was necessary. For cell II, $-\mathbf{E}' = p\mathrm{H} + p\mathrm{Cl} + \text{constant}$. $(\mathrm{d}p\mathrm{Cl}/\mathrm{d}\epsilon)_{\epsilon=1}$ was always small compared to $(\mathrm{d}p\mathrm{H}/\mathrm{d}\epsilon)_{\epsilon=1}$ and was calculated from

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(10) (a) Manufactured by the National Technical Laboratories, South Pasadena, California. (b) Sold by the Precision Scientific Co., Chicago, Ill.

equation 10 which was obtained by differentiation of an equation analogous to (3).

$$2.3026 \left(\frac{\mathrm{d}p\mathrm{Cl}}{\mathrm{d}\epsilon}\right)_{\epsilon = 1} = \mp \frac{c_0}{N} \tag{10}$$

Calculation of dpH/dϵ at the Equivalence Point.—The present differential method for dissociation constants depends for its success on the accurate measurement of the derivative, $(\mathrm{d}p\mathrm{H}/\mathrm{d}\epsilon)_{\epsilon=1}$. Usually the process of obtaining derivatives from experimental data results in considerable loss in accuracy. However in the present case an objective calculation of dpH/dϵ is possible such that dissociation constants are as accurate as those based on conventional measurements[2a] of equal error in **E**′ in systems where standard potentials are known.

The calculation of dpH/dϵ is based on two facts. First, the variation of pH with ϵ in the neighborhood of the equivalence point is approximately linear as is illustrated for a typical experiment in Table II. Therefore one can fit a straight line to experimental data near the equivalence point and calculate an empirical slope s whose magnitude must be close to $(\mathrm{d}p\mathrm{H}/\mathrm{d}\epsilon)_{\epsilon=1}$. Second, using equation 1 or its more convenient expanded form 11 one can predict the variation of pH in the experimental

$$(c_{\mathrm{H}})_{\epsilon = 1 + n\tau} = \tfrac{1}{2}(K' c_0)^{1/2}\left[n + (n^2 + 4)^{1/2} - \left(1 - \frac{n}{(n^2+4)^{1/2}}\right)\tau\right] \tag{11}$$

region and compute a set of correction factors f_c to be applied to the empirical slopes s to obtain $(\mathrm{d}p\mathrm{H}/\mathrm{d}\epsilon)_{\epsilon=1}$. In principle, the correction factors depend on the range of **E**′ used to calculate s, on the spacing of the experimental points, and on the value of τ. In practice, correction factors are quite independent of the **E**′ spacings provided these amount to 0.06–0.10; they vary only slightly with τ; and they depend chiefly on the experimental range of **E**′ values used for the calculation of s.

TABLE II

TITRATION OF SODIUM ACETATE WITH PERCHLORIC ACID,[a] WATER, 25.00°

$\epsilon - 1$	pH + constant
−0.138	0.65
− .106	.57
− .075	.505
− .045	.44
− .013	.365
.019	.28
.050	.205
.080	.14
.112	.07
.142	.00

[a] $c_0 = 1.927 \times 10^{-3}$; $N = 0.05847$; volume at equivalance point, 39.19 ml.; cell I.

In order to derive $(\mathrm{d}p\mathrm{H}/\mathrm{d}\epsilon)_{\epsilon=1}$ from the data near the equivalence point, the slopes s are computed with a probable error of about 1% by the method of least squares using the data within about ±0.30 **E**′ unit of the equivalence point. The exact range in **E**′ used for the calculation of s is noted, a rough estimate of τ is made (the rule $\Delta\epsilon = \tau$ for $\Delta\mathbf{E}' = 0.25$ is usually good enough), and the appropriate correction factor is obtained from Fig. 1 with an accuracy of better than 0.5%. The value of $(\mathrm{d}p\mathrm{H}/\mathrm{d}\epsilon)_{\epsilon=1}$ is given[11] with a probable error of about 1% by equation 12.

$$(\mathrm{d}p\mathrm{H}/\mathrm{d}\epsilon)_{\epsilon=1} = sf_c \tag{12}$$

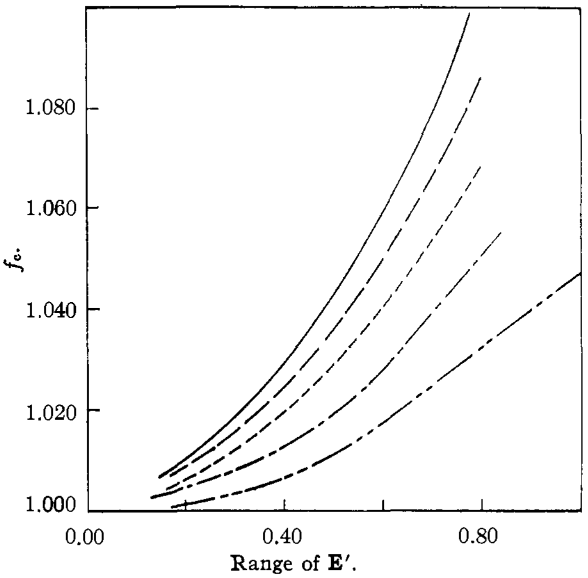

Fig. 1.—Correction factors to empirical slopes for various ranges of **E**′: τ = 0.00, ———; 0.05, — — —; 0.10, - - -; 0.15, — - —; 0.20, — - - —.

Results and Discussion

Table III gives results for acetic acid in water using cell I and Table IV for a number of acids in water using cell II. In the calculation of K_{A} from K_{A}', activity coefficients are estimated by the Debye–Hückel limiting law.[2] At the low ionic strengths used in this work (the ionization of the weak acids is not negligible in computing μ), activity coefficients estimated in this manner seem to be sufficiently accurate, as evident from the absence of significant trends in the computed K_{A} values with μ.[12–17]

TABLE III

RESULTS FOR ACETIC ACID, WATER, 25.0°, CELL I

$10^3 c_0$	Neutral salt × 10^{-3} M	$10^3\,\mu$	$\left(\frac{\mathrm{d}pH}{\mathrm{d}\epsilon}\right)_{\epsilon=1}$	10^5 K_{A}'	$10^5 K_{\mathrm{A}}$
1.315	$NaClO_4$, 1.327	1.478	1.99	1.98	1.81
1.927	$NaClO_4$, 1.976	2.158	2.41	1.89	1.70
3.172	$KClO_4$, 3.404	3.65	2.90	2.07	1.80
4.22	$NaClO_4$, 4.24	4.51	3.44	1.90	1.63
5.21	$NaClO_4$, 5.23	5.54	3.65	2.06	1.73
				Av.	1.73 ± 0.06

The average values of K_{A} for formic acid, benzoic acid, and acetic acid agree well with more precise data in the literature (Table IV). On the other hand, K_{A} for o-nitrophenol appears to be 10–20% high. This discrepancy is significant and points to an important limitation of the differential method. Because the solutions near the equivalence point are weakly buffered when K_{A} is small, the measurements are very sensitive to weakly acidic or basic impurities. In water the most common

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(11) (a) If cell II is used, $(\mathrm{d}pCl/\mathrm{d}\epsilon)_{\epsilon=1}$ must first be subtracted from s (see equation 10). (b) The correction factors in Fig. 1 are computed as follows. Theoretical values of log c_{H} are calculated from equation 11 for a chosen value of τ and for $n = \pm 1/3, \pm 2/3, \pm 3/3, \ldots$ Straight lines are fitted to the theoretical values of log c_{H} and ϵ by the method of least squares and the slopes compared with the theoretical values of $(\mathrm{d}p\mathrm{H}/\mathrm{d}\epsilon)_{\epsilon=1}$ from equation 8 to obtain f_c for a number of ranges in pH. f_c is then plotted *vs.* pH range in Fig. 1. In computing f_c values, the assumption is made that activity coefficients are constant. Calculations using the Debye–Hückel limiting law indicate that within the precision of our data this procedure is justified.

(12) Saxton and Darken, THIS JOURNAL, **62**, 846 (1940).

(13) (a) Saxton and Meyer, *ibid.*, **56**, 1918 (1934); (b) Brockman and Kilpatrick, *ibid.*, **56**, 1483 (1934).

(14) (a) Harned and Ehlers, *ibid.*, **55**, 652 (1933); (b) Harned and Embree, *ibid.*, **56**, 1042 (1934).

(15) Hantzsch, *Ber.*, **32**, 3071 (1899).

(16) Holleman and Herwig, *Rec. trav. chim.*, **21**, 442 (1902).

(17) Ref. 2, p. 581; Harned and Fallon, THIS JOURNAL, **61**, 2374 (1939).

TABLE IV

RESULTS FOR VARIOUS ACIDS AND BASES, WATER, 25.0°, CELL II

Compound	$10^3 c_0$	$10^3 c_{KCl}$	$10^3 \mu$	$\left(\frac{dpH}{d\epsilon}\right)_{\epsilon=1}$	$10^5 K_A'$		$10^5 K_A$
Formic acid[a]	3.503	0.876	2.483	1.18	19.1		17.0
	5.943	.977	3.091	1.38	22.3		19.6
	13.71	.845	4.186	2.05	20.9		18.0
						Ave.	18.2 ± 0.7
Benzoic acid[a]	2.176	2.015	2.777	1.415	7.40		6.54
	3.249	1.003	1.928	1.74	6.78		6.12
	7.604	0.878	2.313	2.555	6.80		6.08
						Ave.	6.25 ± 0.20
Acetic acid[a]	0.865	1.798	2.050	1.67	1.97		1.78
	3.004	1.007	1.496	2.91	1.97		1.80
	8.95	1.004	1.897	4.96	1.905		1.72
						Ave.	1.77 ± 0.03
p-Nitrophenol[b]	4.573	1.894	1.976	48.3	0.0092		0.0083
	1.194	0.979	1.053	25.8	.0085		.0079
							.0081
p-Benzoylphenolate,[c] K_B	0.774	0.813	1.587	6.34	0.097		0.097
	.984	.620	1.604	6.66	.111		.111
						Ave.	0.104 ± 0.007

[a] More precise values of K_A in the literature—formic acid, 1.767×10^{-4},[14b] 1.824×10^{-4} [12]; benzoic acid, 6.29×10^{-5} [13]; acetic acid, 1.749×10^{-5}.[14a] [b] K_A by conductance, 7.5×10^{-8},[15] 7.0×10^{-8} [16]; K_A from potentiometric data at $^1/_3$, $^1/_2$, $^2/_3$ neutralization, $(6.4 \pm 0.7) \times 10^{-8}$ (present work). [c] K_A for *p*-benzoylphenol from potentiometric data at $^1/_3$, $^1/_2$, $^2/_3$ neutralization, $[10.5 \pm 1.0] \times 10^{-9}$; $K_S = K_A K_B$, $[10.9 \pm 1.2] \times 10^{-15}$. More precise value for K_S, 10.08×10^{-15}.[17]

of these, carbonates and silicates, may cause error at *p*H > 6, but do not interfere in measurements of the stronger acids ($K_A > 10^{-7}$) because of both the better buffering action and the higher acidity at the equivalence point.

Judging by the more precise data for formic, benzoic and acetic acid in the literature (Table IV), the probable error of a single K_A value is 2.6%. This corresponds to an error of 2.4% in K_A' and 1.1% in $(dpH/d\epsilon)_{\epsilon=1}$. On the basis of the precision of the potentiometric data, the probable indeterminate error in $(dpH/d\epsilon)_{\epsilon=1}$ is about 1%, so that the scatter of the experimental points is accounted for.

An illustration of the use of the differential method to obtain data on base dissociation constants is afforded by the study of *p*-benzoylphenol (Table IV). The acid dissociation constant for this weak acid ($K_A = 10^{-8}$) is outside the useful range of the differential method but could be obtained from data at $^1/_3$, $^1/_2$ and $^2/_3$ neutralization after calibration of the cell[2b] with formic, benzoic and acetic acid. The base dissociation constant of *p*-benzoylphenolate was measured by the differential method. The product, $K_A K_B = K_S$, agrees with the more precise value in the literature[17] within experimental error (Table IV).

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