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Author

Avdeef, A.

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Alex Avdeef and Jerome J. Bucher

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Accurate Measurements of the Concentration of Hydrogen
Ions with a Glass Electrode: Calibrations Using the
Prideaux and Other Universal Buffer Solutions
and a Computer-Controlled Automatic Titrator

By

Alex Avdeef*¹ and Jerome J. Bucher
Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

Abstract

Several universal buffer solutions, variably composed of 3-5 mM potassium acetate, potassium dihydrogen phosphate, ethylenediammonium dichloride, and borax, were examined as a convenient and reliable method for calibrating a glass electrode to read true hydrogen ion concentration. From the results of nineteen titrations, 25°C, pH 2 to 12, I .05 to .20 M (KCl), pH meter (adjusted with NBS pH_S 4.008 and 6.865 buffers) readings, pH_m, using a Beckman 39501 combination electrode, can be converted to $-\log[H^+]$, p[H], by

$$pH_m = \Delta' + S' p[H]$$

where $\Delta' = 0.2269 - 1.949 I + 7.756 I^2$, $\sigma(\Delta') = .019$ pH and $S' = 0.9657 + .4752 I - 1.532 I^2$, $\sigma(S') = .0022$. At I 0.1 M $pH_m = .110 + .998 p[H]$. A FORTRAN computer program was coded to calculate Δ' and S' for any titration in the range 0 to 40°C and 0 to 0.3 M (KCl), and for any combination of the four buffer components. A microcomputer-controlled automatic titrator, programmed in BASIC, was used to collect the potentiometric data.

Introduction

A convenient and reliable method for calibrating a glass electrode to read true hydrogen concentration is to measure at least two solutions of accurately known hydrogen concentrations. Provided that the response of the glass electrode to $\log [H^+]$ is linear in the region of interest, the pH_m scale* is defined in terms of true concentration, $p[H]$. The strong-electrolyte buffer systems HCl in water and KOH in water are perhaps the easiest to use. However, in the region pH 2.5-11.5 $[H^+]$ is not accurately known (since this is a buffer-free region). For the purpose of expanding the useful calibration range, one may choose a weak acid whose dissociation constants are accurately known. In the half-neutralization region (maximum buffering) the $p[H]$ can readily be calculated from the dissociation constant. Acetic acid has been widely used for this purpose. Its most useful range is roughly pH 4 to 5. Further extensions involve mixtures of weak acids with dissociation constants distributed uniformly over the entire useful pH range. Prideaux in 1916^{1a} proposed the "universal" buffer solution {acetic acid, phosphoric acid, boric acid}, henceforth abbreviated the APB

* $p[H] = -\log_{10} [H^+]$; pH_m = pH-meter reading after suitable calibration with NBS buffers.

buffer. In a later publication, Prideaux and Ward^{1b} replaced acetic acid by phenylacetic acid, and the latter mixture was used for calibration purposes.^{3,4} Other universal buffer systems have been described.^{4,5}

Even though these universal buffer mixtures have been known for a long time, their use for calibration purposes has been relatively scarce. (The control of pH was a more common application.) This may be due to two factors: 1) the dissociation constants may not have been known accurately enough over a useful range of ionic strengths and temperatures, and 2) the routine computation of the hydrogen concentrations in such universal mixtures may have been too formidable in pre-computer days. McBryde⁶ discussed a useful procedure for p[H] measurements in the estimation of equilibrium constants. His empirical calibration results were confirmed by a more elaborate study by Hedwig and Powell,⁷ who proposed the simple relationship

$$\text{pH}_m = .088(2) + .9951(3) \text{ p[H]} \quad (1)$$

which was observed to be independent of ionic strength in the region $I = .04$ to $.20$ M (NaCl). Here pH_m corresponds to pH-meter reading (meter calibrated with NBS buffers) and the number in parentheses following the parameters is the estimated error in the least significant digit. The lack of ionic strength dependence was remarkable.⁸ Hedwig and Powell used HCl, acetic acid, and ethylenediamine, separately, to determine their relation.

The present study was initially an attempt to substantiate the observations of Hedwig and Powell for our particular electrodes and experimental conditions. Also we wished to re-examine the use of universal buffers for accurate $p[H]$ determinations. We explored the use of the AP, APE, and APB universal buffers (where A = acetate, P = phosphate, E = ethylenediamine, B = boric acid) with each component less than six millimolar in concentration. To our surprise, we find ineluctable support for ionic strength dependence of the glass electrode in the ionic strength range .05 to .20 M (KCl), contrary to the findings of Hedwig and Powell. Also we find that the APE uni-buffer does not accurately predict hydrogen concentration, due to presumed ion-pair interactions of enH_2^{2+} and HPO_4^{2-} . We find that it is possible to extend the accurate $p[H]$ range of the glass electrode from 1.5 to 12.5, provided care is given to measurements in the extreme regions. For this purpose we have employed a computer-controlled automatic titrator of our own design. The method of collecting potentiometric readings by the auto-titrator ensured some minimization of the deleterious effects of time-dependent changes of the asymmetry potential of the glass electrode.⁹ A versatile FORTRAN computer program, GLASS, was coded to treat the data involving the universal buffer solutions, for $I = 0.0$ to 0.3 M (KCl) and $t = 4$ to 40°C (conditions particularly useful to biologically-relevant studies).

The Constants of the Acids

The choice of the uni-buffer components (acetic, phosphoric, ethylenediamine, boric) was dictated by the apparent accuracy of the literature constants (determined with hydrogen electrodes, using junctionless references) and the wide range of ionic strengths and temperatures employed in their determinations. Our computer program has employed these constants in the forms of analytical expressions only as a function of temperature and ionic strength (KCl).

Water. The dissociation constant of water, pK'_w , as a function of temperature and ionic strength was calculated from the 17-parameter empirical expression of Sweeton, Mesmer, and Baes.¹⁰ The use of this constant was necessary when calculating $p[H]$ in basic solutions of known $[OH^-]$ concentration. Also, some literature values of constants (boric acid, phosphoric acid, *vide infra*) were expressed in hydrolysis form and required pK'_w for conversion to a more conventional form. At 25°C, 0.1 M (KCl), $pK'_w = 13.787$ (molar scale).

Acetic Acid. The constants reported by Harned and Ehlers¹¹ and Harned and Hickey¹² were fitted to an empirical expression as a function of temperature (NaCl medium) and ionic strength (KCl medium):

$$\log K = \frac{1240.8}{T} - 3.6241 + .01415 T - .98281 I^{1/2} / (1 + I^{1/2}) \\ + (1.8284 - .0052115 T) I - (1.4907 - .0049174 T) I^{3/2}$$

(molal units, T in °K) (2)

The root-mean-square deviation (RMSD) of the fit was 0.0010. At 25°C, 0.1 M (KCl) $\log K_1 = 4.548$ (molar units). Although the experimental data for the temperature dependence is based on NaCl as the background electrolyte, it is assumed to be valid for KCl as well as for $I < 0.3$ M, $t < 40^\circ\text{C}$.

Phosphoric Acid. The empirical analytical functions for $\log K_1$ (9-parameter) and $\log K_2$ (11-parameter) as a function of temperature and ionic strength were taken from the recent work of Mesmer and Baes.¹³ At 25°C, 0.1 M (KCl), $\log K_1 = 1.898$ and $\log K_2 = 6.740$ (molar units). The analytical expression for $\log K_3$ was fitted to data from various sources. The spectroscopically-determined value at 25°C, $I = 0$ was taken from Vanderzee and Quist.¹⁴ The temperature dependence was assumed to follow the form observed by Bjerrum and Unmack.¹⁵ The ionic strength dependence was set up to incorporate $\log K_3 = 11.74$ at 0.1 M KCl, 25°C.¹⁶ Thus

$$\log K_3 = 13.062 - .0379 t + .0004166 t^2 + (.038 t - 2.95)I^{1/2}$$

(molar units, t in $^\circ\text{C}$) (3)

This equation is not intended to be very accurate for $I > .15$ M and $t > 40^\circ$. But this suffices for our calculation since the contribution to the determination of $[\text{H}^+]$ due to the third dissociation of phosphate (at .005 M) is overshadowed by the buffering of water at $\text{pH} > 11$.

Ethylenediamine. The constants for ethylenediamine were fitted to an analytical form as a function of temperature and ionic strength, using the data of Everett and Pinsent:¹⁷

$$\log K_1 = \frac{2424.1}{T} - .0018133 T + 2.336 - .065979 I^{1/2}/(1 + I^{1/2})$$

$$+ (1.2536 - .002149 T)I - (.6002 - .00067 T)I^{3/2}$$

$$\text{RMSD} = .0029 \quad (4)$$

$$\log K_2 = \frac{1842.5}{T} - .005993 T + 2.4565 + 1.0068 I^{1/2}/(1 + I^{1/2})$$

$$- (1.8657 - .00684 T)I + (2.7493 - .00954 T)I^{2/3}$$

$$\text{RMSD} = .0014 \quad (5)$$

(molar units)

Since the ionic strength dependence¹⁷ was based on NaCl, the validity of the above constants to KCl media is probably limited to $I < .3$ M. At 25°C, 0.1 M (KCl), $\log K_1 = 9.958$ and $\log K_2 = 7.106$ (molar units).

Boric Acid. The analytical function (7- parameter) of Mesmer, Baes, and Sweeton¹⁸ was used in the computer program. At 25°C, 0.1 M (KCl) $\log K_1 = 9.008$ (molar units).

Activity Coefficients of HCl, KOH in KCl Solutions. For the comparison of observed $\text{pH}_m - \text{p}[\text{H}]$ values in this study to what might be expected theoretically, we chose to use $\log \gamma_{\pm} = 1/2(\log \gamma_{\text{HCl}} + \log \gamma_{\text{KOH}})$, where γ_{HCl} and γ_{KOH} are the experimental activity coefficients of HCl and KOH as a function of temperature and ionic strength (KCl medium). The extensive analytical functions of Pitzer and co-workers¹⁹ were incorporated in the computer program.

Method of Calculation

Hydrogen Concentration. The computer program GLASS is coded to solve for $[H^+]$ for any combination of the four buffer components, including the case of water titration (no added buffers). The problem is that of solving a nine-order polynomial expression in $[H^+]$ by the Newton-Raphson method of tangents,²⁰ using $10^{(0.1 - pH_m)}$ as the initial $[H^+]$ value for the iterative process. The polynomial function is stated simply as

$$\mathcal{H} = h - \frac{K'_w}{h} + \sum_i^{NL} \bar{h}_i \mathcal{L}_i \quad (6)$$

where $h = [H^+]$, $\mathcal{H}$ = total hydrogen concentration, NL = number of buffer components, $\mathcal{L}_i$ = concentration of the i^{th} buffer component ($i = A, P, E, B$ to designate the different buffers) and $\bar{h}_i$ is the average number of protons associated with the i^{th} buffer at a particular pH. With the further definitions $\beta_0 \equiv 1$; $D_i \equiv \sum_{j=0}^{NH_i} \beta_j^i h^j$; $G_i \equiv \sum j \beta_j^i h^j$; $J_i \equiv \sum j^2 \beta_j^i h^j$ where NH_i = number of dissociable protons on the i^{th} buffer component, $\beta_j^i = [H_j L_i] / [L_i] [H]^j$, and $\bar{h}_i = D_i / G_i$, one can restate Eq. 6 as the polynomial function

$$\begin{aligned} F(h) &= 0 \\ &= \left(h - \frac{K'_w}{h} - \mathcal{H}\right) D_A D_P D_E D_B + G_A D_P D_E D_B \mathcal{L}_A + D_A G_P D_E D_B \mathcal{L}_P \\ &\quad + D_A D_P G_E D_B \mathcal{L}_E + D_A D_P D_E G_B \mathcal{L}_B \\ &\equiv F_H + F_A + F_P + F_E + F_B \end{aligned} \quad (7)$$

To solve for h iteratively by the present method,

$$h_{\text{new}} = (1 - \frac{F(h)}{dF/d\ln h}) h_{\text{old}}$$

So $dF/d\ln h = dF_H/d\ln h + dF_A/d\ln h + \dots$ which yields the expression

$$\frac{dF(h)}{d\ln h} = (h + \frac{K_w}{h}) F_H \prod_i^{NL} D_i + \sum_i^{NL} [\bar{h}_i (F - F_i) + J_i F_i / G_i] \quad (8)$$

The general form of Eq. 8 readily suggests expansions or changes in the choice of buffer components.

The refinement in $[H^+]$ calculation generally converges within one or two cycles for each point.

Ionic Strength Calculation. Since the constants for the buffer components are functions of ionic strength, the computer program calculates the ionic strength due to contribution of all ionic species present in solution. This is performed iteratively since the concentrations of species depend on the ionic strength assumed to deduce the constants. Two cycles is sufficient for reasonable self-consistency.

The program assumes the buffer components are introduced in the analytic forms CH_3COOK , KH_2PO_4 , $C_2H_4N_2H_4 \cdot 2HCl$, and $Na_2B_4O_7 \cdot 10H_2O$ (borax). Since buffer concentrations are chosen to be dilute ($< .01$ M) borax is treated as if it were

composed of $2 \text{ NaOH} + 4 \text{ B(OH)}_3 + 3 \text{ H}_2\text{O}$ (see discussion in Ref. 18). Thus $\mathcal{L}_B$ is the concentration of B(OH)_3 . Given the above forms,

$$\begin{aligned} I_{\text{APEB}} = & [\text{KCl}] + [\text{KOH}] + \frac{1}{2} \mathcal{L}_B + [\text{H}^+] \\ & + \mathcal{L}_A + \mathcal{L}_P \left(1 + \frac{3 + \beta_1^P h}{D_P}\right) + \mathcal{L}_E \left(\frac{3 \beta_2^E h^2 + \beta_1^E h}{D_E}\right) \end{aligned} \quad (9)$$

The $\frac{1}{2} \mathcal{L}_B$ component is due to the NaOH equivalent present in borax.

Analytical Fit of pH_m as a Function of p[H] , $[\text{H}]$, and $[\text{OH}]$. Once $[\text{H}^+]$ values are calculated for a particular data set, the pH meter readings are fitted by weighted linear least squares to the form

$$\text{pH}_m = \Delta + S \text{p[H]} + j_H [\text{H}^+] + j_{\text{OH}} [\text{OH}^-] \quad (10)$$

The last two terms are only important in the extreme regions of pH (< 2 or > 12) and have in the past been associated with the junction potential of the reference electrode.²¹

We find that these terms also reflect the changes in the asymmetry potential of the glass electrode. If one had perfect Nernstian slope ($S = 1$) for the electrode and if $j_H = j_{\text{OH}} = 0$, then Δ should be ideally equivalent to $-\log \gamma_H$. In practice this equivalency is not met.

There is a provision in the program to vary (by numerical non-linear least squares) the buffer concentrations to minimize the fit of data to Eq. 10. In practice, the calculation of $[H^+]$ will not be successful unless the buffer concentrations are already well determined. Their variation by regression is substantially a cosmetic effect.

Weights. In the analytical fit of pH_m , the data are weighted according to

$$\sigma^2(pH^{OBS}) = \sigma_{const}^2 + (\sigma_{volume} \frac{dpH}{dV})^2 = (weight)^{-1}$$

where we have assumed $\sigma_{const} = .002$ pH and $\sigma_{volume} = .001$ ml. The term dpH/dV is the slope of the titration curve. Thus data in buffer regions receive much greater weight than data near equivalent points. The higher the buffer component concentration, the more weight the buffer pH region receives relative to the regions associated with the buffering of water.

Experimental

Chemicals

Potassium hydrogen phthalate, $KHC_8H_4O_4$, was obtained from the National Bureau of Standards (acidimetric standard). KH_2PO_4 (Mallinckrodt, analyt. grade), $Na_2HPO_4 \cdot 7H_2O$ (Mallinckrodt, analyt. grade), and borax, $Na_2B_4O_7 \cdot 10 H_2O$, (Sigma Chemical Co., 99.9%) were used without further purification.

The 1 M HCl and KOH titrant solutions were prepared from "analytical concentrates" (J. T. Baker Chem. Co.) and were re-standardized as previously described.²³

Crystalline ethylenediamine dihydrogen dichloride, en.2 HCl, was isolated from a concentrated solution of the neutral base (Mallinckrodt, reagent) brought to pH 1 with con. HCl. After drying 1 day over P_2O_5 , a stock solution, 0.1 M, was prepared and kept in an inert atmosphere box. Stock solutions of potassium acetate (Baker) and KH_2PO_4 , both 0.1 M, were also prepared and similarly stored. The buffer solutions used for the titrations were prepared from the carefully standardized stock solutions. Solutions containing boric acid were prepared from borax, which dissociates into the monomeric acid in dilute solutions.¹⁸

Meter Adjustment

The standard NBS pH_m 4.008 phthalate and pH_m 6.865 1:1 phosphate buffers (Ref. 8, Ch. 4) were used to adjust the slope and calibrate functions on the pH meter before each titration. All titrations were carried out in thermostated (25.0°C) beakers which were slowly purged with wet argon to ensure the exclusion of carbon dioxide. The electrode was allowed to stabilize in the neutral buffer (1-4 hrs) before the "calibrate" adjustment was made, after which the phthalate buffer (15 min immersion) was used to set the slope adjustment. Only one electrode was used in this study — the Beckman 39501 glass combination ("Enduroglass," Futura plug) — and over a period of six months, it showed no signs of degradation in response.

Automatic Titrator

The automatic titrator employed in this study was controlled by an Intel 80/10 microcomputer (8080 processor) and included a Corning 112 digital pH meter, a Gilmont 2.5 ml ultra-precise (glass piston) buret coupled to a stepper motor (Superior Electric Co., 25 oz-in. max. torque), a stirring motor, and a constant temperature bath (Haake, KT33). The data collection program was coded in BASIC (Livermore) and had provisions for adding either fixed or variable amounts of titrant (in the latter case, to maintain constant pH between collected points), and for ensuring a stable pH reading (several collected readings linearly fitted to time with the slope used as a criterion of stability: $\text{dpH}/\text{dt} < .005 \text{ pH min}^{-1}$). The volume of titrant can be added in increments as small as $5 \times 10^{-4} \text{ ml}$. The time taken to collect a point is recorded.

The data collection program calculates values of $\bar{h}$ for each point in a way that one can estimate dissociation constants of the species under study as the data are being collected. The observed and calculated results are printed on a teletype and punched on paper tape for further processing on a large computer.

Results

Figure 1 shows the titration curves of the 0.1 M ionic strength solutions (5 mM buffer components). The APB

(Prideaux) system shows a nearly uniform buffering action pH 2.5-11.5. The uniform distribution of species as a function of pH in the APB uni-buffer is shown in Figure 2.

Observed Differences between pH_m and $p[H]$. Table I lists the differences between pH-meter readings (meter set to NBS buffers) and true pH values (calculated from known constants); $\Delta^\circ = pH_m(NBS) - p[H]$. The values are selected at $p[H]$ 2 and 12 and at other pH values centered on the maximum buffering of each component. Along with the Δ° values are listed the experimental $-\log \gamma_H$ values, as defined previously. One can see the largest departures from the "expected" $-\log \gamma_H$ values to be for the cases of titrations containing no initially added KCl (Exp. Nos. H1, A1, P1, E1). $\Delta^\circ < 0$ are observed in the basic pH regions. Figure 3 displays Δ° plots for the AP and APB buffers.

Table II summarizes the fitting of the pH_m values to analytic forms of Eq. 10 (pH 1.5 to 12.5) and Eq. 12 (pH 2 to 12):

$$pH_m = \Delta' + S' p[H] \quad (12)$$

Any single experiment can be fitted to the 4-parameter function (Eq. 10) very well, with $|pH_m^{OBS} - pH_m^{calc}| < .005$ typically. A difficulty arises when one tries to use the fit parameters to predict the response of another titration under similar conditions. The j_H and j_{OH} parameters were least predictable in this case. In the pH_m region 2-12, the latter two parameters were disregarded in obtaining analytical Δ' and S' values.

Figure 4 and 5 show plots of Δ' and S' as a function of ionic strength. The intercepts Δ' seem to have a "check-mark" pattern. If the experiments which had $C_{KCl} = 0$ and also those performed in the "reverse direction" (AP1' and AP2') were disregarded, the observed ionic strength dependence closely parallels that of $-\log \gamma_H$ values (Fig. 4). The ionic strength dependence of the slopes S' can be described with similar qualifications.

A parabolic fit of Δ' vs I and S' vs I produces (for all nineteen titrations)

$$\Delta' = 0.2269 - 1.949 I + 7.756 I^2 \quad (13)$$

$$\sigma(\Delta') = .019 \text{ (pH units)}$$

$$S' = 0.9657 + .4752 I - 1.532 I^2 \quad (14)$$

$$\sigma(S') = .0022$$

The corresponding linear fits result in significantly higher errors: $\sigma(\Delta') = .025$ and $\sigma(S') = .0040$, respectively. At 0.1 M ionic strength, $pH_m = .110 + .9979 p[H]$, using Eqs. 13 and 14.

To test the efficacy of such an analysis Δ' , S' according to Eqs. 13 and 14 were used to convert pH_m data to $p[H]$ basis for experiments A2, P2, E2, and B1. Then $\bar{h}$ values were calculated according to ²²

$$\bar{h} = \frac{pH - [H^+] + K'_w/[H^+]}{I} \quad (15)$$

and the corresponding "formation" curves are shown in Figure 6. The constants evaluated at half-integral values of $\bar{h}$ (Fig. 6) are in excellent accordance with literature values, even for $\log K_3$ of phosphate. Hedwig and Powell discuss at greater length the comparison between constants obtained using a theoretical model (Davies equation for $-\log \gamma_H$) and the empirical procedures.

Summary

We have explored various combinations of stable buffer components, whose proton dissociation constants are accurately known for 0 to 40° and I 0 to 0.3 M (KCl), with the aim of producing a useful universal buffer mixture for the purpose of routinely calibrating pH electrodes. The Prideaux and the acetate-phosphate mixtures are convenient for this purpose. Ideally, an electrode need only be calibrated once, for a particular temperature and ionic strength, with the universal buffer. Thereafter, the Δ and S characteristic parameters should be valid for every titration, as long as the pH meter is adjusted to the same reference pH_S 's, as specified by two NBS buffer solutions for example. The procedure outlined should be particularly useful to temperature-dependent equilibrium studies and also to studies where ionic strength variations are difficult to control, as in the case of $I < .2 \text{ M}$.

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Table I. Observed Differences (Δ°) Between pH_m and $p[H]$.

Exp. No.	$p[H]$ 12.00 $\Delta^\circ [I]$ $-\log \gamma_H$	$p[H]$ 9.96 $\Delta^\circ [I]$ $-\log \gamma_H$	$p[H]$ 9.01 $\Delta^\circ [I]$ $-\log \gamma_H$	$p[H]$ 7.11 $\Delta^\circ [I]$ $-\log \gamma_H$	$p[H]$ 6.74 $\Delta^\circ [I]$ $-\log \gamma_H$	$p[H]$ 4.55 $\Delta^\circ [I]$ $-\log \gamma_H$	$p[H]$ 2.00 $\Delta^\circ [I]$ $-\log \gamma_H$
H1	-.029 [.050] .085						+.092 [.058] .090
H2	+.084 [.100] .108						.099 [.107] .111
H3	.136 [.199] .133						.159 [.203] .134
A1	-.015 [.051] .086					.072 [.050] .086	.125 [.059] .091
A2	+.077 [.100] .077					.096 [.098] .108	.100 [.106] .111
P1	+.020 [.058] .090				.094 [.052] .087		.128 [.060] .091
P2	.076 [.091] .105				.095 [.081] .101		.099 [.086] .103
E1	+.010 [.049] .084	.046 [.050] .085		.104 [.054] .088			.131 [.066] .084
E2	.058 [.090] .104	.061 [.091] .105		.081 [.097] .108			.099 [.110] .112
B1	.107 [.101] .108		.132 [.099] .108				.142 [.108] .111
AP1	.073 [.091] .105				.076 [.080] .101	.082 [.077] .100	.088 [.086] .103
AP2	.087 [.111] .112				.097 [.099] .108	.106 [.096] .108	.115 [.104] .110
AP3	.134 [.144] .121				.130 [.131] .118	.132 [.127] .117	.123 [.135] .119
AP4	.161 [.193] .131				.145 [.179] .129	.144 [.176] .129	.133 [.183] .130
AP1 ^b	.106 [.129] .117				.085 [.100] .109	.066 [.093] .106	.078 [.089] .105
AP2'	.132 [.167] .126				.127 [.137] .120	.093 [.131] .118	.100 [.128] .117
APB1	.114 [.113] .112		.134 [.104] .110		.119 [.101] .109	.126 [.099] .108	.118 [.107] .111
APB2	.130 [.152] .123		.133 [.142] .121		.120 [.139] .120	.101 [.136] .120	.115 [.142] .121
APB3	.139 [.192] .131		.140 [.180] .130		.129 [.177] .129	.142 [.174] .128	.126 [.181] .130

^a $\log \gamma_H = 1/2(\log \gamma_{HCl(KCl)} + \log \gamma_{KOH(KCl)})$, as determined from Pitzer's equations (Ref. 19).

^b AP1' and AP2' were cases where an initially acidic solution ($pH_m \sim 1.5$) was titrated with a standard KOH solution.

All other cases involved the titration of a basic solution ($pH_m \sim 12.5$) with a standard HCl solution.

Table II. Analytical Description of pH-Meter Reading^a

Exp. No.	$\bar{I}^b$	[KCl] initial	$(\mathcal{L}_A, \mathcal{L}_P, \mathcal{L}_E, \mathcal{L}_B) \times 10^3$	GOF ^c	Δ	S	j_H	j_{OH}	Δ'	S'
H1	.055(7)	.000	- - - -	1.62	.109(3)	.9877(3)	1.07(14)	.68(5)	.118(2)	.9879(2)
H2	.111(12)	.067	- - - -	1.21	.099(2)	.9993(3)	.13(6)	-.57(9)	.106(2)	.9978(3)
H3	.208(11)	.168	- - - -	1.41	.170(2)	.9962(3)	-.58(6)	.41(9)	.165(2)	.9968(3)
A1	.052(3)	.000	3.00 - - -	1.24	.106(5)	.9901(5)	3.98(45)	-.06(4)	.157(2)	.9855(2)
A2	.106(10)	.063	5.08 - - -	1.12	.101(2)	.9976(2)	.32(6)	.10(7)	.104(1)	.9974(2)
P1	.059(5)	.000	- 3.22 - -	1.81	.115(4)	.9927(4)	2.61(19)	-.51(7)	.148(2)	.9892(3)
P2	.091(9)	.043	- 4.88 - -	.91	.099(1)	.9991(2)	.21(4)	-.93(9)	.102(1)	.9980(1)
E1	.064(18)	.000	- - 2.98 -	2.17	.164(2)	.9882(3)	.04(7)	-.94(9)	.154(2)	.9880(2)
E2	.105(16)	.057	- - 4.82 -	.52	.112(1)	.9959(1)	-.33(2)	-.42(6)	.108(1)	.9960(1)
B1	.109(11)	.065	- - - 5.39	1.45	.149(2)	.9981(3)	-.19(7)	-1.37(9)	.146(1)	.9969(1)
AP1	.087(8)	.039	5.06 4.91 - -	1.44	.087(2)	.9984(3)	.38(9)	.12(16)	.090(1)	.9985(2)
AP2	.106(8)	.058	4.90 5.02 - -	.78	.135(1)	.9935(2)	.65(5)	1.87(9)	.122(1)	.9963(2)
AP3	.137(8)	.090	4.99 5.48 - -	.62	.128(1)	1.0001(1)	-.52(4)	.25(8)	.120(1)	1.0010(1)
AP4	.185(7)	.141	5.07 4.83 - -	.54	.127(1)	1.0031(1)	-.25(3)	-.30(7)	.125(1)	1.0031(1)
AP1'	.105(17)	.058	5.11 4.95 - -	.78	.030(2)	1.0076(2)	3.40(9)	-.84(7)	.073(1)	1.0033(1)
AP2'	.146(19)	.097	4.95 4.95 - -	.80	.059(2)	1.0087(2)	2.48(9)	-1.67(4)	.093(1)	1.0043(2)
APB1	.107(7)	.058	5.12 4.84 - 5.41	.75	.118(1)	1.0007(2)	-.13(6)	-.86(10)	.117(1)	1.0001(1)
APB2	.144(6)	.097	5.19 4.83 - 5.26	1.01	.098(2)	1.0038(3)	.62(8)	-.75(13)	.112(1)	1.0020(1)
APB3	.182(7)	.136	5.07 4.88 - 5.52	.59	.126(1)	1.0017(1)	-.26(4)	-.51(7)	.121(1)	1.0017(1)

^a $pH_m = \Delta + S p[H] + j_H[H^+] + j_{OH}[OH^-]$ for pH 1.5 - 12.5; $pH'_m = \Delta' + S' p[H]$ for pH 2.0 - 12.0.

^bMean ionic strength. Quantity in () is the RMSD in the least significant digit.

^cGoodness-of-fit.

Figure Captions

- Figure 1. Titration curves for the single and mixed buffer systems, at 5 mM, 0.1 M KCl. The titrant axis is expressed in terms of base equivalents. Experiments are identified in Tables I and II. APE is composed of 1:1:1 acetate-phosphate-ethylenediamine.
- Figure 2. Distribution of species in the APB universal buffer, as a function of pH.
- Figure 3. Plot of the differences between pH meter reading (pH_m) and pH based on $[\text{H}^+]$ concentration ($\text{p}[\text{H}]$) as a function of pH_m for the AP and the APB universal buffers. The "expected" $[\text{H}^+]$ activity coefficients are represented by $-\log \gamma_{\text{H}}$, which are taken to be the logarithm of the geometric mean of the observed activities of HCl and KOH in KCl medium.
- Figure 4. Plot of the intercept parameter, Δ' , as a function of the mean ionic strength, where $\text{pH}_m = \Delta' + S' \text{p}[\text{H}]$.
- Figure 5. Plot of the slope parameter, S' , as a function of the mean ionic strength, where $\text{pH}_m = \Delta' + s' \text{p}[\text{H}]$.
- Figure 6. The observed formation curves ($\bar{h}$ vs pH) for exp. nos. E2, P2, A2, and B1, where the half-integral $\bar{h}$ values are used to determine the pK_a 's.

TITRATION CURVE

ACETATE-PHOSPHATE-BORAX-ETHYLENEDIAMINE-WATER BUFFER SYSTEMS (5 MM IN .1 M KCL)

XBL 785-8948

Fig. 1

XBL 785-8947

Fig. 2

Fig. 3

XBL 785-8946

XBL 785-8945

Fig. 4

Fig. 5

XBL 785-8944

XBL 785-8949

Fig. 6

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TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720