The Modern Meaning of PH

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THE MODERN MEANING OF pH

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I. INTRODUCTION

A. Background

"Plus ça change, plus c'est la même chose." In a review article published more than 30 years ago, the present author stated " . . . several scales, all masquerading under the name pH, are in common use. Many investigators are thinking and computing in terms of one definition and measuring a different quantity."[1] An improvement toward an understanding of the nature of the practical pH value has been seen in the last three decades, but the precise manner of interpreting these values is still largely a mystery. To emphasize this situation, one has only to survey a dozen modern texts used in the teaching of analytical chemistry. The results of such an examination are summarized in Table 1. As observed earlier . . . "this state of confusion results in part from the impossibility of determining exactly . . . the molality and the activity of hydrogen (hydronium) ion for a buffer solution of moderate concentration."[1]

The intervening years have nonetheless served to establish the unquestioned usefulness of the pH value for quality control in commerce and industry, as an index of pathological conditions in the clinical laboratory, and for the determination of the stabilities of compounds of interest to the analytical and inorganic chemist. What meaning has been attached to the pH in these many applications? Often very little, or at best a semiquantitative index of a vague quantity, "the level of acidity". Thus pH has served very well for quality control when products were tested under precisely prescribed conditions. In analogous fashion, the pH of body fluids has been related empirically to health and disease. Only in the study of chemical equilibrium has it been necessary to inquire into the precise nature of the quantity measured.

B. pH — A Fundamental Property of Solutions?

In the 70 years that have elapsed since Sørensen first proposed the pH unit,[2] this index has signified to most users in one way or another, precisely or otherwise, the concentration of "hydrogen ion" in solution. Taken at its face value, this is a concept admirable in its simplicity. It is even suitable viewed from the macroscopic vantage point of thermodynamics. From the structural point of view, however, disturbing thoughts concerning the nature of "hydrogen ion" begin to take form. Surely one does not refer to the concentration of free protons, which must be vanishingly small in aqueous solutions.[3] The structure of the hydrogen ion as a kinetic entity in either aqueous or nonaqueous media is far from clear and in mixed solvents even less so.

The failure of pH to assume a clear identity despite the passage of nearly three fourths of a century can be blamed in large part on the methodology of pH measurement. Originally conceived as a measure of hydrogen ion concentration,

$$pH = -\log c_H \equiv pcH$$

$$pH = -\log m_H \equiv pmH \qquad\qquad (1)$$

Table 1
TREATMENT OF pH IN TWELVE POPULAR TEXTBOOKS OF ANALYTICAL CHEMISTRY

	Number of books
pH definition	
$-\text{Log } c_H$	6
$-\text{Log } a_H$	6
Operational definition presented	4
Use $-\log c_H$ in calculations exclusively	10
Describe method of using activities in calculations	2
Discuss pH in nonaqueous and mixed solvents	2

pH was related to the change in emf (E) of the cell with transference

$$\text{Pt; } H_2 \text{(g) | Reference solution} \,||\,| \, \text{KCl (saturated or 3.5 } M) \,|\,|| \, \text{Unknown solution} \, | \, H_2\text{(g); Pt} \tag{A}$$
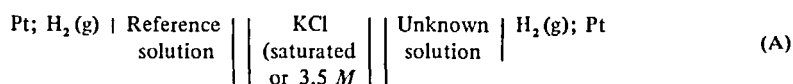
by the ideal equation for the transfer process: H^+ (unknown) $=$ H^+ (reference), namely

$$E = \frac{RT}{F} \ln \frac{c_H(\text{unknown})}{c_H(\text{reference})} \tag{2}$$

As the half cell on the left remained unchanged from one measurement to another, it was convenient to replace it by a reference electrode (a mercury/calomel electrode, for example) in contact with the concentrated KCl solution of the salt bridge, whereupon the pH cell became

$$\text{Hg; } Hg_2Cl_2 \text{(s), KCl (saturated or 3.5 } M) \,|| \, \text{Unknown solution} \, | \, H_2 \text{(g); Pt} \tag{B}$$
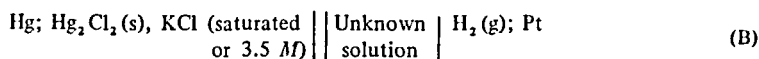
In terms of the present-day "right minus left" convention, the equation for pH thus became

$$pH = \frac{E^{\circ\prime} - E}{(RT \ln 10)/F} \tag{3}$$

where $E^{\circ\prime}$ was found by inserting in Equation 3 values of E determined from measurements of cell B containing one or more reference solutions of known pH. It is but a small step from Equation 3 to the operational definition of pH widely accepted today, namely

$$pH(X) = pH(S) - \frac{E_X - E_S}{(RT \ln 10)/F} \tag{4}$$

Table 2
PRIMARY STANDARDS OF THE NBS pH SCALE AT 15, 25, AND 37°C

	pH(S) at		
Buffer solution	15°C	25°C	37°C
KH tartrate (sat at 25°C)	—	3.557	3:548
KH$_2$ citrate (m = 0.05)	3.802	3.776	3.756
KH phthalate (m = 0.05)	3.999	4.008	4.028
KH$_2$PO$_4$ (m = 0.025), Na$_2$HPO$_4$ (m = 0.025)	6.900	6.865	6.841
KH$_2$PO$_4$ (m = 0.008695), Na$_2$HPO$_4$ (m = 0.03043)	7.448	7.413	7.385
Na$_2$B$_4$O$_7$ (m = 0.01)	9.276	9.180	9.088
NaHCO$_3$ (m = 0.025), Na$_2$CO$_3$ (m = 0.025)	10.118	10.012	9.910

Note: m = molality (mol kg^{-1}). For the sake of brevity, trailing zeros are not given. In those cases, the molality is to be known to four significant figures.

where E_x and E_s refer to the emf of cell B containing the unknown solution and the standard reference solution, respectively. The seven primary standards of the National Bureau of Standards (NBS) pH scale are listed in Table 2, together with their assigned pH(S) values at 25°C.[4,5]

Although the form of these equations has persisted, some changes have occurred in the meaning of the terms they contain and in an understanding of their limitations. The result is to deprive the pH concept of a large portion of its early significance as an exact measure of a useful property of the unknown solution. We may next inquire as to how this development came about.

II. EVOLUTION OF THE pH CONCEPT

A. Fundamental Considerations

It must be remembered that Sørensen proposed the pH unit and the experimental method by which pH values were to be determined early in the 20th century. The pH resulting from Sørensen's experimental procedure may be designated psH. At that time, the modern theory of electrolytes and the role of interionic attraction had not been formulated, and the importance of the activity function in chemical thermodynamics was not yet clear. The developing success of the Debye-Hückel theory in accounting for the properties of dilute solutions of electrolytes led Sørensen and Linderstrøm-Lang to recognize that the psH did not give pcH as intended. The earlier treatment of pH had to be modified in several ways. First, the correct thermodynamic analysis of cell A leads, when the residual liquid-junction potential at the bridge solution is ignored or eliminated, not to Equation 2, but to an equation of similar form where a_H replaces c_H. Formal consistency is then achieved by defining pH by

$$pH = -\log a_H \equiv paH \tag{5}$$

instead of by Equation 1. Finally, the earlier assumption that c_H in solutions of a strong acid such as HCl (or in HCl-NaCl mixtures) is given by αc_{HCl}, where α is the degree of dissociation in the Arrhenius sense, is inconsistent with the theory of complete disso-
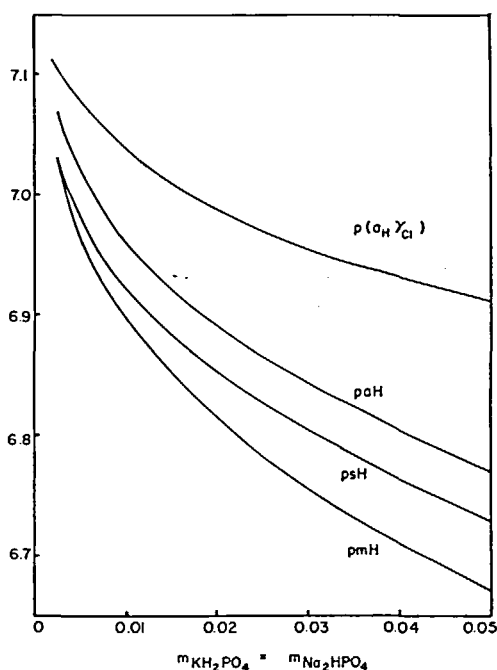
FIGURE 1.   Comparison of acidity functions for equimolal phosphate buffers at 25°C.

ciation of strong electrolytes. It should therefore be replaced by the relationship a_H = $C_H y_H$ or a_H = $m_H \gamma_H$, where y_H and γ_H are activity coefficients on the scales of concentration (molarity) and molality, respectively. For these reasons, the pH numbers (designated psH) based on the Sørensen standard solutions or standard potentials are neither pcH nor paH.

When these changes and a shift to the scale of paH were made, a fundamental difficulty remained; to evaluate $E°'$ in Equation 3, a value of a_H in at least one reference solution was needed. Whereas thermodynamic methods can yield activities for neutral combinations of ions, they are unable to furnish activities of single ionic species. For this reason, the new unit, paH, failed to replace completely the Sørensen scale. Practical pH measurements based on either of the two scales lacked the clear significance that should characterize a fundamental property of the solution. Nevertheless, both scales were useful, providing reproducible pH numbers and a qualitative index of changes of acidity.

The values of psH, paH, and pmH for equimolal phosphate buffer solutions at 25°C are compared in Figure 1 as a function of the molality of the buffer components. The nature of the fourth unit, $p(a_H \gamma_{Cl})$, will be discussed later.

B. Reproducibility

As MacInnes pointed out some years later, "In possibly all but one case in a thousand it is not necessary to consider the meaning of pH in terms of solution theory at all, but only to accept the numbers as a practical scale of acidity and alkalinity."' Reproducible numbers for the pH of a process or product are the primary requirement in industry or quality control procedures, as these numbers can be correlated with successful performance in an empirical way. In these instances, neither the concentration nor activity of hydrogen ions is of any interest or significance. The operational definition of pH, Equation 4, would therefore meet the requirements of a large frac-

tion of routine pH measurements, regardless of the numbers assigned to the pH(S) of the reference solutions with which the equipment was standardized. Two questions come to mind: (1) is it worthwhile to attempt to endow pH(X) with fundamental meaning in the light of the small fraction of measurements where an interpretation of pH is needed and possible, and (2) if so, how can a useful scale of hydrogen ion activity be defined? Analytical chemists, coordination chemists, biophysicists, and others have answered yes to the first question. Possible answers to the second will now be considered. It is here that one must seek the modern meaning of pH..

III. ELECTROMETRIC METHOD OF MEASUREMENT

From the earliest days, the electrometric method has been favored for the determination of pH, and it rightfully assumes primary importance in the definition of this quantity. The determination of pH with indicators is often useful but of secondary nature. Indicator methods and kinetic pH techniques must be standardized in terms of potentiometric procedures. It is thus instructive to examine in some detail the nature of the emf response of pH cells to changes in acidity of the solution placed in that cell. In so doing, we shall hope to discover which form of hydrogen ion function is most directly consistent with the measured quantity, the cell emf.

A. Thermodynamics of the pH Cell

Modern measurements of pH utilize, in the vast majority of instances, the convenient and versatile glass electrode. Thanks to modern technology, the potential of the external surface of this membrane electrode parallels to a remarkable degree that of the hydrogen gas electrode, the primary reference for hydrogen ion measurements. By this, one means that the potential response simulates very well that for the electron-transfer half reaction $2H^+ + 2e = H_2(g)$. Its potential (E_H) changes with hydrogen ion activity in accordance with the theoretical Nernst slope,

$$E_H = E^\circ - \frac{RT}{F} \ln \frac{1}{a_H} \tag{6}$$

Whereas, by convention, $E^\circ = 0$ for the hydrogen electrode, it will not usually be so for a glass electrode. Moreover, the response of the glass electrode may be found to be imperfect when compared with that of the primary hydrogen electrode. It is often possible to apply corrections for this defect and achieve accurate results. Thus for simplicity in thermodynamic analysis, one can write the pH cell schematically as cell B, already formulated.

Other reference electrodes, especially the silver-silver chloride electrode, may constitute the left-hand element, and the KCl solution, though concentrated, is often under-saturated (for example, 3.5 *M*). The pH cell used in most modern practice is nonetheless essentially a cell consisting of a reference electrode of constant potential, a liquid junction, and an indicator electrode responding to hydrogen ion activity in the manner of Equation 6.

There are three sources of potential difference in cell B. These are the potentials across the metal/solution phase boundaries at the indicator electrode (E_H) and the reference electrode (E_R) and the liquid-junction potential (E_j) across the liquid-liquid boundary. The total cell emf E is given in terms of the modern "right minus left" convention[8] by

$$E = E_H - E_R + E_j \tag{7}$$

At constant temperature and pressure and over short periods of time, the standard potential of the indicator electrode in Equation 6 and the reference electrode potential remain unchanged:

$$E^{\circ} - E_R = \text{constant} \equiv E^{\circ\prime} \tag{8}$$

Furthermore, the liquid-junction potential arises from unequal diffusion of ions in the two directions across the boundary. Equation 8 can then be written

$$E = E^{\circ\prime} - \frac{RT}{F} \ln \frac{1}{a_H} - \frac{RT}{F} \int_A^B \sum \frac{t_i}{a_i} \, d\ln a_i \tag{9}$$

where i represents each ionic species, of charge z_i, present on either side of the liquid-liquid boundary. The transference numbers (t_i) are given signs which depend on the direction in which diffusion takes place between the end solutions A and B.

Postponing for the moment a consideration of the precise nature of the liquid-junction potential, one can write

$$paH = \frac{(E^{\circ\prime} + E_j) - E}{2.3026RT/F} \tag{10}$$

or

$$pmH = \frac{(E^{\circ\prime} + E_j) - E}{2.3026RT/F} + \log \gamma_H \tag{11}$$

If the scale of molar concentration is used, pmH and γ_H are replaced by pcH and y_H.

It is evident that neither Equation 10 nor Equation 11 offers a simple and direct derivation of paH or pmH from the emf of cell B. It is not inconceivable that $E^{\circ\prime}$ could be evaluated and rendered constant for lengthy periods. Estimation of the activity coefficient γ_H, which depends on ionic strength, composition with respect to counter ions, etc., or of E_j (Equation 9, last term) is nonetheless completely impractical, especially for routine measurements.

A comparison of Equations 10 and 11 demonstrates that the hydrogen ion activity is formally related more simply to the cell response (E) than is pmH. Furthermore, Equation 10 emphasizes the interdependence of paH and E_j. In other words, paH is uniquely defined only if E_j is known; conversely, adoption of a scale of paH is necessary and sufficient to fix the values of the liquid-junction potentials involved. Harned referred to this as an "interesting perplexity".[9] It has also been called a "dilemma from which there is apparently no escape."

A "true" or "absolute" hydrogen ion activity thus cannot be derived from measurements of cell B, given the present state of affairs. If, however, two different solutions of similar compositions with respect to a_i and t_i were placed in cell B, one might expect E_j to be the same in both, as is $E^{\circ\prime}$. The effectiveness of concentrated KCl solutions in reducing and rendering constant the liquid-junction potential has long been known.[10] In fact, Bjerrum[11] proposed an extrapolation to $1/c_{KCl} = 0$ of plots of E vs. $1/c_{KCl}$ as a practical approach to the complete elimination of liquid-junction effects. If one solution is regarded as a standard of reference (S) and the other as an "unknown", X, the difference of paH is

$$paH(X) - paH(S) = \frac{E_S - E_X}{2.3026RT/F} + \frac{E_j(X) - E_j(S)}{2.3026RT/F} \tag{12}$$

B. The Operational pH Scale

Under ideal conditions, when E_j is either rendered constant or eliminated, one obtains the operational definition of pH set forth earlier in Equation 4. Let us consider once more the *raison d'être* and nature of this definition.

1.   It is based on an attempt to measure *differences* of pH, formally defined as $-\log a_H$, through emf measurements of cell B.
2.   This difference has quantitative significance only insofar as E_j remains unchanged when solution S is replaced by solution X.
3.   Only under these rare and ideal circumstances does pH(X) derive significance from pH(S) or paH(S) which, being essentially nonthermodynamic (or at best quasithermodynamic), must have a defined or conventional basis.
4.   The operational definition fulfills the primary requirement of reproducibility.

This last consideration means that the operational pH scale satisfies the needs of a vast majority of commercial and industrial applications. It says nothing concerning the manner in which pH(S) is to be arrived at; for most routine pH measurements, it is only necessary that the same values of pH(S) for the reference solutions be adopted by all users. The number of instances where pH measurements can justifiably be given a fundamental interpretation is indeed small but nonetheless important. They include equilibrium studies leading to pK values for acid/base systems, stability constants of metal/ligand complexes, research in enzyme processes, biomedical studies and clinical investigations, and the like. For maximum usefulness in these applications, the nature of the standard pH must be clearly defined and every effort made to assure that the residual liquid-junction potential (the last term of Equation 12) is minimized. We shall return to this aspect of pH measurement later in this review.

In essence, the operational formula comes closest to qualifying as the "modern" definition of pH. Coupled with a universally accepted set of reference standards, it is capable of providing pH numbers reproducible from time to time and from place to place. Its faults rest on the side of interpretation. Obviously, the operational pH is not pcH. Less obviously perhaps, it is paH only when the residual liquid-junction potential is zero. One may say that pH is now defined operationally rather than by either pcH or paH (Equations 1 and 5), with the qualification that pH *approaches* a conventional paH under ideal conditions of measurement. The scale of conventional activity is that adopted in the assignment of pH(S) values to the reference standards.

Two points of view concerning the operational pH scale prevail today. One maintains that reproducibility of pH numbers should be the sole, or at least the overriding, consideration and that the numbers adopted for pH(S) of the reference solutions have no fundamental meaning in terms of the properties of the reference buffers themselves. The other admits the necessity for reproducibility in pH measurements, but feels that it is worthwhile to assure that, for the relatively small number of ideally constituted media, pH will fall on a scale the nature of which is understood. Although these desirable conditions are rarely met, many practical pH values can profitably be considered to be approximate values of paH. The difference in these views is clearly dependent on the relative importance ascribed to the interpretation of pH numbers. We shall next examine the nature of a conventional scale of paH on which meaningful values of pH(S) can be based.

IV. SINGLE ION ACTIVITY

The task of establishing paH values for reference buffer solutions is a formidable one for which thermodynamics offers no unique solution. Curiously, the early at-

tempts to define arbitrary but useful scales of single ion activity were met with a certain amount of scorn and even intimidation on the part of the pure thermodynamicists, while attempts to evaluate liquid-junction potentials were considered permissible. In 1930, Guggenheim[12] expressed the view that the ionic activity coefficient could never be more than a mathematical device. Others, including Brønsted, countered with the suggestion that this activity coefficient has a meaning as well defined as the activity coefficient of a neutral molecule.[13,14] Kortüm[15] felt that activity coefficients of ions in very dilute solutions partake of the properties of mean activity coefficients and should be considered identical in magnitude to the latter. In his later years, Guggenheim modified his earlier views to the extent of recognizing the usefulness of conventional ionic activities in establishing a standard pH scale. In 1960 he wrote[16] "Some people may wish to abbreviate $pm_H\gamma_H$ . . . to paH. Other people have strong objections to this notation because it may revive controversies of the days before the nature of pH was properly understood." One may say with some justification that the failure of thermodynamics to offer a guide has been overemphasized.[17] It is well understood that activities of individual ionic species are necessarily conventional, but this arbitrary quality may not be as serious a limitation as it has been considered in the past.

The pH number, of course, has in itself little absolute significance. As the negative of the logarithm of a product of a concentration (c or m) and an activity coefficient (y or γ), it acquires its magnitude from the numerical scale adopted for the latter. The ultimate use of paH numbers depends either on a subsequent correlation with phenomena such as product quality or human pathology or the conversion of these numbers into concentrations of hydrogen ion or other quantities with a clearly understood meaning. Experimental pH measurements are nonetheless widely applied to the determination of thermodynamic equilibrium data such as pK values, on the assumption that they represent $-\log a_H$ (paH). From the mass law, the equilibrium constant (K) for the process

$$A \leftrightarrows B + H^+ \qquad (13)$$

is formulated as follows:

$$pK = paH + \log \frac{mA}{mB} + \log \frac{\gamma_A}{\gamma_B} \qquad (14)$$

The magnitude of the equilibrium constant is fixed by the choice of thermodynamic standard state and by the temperature and pressure. In order that Equation 14 shall be obeyed, a self-consistent scale of γ_H, γ_A, and γ_B is required, and the absolute values of these activity coefficients are unimportant. To establish such a scale, it is sufficient to fix the numerical value of the activity coefficient of one ionic species alone; this is because mean activity coefficients of neutral combinations of ions are, in theory, accessible by a variety of thermodynamic means in any given medium.

Although scales of single ion activity must have an arbitrary basis, there are obvious advantages in defining the activity such that it is reasonable in the light of solution theory. For this reason, one endows the single ion activity with the behavior characteristic of the mean activity coefficient. Thus the single ion activity coefficient approaches unity as the ionic strength goes to zero, so that a_i becomes equal to m_i and paH approaches pmH, as seen in Figure 1. It is convenient to retain these conditions for dilute solutions in nonaqueous and mixed solvents as well. This requires a change in thermodynamic standard state which, in turn, alters the value of pK in Equation 14.

This matter will be considered again later in this review, but let us now turn for a

moment to the use of paH or a_H in the treatment of a chemical equilibrium such as that of Equation 13. Three different equilibrium constants are in common use. They are the thermodynamic constant K, set forth in Equation 14.

$$K = \frac{a_H a_B}{a_A} \tag{15}$$

the "incomplete equilibrium constant" or "apparent constant" K',

$$K' = K\frac{\gamma_A}{\gamma_B} = a_H \frac{m_B}{m_A} \tag{16}$$

and the concentration equilibrium constant or "classical constant" K_c

$$K_c = K\frac{\gamma_A}{\gamma_H \gamma_B} = \frac{m_H m_B}{m_A} \tag{17}$$

Quite evidently, both K' and K_c vary with the ionic strength and the values of the activity coefficients of the species taking part in the equilibrium process. The apparent constant K' has been widely used in studies of acid-base equilibria, as it can be derived readily from the experimental pH (assumed to be paH) and the molalities m_A and m_B of the conjugate species. The K' is evidently a kind of formal equilibrium constant applicable only to solutions in which the ratio $\gamma_A:\gamma_B$ or, as a first approximation, the ionic strength is fixed. These conditions appear to be satisfactorily met in most "constant ionic strength media", such as 1 M NaClO$_4$, synthetic seawater, and the like.

When the objective is clearly the acquisition of thermodynamic data, the use of *operational pH measurements is questionable. Entirely apart from experimental uncertainties* in the use of the pH cell (glass electrode errors, residual liquid-junction potentials, and the like), in so doing one is in the position of inserting a nonthermodynamic step that is clearly unnecessary to the measurement. It can only be justified on the basis of convenience at some sacrifice of accuracy. For some of these applications suitable thermodynamic acidity functions exist and should be used when possible. Perhaps the most useful is $p(a_H\gamma_{Cl})$, proposed by Guggenheim[12] and Hitchcock.[18] This function can be derived easily for strong acid systems as well as buffer solutions in a variety of media from measurements of the emf of cells without liquid junction, for example,

$$\text{Pt; H}_2\text{ (g, 1 atm) I Buffer } (m_A, m_B), \text{ Cl}^-(m_C) \text{ I AgCl; Ag} \tag{C}$$
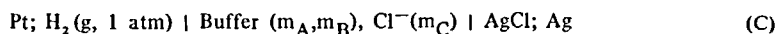
when the standard emf E° and chloride molality m_C are known:

$$p(a_H\gamma_{Cl}) = \frac{E - E°}{2.3026RT/F} + \log m_C \tag{18}$$

Values of $p(a_H\gamma_{Cl})$ in a variety of buffer solutions have been tabulated elsewhere.[19,20] Some years ago, the author and Schwarzenbach showed how $p(a_H\gamma_{Cl})$ could be coupled with a spectrophotometric determination of m_A/m_B to evaluate thermodynamic pK values free from the uncertainties of liquid-junction potentials.[21] The $p(a_H\gamma_{Cl})$ values of 1:1 phosphate buffer solutions are plotted in Figure 1 for comparison with pcH,

psH, and paH. For buffers composed of a monobasic acid and its salt, $p(a_H \gamma_{Cl})$ changes little with ionic strength.[1,22]

A. Conventional Activity Scales

1. Residual Liquid-Junction Potentials

The need for a scale of single ion activity coefficients has long been felt. It arose in part from a desire to evaluate diffusion potentials across liquid-liquid boundaries, which depend on the charges, activities, and mobilities of each of the diffusing ion species. From Equation 12 it may be seen that true differences in paH could be obtained if the residual liquid-junction potential, $E_j(X) - E_j(S)$, could be evaluated, either from experiments or theory. In a classic study of the concentrtion cell with liquid junction,

$$Ag; AgCl \mid MCl \ (c_1) \mid \mid MCl \ (c_2) \mid AgCl; Ag \qquad \text{(D)}$$

MacInnes[23,24] attempted to separate the liquid-junction potential (E_j) from the total cell emf (E), thus obtaining the potential difference between the right and left electrodes, $E_r - E_l$:

$$E = E_r - E_l + E_j \qquad \text{(19)}$$

The test was based on the supposition that $E_r - E_l$ should be nearly independent of the nature of the cation M^+ in dilute solutions ($c < 0.06$ mol dm^{-3}), since the Ag; AgCl electrodes are reversible to chloride ions. If the cation transference number t_+ can be considered constant in the range of concentration from c_1 to c_2, one can write

$$E_j = \frac{RT}{F} \left[t_+ \ln \frac{a_M(1)}{a_M(2)} - (1 - t_+) \ln \frac{a_{Cl}(1)}{a_{Cl}(2)} \right] \qquad \text{(20)}$$

Even with a knowledge of transference numbers, an evaluation of E_j requires additional information concerning single ionic activity coefficients. It is reasonable to expect these single ionic activity coefficients to behave in a manner similar to the mean activity coefficients of the electrolytes composed of these ions. Thus MacInnes used the convention

$$a_M = a_{Cl} = a_{MCl} \qquad \text{(21)}$$

for the analysis of data for cell D. By combination of Equation 20 with the equations for both the emf (E) and E_j, he obtained

$$E_j = E \frac{2t_+ - 1}{2t_+} \qquad \text{(22)}$$

Liquid-junction potentials between pairs of chloride solutions with the same cation were widely different, as shown in Table 3, but the electrode potentials, $E_r - E_l$, appeared to be nearly independent of the cation (Na^+, K^+, or H^+). This observation suggests that the calculation of the liquid-junction potentials between different concentrations of the same electrolyte by Equation 20 is successful.

Attempts to evaluate the potentials across heteroionic junctions are not as fruitful.

Table 3

ELECTRODE POTENTIALS ($E_r - E_l$) AND LIQUID-JUNCTION POTENTIALS (E_j) DERIVED FROM CONCENTRATION CELLS OF TYPE D[24]

Conc (mol dm⁻³)					
c_1	c_2	MCl	E(mV)	E_j(mV)	$E_r - E_l$ (mV)
0.02	0.01	NaCl	13.22	−3.69	16.9
		KCl	16.56	−0.34	16.9
		HCl	28.05	11.07	17.0
0.04	0.05	NaCl	39.63	−11.09	50.7
		KCl	49.63	−1.00	50.6
		HCl	84.16	33.22	50.9
0.06	0.04	NaCl	7.50	−2.18	9.7
		KCl	9.44	−0.20	9.6
		HCl	16.25	6.45	9.8

Table 4

COMPARISON OF FREE-DIFFUSION WITH TWO TYPES OF COMMERCIAL REFERENCE ELECTRODES AT 25°C — EMF IN mV[a] OF CELLS OF THE TYPE: Hg; Hg_2Cl_2,KCl (SATURATED) ‖ SOLUTION ‖ COMMERCIAL REFERENCE ELECTRODE

Solution	Type of commercial electrode				
	Fiber			Porous plug	
	1	2	3	1	2
HCl, 0.1 M	−1.3	−1.0	−0.1	−0.3	+0.1
Phthalate buffer, pH 4	0	0	0	0	0
Phosphate buffer, pH 7.4	+0.3	+0.7	+0.1	+2.9	+2.0
Borax buffer, pH 9.2	−0.1	0	+0.3	+2.4	+1.2
NaOH, 0.1 M	+1.0	+1.3	+1.3	+1.7	+2.2

[a]   Values normalized to E = 0 in phthalate buffer at pH 4.

Not only are calculations based on the Planck[25] and Henderson[26] models less satisfactory,[27] but also in practice differences appear among individual junctions and among commercial junctions of varying designs. The most stable and reproducible liquid junctions seem to be those formed in such a way that mixing by convection is avoided. A free-diffusion junction formed in a 1- to 3-mm vertical capillary with the concentrated bridge solution beneath the more dilute solution has been found to be very satisfactory.[28,29] Unfortunately, a steady state of diffusion, believed to be essential to maximum reproducibility, is rarely achieved in reference electrodes of commercial design. Consequently, these electrodes may yield data at variance with those obtained with capillary junctions. This is apparent in Table 4, where five commercial reference elec-

trodes of two different types are compared with the capillary junction over a range of pH.[30]

The potential E_j developed across a liquid-liquid boundary

$$\text{Solution A} \mid \mid \text{KCl (saturated) (B)}$$

when one faraday of charge is passed reversibly across the interface will be a function of the activities of the ions on both sides of the boundary and of the fraction of the current carried by each ionic species. A boundary is never perfectly sharp, however; diffusion produces a steady-state condition characterized by an indefinite number of boundary layers. The junction potential is therefore given by an integral of the form (compare Equation 9)

$$E_j = - \frac{RT}{F} \int_A^B \Sigma \frac{t_i}{z_i} \, d\ln a_i \qquad (23)$$

Probably the most useful integral form of Equation 23 is the Henderson equation, derived on the assumption that the junction consists of a continuous series of solutions produced by mixing solutions A and B. If the activities of the ions in these two end solutions are taken equal to their concentrations, the transference numbers are expressed in terms of limiting equivalent conductances, λ_i°, and ion concentrations c_i are in equiv dm^{-3}, one finds for the boundary between A and B the expression

$$E_j = \frac{RT}{F} \frac{\Sigma c_+ \lambda_+^\circ - \Sigma c_- \lambda_-^\circ + 11.6}{\Sigma c_+ \lambda_+^\circ z_+ + \Sigma c_- \lambda_-^\circ z_- - 623} \ln$$

$$\frac{\Sigma c_+ \lambda_+^\circ z_+ + \Sigma c_- \lambda_-^\circ z_-}{623} \qquad (24)$$

In Equation 24, the values of c, λ°, and z are those for the cations and anions of solution A; the corresponding values for the saturated solution of KCl are incorporated in the numerical constants.

Some liquid-junction potentials calculated by Equation 24 are collected in Table 5. The effect of buffer concentration, acid/base type, and mobility of the buffer ions (A$^-$ or BH$^+$) is illustrated by the data given. The residual liquid-junction potential error in a pH measurement results from the difference in $\overline{E_j}$ between measurements with the standard and unknown solutions. Its magnitude is given by $[E_j(X) - E_j(S)]/59.16$ at 25°C, where E_j is in mV; this error in pH may be designated E_j for convenience. The calculations involve assumptions concerning ionic mobilities and distributions through the boundary. Likewise, interionic effects are ignored. Nevertheless, it is evident that a wide disparity between the $c\lambda^\circ$ products for the charged species of the "unknown" and the standard solution will be accompanied by an exaggerated residual liquid-junction potential. This is especially true if the unknown buffer and the standard buffer are of different acid-base charge types.

It is difficult to test the validity of these predictions. In the author's opinion, comparisons with conventional ion activities determined from cells without liquid junction in relatively dilute solutions (ionic strength 0.16 or less) provide a more reliable estimate of residual liquid-junction potential errors than does the Henderson equation.[29] Both approaches lend support to the use of concentrated bridge solutions to minimize the value of $E_j(X) - E_j(S)$, although complete elimination of this error is rarely possible.

Table 5
CALCULATED DIFFUSION
POTENTIALS ACROSS
JUNCTIONS OF THE TYPE
BUFFER SOLUTION ‖ KCl
(SATURATED) AT 25°C; EFFECT
OF BUFFER CONCENTRATION
AND MOBILITY OF THE
BUFFER IONS

Buffer solution	E_j (mV)
0.01 M CH_3COOH, 0.01 M CH_3COONa	3.2
0.05 M CH_3COOH, 0.05 M CH_3COONa	2.5
0.1 M CH_3COOH, 0.1 M CH_3COONa	2.2
0.01 M NH_4Cl, 0.01 M NH_3	2.9
0.05 M NH_4Cl, 0.05 M NH_3	2.1
0.1 M NH_4Cl, 0.1 M NH_3	1.8
0.05 M KH_2 citrate	2.8
0.05 M KH phthalate	2.6
0.025 M KH_2PO_4, 0.025 M Na_2HPO_4	1.7
0.025 M $NaHCO_3$, 0.025 M Na_2CO_3	1.8
0.05 M Tris·HCl, 0.05 M Tris	1.9
0.05 M HA, 0.05 M NaA	
λ°_A = 60	2.2
λ°_A = 50	2.4
λ°_A = 40	2.5 ·
λ°_A = 30	2.7
0.05 M B·HCl, 0.05 M B	
λ°_{BH} = 60	2.1
λ°_{BH} = 50	2.0
λ°_{BH} = 40	1.9
λ°_{BH} = 30	1.9

2. Mean Activity and Ionic Activity

The satisfactory constancy of $E_r - E_l$ for cell D, as shown in Table 3, may be taken as supporting the validity of the convention of Equation 21, insofar as one is dealing with dilute solutions of the same electrolyte. Measurements of this sort led to the MacInnes convention,[31] proposed in 1919:

$$a_K = a_{Cl} = a_{KCl} \tag{25}$$

Still widely used, this convention permits the substitution of $\gamma_\pm$(KCl) at a given ionic strength (I) for γ_K or γ_{Cl} in other solutions of the same ionic strength. The approximate equality of the mobilities of K^+ and Cl^- ions in dilute aqueous solutions justified the choice of KCl as a reference electrolyte. Somewhat later, Guggenheim[12] proposed a more general convention applicable to both single electrolytes and to mixtures of several ion species. According to this approach to the problem, single ionic activity coefficients in mixtures were expressed as weighted functions of mean activity coefficients and ratios of activity coefficients of ions of like charge, data not commonly available. In the case of a single electrolyte MCl, however, this convention reduces to the simple relationship set forth in Equation 21.

3. Theoretical Calculations

In the so-called "Debye-Hückel region" of low ionic strength (I < 0.01) there is little doubt that Equations 21 and 25 are valid for completely dissociated electrolytes. Between I = 0.01 and I = 0.1, mean activity coefficients can be expressed with considerable success by the "extended Debye-Hückel equation" with adjustable ion-size parameter $\overset{\circ}{a}$. Consequently, activity coefficients of ions (i) are often calculated by

$$\log \gamma_i = \frac{-Az_i^2 I^{1/2}}{1 + B\overset{\circ}{a}I^{1/2}} \qquad (26)$$

with estimated values of $\overset{\circ}{a}$. For this, some guidance was offered by Kielland, who compiled a table of values of the ion-size parameter for many common ions.[32] A value of $9\overset{\circ}{A}$ was assigned to H^+ and $3\overset{\circ}{A}$ to Cl^-. Kielland's estimates of $\overset{\circ}{a}$ were based on information from crystal radii, hydration numbers, mobilities, and deformabilities of ions. They have been widely used in spite of their empirical nature. The constants A and B of the Debye-Hückel theory which appear in Equation 26 are functions of the temperature and the dielectric constant and density of the solvent.

The NBS method for establishing standard values of paH will be discussed later in this review. The activity coefficient of chloride ion in selected reference buffer solutions is required. Because of buffer action, a wide range of pH values can be covered with solutions of ionic strength less than 0.1. Ionic activity coefficients in these relatively dilute solutions (where the interpretation of pH measurements is most likely to be successful) may be expected to display greater regularity than at higher ionic strengths, where specific ion-ion interactions become pronounced. Bates and Guggenheim[16] proposed as a "pH convention"

$$\log \gamma_{Cl} = \frac{-AI^{1/2}}{1 + 1.5I^{1/2}} \qquad (27)$$

applicable at ionic strengths (I) of 0.1 or less. It was intended that this convention would be used to assign pH(S) values to selected standard reference solutions at all temperatures, with appropriate changes in the Debye-Hückel slope constant A. The coefficient 1.5 in the denominator, corresponding to $B\overset{\circ}{a}$ in Equation 26, implies an ion-size parameter of $4.57\overset{\circ}{A}$ in water at 25°C or somewhat higher than the value selected by Kielland. In the range of intended use, Equation 27 furnishes values of γ_{Cl} which are nearly the same as the mean activity coefficient of NaCl in its aqueous solutions. When this convention is applied to nonaqueous and mixed solvents (e.g., $H_2O/$ methanol mixtures), it has been deemed reasonable to modify it to reflect changes in both Debye-Hückel constants A and B. Thus, $\overset{\circ}{a} = 4.57\overset{\circ}{A}$ has been retained, but $B\overset{\circ}{a}$ is no longer 1.5.

The values of the mean activity coefficients of the halogen acids, alkali halides, and alkali hydroxides decrease in accordance with the predictions of theory in dilute solutions as the ionic strength increases. At molalities in excess of 0.5 mol kg^{-1}, however, this decrease is arrested, and the values of the activity coefficients of many unassociated electrolytes pass through a minimum and increase at higher concentrations. Presumably values for the individual ionic activity coefficients follow a similar pattern. It is evident that equations of the form of Equation 26 are inadequate to account for this behavior, which is related to specific ion-ion interactions and to ion-solvent interactions (solvation). These factors have an important influence on the activity in concentrated solutions.

The Brønsted-Guggenheim specific interaction treatment[33,34] and the Davies equation[35] remedy this defect, to some degree, in an empirical fashion. They append a term linear in ionic strength (namely, $+\beta I$ or $+0.3[z_+z]I$, respectively) to a simplified form of Equation 26, where $B\overset{\circ}{a}$ is set equal to 1. The coefficients β, termed interaction coefficients, may be combined to yield mean activity coefficients for cation/anion pairs in mixtures of electrolytes. This treatment is most successful at ionic strengths not exceeding 0.1, but it has been shown to be remarkably useful for predicting the thermodynamic properties of electrolytes in seawater at ionic strengths as high as 0.7.[36,37] These equations offer little or no guidance, however, in separating mean activity coefficients into their ionic contributions.

4. Hydration Treatment

In using the Debye-Hückel theory, one is attempting to estimate the departures from ideal behavior resulting from the long-range electrostatic ion-ion interactions that predominate in dilute solutions. Bjerrum pointed out many years ago[38] that most ionic species are solvated and when this is the case, a certain amount of solvent is, in effect, removed from the bulk solvent. This amount of solvent is bound in the primary solvation layer and becomes a part of the ionic entity. As a consequence, effective ion concentrations are greater than the stoichiometric concentration. The result is a minimum in the activity coefficient and an increase at higher concentrations. The magnitude of the increase is governed by the hydration number (h) for the electrolyte.

Stokes and Robinson[39] and Glueckauf[40] have been able to account for the observed mean activity coefficients of strong electrolytes up to high concentrations in water by introducing an adjustable hydration number, in addition to the ion-size parameter of the electrostatic term. The equation of Stokes and Robinson is as follows:

$$\log \gamma_\pm = f_{DH} - \frac{h}{\nu} \log a_w - \log [1 + 0.018 (\nu - h) m] \qquad (28)$$

where f_{DH} is the electrostatic (Debye-Hückel) term of the form of Equation 26, ν is the number of ions from each molecule of electrolyte, and a_w is the activity of water in the solution. A constant value of the hydration number could be used up to a molality (m) of approximately 12/h. By regression analysis, it was possible to derive hydration numbers for a series of unassociated electrolytes from data for mean activity coefficients.

With the development of ion-selective electrodes, a demand arose for scales of single ion activity extending well above the $I = 0.1$ limit of the pH convention given in Equation 27. Robinson recognized that the hydration treatment could form the basis for self-consistent scales of this sort, provided the hydration number of one ionic species were known. Analysis of the values of h for the alkali halides[41,42] offers evidence that the effective primary hydration numbers of Cl^-, Br^-, and I^- are, on the average, close to zero. It was therefore suggested that the convention $h_{Cl} = 0$ be adopted. On this basis, h_H, h_{Na}, and h_K are about 7, 3.5, and 2.

It is possible to show that the individual contributions of cation and anion to the mean activity coefficient of a 1:1 electrolyte MX are given by

$$\log (\gamma_M/\gamma_{MX}) = 0.00782 (h_M - h_X) m\phi \qquad (29)$$

and

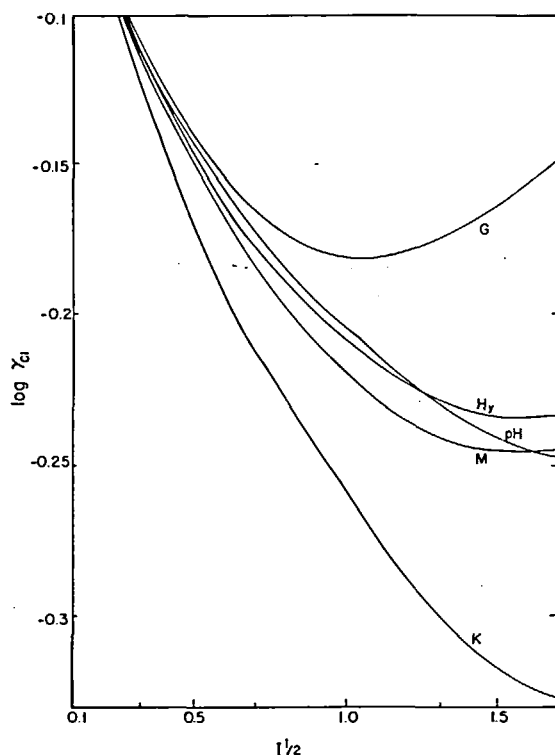$$\log (\gamma_X/\gamma_{MX}) = 0.00782 (h_X - h_M) m\phi \qquad (30)$$

FIGURE 2.   Comparison of five conventions for λ_{cl} in solutions of sodium chloride. G, Guggenheim; Hy, hydration theory; pH, pH convention; M, MacInnes; K, Kielland.

where ϕ is the osmotic coeficient; values of ϕ for many electrolytes have been tabulated.[43] Since values of mean activity coefficients in buffer-chloride mixtures are rarely known, it is difficult to use these equations to derive paH from $p(a_H\gamma_{cl})$. For log γ_{cl} in 0.1 m solutions of HCl, NaCl, and KCl, however, they lead to values of -0.104, -0.112, and -0.115, respectively, as compared with -0.110 given by the pH convention, Equation 27. In view of the specificity of short-range ion-ion interactions, a convention that ascribes different values to γ_{cl} in these three solutions, even at a molality as low as 0.1 mol kg^{-1}, is more reasonable than one taking no account of the nature of the oppositely charged counter ions. Figure 2 is a plot of γ_{cl} in solutions of NaCl, based on the various conventions discussed above.

V. STANDARD REFERENCE VALUES FOR paH

A. NBS "Multistandard" pH Scale

When the NBS set out to establish a standard scale of pH, these matters were of primary concern. Various approaches, including those discussed here, were examined in detail.[1] In view of the experimental difficulties and theoretical uncertainties of the liquid junction, it was decided to base the primary standard scale of pH on emf measurements of cells without liquid junction. The cell with hydrogen and silver-silver chloride electrodes, cell C, was known to be highly reproducible and had been applied extensively by Harned and his associates to obtain reliable thermodynamic data for electrolytes, both in water and in mixed solvents.[44,45] Hitchcock had proposed its use

to obtain values of the acidity function $p(a_H\gamma_{Cl})$, and Hamer and Acree had visualized its use in the practical measurement of paH.[46] From Equation 18,

$$paH = \frac{E - E^\circ}{2.3026RT/F} + \log m_{Cl} + \log \gamma_{Cl} \tag{31}$$

The standard emf E° being known from studies of cell C containing dilute solutions of HCl, it is only necessary to choose a convention for γ_{Cl}.

Several conventions were compared, using data from cell C and the corresponding cells with Ag/AgBr and Ag/AgI electrodes.[47] It was shown that paH values based on a number of reasonable conventions for the single ion activity coefficient varied by less than ± 0.01 unit when the ionic strength did not exceed 0.1. This conclusion may also be drawn from Figure 2. Consequently, the standard scale was fixed by a series of dilute buffer solutions whose pH(S) values were assigned an uncertainty of ±0.01 unit.

With the passage of time, it was recognized that an average of several conventions for γ_{Cl} was no more advantageous than the choice of a single convention. Moreover, rapid advances in electronic technology brought a demand for pH measurements with third-decimal reproducibility. This led to the selection by Bates and Guggenheim,[16] on behalf of two commissions of the International Union of Pure and Applied Chemistry (IUPAC), of the convention set forth in Equation 27.
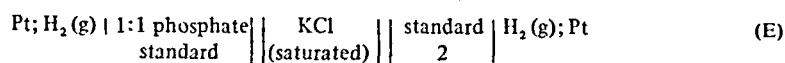
The standardization procedure adopted by the NBS to obtain pH(S) values for reference solutions then consisted of four steps:

1.   Measurement of the emf E for the reference buffer ($I \leqslant 0.1$) with addition of alkali chloride in several small concentrations; calculation of $p(a_H\gamma_{Cl})$ by Equation 18
2.   Extrapolation of $p(a_H\gamma_{Cl})$ to $m_{Cl} = 0$
3.   Calculation of paH from Equation 31 by introduction of the pH convention, Equation 27
4.   Identification of this conventional paH for selected reference solutions with pH(S) in the operational definition of pH, Equation 4 (detailed discussion in Reference 48)

The seven primary standard reference solutions are listed in Table 2. One of these, potassium hydrogen tartrate, is of poor stability and it was intended that it be replaced by another, potassium dihydrogen citrate, with pH in the same range (3.5 to 3.7). There was difficulty, however, in acquiring citrate of the requisite purity and proper composition and, unlike the materials for preparing the other six solutions, KH_2 citrate has not been made available in the Standard Reference Materials series.

The pH scale defined by the NBS standards is evidently a "multistandard scale". In theory, any two reference solutions can be used to fix the practical scale of pH. Indeed, it is believed that each assigned standard value is an equally valid estimate of the conventional paH. Nevertheless, slight inconsistencies in the standardization of the operational pH scale (Equation 4) are unavoidable, in view of the differences in residual liquid-junction potential when one solution replaces another.

The magnitude of these inconsistencies is revealed by measurements of the emf of cells containing two of the standard buffers. For example, the emf of the following cell may serve:
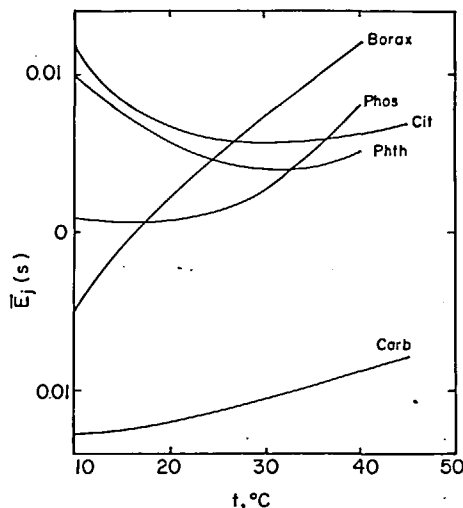
$$\text{Pt; } H_2\text{ (g) } | \text{ 1:1 phosphate} \underset{\text{standard}}{|} \underset{\text{(saturated)}}{| \text{ KCl } |} \underset{2}{|| \text{ standard } |} H_2\text{ (g); Pt} \tag{E}$$

FIGURE 3.   Residual liquid-junction potential
errors (in pH units) for five NBS standard buff-
ers as determined in cell E vs. the equimolal
phosphate solution. Phos, 1:3.5 phosphate; Cit,
KH_2 citrate; Phth, KH phthalate; Carb, carbon-
ate.

If the paH value of the phosphate buffer is accepted, the cell emf furnishes the opera-
tional pH of Standard 2, which can then be compared with the assigned paH of that
standard to obtain an estimate of the error due to the residual liquid-junction potential.
The results of such measurements are shown in Figure 3. The liquid junctions were
formed in vertical capillaries and had cylindrical symmetry. The ordinate $(\bar{E}_j)$ repre-
sents pH(cell E) − paH, where paH is the standard value for each buffer solution
derived from Equations 27 and 31; it is the residual liquid-junction potential error in
pH units.

   Except for the carbonate buffer, the inconsistencies are uniformly less than 0.01 unit
at 25°C, but slightly larger differences are found at low and high temperatures. They
indicate the magnitude of the unavoidable residual liquid-junction potentials of the
pH cell when any two different buffers — standard or unknown — are compared.
Furthermore, they give a clue to the errors inherent in the use of such a cell.

B. "Single-Standard" pH Scale

   The NBS multistandard pH scale has been widely used and adopted by several na-
tional standardizing bodies and in some international standard methods as well. It has,
for example, been adopted in the U.S. by the American Society for Testing and Mate-
rials (ASTM)[49] and has received the endorsement of the IUPAC.[50] Nevertheless, the
British Standards Institution (BSI) has preferred to define the standard pH in a slightly
different way,[51] based on the values for only one of the NBS standards (potassium
hydrogen phthalate, molality 0.05 mol kg⁻¹) together with the Nernst slope, 2.3026RT/
F V pH⁻¹. This variation in procedure was earlier not considered serious, in view of
the unavoidable uncertainties in residual liquid-junction potential. In 1960, U.S. and
BSI representatives, in a report to the IUPAC, agreed that "In their essential elements,
the . . . standards are in agreement; only differences of detail exist."[6]

   This statement was valid as long as pH standards were assigned uncertainties of
±0.01 unit, but with the adoption of a convention leading to the third decimal in

Table 6
COMPARISON OF pH STANDARDS OF THE
BSI "SINGLE-STANDARD" SCALE WITH
THOSE OF THE NBS "MULTISTANDARD"
SCALE AT 25°C

Solution (molality)	BSI value	ΔpH (NBS−BSI)
KH tartrate (saturated at 25°C)	3.556	· 0.001
KH phthalate (0.05)	4.005·	0.003
KH₂PO₄ (0.025), Na₂HPO₄ (0.025)	6.857	0.008
KH₂PO₄ (0.008695), Na₂HPO₄ (0.03043)	7.406	0.007
Na₂B₄O₇ (0.01)	9.182	−0.002
NaHCO₃ (0.025), Na₂CO₃ (0.025)	9.995	0.017

Primary standard; the remainder are classified as secondary
standards of the BSI pH scale.

pH(S), differences in the two approaches could no longer be ignored. An effort has now been launched by U.K. representatives, through IUPAC and other international standardizing bodies, with the aim of replacing the multistandard scale by the single-standard scale in worldwide practice.[52]

The use of a single primary standard, together with the Nernst slope, is attractive from the philosophical view, and the proponents of this scale regard the NBS multistandard scale as "overdetermined". Supporters of the multistandard scale agree that a single standard would suffice if all solutions displayed the same liquid-junction potential. In actual fact, they do not. To a large degree, the difference in view is related to the relative importance attached to reproducibility vs. interpretation of the pH numbers obtained in terms of conventional hydrogen ion activities. A detailed examination of the differences between these two approaches is thus warranted.

The phthalate reference solution, the single standard, is assigned values based, as in the NBS approach, on emf measurements of cell C and the convention of Equation 27. To avoid reduction of phthalate, the hydrogen electrodes in cell C must be coated with palladium black instead of platinum black. In a recent careful study, Bütikofer and Covington have redetermined paH for this buffer solution and critically examined earlier determinations.[53]

In the single-standard procedure, other buffers needed to fix the pH scale in practice are termed secondary buffers. Their pH values are assigned by emf measurements in the usual pH cell (type B), standardized with the primary standard solution. The liquid junctions are of the reproducible vertical capillary type for this purpose. The pH of the secondary standards is then derived by the operational formula, Equation 4, from the pH of the primary standard and the Nernst slope. No inconsistencies in the standard scale are thus apparent; the residual liquid-junction potential error, if any, is included in the pH assigned to the secondary standards. A comparison of BSI and NBS values for several buffer solutions was made by Alner and Greczek some years ago.[28] The BSI pH values have recently been modified[52] in the light of a redetermination of the pH of the primary standard[53] and are given in Table 6. The differences from the NBS values are negligible, for the most part, at 25°C between pH 3.5 and pH 10, but may exceed 0.03 unit if extended to low and high pH. In these regions of high acidity or alkalinity, the residual liquid-junction potential becomes appreciable due to the in-

creasing concentration of the highly mobile H^+ and OH^- ions. For this reason, the primary standards of the NBS scale (Table 2) are limited to the intermediate pH range.

C. Critique of Two Approaches to pH Standardization

One must bear in mind that the primary objective of pH standardization is reproducibility of the experimental pH, with the secondary objective of a meaningful interpretation. A detailed examination of these two approaches — the multistandard and the single-standard scale — reveals several difficulties. Some of these are common to both approaches, while others apply most directly to one approach or the other.

1. Reproducibility

There is good evidence that residual liquid-junction potentials between two given solutions are highly reproducible when the junctions are of the free-diffusion type with cylindrical symmetry, such as are formed in a vertical capillary tube. Since the pH(S) of the secondary standards of the single-standard scale is determined in a cell with liquid junction with the aid of a junction formed in this way, no inconsistencies appear in the standard scale of pH(S). If different standards of the multistandard scale, each individually based on the conventional paH, are used to standardize the cell, slightly different results are obtained. Figure 3 reveals the magnitude of these differences, and Table 6 offers an estimate of the uncertainties attributable to the existence of two sets of standard values.

In general, these differences are not great. More serious, however, are the errors encountered in pH measurements made with the types of commercial reference electrodes commonly used in pH meters. It may be judged from Table 4 that the residual liquid-junction potentials encountered with the capillary junction and with some commercial reference electrodes may differ by as much as 0.02 pH unit. Still larger errors have been reported with combination electrodes.[54] These errors combine with defects, if present, in the potential/pH slope of the glass electrode used in most practical pH potentiometry. For this reason, dual standardization of the pH meter, bracketing, if possible, the pH(X) values, is to be recommended.

2. Interpretation of pH Values

The multistandard scale applies the convention of Equation 27 to each of several standard reference solutions; the single-standard scale applied it to 0.05 m potassium hydrogen phthalate alone. In the former, pH(S) is a conventional paH, equally valid for each reference solution; the secondary standards of the latter include the residual liquid-junction potential error between each separate secondary standard and the single primary standard. The NBS multistandard approach can be used, in principle, also to obtain conventional paH values for buffer solutions of pH lower than 3.5 and higher than 10. This has been done for potassium tetroxalate (pH 1.6)[55] and for calcium hydroxide (pH 12.4)[56] as well as for certain amine buffers of the charge type BH^+,B (e.g., tris(hydroxymethyl)aminomethane, pH 7.4 at 37°C).[57] In addition, certain ampholytes have been suggested for use as reference solutions in "isotonic saline", I = 0.16.[29] In these instances, abnormal liquid-junction potentials in practical pH measurements have led to the designation "secondary standards" for these solutions. Their uses are threefold: (1) to provide enhanced reproducibility at low and high pH, (2) if the liquid-junction potential is primarily a function of H^+ or OH^- concentration, accurate pH measurements (in terms of paH) will result from a close matching of the pH of the standard to that of the unknown solutions, and (3) these standards of paH are useful for measurements where no liquid-junction potential is involved, as in the spectrophotometric determination of pK values (see above).

Thus one may conclude that the multistandard scale, rightly or wrongly, places more emphasis on the interpretation of the measured pH than does the single-standard scale, the values of which, in order to provide enhanced internal consistency, include the unknown liquid-junction potential error between primary and secondary standards. Yet a precise interpretation of pH in terms of paH is usually impossible at low and high pH, and secondary standards are useful in assuring improved reproducibility in these regions of the pH scale.

In the author's opinion, the conventional definition of the activity coefficient is a unifying factor that can be dealt with more straightforwardly than can the residual liquid-junction potential. In spite of the uncertainties in its determination, pH(X) on the multistandard scale approaches the conventional paH under ideal conditions, and the formal role of this quasithermodynamic quantity in equilibrium processes is clearly defined.

VI. pH IN CONSTANT IONIC STRENGTH MEDIA

Our discussion to this point has dealt with pH in dilute aqueous solutions. Many, if not most, routine pH measurements do not fall in this category. Important in commerce and industry are measurements in soils, brines, alcohol-water mixtures, suspensions, gels, tissues, and the like. In these cases, fundamental interpretations in terms of hydrogen ion are impossible and often unnecessary. The pH meter is standardized with aqueous reference solutions, reproducibility is the prime consideration, and the numbers obtained are correctly "the pH" of these diverse media.

The need for an interpretation of pH is, however, not limited to dilute aqueous solutions. Salt solutions of constant composition (clinical fluids, seawater, etc.) and mixed solvent media (alcohol-water solvents) are examples of systems where an interpretation of pH may be desired.

The term "constant ionic medium" implies a rather high and constant ionic strength, together with a substantially fixed composition. When reactions among solutes present in small concentrations relative to the total ionic strength take place in such a medium, changes in activity coefficients may be "swamped out". In addition, the potential at a liquid junction between such a medium and a concentrated bridge solution, such as saturated KCl, is stabilized.

Coordination chemists have made extensive use of constant ionic media in the study of the stabilities of metal-ligand complexes.[58,59] The simplifications afforded may make it feasible to determine pcH, from which concentration equilibrium constants K_c can be derived (see Equation 17). For this purpose, reference solutions of hydrogen ion concentration in the constant ionic medium must be available. Alternatively, it has been common practice to measure the operational pH using the NBS standards or the single-standard scale and to label the equilibrium constants so obtained as "apparent" constants. Extensive data for pK in seawater have been obtained in this way. The effect of pH scales on equilibrium constants in seawater has long been of concern.[60-62]

When a particular constant ionic medium such as 1 M NaClO$_4$ or seawater is to be studied repeatedly, a shift in standard state is inconvenient, so that activity coefficients approach unity as the concentration of "solute" approaches zero in the pure ionic medium (the "solvent"). Sillén suggested that activity coefficients on this scale would stay near unity as long as the concentrations of reactants remained less than about 10% of the concentrations of the medium ions.[63] Biedermann[64] has also set an upper limit of 0.1 M, provided the ionic medium is at least 1 M in concentration. Thermodynamic equilibrium constants and paH referred to this standard state are identical with K_c and pcH when the "solute" concentration is low.

Table 7

EVIDENCE FOR THE STABILIZATION
OF THE LIQUID-JUNCTION
POTENTIAL BY SYNTHETIC
SEAWATER

	ΔE, mV	
	H₂ electrode	Glass electrode
HCl (SwI) to Tris (SwII)	366.1	366.4
Without l.j.		
With l.j.	365.1	366.2
HCl to Bis (SwII)	410.7	411.0
Without l.j.		
With l.j.	410.1	410.8

Under certain conditions, useful values of pcH and pmH in constant ionic media can be determined by the operational formula. Thus

$$pmH~(X) = pmH~(S) - \frac{E_X - E_S}{2.3026RT/F} \tag{32}$$

The calculation of values for pmH(S) for reference buffer solutions in ionic media from cells with liquid junction[65,66] and cells without liquid junction has been considered in detail elsewhere.[67] The concept of the hydrogen ion concentration or molality is more easily understood and used than is that of the single ionic activity. Its role in equilibrium processes is clear and its application straightforward.

Seawater of 3.5% salinity may be considered as a constant ionic medium with ionic strength of 0.66 to 0.7. The thermodynamic properties of normal seawater are nearly the same as those of synthetic saline mixtures consisting only of NaCl, Na₂SO₄, and MgCl₂ in the proper proportions.[68] This conclusion is supported by the data shown in Table 7, demonstrating that synthetic seawater stabilizes the liquid-junction potential. Two synthetic seawaters of identical ionic strength corresponding to a salinity of 3.5% were prepared. One (SwII) was composed of NaCl, Na₂SO₄, MgCl₂, CaCl₂, and KCl in the proper proportions. Sodium sulfate was omitted from the other (SwI) and replaced by equivalent quantities of NaCl and NaClO₄ in order to avoid HSO₄⁻ formation in acidic media. Measurements were made in dilute HCl and in a number of buffer solutions with pH from 4 to 9 using both hydrogen electrodes and glass electrodes in cells of type B (with liquid junction) and type C (without liquid junction). The differences in emf (ΔE) between the acidic solution and two dilute alkaline buffers (Tris, 2-amino-2-hydroxymethyl-1,3-propanediol, pH 8.2; and Bis, 2-amino-2-methyl-propanediol, pH 8.9 at 25°C) were nearly identical and independent of the presence or absence of the liquid junction.[69]

As a consequence of the apparent stabilization of the liquid-junction potential and activity coefficients by the saline medium, the calculation of differences of pmH in seawater by the operational formula, Equation 32, is feasible. Standard potentials of cell C in synthetic seawater have been determined[70] and applied to the assignment of reference pmH values for Tris buffers intended for the standardization of acidity measurements in marine systems at salinities from 3.0 to 4.0%.[71]

Measurements of pH in biological and clinical media and in "isotonic saline" are of importance in the health-related fields. These media usually have a fairly constant
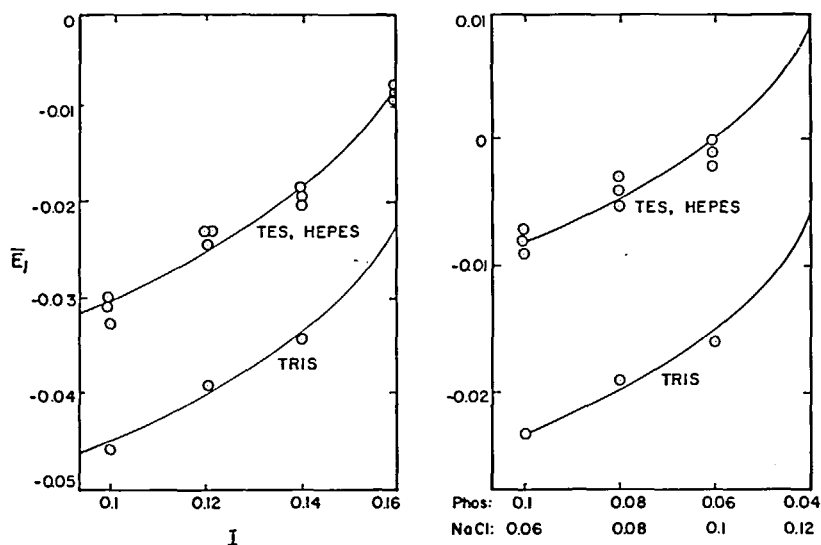
FIGURE 4.   Residual liquid-junction potential errors (in pH units) for four buffer solutions of ionic strength 0.16 as a function of the ionic strength and composition of the standard reference solution. 1:1 and 1:2 TES and 1:2 HEPES buffers contained 0.12 *m* NaCl. 1:3 Tris buffer contained 0.11 *m* NaCl. The reference standard was a phosphate buffer (1:1) and, except for I = 0.1 (left-hand plot), also contained NaCl. Right-hand plot: standard buffers of constant ionic strength 0.16; abscissa indicates contributions of 1:1 phosphate and NaCl to the total ionic strength.

ionic strength in the vicinity of 0.16. This is somewhat too high to expect the operational pH determined relative to the customary aqueous standards to approach closely to $-\log a_H$, although excellent reproducibility may be assured by the use of secondary standards with pH in the physiological range. Furthermore, the ionic strength, though substantially constant, is too low to assure the stabilization of activity coefficients and liquid-junction potentials as does seawater. A recent study[29] suggests that standard buffers of ionic strength 0.16, containing NaCl, can be assigned conventional paH values with little uncertainty, in effect placing them on the NBS scale. These special "isotonic standards" substantially eliminate the residual liquid-junction potential error in clinical pH measurements. Thus a useful interpretation of pH measurements in these media is possible.

The effect of ionic strength and composition of the standard on the residual liquid-junction error $\overline{E}_j$ (in pH units) at I = 0.16 is shown in Figure 4. Once again, $\overline{E}_j$ is given by the difference between the operational pH from cell D and the paH derived from the cell without liquid junction (cell C). For this purpose, the pH convention was extended to I = 0.16; the validity of this extension was confirmed by independent evidence. The figure shows that the error due to residual liquid-junction potentials is reduced by matching the compositions of the buffer/NaCl standards to those of the "unknown" TES, HEPES, and Tris solutions, which contained NaCl at molalities of 0.11 or 0.12 mol kg⁻¹. Abnormal liquid-junction potentials with Tris buffers are well known; they are possibly caused by a low mobility of the Tris·H⁺ ion.[72] However, a difference due to buffer charge type cannot be ruled out. Both TES and HEPES are ampholytes, forming buffer solutions of the acid/base type A^+B^-, while Tris buffers are representative of type A^+B^0. Nevertheless, the ampholytes behave in a manner consistent with the behavior of the phosphate standards, of type A^-B^-.

VII. pH IN NONAQUEOUS AND MIXED SOLVENTS

Some years ago, Van Uitert and Haas[73] achieved a practical standardization of pH measurements in dioxane-water media, and their approach, though approximate, is of continuing value. In essence, it leads to a scale of pcH based on a series of calibration curves obtained with HCl solutions of known concentration and HCl-salt mixtures in the mixed solvents. For each mole fraction of dioxane, the difference (termed log U_H) between the operation pH and the known pcH (assuming ion association to be negligible) was determined. Allowance was made for the change of log U_H with ionic strength.

It is more difficult to set up activity pH scales and reference solutions in nonaqueous and mixed solvents than in water. It is usually convenient to shift the standard state in such a way that the activity coefficients (γ_s) of solute species approach unity at low ionic strengths in the medium concerned rather than in pure water. Then

$$\gamma_s = \gamma_w/\gamma_t \tag{33}$$

where γ_w is the activity coefficient referred to the standard state of aqueous solutions and γ_t is the "transfer activity coefficient",[74] formerly known as the "medium effect".[75] This quantity is fixed by the Gibbs energy of transfer, $\Delta G_t°$, of the species (i) in question from the standard state in water to the new standard state in the non-aqueous or mixed solvent(s):

$$\Delta G_t° = \nu RT \ln \gamma_t(i) \tag{34}$$

In Equation 34, ν is the number of ions from one molecule of the solute species.

It is now clear that activity pH may be defined in two different ways, namely

$$paH = -\log m_H\gamma_w(H) = -\log m_H \cdot \gamma_s(H) \cdot \gamma_t(H) \tag{35}$$

and

$$paH^* = -\log m_H\gamma_s(H) = paH + \log \gamma_t(H) \tag{36}$$

where the asterisk is a reminder that a shift from the customary standard state has taken place.[76] Evidently paH* is a pmH value corrected for the salt effects embodied in $\gamma_t(H)$. The relationship is exactly the same as that between paH and pmH in aqueous solutions, as shown in Figure 1.

The use of a plurality of standard scales is well illustrated by the studies of acidity in mixed solvents, carried out by Hallé, Gaboriaud, and Schaal.[77,78] Electromotive force measurements of the cell (where solvent s was a mixture of water with DMSO or water with N-methylacetamide)

Pt; H₂ or glass electrode	Solution X in s	KCl, saturated in s	KCl, saturated in H₂O	Calomel	(F)
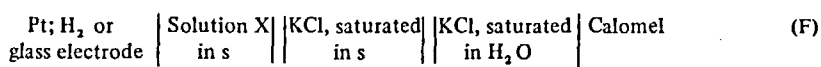
were used to determine values of the negative logarithm of the activity of solvated protons, designated pS*. Standard emf values were obtained from a study of dilute HCl solutions in each solvent mixture. The ionic strength was generally low enough (about 0.01) to permit activity coefficients to be estimated by the Debye-Hückel limit-
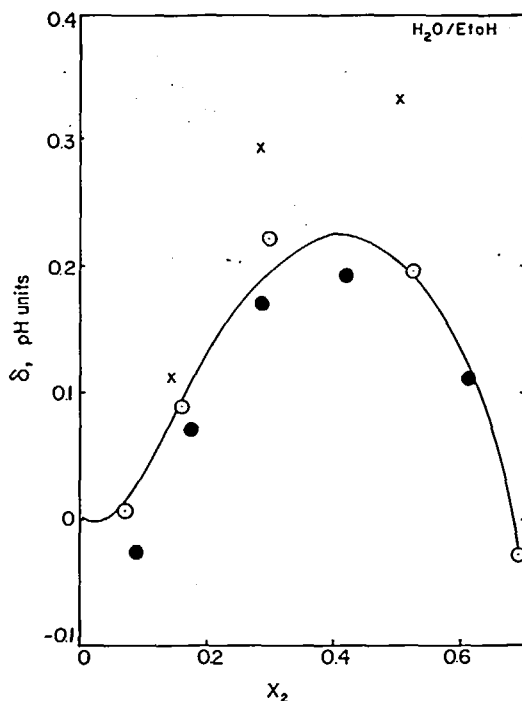
FIGURE 5.   Correction term (δ) for pH measurements
made in H$_2$O/ethanol mixed solvents as a function of
the mole fraction of ethanol. O, Reference 80; ●, Reference 81; X, Reference 82.

ing law. From the data for strong acids, strong bases, and buffer solutions, autoprotolysis constants and pK values for a considerable number of weak electrolytes were determined. The standard state and standard emf used varied with solvent composition. If the combined liquid-junction potentials remained constant for all solutions in the same medium (as the authors believed), it is apparent that pS$^+$ corresponds to paH*.

Let us now examine further the nature of the two quantities defined by Equations 35 and 36. Measurements of cells both with and without liquid junction may be combined with little ambiguity, it has been shown,[79,80] to arrive at a quantity to which both the liquid-junction potentials and the transfer activity coefficient of the proton make a contribution. We have designated this quantity δ.[80]

$$\delta \equiv \frac{E_j (s) - E_j (w)}{2.3026RT/F} - \log \gamma_t (H) = \bar{E}_j - \log \gamma_t (H) \qquad (37)$$

Here $E_j(s) - E_j(w)$ represents the change in potential across the junction: dilute buffer ‖ KCl, (saturated in H$_2$O) when the aqueous buffer is replaced by the buffer in solvent s; $\bar{E}_j$ is expressed in pH units.

Values of δ for water/ethanol solvents are plotted in Figure 5 as a function of the mole fraction of ethanol. The plot shows results obtained by two different methods in three laboratories.[80-82] When the mole fraction (x_2) of ethanol exceeds 0.7, the values of δ drop sharply and may fall below −2 in pure ethanol.

Table 8
LIQUID-JUNCTION POTENTIALS BETWEEN BUFFER SOLUTIONS IN WATER/ETHANOL SOLVENTS AND SATURATED AQUEOUS KCl AT 25°C[83]

x_2*	E_J (mV)
0	0
0.070	5
0.163	−2
0.298	−27
0.519	−37
0.696	−33
1.0	−73

* Mole fraction of ethanol.

When one uses the operational pH scale with aqueous standards to determine pH in nonaqueous and mixed solvents, he is attempting a measurement of paH, for his standards of reference are based on the aqueous standard state. He is nonetheless doomed to failure, for the residual liquid-junction potential error will, it seems certain, be large.[83] The conclusion of Schwabe and Geisler[84] that interfacial potentials are negligible cannot be substantiated.[85]

Formally, this operational pH differs by an amount $\overline{E}_j$ from the "true" paH,

$$paH = pH - \overline{E}_j \tag{38}$$

whereas it differs from the "true" paH* by an amount δ:

$$paH^* = pH - \delta \tag{39}$$

Since the correction terms δ are more accessible than either $\overline{E}_j$ or $\gamma_t(H)$, Equation 39 offers a possible route to paH* values without the need for reference solutions in each different solvent medium. Nevertheless, the highest reproducibility in pH measurements cannot be achieved if the electrodes are immersed in an aqueous medium for standardization and then moved suddenly to a medium of different water activity.

To evaluate the residual liquid-junction potential error (first term on the right of Equation 37), one needs to know the transfer activity coefficient for the proton. Various approaches to the determination of this quantity have been utilized.[75,81,86,87] In recent years, however, the tetraphenylborate method has shown increasing promise. This approach is based on the assumption of equivalence of the transfer activity coefficients of the cation and anion of reference electrolytes such as tetraphenylarsonium tetraphenylborate and tetraphenylphosphonium tetraphenylborate. The theoretical calculations of Kim[88] lend support to this procedure, confirming the approximate equivalence of the solvation energies of the tetraphenylarsonium and tetraphenylborate ions. If one adopts the tetraphenylarsonium and tetraphenylphosphonium salts as reference electrolytes, the residual liquid-junction potentials between dilute buffer solutions in water and in water-ethanol solvents may contribute an error exceeding 1 pH unit in alcohol-rich media, as the data of Table 8 illustrate.[83]

Strict intercomparisons of pH numbers in different solvents would require that a single reference state be maintained for all media. The paH would fulfill this requirement if experimental problems associated with the boundary potential did not arise.
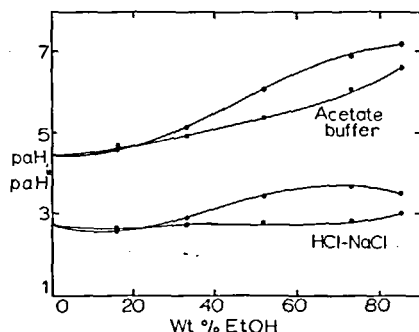
FIGURE 6.   Comparison of paH (dots) with paH* (squares) in water/ethanol solvents.

An alternative solution to the problem would be provided by the availability of transfer energies or transfer activity coefficients for the proton in all solvent media of interest. A complete answer must await the elucidation of the varied interactions between solutes and solvents of different structures and properties. It is impossible at the present time to set up reference buffer solutions for paH(S) with which to standardize an operational scale capable of providing a meaningful intercomparison of acidities in solvent media of widely different compositions.

The estimation of γ_s in dilute solutions poses less of a problem than does the evaluation of γ_t. At low ionic strengths, where long-range electrostatic ion-ion interactions predominate, the Debye-Hückel theory is useful. It is therefore possible to establish standards of paH* by a procedure precisely analogous to that by which the NBS standards of paH in aqueous solutions were assigned.[5,76,89] The standard emf E°* for cell C in each solvent medium is required for the calculation of $p(a_H\gamma_{Cl})^*$ by Equation 18. The convention of Equation 26 is retained, with appropriate changes in the constants A and B, which vary with temperature, dielectric constant, and density of the medium. This procedure, with $\mathring{a} = 4.57\mathring{A}$ as in water, has been used to standardize an operational scale of pH* in 50 wt % water/methanol[89]

$$pH^*(X) = pH^*(S) - \frac{E_X - E_S}{2.3026RT/F} \qquad (40)$$

A similar procedure has led to standard reference solutions for pD in deuterium oxide.[90]

deLigny and co-workers[82,91] have recommended reference solutions for pH* in both H_2O/methanol and H_2O/ethanol mixtures over a considerable range of solvent compositions. Their experimental procedure was very similar to that just described. To reduce the uncertainty in the choice of a convention for γ_{Cl}^*, however, they chose buffers of low ionic strength (about 0.01) and calculated γ_{Cl}^* by the Debye-Hückel equation with extended terms.[92]

Operational scales of this sort are successful only if the potential across the junction — buffer in solvent s ‖ KCl, saturated in H_2O — is reasonably constant as the buffer and pH* are changed without altering the composition of the solvent s. This has been shown to be the case in H_2O/methanol mixtures from 0 to 68 wt % methanol.[80]

It is unfortunately true that a single "universal" pH scale for all solvents cannot be realized at the present time. For certain alcohol-water media, however, reliable values of the transfer activity coefficient of the proton $\gamma_t(H)$ permit paH to be derived from

paH* by Equation 36. Figure 6 compares paH for a dilute acetate buffer and for dilute mixtures of HCl and NaCl with their paH* values in water/ethanol solvents. The experimental data were obtained by Bates and Schwarzenbach,[93] and the transfer activity coefficients are the mean values based on the reference electrolytes tetraphenylarsonium tetraphenylborate and tetraphenylphosphonium tetraborate.[83] The calculations of paH* were made by Equations 18, 26, and 36.

The practical alternative to a universal paH scale is to base the pH scale on a different standard state in each solvent medium or each mixed solvent composition. This unit is designated pH*. In so doing, one preserves the significance of relative acidity in the same solvent while sacrificing the possibility of an exact comparison of acidities in different media. Measurements of pH* can be made with aqueous standards by Equation 39, provided δ corrections have been tabulated for the solvents and solvent mixtures concerned. Otherwise, one uses standards of pH* based on a determination of the conventional paH* for reference solutions in solvents of the same compositions as those of the "unknowns". Reproducible data may be expected, but the same restrictions hold as for measurements in aqueous solutions, namely, no interpretation is allowable unless the unknown solutions match closely the standards with respect to low ionic strength, pH range, temperature, and solvent composition. When these ideal conditions are approached, the experimental pH* should be regarded as approaching $-\log a_H^*$ and can be so used in equilibrium calculations along with activity coefficients consistent with the convention for γ_{Cl} (e.g., Equation 26) on which the reference values were based.

VIII. CONCLUSIONS

One may well despair of ever finding a concise and fully adequate answer to the question "How is pH defined?" The following points must be borne in mind.

1. The experimental pH value for an "unknown" (X) is an operational quantity derived from the relationship

$$pH\ (X) = pH\ (S) - \frac{E_X - E_S}{2.3026RT/F}$$

where E_x and E_s represent the emf of a pH cell

Reference electrode	Solution X or standard S	H_2 electrode, glass electrode, or other indicator electrode for H^+ ions

containing solution X or a standard reference solution (S) of assigned pH(S).

2. The pH(S) values for each of the reference solutions of the NBS "multistandard" scale represent $-\log a_H$, where a_H is a defined or conventional hydrogen ion activity. Small differences in the standardization of the above cell with liquid junction, depending on which standard is chosen, may therefore be found. Under ideal conditions (pH 3.5 to 10, ionic strength 0.1 or less, aqueous solvent) such that the residual liquid-junction potential can be neglected, however, the experimental pH falls on, or close to, this conventional activity scale and can be so interpreted.

3. The pH(S) values for the primary standard of the British "single-standard" scale

are also based on −log a_H, but other secondary standards are assigned values determined by the operational formula with the pH cell above. Consequently, these values include a residual liquid-junction potential and the interpretation of experimental pH(X) values is less straightforward. Primary and secondary standards, however, should furnish the same standardization of the pH cell.

4. The operational pH is free from restrictions as to the ionic strength, solvent medium, and the like. However, severe limitations are placed on the interpretation of pH numbers, as mentioned above. Nevertheless, the useful interpretation of pH in certain "constant ionic media", e.g., clinical fluids (I = 0.16), may be improved by the establishment of conventional activity standards especially for these media.

5. In constant ionic media of elevated ionic strength (e.g., 1 M NaClO$_4$, seawater, etc.), an operational scale of hydrogen ion concentration or molality, pcH or pmH, is a practical expedient.

6. The interpretation of operational pH values in nonaqueous and mixed solvent systems measured with dilute aqueous standards is not usually successful. It is likewise not feasible to determine reference values of paH in these media if the aqueous standard state is to be retained. Activity standards pH*(S) based on a different standard state in each medium can nonetheless be set up and provide a practical alternative to a "universal" pH scale. With these, operational scales of pH* can be defined. The pH* is not a single scale but a succession of independent scales. Consequently, pH* does not permit a comparison of acidities in different solvent media.

7. Students should be instructed (1) that pH is defined operationally, as set forth above; (2) that in dilute solutions of simple solutes pH may be regarded to approach a conventional −log a_H; and (3) that for equilibrium calculations at ionic strengths (I) less than 0.1 activity coefficients of ions (i) of charge z_i can be estimated by the Debye-Hückel equation in the form

$$\log \gamma_i = \frac{-Az_i^2 I^{\frac{1}{2}}}{1 + 1.5I^{\frac{1}{2}}}$$

ACKNOWLEDGMENTS

REFERENCES

1. Bates, R. G., *Chem. Rev.*, 42, 1 (1948).
2. Sørensen, S. P. L., *Biochem. Z.*, 21, 131, 201 (1909); *C. R. Trav. Lab. Carlsberg*, 8, 1, (1909).
3. Kolthoff, I. M., *Recl. Trav. Chim. Pays-Bas*, 49, 201 (1930).
4. Bates, R. G., *J. Res. Natl. Bur. Stand.*, 66A, 179 (1962).
5. Bates, R. G., *Determination of pH, Theory and Practice*, 2nd ed., John Wiley & Sons, New York, 1973, 73.
6. Sørensen, S. P. L. and Linderstrom-Lang, K., *C. R. Trav. Lab. Carlsberg*, 15(6) (1924).
7. MacInnes, D. A., *Science*, 108, 693 (1948).

8. IUPAC, *Manual of Symbols and Terminology for Physicochemical Quantities and Units*, Pergamon Press, Oxford, 1979, 28.

9. Harned, H. S. in *A Treatise on Physical Chemistry*, Vol. 2, Taylor, H. S., Ed., D. Van Nostrand, New York, 1924, 782.

10. Guggenheim, E. A., *J. Am. Chem. Soc.*, 52, 1315 (1930).

11. Bjerrum, N., *Z. Physik. Chem. (Leipzig)*, 53, 428 (1905); *Z. Elektrochem.*, 17, 389 (1911).

12. Guggenheim, E. A., *J. Phys. Chem.*, 34, 1758 (1930).

13. Brønsted, J. N., Delbanco, A., and Volqvartz, K., *Z. Physik. Chem. (Leipzig)*, A162, 128 (1932).

14. Frank, H. S., *J. Phys. Chem.*, 67, 1554 (1963).

15. Kortüm, G., *Elektrolytlosungen*, Becker und Erler Kom.-Ges., Leipzig, 1941, chap. 12.

16. Bates, R. G. and Guggenheim, E. A., *Pure Appl. Chem.*, 1, 163 (1960).

17. Bates, R. G., *Denki Kagaku*, 46, 480 (1978).

18. Hitchcock, D. I., *J. Am. Chem. Soc.*, 58, 855 (1936).

19. Bates, R. G. and Gary, R., *J. Res. Natl. Bur. Stand.*, 65A, 495 (1961).

20. Bates, R. G., *Determination of pH, Theory and Practice*, 2nd ed., John Wiley & Sons, New York, 1973, appendix table 7.

21. Bates, R. G. and Schwarzenbach, G., *Helv. Chim. Acta*, 37, 1069 (1954).

22. Bates, R. G. and Smith, E. R., *J. Wash. Acad. Sci.*, 38, 61 (1948).

23. MacInnes, D. A., *J. Am. Chem. Soc.*, 37, 2301 (1915).

24. MacInnes, D. A., *The Principles of Electrochemistry*, Dover Publications, New York, 1961, 224.

25. Planck, M., *Ann. Physik*, 39(3), 161 (1890).

26. Henderson, P., *Z. Physik. Chem. (Leipzig)*, 59, 118 (1907); 63, 325 (1908).

27. Morf, W. E., *Anal. Chem.*, 49, 810 (1977).

28. Alner, D. J., Greczek, J. J., and Smeeth, A. G., *J. Chem. Soc. A*, 1205 (1967).

29. Bates, R. G., Vega, C. A., and White, D. R., Jr., *Anal. Chem.*, 50, 1295 (1978).

30. White, D. R., Jr., unpublished data, University of Florida, Gainesville, 1979.

31. MacInnes, D. A., *J. Am. Chem. Soc.*, 41, 1086 (1919).

32. Kielland, J., *J. Am. Chem. Soc.*, 59, 1675 (1937).

33. Guggenheim, E. A., *Phil. Mag.*, 19(7), 588 (1935).

34. Guggenheim, E. A. and Turgeon, J. C., *Trans. Faraday Soc.*, 51, 747 (1955).

35. Davies, C. W., *Ion Association*, Butterworths, London, 1962, 39.

36. Whitfield, M., *Deep Sea Res.*, 21, 57 (1973).

37. Whitfield, M., *Mar. Chem.*, 3, 197 (1975).

38. Bjerrum, N., *Z. Anorg. Allg. Chem.*, 109, 275 (1920).

39. Stokes, R. H. and Robinson, R. A., *J. Am. Chem. Soc.*, 70, 1870 (1948).

40. Glueckauf, E., *Trans. Faraday Soc.*, 51, 1235 (1955).

41. Bates, R. G., Staples, B. R., and Robinson, R. A., *Anal. Chem.*, 42, 867 (1970).

42. Bates, R. G. and Robinson, R. A., in *Ion-Selective Electrodes*, Pungor, E., Ed., Akadémiai Kiadó, Budapest, 1978.

43. Robinson, R. A. and Stokes, R. H., *Electrolyte Solutions*, 2nd ed., Butterworths, London, 1970, appendix 8.10.

44. Harned, H. S. and Ehlers, R. W., *J. Am. Chem. Soc.*, 54, 1350 (1932); 55, 652 (1933).

45. Harned, H. S. and Embree, N. D., *J. Am. Chem. Soc.*, 57, 1669 (1935).

46. Hamer, W. J. and Acree, S. F., *J. Res. Natl. Bur. Stand.*, 23, 647 (1939).

47. Bates, R. G., *J. Res. Natl. Bur. Stand.*, 39, 411 (1947).

48. Bates, R. G., *Determination of pH, Theory and Practice*, 2nd ed., John Wiley & Sons, New York, 1973, chap. 4.

49. ASTM, *Standard Test Method for pH of Aqueous Solutions With the Glass Electrode*, ANSI/ASTM E70-78, ASTM, Philadelphia, 1978.

50. IUPAC, *Manual of Symbols and Terminology for Physicochemical Quantities and Units*, Pergamon Press, Oxford, 1979, 30.

51. BSI, *Specification for pH Scale*, British Standard 1647:1961, British Standards Institution, London, 1961.

52. Covington, A. K., unpublished reports to IUPAC, ISO, and IEC, 1978—1979.

53. Bütikofer, H. P. and Covington, A. K., *Anal. Chim. Acta*, 108, 179 (1979).

54. Ladenson, J. H. and Bell, C. E. Jr., *Clin. Chem. (Winston-Salem, N.C.)*, 21, 255 (1975).

55. Bower, V. E., Bates, R. G., and Smith, E. R., *J. Res. Natl. Bur. Stand.*, 51, 189 (1953).

56. Bates, R. G., Bower, V. E., and Smith, E. R., *J. Res. Natl. Bur. Stand.*, 56, 305 (1956).

57. Durst, R. A. and Staples, B. R., *Clin. Chem. (Winston-Salem, N.C.)*, 18, 206 (1972).

58. Schwarzenbach, G., *Helv. Chim. Acta*, 33, 947 (1950).

59. Rossotti, F. J. C. and Rossotti, H., *The Determination of Stability Constants*, McGraw-Hill, New York, 1961.

60. Hawley, J. E. and Pytkowicz, R. M., *Mar. Chem.*, 1, 245 (1973).
61. Almgren, T., Dyrssen, D., Elgquist, B., and Johansson, O., *Mar. Chem.*, 4, 289 (1976).
62. Bates, R. G. and Culberson, C. H., in *The Fate of Fossil Fuel CO₂ in the Oceans,* Andersen, N. R. and Malahoff, A., Eds., Plenum Press, New York, 1977, 45.
63. Sillén, L. G., in *Equilibrium Concepts in Natural Water Systems,* Stumm, W., Ed., Advances in Chemistry Series No. 67, American Chemical Society, Washington, D.C., 1967, 45.
64. Biedermann, G., in *The Nature of Seawater,* Goldberg, E. D., Ed., Physical and Chemical Science Reports No. 1, Dahlem Konferenzen, Berlin, 1975, 339.
65. Biedermann, G. and Sillén, L. G., *Ark. Kemi,* 5, 425 (1953).
66. McBryde, W. A. E., *Analyst (London),* 94, 337 (1969); 96, 739 (1971).
67. Bates, R. G., *Determination of pH, Theory and Practice,* 2nd ed., John Wiley & Sons, New York, 1973, chap. 9.
68. Hansson, I., Ahrland, S., Bates, R. G., Biedermann, G., Dyrssen, D., Högfeldt, E., Martell, A. E., Morgan, J. J., Schindler, P. W., Warner, T. B., and Whitfield, M., in *The Nature of Seawater,* Goldberg, E. D., Ed., Dahlem Konferenzen, Berlin, 1975, 263.
69. Bates, R. G. and Macaskill, J. B., in *Analytical Methods in Oceanography,* Gibb, T. R. P., Jr., Ed., Advances in Chemistry Series No. 147, American Chemical Society, Washington, D.C., 1975, 110.
70. Khoo, K. H., Ramette, R. W., Culberson, C. H., and Bates, R. G., *Anal. Chem.*, 49, 29 (1977).
71. Ramette, R. W., Culberson, C. H., and Bates, R. G., *Anal. Chem.*, 49, 867 (1977).
72. Klein, S. D. and Bates, R. G., *J. Solution Chem.*, 9, 289, 1980.
73. Van Uitert, L. G. and Haas, C. G., *J. Am. Chem. Soc.*, 75, 451 (1953).
74. Trémillon, B. and Coetzee, J. F., *Pure Appl. Chem.*, 50, 591 (1978).
75. Popovych, O., *Crit. Rev. Anal. Chem.*, 1, 73 (1970).
76. deLigny, C. L., Luykx, P. F. M., Rehbach, M., and Wieneke, A. A., *Recl. Trav. Chim. Pays-Bas,* 79, 699 (1960).
77. Hallé, J. C., Gaboriaud, R., and Schaal, R., *Bull. Soc. Chim.,* 1851 (1969); 2047 (1970).
78. Hallé, J. C., Harivel, R., and Gaboriaud, R., *Can. J. Chem.,* 52, 1774 (1974).
79. deLigny, C. L., and Rehbach, M., *Recl. Trav. Chim. Pays-Bas,* 79, 727 (1960).
80. Bates, R. G., Paabo, M., and Robinson, R. A., *J. Phys. Chem.*, 67 1833 (1963).
81. Gutbezahl, B. and Grunwald, E., *J. Am. Chem. Soc.*, 75, 565 (1953).
82. Gelsema, W. J., deLigny, C. L., Remijnse, A. G., and Blijleven, H. A., *Recl. Trav. Chim. Pays-Bas,* 85, 647 (1966).
83. Popovych, O., Gibofsky, A., and Berne, D. H., *Anal. Chem.*, 44, 811 (1972).
84. Schwabe, K. and Geisler, H., *Electrochim. Acta,* 12, 147 (1967).
85. Alfenaar, M. and deLigny, C. L., *Electrochim. Acta,* 13, 662 (1968).
86. Parker, A. J., *Chem. Rev.*, 69, 1 (1969).
87. Popovych, O. and Dill, A. J., *Anal. Chem.*, 41, 456 (1969).
88. Kim, J. I., *J. Phys. Chem.*, 82, 191 (1978).
89. Paabo, M., Robinson, R. A., and Bates, R. G., *J. Am. Chem. Soc.*, 87, 415 (1965).
90. Paabo, M. and Bates, R. G., *Anal. Chem.*, 41, 283 (1969).
91. deLigny, C. L., Luykx, P. F. M., Rehbach, M., and Wieneke, A. A., *Recl. Trav. Chim. Pays-Bas,* 79, 713 (1960).
92. Gronwall, T. H., LaMer, V. K., and Sandved, K., *Phys. Z.*, 29, 358 (1928).
93. Bates, R. G. and Schwarzenbach, G., *Helv. Chim. Acta,* 38, 699 (1955).