# DEFINITIONS OF pH SCALES[1]

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## I. INTRODUCTION

There is an increasing demand for accurate pH measurements in industry as well as in the research laboratory. Commercial pH meters, some of which are claimed to yield pH values reproducible to 0.005 pH unit, are found in nearly every laboratory where chemical analyses and tests are performed. These instruments almost universally utilize glass electrodes and calomel electrodes. They measure the acidity or alkalinity of the aqueous solution under examination with reference to a standard buffer solution with which the meter is calibrated from time to time.

Unfortunately, progress toward an accepted definition of pH has not kept pace with the development of devices for pH measurement, and a given solution may be assigned different pH values in different laboratories. Although adoption of different symbols has been urged (88, 98, 153), 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. This state of confusion results in part from the impossibility of determining exactly

either $-\log m_H$ or $-\log a_H$, where $m_H$ and $a_H$ are, respectively, the molality and the activity of hydrogen (hydronium) ion,[2] for a buffer solution of moderate concentration.

A large part of the present confusion would be removed if, by general agreement, a single scale of pH were adopted. It is the purpose of this paper to set forth the advantages and limitations of several possible units of acidity, in an effort to choose the most suitable scale. The assumptions that underlie the calculation of hydrogen-ion activity from the electromotive force of cells with and without liquid junction will be discussed.

## II. THE SØRENSEN pH AND SCALES OF CONCENTRATION AND ACTIVITY

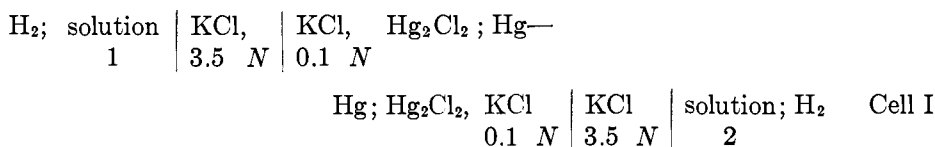Sørensen (149) defined the pH value, which will be written pcH, as

$$pcH \equiv -\log c_H \tag{1}$$

where $c$ is the molar concentration. We shall see presently that the pH value obtained by the operations and calculations specified by Sørensen is not, as he intended, a measure of hydrogen-ion concentration.
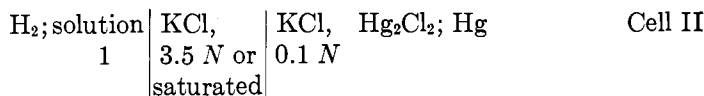
When the pH unit was first defined, it was believed that the partial molal free energy of transfer of hydrogen ion, $\Delta F$, could be expressed exactly by the classical equation,

$$\Delta F = RT \ln (c_{H_1}/c_{H_2}) = -\mathbf{F}E \tag{2}$$

where $\mathbf{F}$ is the faraday, $R$ and $T$ are, respectively, the gas constant and the absolute temperature, and $E$ is the electromotive force of the concentration cell,

$$H_2; \text{ solution} \left| \begin{matrix} KCl, \\ 3.5 \ N \end{matrix} \right| \begin{matrix} KCl, & Hg_2Cl_2 ; Hg- \\ 0.1 \ N \end{matrix}$$

$$Hg; Hg_2Cl_2, KCl \left| \begin{matrix} KCl \\ 0.1 \ N \end{matrix} \right| \begin{matrix} \text{solution}; H_2 \quad \text{Cell I} \\ 3.5 \ N \end{matrix} \begin{matrix} \\ 2 \end{matrix}$$

corrected for the liquid-junction potentials between 3.5 $N$ potassium chloride and solutions 1 and 2. The liquid junctions in cell I are indicated by vertical lines. Sørensen (150, 151, 152) based his pH scale on E.M.F. measurements of cell I with the use of solutions of hydrochloric acid and mixtures of hydrochloric acid and sodium or potassium chlorides as solution 1. It was assumed that the values of $c_{H_1}$ in these reference solutions were given by $\alpha M$, where $M$ was the molar concentration of hydrochloric acid, and $\alpha$, the classical degree of dissociation of hydrochloric acid, was computed from measurements of electrolytic conductance. For convenience, this standard was expressed in terms of $E^0$, the electromotive force of the cell,

$$H_2; \text{solution} \left| \begin{matrix} KCl, \\ 3.5 \ N \text{ or} \\ \text{saturated} \end{matrix} \right| \begin{matrix} KCl, & Hg_2Cl_2; Hg \\ 0.1 \ N \end{matrix} \qquad \text{Cell II}$$

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[2] The term "hydrogen ion" will hereafter refer to the hydrated proton. The term "pH measurement" will refer to measurements of acidity in general, without indicating the scale used.

when the hydrogen-ion concentration in solution 1 was 1 normal. The liquid-junction potential is not included in the value of $E^0$. Cell II could then be used, it was supposed, to compute the pH values of other solutions by the following equation,

$$E = E^0 - \frac{RT}{\mathbf{F}} \ln c_{\mathbf{H}} \qquad (3)$$

in which $E$ is again corrected for the difference of potential across the liquid junction.

Conversion of equation 3 to common logarithms and substitution of Sørensen's definition of pH and his value of $E^0$ for cell II at 25°C. (149, 152, 153) gives

$$psH \equiv \frac{E - 0.3376}{0.05914} \qquad (4)$$

The pH values computed by this equation will be designated psH.

The advent of modern chemical thermodynamics and new concepts of electrolytic solutions clarified the meaning of psH in some degree but did not offer a unique solution to the problem of measuring acidity. Modified definitions of pH have appeared but have failed to supplant the older ones. The activity has superseded the concentration in equations for free energy, and it is now realized that neither the activity nor the concentration of hydrogen ion can be derived from $\alpha M$ for a solution of a strong acid, yet Sørensen's pH scale continues to be commonly used. It is evident that the psH value is neither $-\log c_{\mathbf{H}}$ nor $-\log \mathbf{a_H}$.

From the form of the newer free-energy equation, it was reasonable to define a new pH value (153),

$$paH \equiv -\log \mathbf{a_H} \qquad (5)$$

where $\mathbf{a_H}$ is $f_{\mathbf{H}} c_{\mathbf{H}}$ or $f_{\mathbf{H}} m_{\mathbf{H}}$ and $f$ is the activity coefficient corresponding to the scale of concentration.[3] The psH value is nearly equal to $-\log 1.1 \mathbf{a_H}$ (84, 90, 153). Hence

$$paH = psH + 0.04 \qquad (6)$$

Equation 6 is very satisfactory from a practical viewpoint as a formula for converting to the activity basis the extensive tables of Sørensen values given by Clark (25), Britton (19), and others.

Adoption of equation 5 as the definition of an acidity function obviously will not, of itself, fix a scale of paH. If cell II or a similar one is used, the standardiza-

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[3] The standard state of unit activity coefficient at infinite dilution requires that activity on the scales of volume concentration ($M$, $N$, or $c$) and on the molal ($m$) scale shall be related by $\mathbf{a}_M = \mathbf{a}_m d^0$, where $d^0$ is the density of water. Thus, for a given solution,

$$(paH)_m - (paH)_M = \log d^0$$

At temperatures below 25°C., paH values on the two scales differ by 0.001 or less. At 60°C. the difference is 0.007, and at 100°C., 0.019. The value of $E^0$ likewise reflects a change in standard state and scale of concentration. Hereafter the molal scale will be used. All values of E.M.F. are given in international volts.

tion of the scale will depend upon whether an attempt is made to evaluate the potential difference at the liquid junction and the manner in which the evaluation or correction is made. In the use of cell II to determine differences of $-\log a_H$, as is usually done, the problem is formally simplified but remains unsolved. A consideration of the thermodynamics of the cell reveals why this is so.

The chemical reaction in cell II, apart from ion transfer across the liquid junctions, is

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Hg_2Cl_2(s) = Hg(l) + H^+ \text{ (in solution 1)} + Cl^- \text{(in 0.1 } N \text{ KCl)} \quad (7)$$
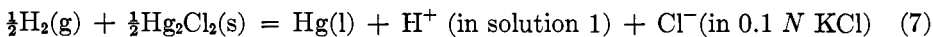
The observed E.M.F. of the cell, $E$, corrected to a partial pressure of 760 mm. of hydrogen, is given by

$$E = E^0 - \frac{2.303RT}{F} \log a_H a_{Cl} + E_j \tag{8}$$

or

$$\frac{F(E - E^0 - E_j)}{2.303RT} = \text{paH} - \log a_{Cl} \tag{8a}$$

where $E_j$ is the algebraic sum of the liquid-junction potentials. It should be noted that $E^0$ now refers to the standard state of unit activity instead of unit concentration. It is the electromotive force of a hypothetical cell of type II, corrected for the liquid-junction potential, in which each of the reactants and products of the cell reaction is present at unit activity.

In equation 8, $a_H$ represents the activity of hydrogen ion in solution 1, and $a_{Cl}$ is the activity of chloride ion in the solution of potassium chloride in contact with the calomel electrode. Hence $a_H a_{Cl}$ is not accessible to direct measurement, and $E_j$ cannot be obtained from equation 8. Furthermore, $E_j$ can never be calculated without an extrathermodynamic assumption to relate the activity coefficients of the ions. Partial corrections, made without consideration of the activity coefficients of ions transferred across the boundary, may in unfavorable instances even be worse than no corrections (43). Accurate determinations of $-\log a_H$ by means of concentration cells with transference are, however, possible under certain conditions with the aid of the Debye–Hückel limiting law in the region of its validity (at ionic strengths of 0.002 or below).[4] In certain special cases, a function of the electromotive force can be extrapolated to a limiting condition that is amenable to thermodynamic treatment (120, 121, 122). The difference of paH between two solutions is, by equation 8a,

$$\frac{F(E_1 - E_2)}{2.303RT} = (\text{paH})_1 - (\text{paH})_2 + \frac{F(E_{j_1} - E_{j_2})}{2.303RT} \tag{9}$$

[4] Kortüm (93) has discussed this method of calculating the liquid-junction potential and the related experiments of Hermans (71, 72, 73). Unfortunately, only the potential at the interface between simple solutions of the same electrolyte can be obtained, and the ionic strengths must be extremely low. In this connection, the computation of diffusion potentials and ionic activity coefficients described by Szabó (155, 156, 157) is of interest.

If the last term of equation 9 can be reduced to small values, a difference of paH can be obtained. Standardization of the cell with a solution of known or assigned paH then makes it possible to compute the paH of the second or unknown solution.

The activity of chloride ion, $\mathbf{a}_{Cl}$, in equation 8a is unknown. It is constant, however, when the same reference electrode is used. For this reason it will be convenient to define a quantity, $E^{0\prime}$, as follows:

$$E^{0\prime} \equiv E^0 - \frac{2.303RT}{\mathbf{F}} \log \mathbf{a}_{Cl} \tag{10}$$

From equations 8a and 10 we have

$$\text{paH} = -\log f_H m_H = \frac{\mathbf{F}(E - E^{0\prime} - E_j)}{2.303RT} = \frac{E - (E^{0\prime} + E_j)}{k} \tag{11}$$

and the equivalent expression,

$$E^{0\prime} + E_j = E - k \,(\text{paH}) \tag{11a}$$

The symbol $k$ will be written for $2.3026RT/\mathbf{F}$. At 25°C., equation 11 becomes[5]

$$\text{paH} = \frac{E - (E^{0\prime} + E_j)}{0.05914} \tag{12}$$

The form of equation 12 is identical with that of equation 4.

Use of equations 11 and 12 to determine the paH of so-called unknowns entails the use of previously determined values of $E^{0\prime} + E_j$ or a redetermination of $E^{0\prime} + E_j$ at the time of measurement by calibration of the cell with a reference solution of known or assigned paH (equation 9). These two procedures will receive further attention in a later section. The equality of the potential difference across the junctions, reference|KCl and unknown|KCl, is implied in both.

A 3.5 $M$ solution of potassium chloride or saturated solution (4.80 $m$ or 4.16 $M$ at 25°C.) is customarily interposed between the unknown solution and the reference electrode of cell II in an attempt to reduce the magnitude of the junction potentials, and presumably the differences among the potentials, between potassium chloride and the many different solutions that are employed as standards and unknowns. A concentrated solution of ammonium nitrate is not as effective as saturated potassium chloride for this purpose (15), but mixed chlorides and nitrates appear to possess certain advantages (106). The bridge solution of potassium chloride is often regarded as reducing the residual liquid-junction potential to a few tenths of a millivolt, when the pH of each solution forming the boundary is greater than 3 and less than 11 (88, 123).

The inequalities among the mobilities of ions other than hydrogen and hydroxyl are not large. When the buffer solution is neither strongly acid nor strongly alkaline, the concentrations of these excessively mobile ions are negligible. The tendency is toward a small, though constant, diffusion potential rather than complete elimination of it (25).

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[5] Values of $k$ at other temperatures can be found in reference 105.

Inasmuch as the equality of the potentials at the interfaces between a saturated solution of potassium chloride and two different buffer solutions can never be affirmed, a series of buffer standards of known paH (if these values can be assigned) will yield a scale for the most part lacking in thermodynamic rigor. The residual error in paH, equal to $(E_{i_1} - E_{i_2})/0.05914$ at 25°C., cannot readily be avoided. Bjerrum (14, 15) has attempted to eliminate the diffusion potential by using both 1.75 $M$ and 3.5 $M$ potassium chloride as bridge solutions in cell II. The observed difference in electromotive force was employed as an extrapolation term to render the elimination more complete than could be obtained with a saturated solution of potassium chloride alone.

Sørensen and Linderstrøm-Lang (153) found that the Bjerrum extrapolation gave substantially the same result as the interposition of saturated potassium chloride, so long as the solutions studied were neither very acid nor very alkaline. Only when the observed difference of electromotive force is small is there justification for assuming that the liquid-junction potential has been eliminated by the Bjerrum extrapolation (2, 18). A solution formed by saturating the electrode liquid with potassium chloride has sometimes been interposed between the electrode liquid and the bridge of saturated potassium chloride in an attempt to reduce the liquid-junction potential (111, 112). In his monograph, Clark advocated the universal use of the bridge solution of saturated potassium chloride and the abandonment of all attempts to correct the electromotive force for diffusion potentials in the determination of psH (25). Michaelis (110), in recommending the use of saturated potassium chloride, admits the possible advantage of the Bjerrum extrapolation in measurements of solutions in which the concentration of hydrogen ion or hydroxyl ion exceeds 0.001 gram-ion per liter.

### III. pH SCALES WITH THERMODYNAMIC SIGNIFICANCE

All thermodynamic methods yield mean activity coefficients, $f_{\pm}$, and not ionic activities. A scale of paH must therefore embrace a non-thermodynamic formula which permits an ionic activity coefficient to be derived from an experimentally determined combination of activity coefficients of two or more ionic species. A plausible separation for dilute solutions of a uni-univalent electrolyte is

$$f_+ = f_- = f_{\pm} \tag{13}$$

For some standard buffer solutions, in which the total salt concentration may exceed 0.1 $m$, such an assumption is certainly not justified.

The definition of a unit of acidity, ptH, with thermodynamic meaning,

$$\text{ptH} \equiv -\log m_{\text{H}} f_{\pm} \tag{14}$$

avoids a part of this difficulty. Equation 14 is formally less objectionable than equation 5. The ptH value has significance, however, only in those solutions for which the mean activity of acid can be measured or calculated, and this is not always a simple task. In mixtures, the term "mean activity coefficient of acid" is ambiguous, unless the particular anion to be associated with the hydrogen ion is specified. The ptH value is evidently related to paH by

$$\text{ptH} = \text{paH} + \log (f_{\text{H}}/f_{\pm}) \tag{15}$$

Hitchcock (74) has suggested the use of cells without liquid junction of the type,

$$\text{H}_2; \frac{\text{solution}}{\text{containing Cl}^-}, \text{AgCl}; \text{Ag} \qquad \text{Cell III}$$
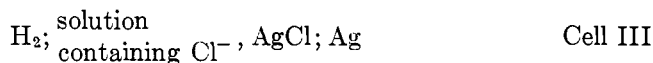
for the determination of acidity. The unknown solution must contain chloride ion in an amount known within 1 per cent, if an accuracy within a few thousandths of a pH unit is to be attained. It must also be free of substances that disturb the potential of the silver–silver chloride electrode (126) or that are catalytically reduced at the hydrogen electrode (46). The solution should preferably be free of dissolved air (147).

The electromotive force of cell III is given by

$$\frac{\text{F}(E - E^0)}{2.3026RT} + \log m_{\text{Cl}} = -\log (f_{\text{H}} f_{\text{Cl}} m_{\text{H}}) \qquad (16)$$

Guggenheim (34) and Hitchcock (74) have pointed out the advantage of a unit of acidity which will be called pwH,

$$\text{pwH} \equiv -\log (f_{\text{H}} f_{\text{Cl}} m_{\text{H}}) \qquad (17)$$

and which can be determined exactly from measurements of cell III or a similar cell without liquid junction. This unit retains its significance at high ionic strengths. Inasmuch as pwH is $-\log (m_{\text{H}} f_{\text{HCl}}^2)$, where $f_{\text{HCl}}$ is the mean activity coefficient of the ions of hydrochloric acid, it differs numerically from paH and ptH in solutions of moderate concentration.

The scale defined by equation 17 in terms of the electromotive force of cell III would appear to solve many of the uncertainties of pH measurement. In a great number of instances, however, this procedure is impractical. The cell with liquid junction, in spite of its theoretical difficulties, remains the most convenient and widely used means for measuring the acidity of aqueous solutions.

The approximate relationships among paH, psH, and pcH are given by

$$\text{paH} = \text{psH} + 0.04 = \text{pcH} + \phi(\mu) \qquad (18)$$

where $\phi(\mu)$ represents some function of ionic strength. The appearance of this last term in equation 18 emphasizes the fact that there can be no constant difference between $\text{a}_{\text{H}}$ and $c_{\text{H}}$. The relationships among these three scales and the pwH scale are shown in figure 1, where the pH values of acetic acid–sodium acetate mixtures at 25°C. are plotted as a function of concentration.

Let us examine further the nature of pwH. Combination of equation 17 with the mass-law equation for the dissociation of a weak acid, HA, gives

$$\text{pwH} = \text{p}K - \log (m_{\text{HA}}/m_{\text{A}}) - \log (f_{\text{HA}} f_{\text{Cl}}/f_{\text{A}}) \qquad (19)$$

where $\text{p}K$ is the common logarithm of the reciprocal of $K$, the dissociation constant. When HA is a monobasic acid, the last term of equation 19 is small. If, further, the buffer ratio is unity, pwH is approximately equal to $\text{p}K$ at all concentrations. The upper curve of figure 1, calculated from the author's measurements of cells of type III, illustrates the approximate constancy of pwH

for mixtures of acetic acid and sodium acetate. The pwH values are, however, about 4.76, or slightly greater than p$K$, which is 4.756 at this temperature (56). Obviously this constancy detracts from the usefulness of pwH as a practical unit of acidity. As shown in figure 1, a change of 30 per cent in the hydrogen-ion concentration (0.16 in pcH) has no perceptible effect upon pwH. When HA is the primary or secondary anion of a dibasic or tribasic acid, pwH changes with ionic strength, but less sharply than do pcH, paH, and psH.

The paH and psH numbers were computed from E.M.F. measurements of hydrogen–calomel cells with liquid junction (36, 76, 102) by equations 4 and 12 with the aid of published values of $E^{0'} + E_j$ (76, 102). In the evaluation of pcH
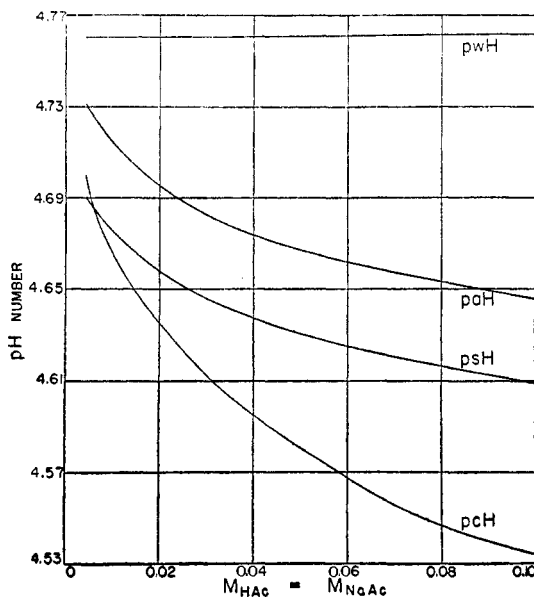


Fig. 1. pH values for acetate buffers on four different scales as a function of concentration at 25°C.

from paH, it was assumed that $f_H$ at a particular ionic strength, $\mu$, could be computed from the Debye–Hückel equation (29), written as follows:

$$-\log f_H = 0.509 \sqrt{\mu}/(1 + 1.3\sqrt{\mu}) \tag{20}$$

At infinite dilution, pcH and paH are, of course, identical. Before that limit is reached, however, the solute is so attenuated that the acid is highly dissociated and the buffering action largely disappears. The pH of the solution then approaches that of the solvent alone.

The simple expressions for computing psH and paH (equations 4 and 12) are of the same form. It is evident that a change in $E^{0'} + E_j$ (equations 11 and 12) results in a shift of the pH scale. By choice of a suitable value for this potential, the pH number computed from the same electromotive force can be made to

conform to the scale of either psH or paH. Table 1 lists these values of $E^{0'} + E_j$ for cell II and for the corresponding cell with a saturated calomel electrode:

$$\text{H}_2;\ \text{solution 1}\ |\ \text{KCl (satd.), Hg}_2\text{Cl}_2;\ \text{Hg} \qquad \text{Cell IV}$$
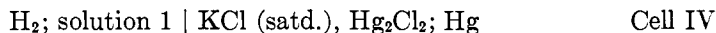
### IV. CHOICE OF A STANDARD pH SCALE

The pH measurement of unknown solutions by means of cells with liquid junction always involves an uncertainty of 0.02 unit or more, as a consequence of the unknown residual liquid-junction potential. The consistent use of a single standard scale by all investigators will result, however, in elimination of the differences among scales. Figure 1 shows that these differences may amount to 0.04 to 0.1, or even more at high ionic strengths. Only when pH is referred, by general agreement, to a single value of $E^{0'} + E_j$ at a particular temperature, or to a single series of standards, will the present confusion be lessened (51).

TABLE 1

*Values of $E^{0'} + E_j$ for different pH scales at 25°C.*

| SCALE UNIT | $E^{0'} + E_j$ | |
|---|---|---|
| | Cell II | Cell IV |
| | *volts* | *volts* |
| pcH...................... | About 0.3400* | About 0.2488* |
| psH...................... | 0.3376 | 0.2464 |
| paH, ptH............... | 0.3353 to 0.3358† | 0.2441 to 0.2446† |

\* Computed from the data of Hitchcock and Taylor (76) for 0.1 $M$ hydrochloric acid and a mixture of 0.01 $M$ hydrochloric acid with 0.09 $M$ potassium chloride. $E^{0'} + E_j$ can have no constant value for the pcH scale.

† References 76 and 102.

The Sørensen scale and other "conventional" scales that are based upon neither $c_H$ nor $a_H$ serve satisfactorily for reproducible comparisons of the results of different workers. Yet pH is used extensively in rough quantitative calculations involving chemical equilibrium. The engineer and chemist need to know insofar as possible the character of the quantity being measured. Scales of pcH, paH, and ptH answer these requirements in greater or less degree.

The lack of agreement on the most suitable scale of acidity stems from the far-reaching influence of hydrogen ion upon diverse chemical phenomena. It would not be surprising to learn, for example, that investigators of catalysis and of the kinetics of reactions preferred to know the hydrogen-ion concentration of of the solutions with which they work. Likewise, the activity of hydrogen ion would prove of considerable usefulness in studies of chemical equilibrium and electrodeposition. In many instances, $m_H f_\pm^2$ is of importance (34). The negative logarithm of this quantity has the same dimensions as pwH. Although pwH retains its significance at high ionic strengths, there are objections to its general use as a unit of acidity, as we have indicated.

Insofar as they are based upon values of $E^{0'} + E_j$ (equation 11) found by

extrapolation to zero ionic strength where equation 13 obtains, paH and ptH are numerically equal. Guggenheim has pointed out (34) that cells of types II and IV, and thus the pH meter, measure a quantity which might be designated $c_H f_?$, where $f_?$ is much more complicated than $f_\pm$, inasmuch as it depends upon transport numbers of the ions in the cell. Neither $f_H$ nor $f_\pm$ can be derived from $f_?$, and any practical standardization of paH or ptH will be theoretically unsatisfactory.

There remains the possibility of computing the hydrogen-ion concentration ($c_H$ or $m_H$) of a buffer solution accurately (54, 75, 82). In this matter the optical method can offer considerable help (40, 41, 81, 83). The determination of $m_H$ could not, however, be applied conveniently to unknown mixtures.[6]

A change of $E^{0\prime} + E_j$ in equation 12 effects the upward or downward displacement of curves such as those of paH and psH (figure 1). Evidently it would be impossible to calculate pcH from a simple equation of the form of equation 11. To do this a knowledge of $f_H$ is required, and the ionic strength must be known before $f_H$ can even be estimated.

Although the importance of the hydrogen-ion activity in chemical equilibria has been widely recognized, there has been some reluctance to abandon the conventional psH scale. Thus Sørensen and Linderstrøm-Lang (153) in first defining the activity scale felt it premature to introduce the activity principle in place of the concentration principle generally. However, the psH scale, to which the great mass of published data refers, is unfortunately not a scale of concentration at all. Kolthoff, one of the early advocates of paH (87, 88, 90), recommends the adoption of an activity scale only when standard values shall be recognized internationally (86).

In the past twenty years, however, the situation has become still more confused. It has been urged that attention be directed in published work to the meaning of the pH values and to the details of their determination (25, 114, 115, 143), but this advice appears often to have gone unheeded. The activity scales defined by Hitchcock and Taylor (76, 77) and MacInnes, Belcher, and Shedlovsky (102) have found more and more use, and standards whose paH values are based upon measurements of cells without liquid junctions have been issued by the National Bureau of Standards. Furthermore, the initial step toward international endorsement of the activity scale has been taken (148). Nevertheless, many pH measurements are still based on the conventional scale defined by Sørensen.

Some eight years after the appearance of the third edition of his widely used monograph, Clark, in a discussion of the nature of the pH scale, wrote (26), ". . . we can remove some confusion by doing away with its form and preserving its substance." The possibility of employing an electromotive force, as in oxidation–reduction systems, or the Gibbs chemical potential in place of pH numbers

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[6] Kilpatrick and coworkers (81, 82, 83) have compared the colorimetric, electrometric, and catalytic methods for determining $m_H$ in benzoate and acetate buffer solutions with added potassium chloride and have obtained concordant results up to an ionic strength of 2 for the benzoate system and 3 for the acetate system.

was considered.  Clark suggests that the latter quantity, closely allied to paH, might be derived from the electromotive force of cells without liquid junction. The fundamental difficulty of determining the activity coefficient of a single species will, in his view, "be met by sensible adjustments to approximation theory."

The shift from psH to paH involves merely a shift of $E^{0\prime} + E_j$ by an amount which corresponds approximately to an increase of 0.04 in pH (compare equation 12 and figure 1).  The psH has virtually no meaning.  The paH value has in itself no significance in terms of physical reality, yet its rôle in chemical equilibria is simply and unequivocally defined.  For these reasons, the general adoption of the activity scale seems warranted.

### V. PRIMARY AND SECONDARY STANDARDS

Examination of the problem of calculating paH from the electromotive force of cells with liquid junction reveals that the precision of a series of measurements, which are essentially comparisons with a standard of assigned paH value, can be enhanced by use of several standards of different paH.  For the control laboratory, this procedure is of advantage in reducing errors imparted by differences in temperature and by the wrong adjustment of a pH meter to the theoretical slope of pH with respect to electromotive force (10).  Calibration with two buffer solutions of different pH is also of value in demonstrating the proper functioning of the electrodes.  The accurate examination of strongly alkaline solutions, where the glass-electrode error is a factor, requires especial care in the selection of buffers (30).  It is obviously important that these standards be consistent with each other and define a paH scale that is uniform over its whole range.

The commonly used pH standards are solutions that can be easily prepared from pure, stable, crystalline buffer salts.  These buffer solutions are of varying types and compositions.  The definition of a uniform paH scale in terms of all of these standards is difficult, inasmuch as the specific behaviors and individual characteristics of ions disappear only at dilutions so great as to be generally inaccessible to experiment.  The usefulness of two series of standards is thus apparent.  The first group would be composed of primary standards of similar composition and low concentration, whose paH values could be closely fixed. Other convenient secondary, or practical, standards, composed of stable buffer salts of different types and concentrations, would make up the second group. The primary standards would serve for a determination of $E^{0\prime} + E_j$.  The paH of the secondary standards would be determined by careful comparison with the primary group.

Specifications for standardizing practical pH measurements have been set forth by Clark in his monograph (25).  These directions would be modified only by the substitution of a new set of values of $E^{0\prime} + E_j$, consistent with the primary paH standards.  No correction for the liquid-junction potential is necessary.  As yet no standard potentials applicable to all strong acid–salt mixtures or to strong bases can be recommended.  If there is any departure from standard procedure

in the determination of the pH values included in published material, a statement of the essential modifications should be made.

In the sections to follow, some possible methods of establishing a uniform series of primary standards and assigning to them acidity values that closely approximate $-\log a_H$ will be compared. The calculation of paH from E.M.F. measurements of hydrogen–calomel cells with transference will be considered first.

## VI. THE HYDROGEN–CALOMEL CELL WITH LIQUID JUNCTION

It has been seen that the activity scale appears to be the most generally useful one for measuring the acidity of aqueous solutions. We shall now consider means of standardizing electrometric pH instruments to yield values that correspond as closely as possible to this scale. As pointed out in an earlier section, there are two methods of approach: choice of $E^{0\prime} + E_j$, or evaluation of the paH values of one or more standard reference solutions.

### A. The liquid-junction potential

The paH value is usually derived from the electromotive force of cells of types II or IV. The cell with saturated calomel electrode is generally used in the pH meter, and the hydrogen electrode is replaced by the versatile glass electrode. The electromotive force of the cell with liquid junction is a complicated function of the concentrations and transference numbers of each ionic species present in the electrode solutions and in the transition layers which form the boundary (85). The potential, $E_j$, at the liquid junction between two solutions I and II is given by

$$E_j = -k \int_{\mathrm{I}}^{\mathrm{II}} \sum (T_i/z_i)\, \mathrm{d} \log f_i m_i \qquad (21)$$

where $T_i$ is the transference number of the ion whose valence is $z_i$ and the summation is made for all ions in the boundary.

As has often been pointed out (36, 52, 100, 139, 159), the evaluation of individual ionic activity coefficients requires an exact knowledge of $E_j$, and the value of $E_j$, in turn, rests upon a knowledge of the ionic activity coefficients. The electric potential difference between two points in different media has not yet been defined in terms of physical realities (32, 33), and the activity coefficient of an ion is not an experimental quantity but a mathematical device (159). MacInnes regards as extreme the view that single ion activities have no physical meaning (101) and points to their usefulness as mathematical concepts in visualizing cell mechanisms. The problem of computing $E_j$ is, however, incapable of solution unless an assumption from outside the realm of thermodynamics is introduced.

One of the common assumptions, that suggested by MacInnes (99), asserts the equality of the activity coefficients of the ions of potassium chloride in a pure solution of the salt of any concentration. The ionic activity coefficient is assumed not to be influenced by the presence of other ions with which the ion in question may be associated in other mixtures where the same concentration of the ion is maintained. Thus the chloride-ion activity is considered to be the

same in a solution of any chloride as in a solution of potassium chloride of the same chloride concentration. The activity coefficients of the ions of uni-univalent electrolytes have often been set equal to the mean activity coefficients. In other words, the validity of equation 13 at all ionic strengths is assumed. Although used earlier by others, this second assumption was generalized by Guggenheim and is now usually associated with his name.

Either of these postulates makes possible a calculation of the potential difference across junctions the structure of which corresponds to certain models, provided that the mean activity coefficients of the electrolytes and the transference numbers of the ions in the mixtures composing the transition layers are known. Nevertheless, the calculation is awkward at best, and the necessary information is not usually available. In spite of these limitations, the liquid-junction potentials that can be computed for certain simple cases from available experimental data and non-thermodynamic assumptions are not at all unreasonable. For this reason, the calculation deserves further consideration here.

The liquid-junction potential given by equation 21 can be separated into an ideal part, $E_m$, and a non-ideal part, $E_f$:

$$E_j = E_m + E_f \tag{22}$$

The equations of Henderson (69, 70) and Planck (124) yield only the ideal term, $E_m$. No activity coefficients are used in calculating $E_m$, and consequently no assumption, apart from the character of the distribution of the ions in the boundary, is involved. When strong acids are present at concentrations up to 0.1 $M$, $E_f$ may amount to a third of $E_j$, or more. Hamer's calculation (42) by the graphical method of Harned (52) suggests that $E_f$ may be only 0.1 to 0.2 mv., or about 5 per cent of $E_j$, when the junction is formed between saturated potassium chloride and acetate buffers. Unfortunately, the computation of $E_j$ is markedly affected by errors in the transference numbers (18, 36), and too few data are available to demonstrate whether $E_f$ is likewise small when other weak acid systems are involved.

MacInnes and Longsworth (101, 103) found essentially the same values for the potentials at the junctions between different concentrations of the same electrolyte—sodium chloride, potassium chloride, or hydrochloric acid—regardless of whether the computations of ionic activity coefficients were based upon the MacInnes or the Guggenheim assumptions. In this connection, it should be remembered that the manner in which the junction is formed has little effect upon $E_j$ when the boundary is formed between different solutions of the same electrolyte. It has been shown (42, 103) that the calculated $E_j$ for the junction: HCl (0.1 $M$) | KCl (satd.) is 2.0 mv. when the computation is based on the Guggenheim assumption, and 2.8–2.9 mv. on the MacInnes assumption. It makes a decided difference which convention is adopted. The assumed structure of the boundary has little influence, however, on the calculated potential of the cell. Junctions formed from potassium chloride and a buffer solution are still more complex, and the computation of $E_m$ requires information or assumptions regarding the distribution of the electrolytes in the transition layers. The equa-

tions are therefore of little practical value in the determination of the pH of a reference buffer for pH standardization. As we shall see, practical standardizations of the hydrogen–calomel cell need not involve a calculation of the liquid-junction potential.

### B. Previous standardizations of the paH scale

It is evident that $E^0$ in equations 8a and 10 is the negative of the standard potential of the mercury–mercurous chloride electrode. The value of $E^0$ is found to be 0.2679 v. at 25°C. by adding 0.0455 v., the electromotive force of the silver chloride–calomel cell without liquid junction (31, 128), to 0.2224 v., the standard potential of the hydrogen–silver chloride cell (58). Both the MacInnes assumption and the Guggenheim assumption justify the substitution of $a_{KCl}$, the product of the molality of potassium chloride at the calomel electrode and its stoichiometrical activity coefficient, for $a_{Cl}$ in equation 10. The molalities of potassium chloride in the 0.1 $N$ and saturated solutions are, respectively, 0.1005 and 4.804 (140). If we accept the values 0.769 and 0.588 for the activity coefficient of potassium chloride in these solutions (55, 140, 146), we find by equation 10 that $E^{0'}$ is 0.3337 v. for the 0.1 $N$ calomel electrode and 0.2412 v. for the saturated calomel electrode. This same value of $E^{0'}$ for the cell with hydrogen electrode and the 0.1 $N$ calomel electrode was chosen by Guggenheim and Schindler (36) and by Hamer (42). The former based their choice wholly, and the latter in part, upon the explicit assumption of a relationship between $a_{Cl}$ and $a_{KCl}$ such as we have used here.

Equation 11 may be regarded as a conventional definition of $f_H$ and of $E^{0'} + E_j$. The value of one depends on the value assigned to the other. It is evidently possible to measure the electromotive force of cell II or IV when solution 1 contains only strong acids (so that $m_H$ is known), to evaluate $f_H$ from the known mean activity coefficients and an assumption such as those of MacInnes and Guggenheim, and thus to calculate $E^{0'} + E_j$. Each different value of $E^{0'} + E_j$ constitutes a different basis for a scale of paH.

Guggenheim and Schindler (36) chose $E^{0'} = 0.3337$ v. as the basis of their paH scale, because this potential was found to yield values for $f_H$ (equation 11) in 0.1 $M$ hydrochloric acid and in mixtures of 0.01 $M$ hydrochloric acid with 0.09 $M$ sodium and potassium chlorides that were nearly the same as those calculated with the aid of the MacInnes convention. The Henderson equation was used to compute $E_j$. It is readily shown that the Guggenheim convention would have led to a value of 0.3329 v. From the paH values given by Guggenheim and Schindler for three acetate buffers and three phosphate buffers, we find by equation 11a an average $E^{0'} + E_j$ of 0.3345 ± 0.0005 v.

Electromotive-force measurements of hydrochloric acid and buffer solutions of acetates were shown by Hamer (42) to lead to approximately the same value of $E^{0'}$ (0.3337 v.) as that given above for cell II. For the cell with a saturated calomel electrode (type IV), the strong acids yield 0.2407 v., whereas buffered solutions give 0.2414 v. Two values of $E^{0'} + E_j$ were chosen for each of the two types of cell. The contributions of both $E_m$ and $E_f$ to the liquid-junction

potential (compare equation 22) were considered. The computation of $E_f$ was based on the MacInnes assumption. Of the two values for cell II, 0.3369 v. was intended to apply to measurements of solutions that contained strong acids, and 0.3346 v. was recommended for measurements with buffered solutions that contain weak acids.[7] Experimental evidence furnishes ample support for such a dual set of values. Actually, $E^{0\prime} + E_j$ for various mixtures containing strong acids appears to vary too widely to permit the paH of all mixtures of that class to be calculated with the use of any single value of the standard potential.

Sørensen and Linderstrøm-Lang (153), in defining the first scale of paH, based their choice of the standard potential of cell II upon an extensive series of electromotive-force measurements of cells that contained mixtures of hydrochloric acid and sodium or potassium chloride. Each measured E.M.F. value was corrected for the liquid-junction potential by means of the Bjerrum extrapolation. The activity coefficient of the hydrogen ion was computed by Brønsted's equation (22) and the earlier cube-root formula of Bjerrum (16). A value of 0.3357 was selected for $E^{0\prime}$ at 18°C. At 25°C., $E^{0\prime}$ becomes 0.3353 v. It was suggested that the Bjerrum extrapolation be employed in measurements of paH. In later work (154) these authors themselves used a bridge of saturated potassium chloride between buffered solutions and the reference electrode and made no correction of the measured electromotive force. It is possible, however, that Sørensen and Linderstrøm-Lang would retain the extrapolation procedure in measurements with mixtures containing strong acids. If we are to assume that they intended the same standard potentials as were recommended in their earlier paper (153) to apply to measurements of buffered solutions by their later procedure, $E^{0\prime} + E_j$ is 0.3353 v.

Substitution of a solution of potassium chloride saturated at 25°C. for the 3.5 $M$ bridge solution appears to alter the electromotive force of cell II by only 0.1 mv. (42). For this reason, the concentration of the bridge solution will not usually be specified, so long as it is 3.5 $M$ or greater.

Scatchard (136) assumed an unchanging potential across a flowing junction between a saturated solution of potassium chloride and solutions of hydrochloric acid as the concentration of the latter was reduced from 0.1 $M$ to zero, in which limit $f_H$ is unity by definition. Electromotive-force measurements of cells of the type,

$$\text{Ag; AgCl, HCl } (m) \mid \text{KCl (satd.), Hg}_2\text{Cl}_2; \text{Hg} \qquad \text{Cell V}$$
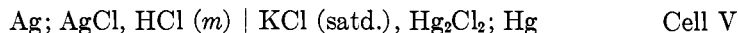
were made, and $E'$, that is, $E + k \log m$, was plotted as a function of the square root of the molality and the limiting value at zero concentration obtained. Addition of 0.2226 v., the standard potential of the hydrogen–silver chloride cell (135), gave 0.2454 v. for $E^{0\prime} + E_j$ (cell IV) at 25°C. Inasmuch as this treat-

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[7] The potentials recorded in the last column of table VI of Hamer's paper refer to the cell in which the junction is made directly between 0.1 $N$ potassium chloride and solution 1 without interposition of saturated potassium chloride. The values of $E^{0\prime} + E_j$ given here for cell II were therefore computed from the corresponding potentials of cell IV, given in column 2 of the same table, by addition of 0.0912 v. (102).

ment of the cell with liquid junction requires no *a priori* statement relating the ionic activity coefficients, Scatchard was able to compute $f_H$ and $f_{Cl}$ in the solutions of hydrochloric acid used in the cells. These experimental activity coefficients were in excellent accord with those based upon the MacInnes assumption at concentrations of acid not exceeding 0.2 molal.

The assumption of an unchanging liquid-junction potential and the validity of Scatchard's extrapolation are open to question (30). It is of interest, however, that a later determination of $E^{0\prime} + E_j$ from similar measurements (76), with the employment of the Debye–Hückel equation in the extrapolation, led to a value, 0.2450 v., in reasonably good agreement with that found by Scatchard. If the most recent value of $E^0$ for the hydrogen–silver chloride cell (58) is combined with Scatchard's extrapolated value for cell V, $E^{0\prime} + E_j$ becomes 0.2452 v., and the agreement of the two investigations is quite satisfactory. Inasmuch as the electromotive force of the cell,

$$\text{Hg; Hg}_2\text{Cl}_2, \text{ KCl (satd.)} \mid \text{KCl (0.1 } N), \text{ Hg}_2\text{Cl}_2; \text{ Hg} \qquad \text{Cell VI}$$
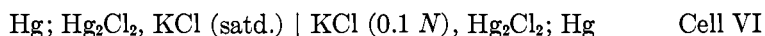
has been found to be 0.0912 v. at 25°C. (18, 102, 130), we are able to compute $E^{0\prime} + E_j$ for cell II from the corresponding quantity for cell IV. Addition gives 0.3364 v. for this potential.

By measurement of the electromotive force of a concentration cell with transference, Kolthoff and Bosch (90) concluded that a paH value of 2.075 should be assigned to the standard reference mixture, 0.01 $M$ hydrochloric acid and 0.09 $M$ potassium chloride. This reference solution was compared experimentally with a solution of hydrochloric acid so dilute (0.001 $M$) that $f_H$ would be practically identical with the known mean activity coefficient of the acid. A correction was made for $E_m$, the ideal part of the diffusion potential. The E.M.F. of cell II with 0.01 $M$ hydrochloric acid and 0.09 $M$ potassium chloride as solution 1 is 0.4583 v. at 25°C. This is the mean of three closely agreeing measurements, 0.45830 found by Guggenheim and Schindler (36), 0.4584 by Bjerrum and Unmack (18), and 0.4582 computed from the E.M.F. of cell IV given by Hitchcock and Taylor (76). From equation 11a, therefore, $E^{0\prime} + E_j$, the basis of Kolthoff's paH scale (90, 91), is found to be 0.3356 v.

Bjerrum and Unmack (18) based their computation of paH on an extensive series of electromotive-force measurements for which solutions of hydrochloric acid and mixtures of hydrochloric acid with sodium and potassium chlorides were used in cells of type II. Similar data of other investigators were critically examined. Each electromotive-force value was corrected by means of the Henderson equation for $E_m$, the ideal part of the liquid-junction potential. The determination of $E^{0\prime}$ was made by a double extrapolation, as follows: The limiting value of $E + k \log c_H$ at zero acid concentration was first determined for each of several series of acid–salt mixtures of constant total concentration, $c$. These quantities were then plotted as a function of $c$, and $E^{0\prime}$, the limit at $c = 0$, was obtained by extrapolation with the aid of the Debye-Hückel equation. An examination of the data of Bjerrum and Unmack confirms the observation of Hitchcock and Taylor (76) that these three types of solutions yield somewhat

divergent results for $E^{0'} + E_j$ and that the difficulty is not remedied by a correction for $E_j$, or at least for the ideal term, $E_m$. Nevertheless, Bjerrum and Unmack chose $E^{0'} = 0.3360$ v. at 25°C. as most generally applicable to measurements of all types of solutions. From their paH values for several phosphate and citrate buffer solutions, $E^{0'} + E_j$ is found by equation 11a to be approximately 0.3364 v.

Two solutions that contained hydrochloric acid, four buffer solutions, and a solution of calcium hydroxide were studied by Manov, DeLollis, and Acree (108) by measurements of cells of types III and IV. A silver–silver chloride electrode immersed in an air-free saturated solution of potassium chloride was substituted for the saturated calomel electrode of the latter cell. The paH values of the seven solutions were computed from the electromotive force of the cell without liquid junction with the aid of earlier data for the phthalate, phosphate, phenolsulfonate, and borate systems (6, 12, 47, 107). The values of $E^{0'} + E_j$ for cell II can be obtained by adding 0.0455, the difference between the standard potentials of the calomel and silver–silver chloride electrodes (31), and 0.0912, the E.M.F. of cell VI, to $E^{0'} + E_j$ computed by these investigators. In this way, $E^{0'} + E_j$ for cell II is found to be 0.3358 v. for the solutions of strong acid, 0.3346 ± 0.0004 for the buffer mixtures, and 0.3336 for the solution of calcium hydroxide, a strong base. The fact that moderate concentrations of hydrogen ion effect an elevation of $E^{0'} + E_j$ above the value found with solutions whose pH is between 3 and 11 is well recognized. It is, therefore, not at all surprising to find that the excessively mobile negative ion, hydroxyl, lowers the value of $E^{0'} + E_j$.

Cohn, Heyroth, and Menkin (28), in an analysis of E.M.F. data for mixtures of acetic acid and sodium acetate, demonstrated the influence of a change in $E^{0'} + E_j$ on the determination of pK for acetic acid. "Apparent" pK values at finite concentrations were computed from the measured paH by the mass·law equation. The true pK was obtained by extrapolation to infinite dilution, with the aid of the Debye–Hückel equation. When 0.3380 v. was used for $E^{0'} + E_j$ at 18°C., pK was found to be 4.730, and when 0.3360 v. was used a value of 4.765 resulted. In order to obtain the true pK, 4.757 at 18°C. (56, 57), it would therefore be necessary to use $E^{0'} + E_j = 0.3365$ v. At 25°C., this potential becomes 0.3361 v. (25).

By a similar procedure, Kauko and coworkers (79, 80) assigned different paH values to the reference solution, 0.01 M hydrochloric acid, 0.09 M potassium chloride, and determined the resultant effect upon pK for the first dissociation step of carbonic acid. In this way they chose 2.087 as the correct paH of the reference solution. If E for cell II is again taken as 0.4583 v. at 25°C., $E^{0'} + E_j$ is found by equation 11a to be 0.3350 v.

Two other scales based upon thermodynamic dissociation constants deserve consideration in some detail. The first of these is based upon the work of Hitchcock and Taylor (76, 77), who measured the E.M.F. at 25°C. of cells of type IV containing acetate, phosphate, borax, and glycolate buffer solutions at each of several dilutions. Cells of the type,

$$\text{H}_2 ; \text{ buffer solution } | \text{ KCl (satd.) } | \text{ HCl (0.1 } M\text{)}; \text{H}_2 \qquad \text{Cell VII}$$
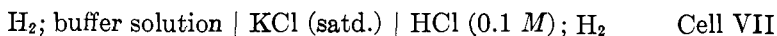
were also measured at 38°C. Several concentrations of acetates, phosphates, and borax comprised the buffer solutions used in the half-cell on the left. Measurements of cell VII, for which the buffer solution was replaced by (a) 0.1 $M$ hydrochloric acid, (b) 0.01 $M$ hydrochloric acid and 0.09 $M$ sodium chloride, and (c) 0.01 $M$ hydrochloric acid and 0.09 $M$ potassium chloride were made at 25° and 38°C. Additional solutions, formed by diluting these three with water, were also studied.

The second scale is that of MacInnes, Belcher, and Shedlovsky (102), who studied acetate buffer solutions by means of E.M.F. measurements of cell II at 12°, 25°, and 38°C. These data were supplemented by a series of measurements made with chloroacetate buffer solutions at 25°C.

Hitchcock and Taylor used paH, and MacInnes, Belcher, and Shedlovsky ptH, in the formal equations for determining $E^{0'} + E_j$. If the buffer solution is composed of a weak monobasic acid, HA, together with its salt, the dissociation constant, $K$, and the "incomplete" dissociation constant ("unvollständige Dissoziationskonstante" of Bjerrum and Unmack (18)), $K'$, are given by

$$\mathrm{p}K' = \mathrm{p}K + \log \frac{f_\mathrm{A}}{f_\mathrm{HA}} = \mathrm{paH} - \log \frac{c_\mathrm{A}}{c_\mathrm{HA}} \tag{23}$$

and

$$\mathrm{p}K' = \mathrm{p}K + \log \frac{f_\pm}{f_\mathrm{HA}} = \mathrm{ptH} - \log \frac{c_\mathrm{A}}{c_\mathrm{HA}} \tag{24}$$

where $\mathrm{p}K$ and $\mathrm{p}K'$ are as usual the common logarithms of $1/K$ and $1/K'$. The two different definitions of the unit of acidity lead to equations of identical form. In either case, $\mathrm{p}K'$ is a linear function of the square root of the ionic strength in dilute solutions, and its value at zero ionic strength is $\mathrm{p}K$. As equation 23 shows, the difference between $\mathrm{p}K'$ and $\mathrm{p}K$ affords a measure of the ratio of the activity coefficients of the buffer components (27, 68).

Hitchcock and Taylor expressed $E^{0'} + E_j$ in terms of $\mathrm{p}K$ by combining equations 11 and 23. The effect of activity coefficients was removed by extrapolation to zero ionic strength with the use of the Debye–Hückel equation. MacInnes, Belcher, and Shedlovsky employed assumed values of $E^{0'} + E_j$ to compute ptH by the right-hand side of equation 11. The corresponding values of $\mathrm{p}K'$ obtained from equation 24 yielded a provisional $\mathrm{p}K$ by suitable extrapolation. As Cohn, Heyroth, and Menkin (28) have shown, the proper $E^{0'} + E_j$ will be that which, by trial, furnishes the known $\mathrm{p}K$.

As a basis for a scale of pH, MacInnes, Belcher, and Shedlovsky found $E^{0'} + E_j$ for cell II to be 0.3358 v. at 25°C., 0.3352 v. at 38°C., and 0.3364 v. at 12°C. For the corresponding cell with a saturated calomel electrode (cell IV), $E^{0'} + E_j$ is found to be 0.2446 v. at 25°C. by subtraction of 0.0912 v., the E.M.F. of cell VI. In the computation of paH, Hitchcock and Taylor use 0.2441 v. for $E^{0'} + E_j$ of the cell with the saturated calomel electrode (type IV). The corresponding value for cell II is 0.3353 v. The two pH scales differ, therefore, by 0.008 unit. These potentials are in acceptable agreement with 0.3353 v., sug-

gested by Sørensen and Linderstrøm-Lang (153, 154) as the basis for a paH scale at 25°C.

These scales achieve some measure of thermodynamic significance without sacrifice of utility. No estimate of diffusion potentials is required. The paH cannot be proved to be consistent with p$K$, however, at any concentration accessible to direct measurement. The observed change of p$K'$ with ionic strength is, nevertheless, approximately that expected from theory, except for the most dilute buffer solutions. This treatment should yield identical paH and ptH values, and the difference found is probably to be ascribed chiefly to the extrapolation, as we shall see presently. All buffer solutions are not found to yield the same $E^{0'}$, presumably because of marked differences in the mobilities of the ions and, hence, in the liquid-junction potential.

TABLE 2

*Standard potentials of cell II at 25°C.*

| REFERENCE | YEAR | $E^{0'}$ | $E^{0'} + E_j$ | REMARKS |
|---|---|---|---|---|
| | | *volts* | *volts* | |
| Sørensen and Linderstrøm·Lang (153).... | 1924 | 0.3353 | | |
| Scatchard (136)........................ | 1925 | | 0.3364 | |
| Sørensen, Linderstrøm·Lang, and Lund (154)............................ | 1927 | | 0.3353 | |
| Cohn, Heyroth, and Menkin (28)........ | 1928 | | 0.3361 | |
| Bjerrum and Unmack (18).............. | 1929 | 0.3360 | 0.3364 | |
| Guggenheim and Schindler (36)......... | 1934 | 0.3337 | 0.3345 | |
| Hamer (42)........................... { | 1937 | 0.3337 | 0.3346 | Buffered solutions |
| | | | 0.3369 | Strong acids |
| Kauko and Airola (79)................. | 1937 | | 0.3350 | |
| Hitchcock and Taylor (76)............. { | 1937 | | 0.3353 | Buffered solutions |
| | | | 0.3362 | Hydrochloric acid |
| MacInnes, Belcher, and Shedlovsky (102)............................. | 1938 | | 0.3358 | |
| Manov, DeLollis, and Acree (106) ...... { | 1945 | | 0.3358 | Strong acids |
| | | | 0.3346 | Buffered solutions |
| | | | 0.3336 | Calcium hydroxide |

A summary of $E^{0'} + E_j$ is given in table 2. All of the values recorded in the table refer to the cell with the 0.1 $N$ calomel electrode and bridge solution of 3.5 $M$ or saturated potassium chloride (type II) at 25°C. The potentials of the corresponding cell with saturated calomel electrode (type IV) are obtained by subtracting 0.0912 v. from the values listed.

*C. Evaluation of $E^{0'} + E_j$ for buffer solutions at 25°C.*

It is clearly unfortunate that so much of the E.M.F. work with hydrogen-calomel cells has been confined to solutions of strong acids. Although the hydrogen-ion concentration in such solutions is known, the activity of this ion is as undefined as it is in a buffer solution. A single value of $E^{0'} + E_j$ appears to serve satisfactorily for the pH range 3 to 11 (88, 123). Solutions that contain

appreciable amounts of strong acids, however, usually require a somewhat higher value, and scales based exclusively upon strongly acid standards are not accurate over the entire pH range. For this reason, Clark (25) has considered the eventual adoption of a sliding scale of potentials. When the majority of paH determinations involve solutions of weak acids or bases and their salts, it is of unquestioned advantage to utilize a value of $E^{0'} + E_j$ that is based upon measurements of systems of this type (28, 112, 113, 153).

A further analysis of the available electromotive-force data for buffer solutions therefore seems appropriate. For this purpose, the cell measurements of Hitchcock and Taylor (76) were converted, by the addition of 0.0912, to the corresponding data for cell II. Larsson and Adell (95, 96) have studied the effect of neutral salts upon the paH of a large number of monobasic acid buffers at 18°C. by means of electromotive-force measurements of quinhydrone–calomel cells. When their data are corrected for the difference between the potentials of the quinhydrone and hydrogen electrodes it becomes apparent that their calomel electrode was neither the standard 0.1 $N$ electrode nor the saturated type. We are able, fortunately, to compute the corresponding electromotive forces for cell II at 18°C. by addition of 0.7870 v., the difference between their measurement for the mixture of 0.01 $M$ hydrochloric acid and 0.09 $M$ potassium chloride, −0.3312 v., and 0.4558 v. found by Bjerrum and Unmack (18) for the same solution, also at 18°C. The measurements of Guggenheim and Schindler (36) and of MacInnes, Belcher, and Shedlovsky (102) will also be considered.

The paH numbers computed from electromotive-force measurements of cells without liquid junction, or from thermodynamic dissociation constants, become increasingly accurate as the ionic strength decreases. There seems good reason to suppose that the paH so derived is, in most instances, accurate within 0.005 unit at ionic strengths of 0.01 or below. If the Debye–Hückel equation, with ion-size parameter, $a_i$, arbitrarily chosen as 4 Å. (equation 20), is substituted for log $f_{A^-}$, the mass law yields the following expression for the paH of a mixture of monobasic acid, HA, and its salt,

$$\text{paH} = \text{p}K + \log \frac{m_A}{m_{HA}} - \frac{A\sqrt{\mu}}{1 + 4B\sqrt{\mu}} \tag{25}$$

in which the activity of the uncharged acid molecules has been set equal to their molality. The constants $A$ and $B$ vary with temperature (105, 138). In dilute solutions the error in the paH that results from such a choice of a reasonable, though probably incorrect, value for the coefficient of the $B\sqrt{\mu}$ term in the denominator of the last term of equation 25 is unimportant. At intermediate ionic strengths it becomes appreciable.

Guggenheim's equation (35) for the mean activity coefficients of strong uni-univalent electrolytes is

$$-\log f_{\pm} = \frac{A\sqrt{\mu}}{1 + \sqrt{\mu}} + \lambda\mu \tag{26}$$

This relation represents observed activity coefficients at 0°C. successfully at concentrations up to 0.1 $M$. At a given ionic strength all specific differences among electrolytes are evidently embodied in the coefficients, $\lambda$, of the linear term. If, like $f_{\pm}$, the true activity coefficient of the anion A, $f_A$, and the approximate value, $f_A'$, computed from the Debye–Hückel equation with a value of 4 for $a_i$, can likewise be expressed by Guggenheim's equation, the error, $\Delta(\text{paH})$, will be

$$\Delta(\text{paH}) = \log f_A - \log f_A' = (\lambda' - \lambda)\mu \qquad (27)$$

The error in paH will therefore be a linear function of ionic strength when the ionic strength does not exceed 0.1.

The results of computations of $E^{0'} + E_j$ for cell II by equation 11a are given in table 3. The paH values for phosphate and borax buffers were taken from previous publications (8, 109). In all other cases, paH was computed by equation 25. Standard potentials computed at 18°C. were corrected to 25°C. by subtraction of 0.0004 v. (25).

Some of the data of table 3 are plotted as a function of ionic strength in figure 2. The dotted lines are drawn through the points for acetate solutions (upper line), glycolate solutions (middle line), and chloroacetate solutions (lower line). Some of the results plotted in figure 2 are of doubtful accuracy, and great significance cannot be attached to the relations shown there. The prediction that the error of paH varies linearly with ionic strength seems, however, to be confirmed. At ionic strengths above 0.01, the liquid-junction potential appears to be constant, or also varying in linear fashion. When the ionic strength of the buffer solution is less than 0.01, the situation is somewhat altered and the slopes of the lines change sharply. This discontinuity cannot be ascribed to errors in the calculated paH. It is possible that the liquid-junction potential changes rapidly with concentration when the buffer is very dilute.

It must be remembered that, apart from their aid in the establishment of a linear plot, the calculated values of paH, and hence of $E^{0'} + E_j$, have little meaning above an ionic strength of 0.01. With the exception of the data for phosphates, which appear to be higher than those of the other buffer systems, the curves of $E^{0'} + E_j$ as a function of ionic strength converge well at 0.01 $\mu$, where the calculation of paH is fairly reliable. In view of the sharp change in slope observed for the most dilute solutions, it seems unwise to accord these points much weight in evaluating a standard potential for general use in the practical determination of paH.

The nine buffer mixtures of approximately 0.01 $\mu$ yield, as the data of table 3 show, a mean of 0.3350 ± 0.0002 for $E^{0'} + E_j$. If the two chloroacetate buffers are omitted and only solutions with paH above 3 are included, the average of seven results is 0.3352 ± 0.0001 v. The three dotted lines of figure 2, extended to the axis of ordinates, meet at 0.3353. From all of these considerations, we choose 0.3352 ± 0.0002 as the value of $E^{0'} + E_j$ that appears most suitable for use with buffer solutions composed of weak monobasic acids and their sodium

TABLE 3

*Calculation of $E^{0'} + E_j$ for cell II at 25°C. from E.M.F. measurements of buffer solutions*

| BUFFER SYSTEM | COMPONENT a | COMPONENT b | TEMPER-ATURE | E | pK | paH | $E^{0'} + E_j$ (18°C.) | $E^{0'} + E_j$ (25°C.) | REFERENCES | |
|---|---|---|---|---|---|---|---|---|---|---|
| | *molarity* | *molarity* | °C_ | *volts* | | | *volts* | *volts* | | |
| (a) Acetic acid and (b) sodium acetate | 0.00203 | 0.00203 | 18 | 0.6103 | 4.757 | 4.744 | 0.3363 | 0.3359 | E | (95) |
| | 0.00406 | 0.00406 | | 0.6093 | | 4.731 | 0.3361 | 0.3357 | pK | (56, 57) |
| | 0.00608 | 0.00608 | | 0.6088 | | 4.724 | 0.3360 | 0.3356 | | |
| | 0.00811 | 0.00811 | | 0.6084 | | 4.718 | 0.3359 | 0.3355 | | |
| | 0.01007 | 0.01007 | | 0.6077 | | 4.712 | 0_3356 | 0.3352 | | |
| | 0.01 | 0.01 | 25 | 0.6139 | 4.756 | 4.714 | | 0.3351 | E | (36) |
| | 0.01* | 0_01* | | 0.6097 | | 4.644 | | 0.3352 | pK | (56, 104) |
| | 0_1 | 0.1 | | 0.6101 | | 4.645 | | 0.3354 | | |
| | 0.02 | 0.02 | 25 | 0.6131 | | 4.696 | | 0.3354 | E | (76) |
| | 0_04 | 0.04 | | 0.6119 | | 4.675 | | 0.3354 | | |
| | 0.06 | 0.06 | | 0.6111 | | 4.662 | | 0.3354 | | |
| | 0.08 | 0.08 | | 0.6106 | | 4_651 | | 0.3355 | | |
| | 0_1 | 0.1 | | 0.6102 | | 4.645 | | 0.3355 | | |
| | 0_009 | 0.001 | 25 | 0.5636 | | 3.851 | | 0.3359 | E | (102) |
| | 0.008 | 0.002 | | 0.5811 | | 4.152 | | 0.3356 | | |
| | 0.018 | 0.002 | | 0.5614 | | 3.818 | | 0.3356 | | |
| | 0.016 | 0.004 | | 0.5799 | | 4.135 | | 0.3354 | | |
| | 0.01160 | 0.004717 | | 0.5921 | | 4.340 | | 0.3354 | | |
| | 0.01115 | 0.006181 | | 0.5994 | | 4.468 | | 0.3352 | | |
| | 0.01055 | 0.007594 | | 0.6056 | | 4.576 | | 0.3350 | | |
| | 0.01008 | 0.009134 | | 0.6113 | | 4.672 | | 0.3350 | | |
| | 0.01 | 0.01 | | 0.6140 | | 4.714 | | 0.3352 | | |
| | 0.01015 | 0.01278 | | 0.6195 | | 4.807 | | 0.3352 | | |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| (a) Chloroacetic acid and (b) sodium chloroacetate | 0.001072 | 0.0019 | 25 | 0.5176 | 2.855 | 3.077 | | 0.3356 | $E$ | (102) |
| | 0.006716 | 0.005108 | | 0.4946 | | 2.696 | | 0.3352 | p$K$ | (134, 144) |
| | 0.00784 | 0.00739 | | 0.4995 | | 2.785 | | 0.3348 | | |
| | 0.00868 | 0.01143 | | 0.5075 | | 2.924 | | 0.3346 | | |
| | 0.01169 | 0.01647 | | 0.5084 | | 2.944 | | 0.3343 | | |
| | 0.01443 | 0.01840 | | 0.5056 | | 2.900 | | 0.3341 | | |
| | 0.01006 | 0.01006 | 18 | 0.5031 | 2.836 | 2.912 | 0.3349 | 0.3345 | $E$ p$K$ | (96) (134, 144, 164) |
| (a) Glycolic acid, (a) lithium chloride, and (b) lithium glycolate | 0.01 | 0.01 | 25 | 0.5587 | 3.831 | 3.786 | | 0.3348 | $E$ | (76) |
| | 0.02 | 0.02 | | 0.5564 | | 3.761 | | 0.3340 | p$K$ | (116) |
| (a) Glycolic acid and (b) sodium glycolate | 0.01009 | 0.01009 | 18 | 0.5552 | 3.837 | 3.807 | 0.3354 | 0.3350 | $E$ p$K$ | (96) (116) |
| (a) Lactic acid and (b) sodium lactate, in 0.0118 $M$ NaCl | 0.01 | 0.0094 | 18 | 0.5541 | 3.863 | 3.790 | 0.3353 | 0.3349 | $E$ p$K$ | (96) (117) |
| (a) Formic acid and (b) sodium formate | 0.005 | 0.005 | 18 | 0.5519 | 3.754 | 3.756 | 0.3351 | 0.3347 | $E$ p$K$ | (95) (60) |
| (a) Propionic acid and (b) sodium propionate | 0.0102 | 0.0102 | 18 | 0.6146 | 4.874 | 4.830 | 0.3357 | 0.3353 | $E$ p$K$ | (95) (59) |
| (a) $n$-Butyric acid and (b) sodium $n$-butyrate | 0.01066 | 0.01 | 18 | 0.6095 | 4.809 | 4.739 | 0.3358 | 0.3354 | $E$ p$K$ | (95) (67) |

TABLE 3—*Concluded*

| BUFFER SYSTEM | COMPONENT a | COMPONENT b | TEMPER- ATURE | E | pK | paH | $E^{0\prime} + E_j$ (18°C.) | $E^{0\prime} + E_j$ (25°C.) | REFERENCES | |
|---|---|---|---|---|---|---|---|---|---|---|
| | *molarity* | *molarity* | °C. | *volts* | | | *volts* | *volts* | | |
| (a) Potassium dihydrogen phos- | 0.005 | 0.005 | 25 | 0.7508 | | 7.018 | | 0.3358 | E | (76) |
| phate and (b) disodium hydro- | 0.01 | 0.01 | | 0.7471 | | 6.959 | | 0.3355 | paH | (8) |
| gen phosphate | 0.015 | 0.015 | | 0.7446 | | 6.919 | | 0.3354 | | |
| | 0.02 | 0.02 | | 0.7426 | | 6.886 | | 0.3354 | | |
| | 0.025 | 0.025 | | 0.7409 | | 6.860 | | 0.3352 | | |
| | 0.0025† | 0.0025 | 25 | 0.7534 | | 7.050 | | 0.3365 | E | (36) |
| | 0.025† | 0.025 | | 0.7386 | | 6.833 | | 0.3345 | paH | (8) |
| | 0.05† | 0.05 | | 0.7325 | | 6.741 | | 0.3338 | | |
| Borax | 0.01 | | 25 | 0.8781 | | 9.177 | | 0.3354 | E | (76) |
| | 0.02 | | | 0.8774 | | 9.173 | | 0.3349 | paH | (109) |
| | 0.03 | | | 0.8775 | | 9.176 | | 0.3348 | | |
| | 0.04 | | | 0.8778 | | 9.185 | | 0.3346 | | |
| | 0.05 | | | 0.8783 | | 9.196 | | 0.3344 | | |

\* In 0.09 *M* potassium chloride.

† NaH$_2$PO$_4$ instead of KH$_2$PO$_4$. These solutions also contained sodium chloride at a concentration equal to 0.97 × the molarity of each phosphate.

salts. The corresponding potential for the cell with a saturated calomel electrode (cell IV) is 0.2440 v.[8] For the molar scale of activity, $E^{0'} + E_j$ becomes 0.2439. This value is in good agreement with 0.2441, selected by Hitchcock and Taylor (76).

It is impossible to state what effect a change in the valence type of the buffer system will have upon $E^{0'} + E_j$ and, hence, how generally applicable this standard potential may be in determining the paH of buffered solutions of different and even unknown compositions. If measurements of hydrogen-calomel cells with dilute phosphate buffers were available, it is safe to say that they would furnish a standard potential greater than 0.3360 at an ionic strength of 0.01. The single measurement of Guggenheim and Schindler (36) in the dilute range gives 0.3365. The values of $E^{0'} + E_j$ computed from E.M.F. data (76) for phosphates at higher ionic strengths, together with the paH derived
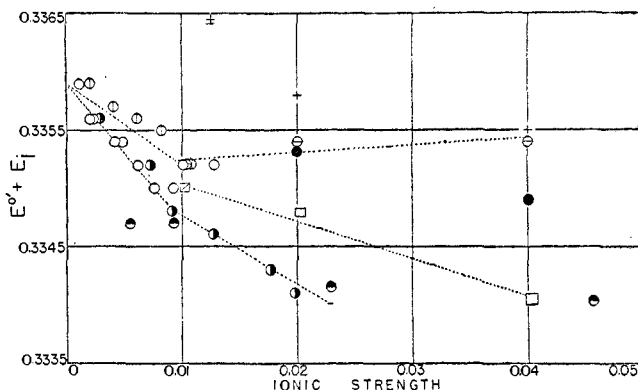


Fig. 2. $E^{0'} + E_j$ for cell II as a function of ionic strength at 25°C. Acetates: ⊖ (36, 76), ⊕ (95), ○ (102). Chloroacetates: ◑ (102). Formates: ⊖ (95). Glycolates: □ (76), ▨ (96). Borates: ● (76). Phosphates: + (76), ± (36).

from measurements of cells without junction, are consistent with the results for monobasic acid systems, as shown in table 3. It is entirely possible that the change in slope that occurs at about 0.01 $\mu$ with acetate and chloroacetate buffer systems becomes apparent at a higher concentration when bivalent anions are present.

Nevertheless, the conclusion that the residual liquid-junction potentials (compare equation 9) may amount to 0.01 to 0.02 paH unit (0.6 to 1.2 mv.) is inescapable. It is clearly impossible to determine the paH of a solution that is "unknown" in every sense of the word with an uncertainty less than ±0.02 unit.

[8] Although the presence of air alters the potentials of calomel and silver–silver halide electrodes in acid solutions, its effect upon only the silver–silver iodide electrode is significant in neutral halide solutions (128, 147, 158).

### D. Determination of the paH of reference solutions

The potential of the saturated calomel electrode is not considered highly reproducible, and the use of this electrode as a standard cannot be recommended (113). Some possible causes of erratic behavior are hysteresis (163) and variations in the grain size of the calomel (162). Hence, one cannot expect always to make use of standard values of $E^{0'} + E_j$ such as are given in the foregoing section. For this reason it is always desirable to redetermine $E^{0'} + E_j$, that is, to standardize the cell, at frequent intervals by measurement of the electromotive force for a solution of known paH. The true standard potential is then unimportant, so long as the calibration remains unchanged.

Nevertheless, electromotive-force measurements of cells of types II and IV in different laboratories agree satisfactorily when the cell solutions are either buffered electrolytes or strong acid–salt mixtures, as a comparison of published data will testify (18, 36, 76, 102). Different choices of $E^{0'}$ or $E^{0'} + E_j$ are chiefly responsible for the lack of agreement on the paH values to be assigned to standard solutions. It is apparent from figure 2 that the choice of 0.3358 by MacInnes, Belcher, and Shedlovsky (102) resulted from the use of experimental data for very dilute buffer solutions. On the other hand, Hitchcock and Taylor obtained 0.3353 by the extrapolation of values obtained at ionic strengths in excess of 0.01. A difference of 0.008 in the paH values computed from the same measured electromotive force is the direct result of this difference of 0.5 mv. in $E^{0'} + E_j$. Except for the dilute acetate buffer, 0.01 $M$ acetic acid and 0.01 $M$ sodium acetate,[9] paH on the scale of Guggenheim and Schindler (36) appears improbably high, because their standard potential is too low.

Our choice of 0.3352 for $E^{0'} + E_j$ rests upon the two following considerations: (a) There is no theoretical explanation for an abrupt change below 0.01 $\mu$ in the slope of the plot of "apparent" paH with respect to ionic strength. We are therefore led to suspect an abnormal change of liquid-junction potential as the solute on one side of the boundary becomes attenuated. (b) It is quite improbable that the paH of the standard 0.01 $M$ acetate buffer computed from measurements of cells without liquid junction is in error by more than ±0.005 unit. This value is 4.714. If $E^{0'} + E_j$ is 0.3352, the paH computed from the electromotive force of the cell with liquid junction is also 4.714. If the higher value, 0.3358, is chosen for the standard potential, however, the paH of this solution is found to be 4.704.

The reference solution that appears to have found most extensive use (18, 79, 90, 94, 153) is the mixture of 0.01 $M$ hydrochloric acid and 0.09 $M$ potassium chloride, often known as "Veibel's solution" (162). Inasmuch as the potential at the boundary of a strong acid mixture such as this and saturated potassium chloride differs somewhat from the potential between a buffer solution and the same bridge solution, this mixture is not to be recommended as a standard for general use.

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[9] Guggenheim and Schindler have apparently made an error in calculating the paH of this buffer solution. The paH value should read 4.71 instead of 4.80 on pages 535 and 538 of their paper (36).

Table 4 illustrates the essential agreement among paH values of buffered solutions computed from the data of Hitchcock and Taylor (H & T) (76) and MacInnes, Belcher, and Shedlovsky (M, B, & S) (102) and those values derived from measurements of cells without liquid junction. The paH in the second and third columns is based upon standard potentials of 0.2440 for cell IV and 0.3352 for cell II. At present it is impossible to say definitely what effect the presence of salts of the higher valence types may have upon the standard potential. Nevertheless, paH values for phosphate buffer solutions have been included in the table for purposes of comparison. Methods by which the paH can be calculated from the electromotive force of cells without liquid junction will be considered in the following section.

TABLE 4

*paH of standard buffer solutions at 25°C.*

$(E^{0'} + E_j = 0.3352)$

| SOLUTION | paH (H & T) | paH (M, B, & S) | paH (FROM CELLS WITHOUT LIQUID JUNCTION) | REFERENCE (CELLS WITHOUT LIQUID JUNCTION) |
|---|---|---|---|---|
| Acid potassium phthalate (0.05 $M$) | 4.010 | 4.010 | 4.005 | (50) |
| Acetic acid (0.01 $M$) and sodium acetate (0.01 $M$) | 4.716 | 4.710 | 4.714 | This paper |
| Acetic acid (0.1 $M$) and sodium acetate (0.1 $M$) | 4.650 | 4.650 | 4.65 ±0.01 | This paper |
| Potassium dihydrogen phosphate (0.01 $M$) and disodium hydrogen phosphate (0.01 $M$) | 6.965 | | 6.959 | (8) |
| Potassium dihydrogen phosphate (0.025 $M$) and disodium hydrogen phosphate (0.025 $M$) | 6.860 | | 6.860 | (8) |
| Borax (0.01 $M$) | 9.180 | | 9.177 | (109) |

VII. THE PAH OF BUFFER SOLUTIONS FROM MEASUREMENTS OF CELLS WITHOUT LIQUID JUNCTION

As indicated in an earlier section, a cell without liquid junction and the pwH scale should be used for determinations of acidity whenever it is possible to do so. The great majority of approximate measurements, however, are made of cells with liquid junction, and the paH scale appears the most suitable for interpreting these results. In view of the relative ease with which accurate E.M.F. measurements of cells without liquid junction can be made over a wide range of temperatures, an effort has been made to use these cells for establishing paH standards with which to calibrate the pH meter and other cells with liquid junction. The assumptions on which these methods are based will be discussed. Inasmuch as the paH definition (equation 5) is used throughout, all of these methods of

calculation are equivalent in dilute solutions. An attempt will be made to determine the limiting value of the ionic strength below which these different assumptions will yield substantially identical paH values.

## A. Electromotive force and pwH

In order to make a comparison with the measurements of cells with liquid junction reported by Hitchcock and Taylor (76, 77) and MacInnes, Belcher, and Shedlovsky (102), some studies of the buffer solutions used by these investigators were undertaken with the use of cells without liquid junction (3). The cells were of type III. In general, the electromotive force was obtained at 0°, 25°, 38°, and 50°C. The value at 0°C. was found by linear extrapolation with the use of the E.M.F. measured at temperatures of 25°C. and a few tenths of a degree above 0°C.

In addition to the buffer solutions studied by Hitchcock and Taylor, cell measurements were made with 0.02 $m$ solutions of potassium dihydrogen citrate and potassium tetroxalate. Potassium bitartrate and potassium tetroxalate separated from the 0.03 $m$ and 0.1 $m$ solutions when these were cooled, so measurements at 0°C. could not be obtained. Molalities were used throughout, but the difference of pH between the weight and volume scales of concentration is less than 0.001 unit and therefore unimportant, so long as the same standard state is employed. Two concentrations of sodium chloride, 0.01 $m$ and 0.005 $m$, were utilized, in order that pwH in the absence of chloride could be obtained by a short extrapolation. These data are summarized in table 5.

The pwH numbers for these buffer solutions are given in table 6, together with those of several other useful buffer solutions that have been studied by measurements of cells of type III. The data for 0.1 $m$ hydrochloric acid and mixtures of 0.01 $m$ hydrochloric acid with 0.09 $m$ sodium and potassium chlorides are included. The pwH values for these were computed from the mean activity coefficient of hydrochloric acid in the mixtures (53). For the other solutions, equation 16 was used. The ionic strengths were obtained, by arithmetical approximations, with the aid of the first dissociation constant of oxalic acid (19) and the first and second constants of tartaric (19) and citric acids (18).

## B. Evaluation of ionic activity coefficients

It is evident from the mass law that

$$-\log (f_{\mathrm{H}} f_{\mathrm{Cl}} m_{\mathrm{H}}) = \mathrm{p}K - \log \frac{m_{\mathrm{HA}}}{m_{\mathrm{A}}} - \log \frac{f_{\mathrm{HA}} f_{\mathrm{Cl}}}{f_{\mathrm{A}}} \qquad (28)$$

in which HA is an uncharged weak acid or an acid anion, and A is the anion with one more negative charge than HA. The last term of this equation will be called $\log f_r$. Expressions for paH are derived by adding $\log f_{\mathrm{Cl}}$ to either side of equation 28:

$$\mathrm{paH} = -\log (f_{\mathrm{H}} f_{\mathrm{Cl}} m_{\mathrm{H}}) + \log f_{\mathrm{Cl}} \qquad (29)$$

and

$$paH = pK - \log \frac{m_{HA}}{m_A} - \log \frac{f_{HA}f_{Cl}}{f_A} + \log f_{Cl} \qquad (29a)$$

In equation 28, both of the terms that contain activity coefficients are physically defined.[10] This significance is lacking, however, in the expressions for paH. To compute $-\log a_H$, a numerical value must be assigned to $f_{Cl}$. An arbitrary assumption must be introduced at this point, for neither $f_{Cl}$ nor $f_{HA}/f_A$ can be evaluated by thermodynamic methods. This assumption should appear reasonable in the light of the modern theory of electrolytes.

TABLE 5

*Electromotive force of the cell: $H_2$; buffer solution, NaCl, AgCl; Ag at 0°, 25°, 38°, and 50°C.*

| BUFFER SOLUTION | NaCl | $E_0$ | $E_{25}$ | $E_{38}$ | $E_{50}$ |
|---|---|---|---|---|---|
| | *molality* | | | | |
| 0.1 $m$ potassium tetrox- alate | 0.01 | | 0.43742 | 0.43895 | 0.44001 |
| | 0.005 | | 0.45491 | 0.45699 | 0.45889 |
| 0.02 $m$ potassium tetrox- alate | 0.01 | 0.45329 | 0.45978 | 0.46197 | 0.46342 |
| | 0.005 | 0.46945 | 0.47736 | 0.48031 | 0.48250 |
| 0.03 $m$ potassium bitar- trate | 0.01 | | 0.55565 | 0.56085 | 0.56585 |
| | 0.005 | | 0.57372 | 0.57965 | 0.58528 |
| 0.1 $m$ potassium dihy- drogen citrate | 0.01 | 0.55691 | 0.56695 | 0.57195 | 0.57638 |
| | 0.005 | 0.57352 | 0.58480 | 0.59058 | 0.59614 |
| 0.02 $m$ potassium dihy- drogen citrate | 0.01 | 0.56000 | 0.57052 | 0.57575 | 0.58058 |
| | 0.005 | 0.57671 | 0.58870 | 0.59475 | 0.60027 |
| 0.1 $m$ acetic acid + 0.1 $m$ sodium acetate | 0.01 | 0.60464 | 0.62242 | 0.63153 | 0.63982 |
| | 0.005 | 0.62082 | 0.64017 | 0.65000 | 0.65897 |
| 0.01 $m$ acetic acid + 0.01 $m$ sodium acetate | 0.01 | 0.60436 | 0.62230 | 0.63145 | 0.63982 |
| | 0.005 | 0.62062 | 0.64013 | 0.65003 | 0.65905 |

The theories of electrolytic solutions offer some guidance in splitting the activity-coefficient terms of equation 28, but their aid is limited in general to dilute solutions. In solutions so dilute that the limiting law of Debye and Hückel is obeyed, the validity of equation 13 can safely be assumed. The limiting law indicates further that the logarithms of ionic activity coefficients are proportional to the squares of the charges on the ions. The Debye–Hückel equations and their extended forms have been conspicuously successful in repre-

[10] If $f_H$ is written in both numerator and denominator, it is evident that log $(f_{HA}f_{Cl}/f_A)$ is 2 log $(f_{HCl}'/f_{HA}')$, where $f_{HCl}'$ and $f_{HA}'$ are, respectively, the mean activity coefficients of hydrochloric acid and of a monobasic weak acid, HA.

TABLE 6

*pwH at 0°, 25°, 38°, and 50°C.*

| SOLUTION | SODIUM CHLORIDE | IONIC STRENGTH | pwH = −log $(f_H f_{Cl} m_H)$ AT | | | | REFERENCE |
|---|---|---|---|---|---|---|---|
| | | | 0°C. | 25°C. | 38°C. | 50°C. | |
| | *molality* | | | | | | |
| 0.1 m hydrochloric acid | | 0.1 | 1.190 | 1.198 | 1.204 | 1.212 | (58) |
| 0.1 m potassium tetroxalate | 0.01 | | | 1.636 | 1.653 | 1.677 | |
| | 0.005 | | | 1.631 | 1.644 | 1.670 | |
| | 0.000 | 0.144 | | 1.626 | 1.635 | 1.663 | |
| 0.02 m potassium tetroxalate | 0.01 | | 2.002 | 2.014 | 2.025 | 2.042 | |
| | 0.005 | | 2.000 | 2.010 | 2.022 | 2.039 | |
| | 0.000 | 0.034 | 1.998 | 2.006 | 2.019 | 2.036 | |
| 0.01 m hydrochloric acid + 0.09 m sodium chloride | | 0.1 | 2.200 | 2.206 | 2.211 | | (53) |
| 0.01 m hydrochloric acid + 0.09 m potassium chloride | | 0.1 | 2.203 | 2.208 | 2.212 | | (53) |
| 0.03 m potassium bitartrate | 0.01 | | | 3.635 | 3.628 | 3.640 | |
| | 0.005 | | | 3.640 | 3.631 | 3.642 | |
| | 0.000 | 0.035 | | 3.645 | 3.634 | 3.644 | |
| 0.1 m potassium dihydrogen citrate | 0.01 | | 3.915 | 3.826 | 3.808 | 3.804 | |
| | 0.005 | | 3.920 | 3.827 | 3.808 | 3.812 | |
| | 0.000 | 0.113 | 3.925 | 3.828 | 3.808 | 3.820 | |
| 0.02 m potassium dihydrogen citrate | 0.01 | | 3.972 | 3.887 | 3.869 | 3.870 | |
| | 0.005 | | 3.979 | 3.893 | 3.876 | 3.876 | |
| | 0.000 | 0.023 | 3.986 | 3.899 | 3.883 | 3.882 | |
| 0.05 m acid potassium phthalate | 0.01 | | 4.085 | 4.090 | 4.113 | 4.152 | (45) |
| | 0.005 | | 4.087 | 4.091 | 4.117 | 4.155 | |
| | 0.000 | 0.053 | 4.089 | 4.092 | 4.121 | 4.158 | |
| 0.1 m acetic acid + 0.1 m sodium acetate | 0.01 | | 4.796 | 4.764 | 4.773 | 4.794 | |
| | 0.005 | | 4.793 | 4.763 | 4.771 | 4.792 | |
| | 0.000 | 0.1 | 4.790 | 4.762 | 4.769 | 4.790 | |
| 0.01 m acetic acid + 0.01 m sodium acetate | 0.01 | | 4.791 | 4.762 | 4.771 | 4.794 | |
| | 0.005 | | 4.790 | 4.762 | 4.771 | 4.793 | |
| | 0.000 | 0.01 | 4.789 | 4.762 | 4.771 | 4.792 | |
| 0.025 m potassium dihydrogen phosphate + 0.025 m disodium hydrogen phosphate | 0.01 | | 7.081 | 6.962 | 6.941 | 6.939 | (8) |
| | 0.005 | | 7.085 | 6.966 | 6.946 | 6.945 | |
| | 0.000 | 0.1 | 7.089 | 6.970 | 6.951 | 6.951 | |

TABLE 6—*Concluded*

| SOLUTION | SODIUM CHLORIDE | IONIC STRENGTH | pwH = −log ($f_H f_{Cl} m_H$) AT | | | | REFERENCE |
|---|---|---|---|---|---|---|---|
| | | | 0°C. | 25°C. | 38°C. | 50°C. | |
| | *molality* | | | | | | |
| 0.01 *m* potassium dihydrogen phos· phate + 0.01 *m* disodium hydrogen phosphate | 0.01 | | 7.139 | 7.021 | 7.000 | 6.999 | (8) |
| | 0.005 | | 7.148 | 7.029 | 7.009 | 7.008 | |
| | 0.000 | 0.04 | 7.157 | 7.037 | 7.018 | 7.017 | |
| 0.05 *m* sodium tetra· borate (borax) | 0.01 | 0.11 | 9.614 | 9.303 | 9.195 | 9.120 | (109) |
| 0.01 *m* sodium tetra· borate (borax) | 0.01 | 0.03 | 9.517 | 9.242 | 9.466 | 9.083 | (109) |

senting the mean activity coefficients of strong electrolytes at intermediate and even high concentrations. No extension of equation 13 is forthcoming, however, nor is any information to be derived from these equations regarding the upper limit of validity of the relationship between the activity coefficients of ions of single and double charge.

In figure 3, the common logarithms of the ratios of the mean activity coefficients of eighteen uni-univalent strong electrolytes to that of hydrochloric acid are plotted as a function of ionic strength. The activity coefficients of the formates were taken from the papers of Guggenheim (35) and those of the other electrolytes from tables given in the monograph of Harned and Owen (64). The logarithms of the ratios of the mean activity coefficients of eight strong electrolytes of the 2–1 and 1–2 valence types to the square of the mean activity coefficient of hydrochloric acid are plotted in figure 4 as a function of ionic strength. Broken lines are drawn when the ratio is known only at an ionic strength of 0.3.

It is evident in figures 3 and 4 that the valence relations of the limiting law for mean activity coefficients hold fairly well in a part of the range where specific effects render the simple limiting equation useless. Although no appreciable individual differences among the mean activity coefficients of many uni-univalent electrolytes are apparent somewhat above the so-called "Debye–Hückel range," it is doubtful that equation 13 can be more than approximately true at higher ionic strengths (36, 161). Kortüm (92), however, believes that the general form of equation 13 for an ion $i$ of charge $z_i$ in an electrolyte which dissociates completely into $\nu_+$ cations and $\nu_-$ anions of valences $z_+$ and $z_-$, respectively,

$$\ln f_i = \frac{\nu z_i^2}{\nu_+ z_+^2 + \nu_- z_-^2} \ln f_{\pm} \qquad (30)$$

where $\nu = \nu_+ + \nu_-$, is valid for all electrolytes up to an ionic strength of 0.01, and for potassium chloride to 0.1.

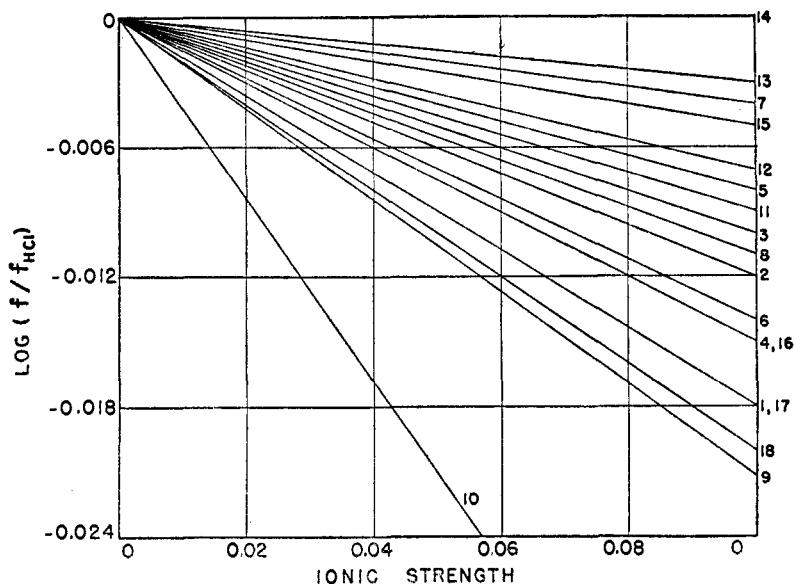Probably the most fruitful expositions of ionic behavior have been made by

FIG. 3. Logarithms of the ratios of mean activity coefficients of strong uni-univalent electrolytes to the mean activity coefficient of hydrochloric acid plotted as a function of ionic strength. Odd numbers indicate sodium salts and even numbers potassium salts. 1, 2—fluorides; 3, 4—chlorides; 5, 6—bromides; 7, 8—iodides; 9, 10—nitrates; 11, 12—for· mates; 13, 14—acetates; 15, 16—thiocyanates; 17, 18—toluenesulfonates.
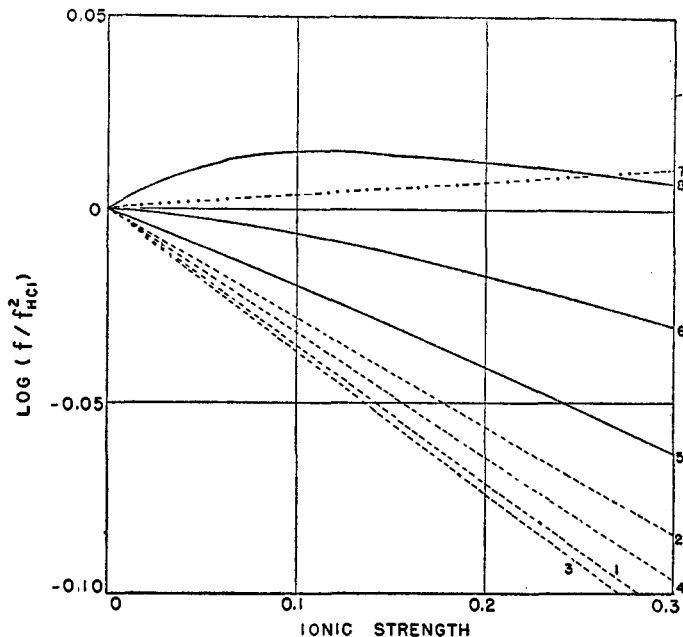


FIG. 4. Logarithms of the ratios of mean activity coefficients of strong electrolytes of the 1–2 and 2–1 valence types to the square of the mean activity coefficient of hydrochloric acid plotted as a function of ionic strength. 1, sodium sulfate (62); 2, lithium sulfate (133); 3, potassium sulfate (133); 4, sodium thiosulfate (133); 5, barium chloride (142, 160); 6, calcium chloride (146); 7, magnesium bromide (132); 8, zinc iodide (4).

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Brønsted.   The first of these is the principle of specific ionic interaction (21).[11] This theory, which has been able to interpret successfully the properties of many mixtures of strong electrolytes, may be summarized by its two postulates: (a) Ions of like charge repel each other so strongly that the interactions of their short-range forces are identical and negligible, and (b) each ion exerts a "salting-out effect" on every other ion in the solution, that is, an effect which tends to increase the activity coefficient.

The first of these postulates leads one to expect only small changes in the last term on the right of equation 28 when an anion, A, is substituted for another of like charge.   This term would be altered, however, by a change in the kinds of cations.   The theory also predicts a linear change of this activity-coefficient term with change of composition, as long as the ionic strength is constant and the kinds of ions remain unchanged.   When the change in composition involves a change of ratio of different cations, however, the activity coefficient may not vary in such a simple manner.   Beyond these considerations, Brønsted's principle offers no assistance in splitting the activity-coefficient term.

Güntelberg and Schiödt (39) and others (20, 82) have pointed out the usefulness in electrometric work of a kinetic principle set forth by Brønsted (23). According to this principle, the activity coefficients of substances present in small amount in a mixture of electrolytes are virtually independent of the quantities of these substances and are determined solely by the salt present in large amount.

The assumptions that have been used to evaluate the individual activity coefficients will be discussed in the sections to follow.   It will be convenient to distinguish among paH values related to these various assumptions.   The symbols $p_1H$, $p_2H$, etc., will be used to differentiate the several paH scales that will be considered.

### C. Estimation of the activity coefficient of chloride ion

It is evidently not impossible to employ cells of type III for the measurement of $-\log m_H$ or $-\log a_H$ of unknown solutions.   In addition to the experimental difficulties attending the use of cells of this kind with solutions of unknown composition, it is necessary to evaluate $f_H f_{Cl}$ or $f_{Cl}$ to compute respectively $-\log m_H$ or $-\log a_H$ from equation 29.   In order that $m_H$ could be calculated, Hamer (42) suggested that $f_H f_{Cl}$ be computed with the aid of Guggenheim's equation (35) for a "standard" electrolyte, the first term on the right of equation 26,

$$\log f_i = -A\sqrt{\mu}/(1 + \sqrt{\mu}) \tag{31}$$

where $i$ represents a single ionic species, or that it be set equal to the square of the mean activity coefficient of sodium chloride at the appropriate ionic strength. Hamer and Acree (44) preferred to use the Hückel equation (78) for computing $f_{Cl}$,

$$\log f_i = \frac{-A z_i^2 \sqrt{\mu}}{1 + B a_i \sqrt{\mu}} + \beta_i \mu \tag{32}$$

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[11] See also Güntelberg (38), Scatchard and Prentiss (141), and chapter 14 of the monograph of Harned and Owen (64).

where $A$ and $B$ are constants at a particular temperature (105, 138) in the water medium and $a_i$ and $\beta_i$ are parameters characteristic of the mixture of ions. With this value for $f_{Cl}$, $\mathbf{a_H}$ could be obtained. In the absence of any information concerning the values of $a_i$ and $\beta_i$, relatively large uncertainties must be ascribed to the pH. For accurate work and for standardization purposes, it is necessary to know these values (44).

Manov, DeLollis, and Acree (107) computed the pH of mixtures of borax and sodium chloride after evaluating $f_{Cl}$ by equation 32 without the term $\beta_i\mu$, which is of secondary importance at low ionic strengths. It was assumed that the activity coefficient of chloride ion in all mixtures of borax and sodium chloride is equal to the mean activity coefficient of sodium chloride in a pure solution of the salt at the same ionic strength. A value of 4.4 was assigned to $a_i$, inasmuch as the first term on the right of equation 32 represents log $f_{NaCl}$ at ionic strengths below 0.05 when this value of $a_i$ is used (24, 141). In a later paper (109), results of measurements with varying ratios of sodium chloride to borax were reported. Equation 32, with the same $a_i$ value (4.4) as before, was used for computing the activity coefficient of chloride ion, but $\beta_i\mu$ was replaced by $-Cm_{Cl}$, where $C$ is the slope of the plot of $pK'$,

$$pK' = (E - E^0)/k + \log (m_{HBO_2}/m_{BO_2}) \tag{33}$$

for a given borate buffer solution with respect to the molality of sodium chloride.

The activity coefficient of chloride ion was in effect set equal to the mean activity coefficient of sodium chloride only when chloride was absent. It is apparent from a consideration of equations 16, 28, 32, and 33 that $f_{Cl}$ at ionic strengths below 0.05 was expressed by

$$f_{Cl} = f_{NaCl}f_r/f_r^0 \tag{34}$$

where $f_r$ is $f_{HBO_2}f_{Cl}/f_{BO_2}$ in a mixture of borax and sodium chloride and $f_r^0$ is the same quantity in a borax solution of the same concentration but without chloride.

The dissociation of $HBO_2$ may not be the only equilibrium of significance in borax buffers of moderate concentration (89). For this reason, the buffer ratio may depart from unity, and incorrect results are then obtained by equation 29a. Under these circumstances, however, the paH computed from equation 29 will approximate the true value, inasmuch as secondary equilibria influence this computation only through a change in ionic strength. When the concentration of borax is 0.01 $M$ or less, the two equations yield substantially the same result.

In order to determine the pH of 0.05 $m$ acid potassium phthalate, Hamer and Acree (45) constructed plots of $-\log f_{Cl}^0$, that is, log $(f_H m_H)^0 -\log (f_H f_{Cl} m_H)^0$, where the superscript zero indicates the value of the quantity extrapolated to zero sodium (or potassium) chloride, as a function of $-\log (f_H f_{Cl} m_H)$, which we have called pwH. Equation 13 was assumed to hold for aqueous solutions of hydrochloric acid and potassium hydroxide up to a molality of 0.2. It was then possible to assign values to log $(f_H m_H)^0$, and hence to $-\log f_{Cl}^0$, in solutions of these strong electrolytes. Straight lines were drawn between $-\log f_{Cl}^0$ in the acid and alkaline solutions at each of several ionic strengths. The value that

corresponded to the appropriate pwH was then interpolated graphically or calculated by means of the equation for the line. The pH of the buffer solution could then, of course, be computed by equation 29. The constants $P$ and $Q$ of the equation

$$pH = (pwH - P)/Q \tag{35}$$

at several ionic strengths are given in their paper. The pH of 0.05 $m$ acid potassium phthalate found in this way agreed well with the paH later assigned to this solution (50) on the basis of extensive studies of the equilibria in the phthalate buffer systems (47, 49).

The activity coefficients of chloride ion in pure solutions of hydrochloric acid and potassium hydroxide found by this means for ionic strengths below 0.1 correspond to those calculated by the first term on the right of equation 32 with 5.6 and 3.4, respectively, for $a_i$. Intermediate values of $a_i$ would be needed for computing $f_{Cl}$ in buffer solutions of intermediate pH. In terms of equation 32, therefore, this method postulates a dependence of $a_i$ and of log $f_{Cl}$ (or log $f_H$) upon the acidity of the solution. Insofar as a decrease of acidity always means a change of composition of the solution away from that of a strong acid and toward that of a strong base, this view is not unreasonable. Hamer and Acree suggest further that the data for the activity coefficient of sodium or lithium hydroxide, instead of potassium hydroxide, be used when sodium and lithium are predominant among the buffer cations. In spite of this refinement, however, the specific effects of ions other than hydrogen, hydroxyl, and the alkalis on the value of $f_{Cl}$ and $f_H$ cannot be ignored.

If $-\log f_{Cl}$ is computed by the first term on the right of equation 32, with arbitrary choice of the value of $a_i$, a unit of acidity that will be termed $p_lH$ can be defined with the aid of equation 29:

$$p_lH \equiv -\log \left( f_H f_{Cl} m_H \right) - A\sqrt{\mu}/(1 + Ba_i\sqrt{\mu}) \tag{36}$$

In agreement with Bjerrum's calculation (17), $a_i$ for most strong uni-univalent electrolytes in aqueous solution is in excess of 3.5, and values over 6 are uncommon with electrolytes of this valence type.[12] For this reason, Bates, Siegel, and Acree (11) chose a value of 4.0 for constructing titration curves of monobasic acids in dilute solutions from measurements of cells of type III without liquid junction.

Obviously the differences of $p_lH$ caused by the choice of different values of $a_i$ disappear in dilute solutions. Consequently, $f_{Cl}$ can be estimated with greater certainty for a dilute buffer than for a solution of higher ionic strength. In table 7 $p_lH$, computed from the data of table 6 by equation 36, is listed for fifteen solutions. Two values, 4 and 6, were used for $a_i$. The paH on the scale of

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[12] The value of $a^*$ (the symbol used in place of $a_i$ when a combination of activity coefficients is being expressed by equation 32) for log $(f_{HP_s}f_{Cl}/f_{P_s})$, where Ps is the bivalent $p$-phenolate sulfonate anion, was found to be 8.0 (12). In calculations of log $(f_{HCO_3}f_{Cl}/f_{CO_3})$, the writer found a value of 10.0 to be consistent with the E.M.F. data of Harned and Scholes (66). Values of 3.5 to 6.0 have been obtained for most other buffer solutions.

TABLE 7

*p₁H from cells without liquid junction compared with paH from cells with
liquid junction*

The upper $p_1H$ value was computed with $a_i = 4$, the lower value with $a_i = 6$

| SOLUTION | p₁H AT | | | | paH, FROM CELLS WITH LIQUID JUNCTION, AT | | REFERENCE (paH) |
|---|---|---|---|---|---|---|---|
| | 0°C. | 25°C. | 38°C. | 50°C. | 25°C. | 38°C. | |
| 0.1 m hydrochloric acid | 1.080 1.094 | 1.084 1.099 | 1.088 1.103 | 1.094 1.109 | 1.085 | 1.082 | (76, 77) |
| 0.1 m potassium tetroxalate | | 1.497 1.516 | 1.504 1.522 | 1.529 1.548 | 1.480 | 1.495 | (76, 77) |
| 0.02 m potassium tetroxalate | 1.925 1.932 | 1.931 1.937 | 1.942 1.949 | 1.957 1.964 | | | |
| 0.01 m hydrochloric acid + 0.09 m sodium chloride | 2.091 2.105 | 2.092 2.107 | 2.095 2.110 | | 2.058 | | (76) |
| 0.01 m hydrochloric acid + 0.09 m potassium chloride | 2.093 2.107 | 2.094 2.109 | 2.096 2.111 | | 2.075 | 2.075 | (76, 77) |
| 0.03 m potassium bitartrate | | 3.569 3.575 | 3.556 3.563 | 3.564 3.571 | 3.567 | | (76) |
| 0.1 m potassium dihydrogen citrate | 3.811 3.826 | 3.709 3.725 | 3.687 3.703 | 3.696 3.713 | 3.719 | | (76) |
| 0.02 m potassium dihydrogen citrate | 3.925 3.929 | 3.835 3.840 | 3.818 3.823 | 3.815 3.821 | | | |
| 0.05 m acid potassium phthalate | 4.002 4.011 | 4.002 4.011 | 4.027 4.036 | 4.064 4.074 | 4.010 4.000 4.000* | 4.025 4.015 | (76, 77) (102) (102) |
| 0.1 m acetic acid + 0.1 m sodium acetate | 4.680 4.694 | 4.648 4.663 | 4.653 4.668 | 4.672 4.687 | 4.648 4.640 4.650* | 4.655 4.635 | (76, 77) (102) (102) |
| 0.01 m acetic acid + 0.01 m sodium acetate | 4.746 4.748 | 4.717 4.720 | 4.725 4.728 | 4.745 4.748 | 4.714 4.700 4.710* | 4.710 | (76) (102) (102) |
| 0.025 m potassium dihydrogen phosphate + 0.025 m disodium hydrogen phosphate | 6.979 6.993 | 6.856 6.871 | 6.835 6.850 | 6.833 6.848 | 6.858 | 6.835 | (76) |

TABLE 7—*Concluded*

| SOLUTION | p$_I$H AT | | | | paH, FROM CELLS WITH LIQUID JUNCTION, AT | | REFERENCE (paH) |
|---|---|---|---|---|---|---|---|
| | 0°C. | 25°C. | 38°C. | 50°C. | 25°C. | 38°C. | |
| 0.01 $m$ potassium dihydrogen phosphate + 0.01 $m$ disodium hydrogen phosphate | 7.079 7.087 | 6.956 6.964 | 6.936 6.943 | 6.933 6.941 | 6.963 | | (76) |
| 0.05 $m$ sodium tetraborate (borax) + 0.01 $m$ sodium chloride | 9.501 9.516 | 9.186 9.201 | 9.075 9.091 | 8.998 9.014 | 9.180† | 9.070† | (76,77) |
| 0.01 $m$ sodium tetraborate (borax) + 0.01 $m$ sodium chloride | 9.448 9.454 | 9.170 9.176 | 9.393 9.399 | 9.008 9.015 | 9.178† | 9.078† | (76,77) |

* At 12°C.
† paH of the buffer without sodium chloride.

Hitchcock and Taylor (76, 77), derived from measurements of cells with liquid junction, is included, as well as the values of MacInnes, Belcher, and Shedlovsky (102) for acid potassium phthalate and the two acetate buffer solutions. Inasmuch as the choice of $a_i$ is almost completely arbitrary, the uncertainty of the p$_I$H must be considered at least as great as the difference between the two p$_I$H scales.

It is of interest to compare p$_I$H obtained from the electromotive force of cell III with paH computed from mean activity coefficients by the conventions of MacInnes and of Guggenheim. Such a comparison is necessarily limited to strong electrolytes. For this purpose we choose 0.01 $m$ and 0.1 $m$ hydrochloric acid and mixtures of 0.01 $m$ hydrochloric acid with 0.09 $m$ sodium and potassium chlorides.

The mean activity coefficient of hydrochloric acid, $f_{HCl}$, in its pure aqueous solution is 0.905 at 0.01 $m$ and 0.796 at 0.1 $m$ (58, 145). The value of this activity coefficient in the two mixtures can be computed from published data (38, 53, 61). According to the Guggenheim convention, $f_H$ is numerically equal to $f_{HCl}$. The mean activity coefficient of potassium chloride is 0.902 and 0.770 at 0.01 and 0.1 $m$, respectively (146). These are also the values of $f_{Cl}$, by the MacInnes assumption, whenever the chloride-ion concentration is 0.01 or 0.1, as it is in each of the four solutions in question. We then compute $f_H$ by the formula, $f_H = f_{HCl}^2/f_{KCl}$, and paH by equation 5. Inasmuch as the logarithms of the mean activity coefficients of both hydrochloric acid and potassium chloride can be satisfactorily expressed in this range of ionic strengths by the last term of equation 36 with suitable choice of $a_i$ (131, 146), these paH values are desig-

nated $p_1H$. The results of these calculations are given in table 8. The $p_1H$ of the two acid–chloride mixtures is appreciably higher than paH derived from cells with liquid junction, as a comparison with the results in table 7 shows.

If we assign arbitrarily a value of 4 to $a_i$ for the computation of log $f_{Cl}$ by the last term of equation 36, we have in reality another convention that is possibly easier to employ in the determination of paH from measurements of cell III than those suggested by MacInnes and Guggenheim. As table 8 shows, this assumption is substantially equivalent to the MacInnes convention for these mixtures of strong electrolytes and for solutions of hydrochloric acid.

Inasmuch as cell III is reversible to the ions of hydrochloric acid, it is not unreasonable to identify $f_{Cl}$ with the mean activity coefficient of hydrochloric acid in the cell solution. Unfortunately, this mean activity coefficient cannot be determined unless $m_H$ is known. The activity coefficient of the acid in a mixture of strong electrolytes of the same ionic strength and composition with respect to cations is likewise often unknown. In the method proposed by Hamer and Acree (45) and discussed earlier in this section, $f_{Cl}$ is set equal to $f_{HCl}$ in a solution

TABLE 8

*$p_1H$ for solutions of hydrochloric acid and acid–chloride mixtures at 25°C.*

| SOLUTION | EQUATION 36 $a_i = 4$ | EQUATION 36 $a_i = 6$ | MAC INNES CONVENTION | GUGGENHEIM CONVENTION |
|---|---|---|---|---|
| 0.01 $m$ HCl | 2.043 | 2.046 | 2.042 | 2.043 |
| 0.1 $m$ HCl | 1.084 | 1.099 | 1.085 | 1.099 |
| 0.01 $m$ HCl 0.09 $m$ NaCl | 2.092 | 2.107 | 2.092 | 2.103 |
| 0.01 $m$ HCl 0.09 $m$ KCl | 2.094 | 2.109 | 2.095 | 2.104 |

of hydrochloric acid of the same ionic strength for computing the paH of solutions whose pwH is in the vicinity of 1 to 2. Log $f_{Cl}$ is then assumed to vary linearly with pwH. When $f_{Cl}$ is identified with $f_{HCl}$, either with or without the linear variation, the paH scale so defined will be called $p_2H$.

$$p_2H \equiv (pwH - P)/Q \tag{35a}$$

$$p_2H \equiv -\log (f_H f_{Cl} m_H) + \log f_{HCl} \tag{35b}$$

### D. Separation of $f_{Cl}$ from the activity-coefficient term

When the buffer solution is composed of the primary and secondary anions of a dibasic or polybasic acid, the experimental values of log $f_r$ can be represented satisfactorily by an equation of the following form (8, 9, 47):

$$\log f_r \equiv \log \frac{f_{HA^-} f_{Cl^-}}{f_{A^{--}}} = \frac{2A\sqrt{\mu}}{1 + Ba^*\sqrt{\mu}} + \beta^* \mu \tag{37}$$

Both $a^*$ and $\beta^*$ are readily obtained from the experimental log $f_r$ by a process of curve fitting. When HA is a monobasic acid, however, the term that contains

$a^*$ disappears from the formal equation for log $f_r$, analogous to equation 37. Because $a^*$ and $\beta^*$, and also $a_i$ and $\beta_i$, possess little physical significance, equations 32 and 37 are useful chiefly as interpolation formulas.

Perhaps the simplest means of splitting $f_r$ to obtain $f_{Cl}$ is to assume the validity of the valence relationships in very dilute solutions, that is, $f_{Cl}^4 = f_{HA^-}^4 = f_{A^{--}}$. Log $f_{Cl}$ is thus set equal to $-\frac{1}{2}$ log $f_r$. In a study of malonate–chloride buffer solutions, Hamer, Burton, and Acree (48) suggested that for the computation of $f_{Cl}$ the experimental values of $a^*$ and $\beta^*$ be identified with $a_i$ and $\beta_i$ of equation 32. It is apparent that the measured activity-coefficient term would then be divided according to the formula,

$$\log f_{Cl} = -\frac{1}{2} \log f_r + \frac{3}{2} \beta^* \mu \tag{38}$$

For the malonate solutions, $\beta^*$ was zero, and the result is the same in this special case as that based upon the assumption of the valence relationships of the limiting law.

In order to compute the paH of equimolal mixtures of potassium dihydrogen phosphate and disodium hydrogen phosphate, Bates and Acree (8) determined $a^*$ and $\beta^*$ for five ratios of the molalities of sodium chloride and phosphate. The values of these two parameters were extrapolated to the limit of zero sodium chloride. The assumption was made that the limiting values, $a^0$ and $\beta^0$, could be used in equation 32 to compute $f_{H_2PO_4}/f_{HPO_4}$,

$$\log \left[ \frac{f_{H_2PO_4}}{f_{HPO_4}} \right]^0 = \frac{3A\sqrt{\mu}}{1 + Ba^0\sqrt{\mu}} + \beta^0 \mu \tag{39}$$

and paH by equation 29a. It was reasoned that the numerical values of the parameters of equation 37 in the absence of sodium chloride would be determined chiefly by the properties of the phosphate buffer. The following formulas are involved in this method of separating $f_{H_2PO_4}/f_{HPO_4}$ from the experimentally defined activity-coefficient term of equation 37:

$$\log \left[ \frac{f_{H_2PO_4}}{f_{HPO_4}} \right]^0 = \frac{3}{2} \log f_r^0 - \frac{1}{2} \beta^0 \mu \tag{40}$$

and

$$\log f_{Cl}^0 = -A\sqrt{\mu}/(1 + Ba^0\sqrt{\mu}) = -\frac{1}{2} \log f_r^0 + \frac{1}{2} \beta^0 \mu \tag{40a}$$

where the superscript zeros indicate the value of the quantity in question in the phosphate buffer without sodium chloride. As equation 40a shows, this treatment implies that the salt-effect term, $\beta_{Cl}\mu$, becomes zero in the absence of chloride.

The appearance in these equations of a term involving $\beta^0$ is unfortunate, inasmuch as $-\beta^*$, the slope of the extrapolation plots, can be varied somewhat by choice of $a^*$ within about $\pm 0.2$, the usual error in establishing the latter. If $f_{Cl}^4 = f_{HA^-}^4 = f_{A^{--}}$ were employed as a separation formula at all concentra-

tions, the last terms of equations 38, 40, and 40a would disappear. From a practical standpoint, this change of assumptions would not have a large effect on the pH values assigned to phosphate buffers, for $\frac{1}{2}\beta^0\mu$ is only 0.003 for a mixture of 0.025 $m$ potassium dihydrogen phosphate and 0.025 $m$ disodium phosphate, and 0.011 for a mixture in which the concentration of each phosphate salt is 0.1 $m$.

Hamer and Acree (47) have computed $\beta_i$ for chloride, acid phthalate, and phthalate ions from the observed change of $\beta^*$ with change of $m_{Ph}/m_{HPh}$ between 1.00 and 2.02 and $m_{Cl}/m_{HPh}$ from 1.0 to 0.093, where Ph is written for phthalate. A constant value of 3.76 for $a^*$ at 0–60°C. was found for all of these different compositions, and this value was therefore assigned to $a_i$ for each ion. The $\beta^*\mu$ term was expressed in terms of ionic $\beta_i$ values,

$$\beta^*\mu = \beta_{Ph}m_{Ph} - \beta_{HPh}m_{HPh} - \beta_{Cl}m_{Cl} \tag{41}$$

by a combination of activity-coefficient equations for each ion written in the form

$$-\log f_i = -A\sqrt{\mu}/(1 + 3.76B\sqrt{\mu}) - \beta_i m_i \tag{42}$$

In this equation the molality of the ion of species $i$ replaces the ionic strength, $\mu$, in the last term of equation 32. The experimental values of $\beta^*$ and the known molalities of the ions were used to set up a series of equations of the same form as equation 41. Each ratio of the three anions gave a different expression, and the three $\beta_i$ constants were obtained by the method of least squares.

The concept of constant $\beta_i$ appears to be at variance with the observed change of $\beta^*$ when a neutral salt, such as potassium nitrate, is added to a buffer–chloride mixture. It has been found that $a^*$ may remain unchanged, but $\beta^*$ is usually different (9). Inasmuch as the addition of neutral salt produces no change in the molalities of the buffer ions or chloride, the observed change cannot be accounted for by the formulation of equation 41, where constant $\beta_i$ is assumed.

Insofar as the treatment of solutions of constant buffer ratio and zero chloride-ion concentration is concerned, this method defines a scale equivalent to that employed to express the paH of the phosphate buffer solutions. The paH values computed by equations 29a and 39 with the limiting parameters for solutions without chloride are identical with the pH given by Hamer and Acree. Since the limiting value of $\beta^*$, namely $\beta^0$, when chloride is absent is $\beta_{Ph}m_{Ph} - \beta_{HPh}m_{HPh}$ by equation 41, the equation for dividing the experimental activity-coefficient term for phthalate solutions without chloride is the same as equation 40a.

These assumptions form the bases of three different pH scales. When the ionic activity coefficients are separated by assuming the validity of the valence relationships of the limiting law, that is, $f_{HA^-}^4 = f_{Cl^-}^4 = f_{A^{--}}$, the paH value of the buffer solution without chloride will be called $p_3H$. It is defined by

$$p_3H \equiv -\log (f_H f_{Cl} m_H)^0 - \frac{1}{2}\log f_r^0$$

$$= pK - \log (m_{HA}/m_A) - \frac{3}{2}\log f_r^0 \tag{43}$$

The separation formula of equation 38 similarly leads to

$$p_4H \equiv -\log (f_H f_{Cl} m_H)^0 - \frac{1}{2} \log f_r^0 + \frac{3}{2} \beta^0 \mu$$

$$= pK - \log (m_{HA}/m_A) - \frac{3}{2} \log f_r^0 + \frac{3}{2} \beta^0 \mu \qquad (44)$$

when chloride is absent, and equation 40a gives

$$p_5H \equiv -\log (f_H f_{Cl} m_H)^0 - \frac{1}{2} \log f_r^0 + \frac{1}{2} \beta^0 \mu$$

$$= pK - \log (m_{HA}/m_A) - \frac{3}{2} \log f_r^0 + \frac{1}{2} \beta^0 \mu \qquad (45)$$

The $p_4H$ values of phosphate–chloride mixtures and of phenolsulfonate–chloride mixtures have been reported (6, 12). The paH of mixtures of acid potassium phthalate, phthalic acid, and potassium chloride (49) was computed from the compositions of the mixtures with the aid of $a_i$ and $\beta_i$ derived in the manner described earlier in this section. Of the published pH values for buffer solutions without chloride, those for mixtures of potassium $p$-phenolsulfonate and sodium hydroxide (7) were computed on the $p_4H$ scale, and those for mixtures of potassium dihydrogen phosphate and disodium hydrogen phosphate (8) and mixtures of acid potassium phthalate and dipotassium phthalate (47) are on the $p_5H$ scale. Inasmuch as the ionic parameters determined from studies of mixtures of primary and secondary phthalates with potassium chloride were used in its determination, the pH of solutions of acid potassium phthalate (50) is also based upon the $p_5H$ scale. These scales are related by the equation:

$$p_4H = p_5H + \beta^0 \mu = p_3H + \frac{3}{2} \beta^0 \mu \qquad (46)$$

The paH values at 25°C. of some chloride-free buffer solutions on the several scales discussed in this section and the foregoing one are given in table 9. In an attempt to estimate $f_{HCl}$ in these buffer solutions for the computation of $p_2H$ by equation 35b, the average of the activity coefficient of hydrochloric acid at zero concentration in solutions of sodium chloride and in solutions of potassium chloride of the appropriate ionic strength has been employed. This quantity was calculated from data given by Harned (53) and by Harned and Hamer (61).

*E. Use of electrodes reversible to bromide and iodide ions*

The chloride ion evidently plays a unique and important rôle in these paH equations. Equimolal mixtures of potassium dihydrogen phosphate and disodium hydrogen phosphate have therefore been studied in an effort to determine to what extent the value of paH on these several scales depends upon the reference electrode and the added halide (5). Electromotive-force measurements of cells analogous to type III,
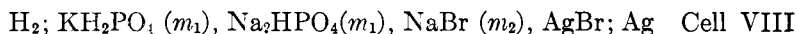
$$H_2; \; KH_2PO_4 \; (m_1), \; Na_2HPO_4(m_1), \; NaBr \; (m_2), \; AgBr; \; Ag \qquad \text{Cell VIII}$$

TABLE 9

*paH of buffer solutions without chloride at 25°C.*

| BUFFER | MOLALITY OF EACH COMPONENT | IONIC STRENGTH | $p_1H$ ($a_i = 4$) | $p_1H$ ($a_i = 6$) | $p_2H$ (EQUATION 35a) | $p_2H$ (EQUATION 35b) | $p_3H$ | $p_4H$ | $p_5H$ |
|---|---|---|---|---|---|---|---|---|---|
| Acid potassium phthalate | 0.05 | 0.053 | 4.002 | 4.011 | 4.008 | 4.007 | | | 4.005 |
| Acetic acid, sodium acetate | 0.01 | 0.01 | 4.717 | 4.720 | 4.717 | 4.718 | | | |
| | 0.1 | 0.1 | 4.648 | 4.663 | 4.660 | 4.657 | | | |
| Acid potassium phthalate, dipotassium phthalate | 0.01 | 0.04 | 5.169 | 5.177 | | 5.172 | 5.170 | 5.164 | 5.168 |
| | 0.02 | 0.08 | 5.098 | 5.111 | | 5.105 | 5.100 | 5.089 | 5.096 |
| | 0.05 | 0.2 | 4.991 | 5.013 | 5.015 | 5.009 | 4.996 | 4.969 | 4.987 |
| | 0.1 | 0.4 | 4.907 | 4.940 | | 4.942 | 4.919 | 4.919 | 4.902 |
| Potassium dihydrogen phosphate, disodium hydrogen phosphate | 0.005 | 0.02 | 7.017 | 7.022 | | 7.017 | 7.018 | 7.019 | 7.018 |
| | 0.01 | 0.04 | 6.956 | 6.964 | | 6.959 | 6.958 | 6.961 | 6.959 |
| | 0.025 | 0.1 | 6.856 | 6.871 | 6.866 | 6.866 | 6.858 | 6.865 | 6.860 |
| | 0.05 | 0.2 | 6.767 | 6.789 | 6.789 | 6.786 | 6.767 | 6.783 | 6.772 |
| | 0.1 | 0.4 | 6.663 | 6.696 | | 6.698 | 6.660 | 6.693 | 6.671 |
| Potassium p-phenolsulfonate, sodium potassium p-phenolate sulfonate | 0.01 | 0.04 | 8.841 | 8.849 | | 8.844 | 8.857 | 8.852 | 8.855 |
| | 0.025 | 0.1 | 8.770 | 8.785 | 8.778 | 8.779 | 8.799 | 8.789 | 8.796 |
| | 0.05 | 0.2 | 8.715 | 8.737 | 8.735 | 8.733 | 8.760 | 8.740 | 8.753 |
| | 0.1 | 0.4 | 8.662 | 8.695 | | 8.697 | 8.730 | 8.691 | 8.717 |
| Borax | 0.01 | 0.02 | 9.177 | 9.182 | 9.176* | 9.177 | | | |
| | 0.025 | 0.05 | 9.172 | 9.181 | 9.172* | 9.176 | | | |

* Reference 109.

and

$$H_2; KH_2PO_4\ (m_1),\ Na_2HPO_4(m_1),\ NaI\ (m_2),\ AgI;\ Ag \qquad \text{Cell IX}$$
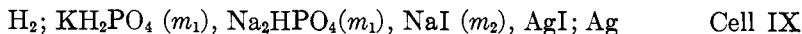
were made at 25°C.

A comparison of the experimental results for solutions that contained sodium halide at a molality equal to that of each phosphate salt with similar data for phosphate–chloride mixtures (8) is made in figure 5. The quantity plotted as ordinate we have called pwH. When the three curves, plotted from measurements at sufficiently high concentrations so that the buffer ratio is always unity,
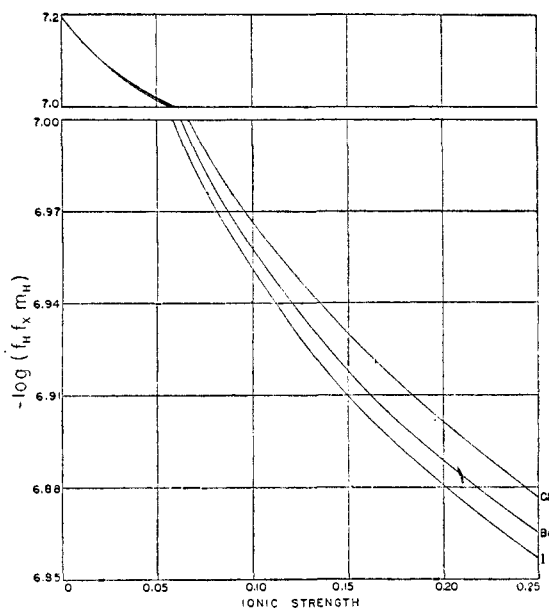


FIG. 5. Observed values of $-\log\ (f_Hf_Xm_H)$ in equimolal phosphate buffers containing sodium halide (NaX) at a molality equal to that of each phosphate salt plotted as a function of ionic strength.

are extended to zero ionic strength they meet at 7.198, the value of $pK$ for the second dissociation of phosphoric acid at 25°C. (6, 8). The separation of these three curves at a given ionic strength decreases as the ratio of halide to phosphate decreases, but the curves fail to meet, if the ionic strength exceeds 0.05, even at zero concentration of halide.

The activity-coéfficient term, $\log f_r$, in phosphate–halide mixtures is defined by

$$\log f_r \equiv \log\ (f_{H_2PO_4}f_X/f_{HPO_4}) \tag{47}$$

where X represents chloride, bromide, or iodide ion. The limiting values of $\log f_r$ in phosphate buffers without sodium chloride, sodium bromide, or sodium iodide were obtained from plots of $\log f_r$ with respect to $m_X/\mu$, as shown in figure 6. This limiting quantity, termed $\log f_r^0$, is listed in table 10. Equation 37 was

used to compute log $f_r$ in the buffer solutions containing sodium chloride. The values of the parameters are to be found in an earlier paper (8).

The convergence of the plots of log $f_r$ at low ionic strengths, though incomplete, is in agreement with a principle of Brønsted (23) referred to earlier in this paper. The activity coefficients of hydrochloric, hydrobromic, and hydriodic acids at zero concentration in a phosphate medium depend as a first approximation only on the specific nature of the phosphate salts.

TABLE 10

*Log $f_r^0$ and $-$ log $(f_H f_X m_H)^0$ for phosphate buffer solutions*

| IONIC STRENGTH | LOG $f_r^0$ | $-$LOG $(f_H f_X m_H)^0$ |
|---|---|---|
| | X = Cl | |
| 0.01 | 0.089 | 7.109 |
| 0.05 | 0.1748 | 7.023 |
| 0.07 | 0.1983 | 7.000 |
| 0.10 | 0.2263 | 6.972 |
| 0.15 | 0.2610 | 6.937 |
| 0.20 | 0.2870 | 6.911 |
| 0.25 | 0.3084 | 6.890 |
| | X = Br | |
| 0.01 | 0.090 | 7.108 |
| 0.05 | 0.1772 | 7.021 |
| 0.07 | 0.2020 | 6.996 |
| 0.10 | 0.2310 | 6.967 |
| 0.15 | 0.2672 | 6.931 |
| 0.20 | 0.2952 | 6.903 |
| 0.25 | 0.3183 | 6.880 |
| | X = I | |
| 0.01 | 0.091 | 7.107 |
| 0.05 | 0.1790 | 7.019 |
| 0.07 | 0.2048 | 6.993 |
| 0.10 | 0.2350 | 6.963 |
| 0.15 | 0.2730 | 6.925 |
| 0.20 | 0.3028 | 6.895 |
| 0.25 | 0.3267 | 6.871 |

The last column of table 10 gives $-$log $(f_H f_X m_H)^0$, obtained from log $f_r^0$ by equation 28, for equimolal phosphate buffer solutions in the absence of halide. Hydrolysis of the secondary anion and ionization of the primary anion are so small that the second term on the right of equation 28 can be ignored.

In order to calculate $p_4H$ and $p_5H$ for phosphate buffer solutions by equations 44 and 45, $\beta^0$ must be found. For this purpose, the values of log $f_r^0$ given in table 10 for the chloride, bromide, and iodide series were fitted to equations of the type:

$$\log f_r^0 \equiv \log \left[\frac{f_{H_2PO_4} f_X}{f_{HPO_4}}\right]^0 = \frac{2A\sqrt{\mu}}{1 + Ba^0\sqrt{\mu}} + \beta^0\mu \qquad (48)$$

The parameters $a^0$ and $\beta^0$, obtained by the method of least squares, are listed in table 11. The average difference, $\Delta$, between the "observed" values of $\log f_r^0$ and those calculated by equation 48 is given in the last column.

The paH of equimolal mixtures of potassium dihydrogen phosphate and disodium hydrogen phosphate on the several scales based upon measurements of cells without liquid junction can now be compared. Table 12 is a summary of
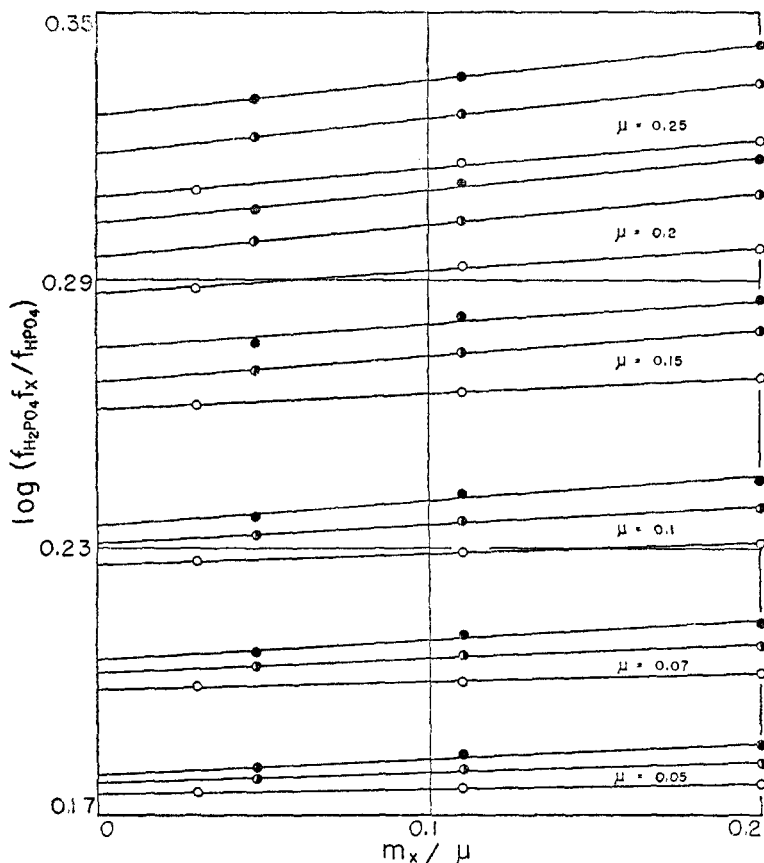


Fig. 6. Log $(f_{H_2PO_4}f_X/f_{HPO_4})$ plotted as a function of the fractional contribution of halide, NaX, to the total ionic strength. For the lower curve of each group, X is chloride; for the middle curve, X is bromide; for the upper curve, X is iodide.

the results computed from cells with silver chloride, silver bromide, and silver iodide electrodes. The differences among paH values on the several scales are negligible at low ionic strengths though appreciable at the higher concentrations. The $p_1$H value is strongly influenced in concentrated solutions by the value of $a_i$ arbitrarily chosen. The $p_2$H was computed from $-\log (f_H f_X m_H)^0$ by equations of the form of equation 35b together with the mean activity coefficients of hydrochloric acid (58), hydrobromic acid (63), and hydriodic acid (65) in their aqueous solutions at the appropriate ionic strength.

It is noteworthy that $-\log (f_H f_X m_H)^0$ decreases as X increases in atomic weight. This change is to be expected if the activity coefficients of the halide ions are in the same order as the mean activity coefficients of the alkali halides and those of

TABLE 11

*Parameters of equation 48 for log $(f_{H_2PO_4}f_X/f_{HPO_4})$ in phosphate buffers without halide*

| X | $a^0$ | $\beta^0$ | $\Delta$ |
|---|---|---|---|
| Cl. | 4.4 | 0.054 | 0.0002 |
| Br. | 4.2 | 0.069 | 0.0000 |
| I. | 4.0 | 0.079 | 0.0003 |

TABLE 12

*paH values for phosphate buffer mixtures: $KH_2PO_4$ ($m_1$), $Na_2HPO_4$ ($m_1$), NaX ($m_2 = 0$), from the E.M.F. of cells without liquid junction at 25°C.*

| $m_1$ | $p_1H$ ($a_i^* = 4$) | $p_2H$ (EQUATION 35b) | $p_2H$ | $p_4H$ | $p_5H$ |
|---|---|---|---|---|---|
| | | X = Cl | | | |
| 0.0125 | 6.935 | 6.942 | 6.936 | 6.940 | 6.937 |
| 0.0175 | 6.900 | 6.910 | 6.901 | 6.907 | 6.903 |
| 0.025 | 6.858 | 6.873 | 6.859 | 6.867 | 6.862 |
| 0.0375 | 6.806 | 6.830 | 6.807 | 6.819 | 6.811 |
| 0.05 | 6.768 | 6.796 | 6.768 | 6.784 | 6.773 |
| 0.0625 | 6.736 | 6.774 | 6.736 | 6.756 | 6.742 |
| | | X = Br | | | |
| 0.0125 | 6.933 | 6.944 | 6.932 | 6.937 | 6.934 |
| 0.0175 | 6.896 | 6.910 | 6.895 | 6.902 | 6.897 |
| 0.025 | 6.853 | 6.873 | 6.852 | 6.862 | 6.855 |
| 0.0375 | 6.800 | 6.829 | 6.798 | 6.814 | 6.803 |
| 0.05 | 6.760 | 6.796 | 6.755 | 6.776 | 6.762 |
| 0.0625 | 6.726 | 6.774 | 6.721 | 6.747 | 6.729 |
| | | X = I | | | |
| 0.0125 | 6.931 | 6.945 | 6.929 | 6.935 | 6.931 |
| 0.0175 | 6.893 | 6.913 | 6.891 | 6.899 | 6.893 |
| 0.025 | 6.849 | 6.876 | 6.845 | 6.856 | 6.849 |
| 0.0375 | 6.794 | 6.834 | 6.789 | 6.807 | 6.794 |
| 0.05 | 6.752 | 6.802 | 6.743 | 6.767 | 6.752 |
| 0.0625 | 6.717 | 6.781 | 6.708 | 6.738 | 6.717 |

the halogen acids. For the same reason, log $f_r^0$ increases from chloride to iodide. Hence, $p_3H$ values computed by equation 43 from measurements of chloride, bromide, and iodide cells differ more from one another than do the values of $-\log (f_H f_X m_H)^0$. This normal decrease of pwH from chloride to iodide is not

satisfactorily compensated in the calculation of $p_4H$ or $p_5H$. Only $p_2H$ exhibits substantial agreement, and this quantity is considerably higher than the other four. Inasmuch as the activity coefficient of hydrochloric acid is lower in the presence of potassium and sodium salts than in pure aqueous solutions of the acid, these $p_2H$ values are understandably too high. Unfortunately, small systematic changes in $\log f_r^0$, within experimental error, may lead to a different $a^0$ and different $\beta^0$ (equation 48), and $p_4H$ and $p_5H$ may be significantly changed thereby (5).
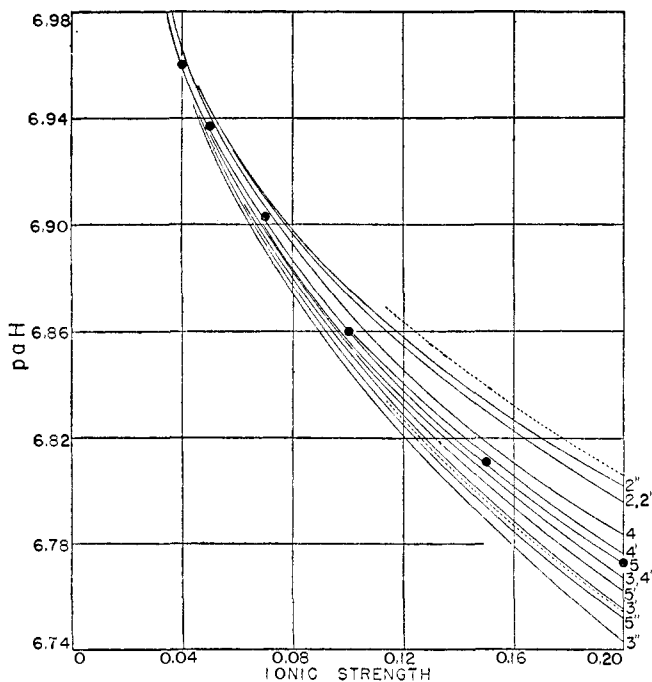


FIG. 7. $p_2H$, $p_3H$, $p_4H$, and $p_5H$ of phosphate buffer solutions as a function of ionic strength. Curves representing the four scales are labeled 2, 3, 4, and 5. The values were derived from the electromotive force of cells with silver–silver chloride electrodes (un·primed), silver–silver bromide electrodes (single prime), and silver–silver iodide electrodes (double prime). The dashed lines indicate the course of the curve of $p_1H$ for $a_i$ values of 8 (upper line) and 3 (lower line).

Figure 7 illustrates the change of $p_2H$, $p_3H$, $p_4H$, and $p_5H$ for equimolal phosphate buffer solutions with changing ionic strength. The lines representing the several scales are labeled 2, 3, 4, and 5. The results derived from bromide cells are marked with a single prime and those from iodide cells with a double prime. Lines unmarked save for the identifying figure represent data from the chloride cells. The upper and lower dashed lines locate the $p_1H$ curve when $a_i$ is arbitrarily assigned the extreme values of 8 and 3 for the computation. The molality of each phosphate salt is one quarter of the ionic strength.

The paH of buffer solutions composed of potassium binoxalate and sodium

oxalate in the molal ratio 1:5 is plotted in figure 8 as a function of ionic strength. The $p_2H$, $p_3H$, $p_4H$, and $p_5H$ curves are again labeled 2, 3, 4, and 5, respectively. The upper dashed line locates the $p_1H$ curve when $a_i$ is 6, and the lower line is computed for $a_i = 4$ (equation 36). The paH was derived from the electromotive force of hydrogen–silver chloride cells without liquid junction (125). The activity coefficient of hydrochloric acid used in the calculation of $p_2H$ by equation 35b was the average of $f_{HCl}$ in aqueous solutions of sodium chloride and
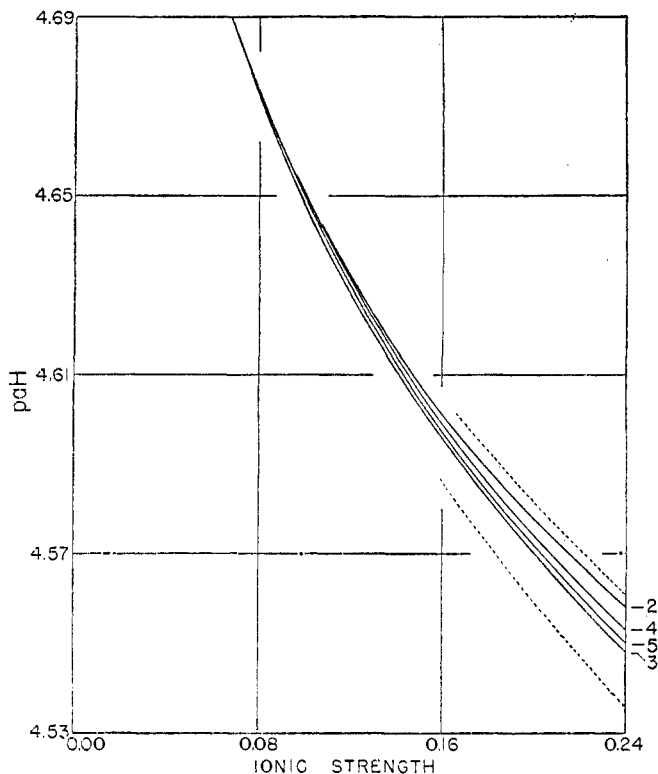


FIG. 8. $p_2H$, $p_3H$, $p_4H$, and $p_5H$ of oxalate buffer solutions as a function of ionic strength. The molal ratio of potassium binoxalate to sodium oxalate is 1:5. The values were derived from the electromotive force of hydrogen–silver chloride cells without liquid junction. Curves representing the four scales are labeled 2, 3, 4, and 5. The dashed lines indicate the course of the curve of $p_1H$ for $a_i$ values of 6 (upper line) and 4 (lower line).

of potassium chloride. It is evident that the four scales agree somewhat more closely for oxalate solutions than for phosphates.

The location of the true $-\log a_H$ in figures 7 and 8 can, of course, never be ascertained. All of these reasonable estimates of $-\log a_H$ agree at ionic strengths below 0.01 to 0.02, however, and there the paH can be said to possess some significance in terms of activity. Thus it may prove desirable to impose an upper limit of 0.02 on the ionic strength of primary standards of paH. Studies of other buffer systems will aid in establishing a limit of general applicability.

## VIII. ESTABLISHMENT OF A UNIFORM SCALE OF pAH

The conditions under which one anion can be substituted for another without a sensible change in the activity-coefficient term are obviously of concern in any attempt to select a series of uniform paH standards. Insofar as ratios of certain ionic activity coefficients are involved, one need not rely wholly on theory. It is important first of all that the ionic strengths and the compositions of the buffer solutions with respect to cations be the same. In general, sodium and potassium ions have similar effects, but lithium, barium, strontium, calcium, and zinc ions produce rather large changes in $(f_{HA}f_{Cl}/f_A)$ (116, 117). If undissociated weak acid is present, its concentration should be the same in each buffer solution (118, 137).

TABLE 13

*Ratios of activity coefficients of halide ions in phosphate buffer solutions compared with ratios of mean activity coefficients of halides and halogen acids in their pure aqueous solutions*

| IONIC STRENGTH | LOG $\dfrac{f_X^0}{f_{Cl}^0}$ | 2 LOG $\dfrac{f_{HX}}{f_{HCl}}$ | 2 LOG $\dfrac{f_{NaX}}{f_{NaCl}}$ | 2 LOG $\dfrac{f_{KX}}{f_{KCl}}$ |
|---|---|---|---|---|
| X = Br |
| 0.05 | 0.002 | 0.006 | | |
| 0.07 | 0.004 | 0.008 | | |
| 0.10 | 0.005 | 0.009 | 0.003 | 0.002 |
| 0.15 | 0.006 | 0.012 | | |
| 0.20 | 0.008 | 0.017 | 0.006 | 0.006 |
| 0.25 | 0.010 | 0.019 | | |
| X = I |
| 0.05 | 0.004 | 0.014 | | |
| 0.07 | 0.007 | 0.020 | | |
| 0.10 | 0.009 | 0.023 | 0.012 | 0.008 |
| 0.15 | 0.012 | 0.033 | | |
| 0.20 | 0.016 | 0.045 | 0.022 | 0.018 |
| 0.25 | 0.019 | 0.051 | | |

### A. Activity coefficients of ions of the same charge

The ratio of the activity coefficient of chloride ion to that of bromide or iodide ion in pure phosphate buffers can be obtained from log $f_r^0$ or from $-\log (f_H f_X m_H)^0$ listed in the tables of the foregoing section:

$$\log (f_X^0/f_{Cl}^0) = \log (f_H f_X m_H)^0 - \log (f_H f_{Cl} m_H)^0 = 2 \log (f_{HX}^0/f_{HCl}^0) \quad (49)$$

As before, the superscripts in equation 49 designate a pure phosphate buffer without halide. The ratios of the ionic activity coefficients in phosphate buffers are compared in table 13 with the ratios of the mean activity coefficients of the sodium and potassium halides and of the halogen acids in their pure aqueous solutions (64).

Electromotive-force measurements likewise furnish a comparison of activity coefficients in equimolal buffer mixtures of acetic acid and sodium acetate with added sodium chloride and potassium iodide. The data of Harned and Ehlers (56) for cell III at 25°C. show that log $(f_{HAc}f_{Cl}/f_{Ac})$ in acetate buffer solutions to which sodium chloride has been added in molality equal to that of each component of the buffer is given by $-0.06 \mu$. Bates and Vosburgh (13) have measured the E.M.F. of the cell,

$$\text{H}_2; \text{HAc } (m_1), \text{NaAc } (m_1), \text{KI } (m_2), \text{Hg}_2\text{I}_2;\text{Hg} \qquad \text{Cell X}$$
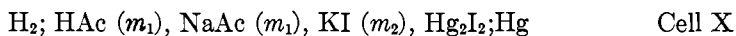
at the same temperature. The ratio $m_2/m_1$ varied from 0.55 to 1.0 in the six buffer solutions studied. Their data show that log $(f_{HAc}f_I/f_{Ac})$ is $-0.14 \mu$ in these mixtures. In this instance, the substitution of iodide for chloride evidently *decreases* the activity-coefficient term, in apparent contradiction of the change in log $f_r^0$ found for phosphate buffer solutions. It must be remembered, however, that the two acetate media differ with respect to the kind and concentration of the cations. An increase in the E.M.F. of cells of types III and IV when potassium ion replaces sodium ion is not an uncommon observation (6, 9, 18, 76, 77). The activity coefficient of hydriodic acid is greater than that of hydrochloric acid in the same cationic environment, and the substitution accordingly increases log $f_r^0$. On the other hand, these results indicate that the activity coefficient of hydriodic acid in an acetate–potassium iodide mixture is smaller than that of hydrochloric acid in an acetate–sodium chloride mixture of the same ionic strength. Unfortunately, the activity coefficient of hydriodic acid in salt solutions has not been measured. Nevertheless, this conclusion is entirely consistent with salt effects upon the activity coefficients of hydrochloric and hydrobromic acids (53, 64).

At ionic strengths below 0.05, the substitution of $f_{Br}$ or $f_I$ for $f_{Cl}$ in the activity-coefficient term, log $f_r^0$, alters that term by an amount hardly greater than the experimental error in the term itself, in accord with the theory of specific ionic interaction. Hitchcock (74) has discussed a suggestion of Scatchard that a cell reversible not only to hydrogen ion but also to another univalent cation be utilized for measuring $m_H$, since the ratio of activity coefficients of two ions of the same charge would be practically unity in solutions of moderate concentration. Redlich and Klinger (129) have studied such a cell: namely,

$$\text{H}_2; \text{solution, TlBr (satd.), AgBr; Ag} \qquad \text{Cell XI}$$

Inasmuch as the molalities of thallous and bromide ions are equal, the E.M.F. of this cell yields a measurement of $a_H (f_{Br}/f_{Tl})^{1/2}$. Unfortunately, the ions appearing in the activity-coefficient ratio are of unlike charge. For this reason, the ratio may depart from unity at relatively low ionic strengths. When the solubility of thallous bromide in the solution is known, $m_H f_H/f_{Tl}$ can also be determined. The numerical values of this quantity should be approximately equal to $m_H$ at low and moderate concentrations, for the hydrogen ion and thallous ion bear the same charge and their concentrations are small with respect to the total salt concentration.

A comparison of $\log f_r \equiv \log (f_{HA}f_{Cl}/f_A)$, where HA is a weak monobasic acid and A its univalent anion, for five buffer systems with $\log f_r$ for mixtures of acetic acid, sodium acetate, and sodium chloride (56, 57) is shown in figure 9. The term $\log (f_{HA}f_{Ac}f_{Cl}/f_{HAc}f_A f'_{Cl})$, where $f'_{Cl}$ is the activity coefficient of chloride ion in the reference buffer of acetic acid (HAc) and sodium acetate, is plotted as a function of ionic strength. This activity-coefficient term is the difference between $\log f_r$ for the two buffer–chloride systems that are being compared. The data are taken from the literature and relate, in general, to mixtures in which the
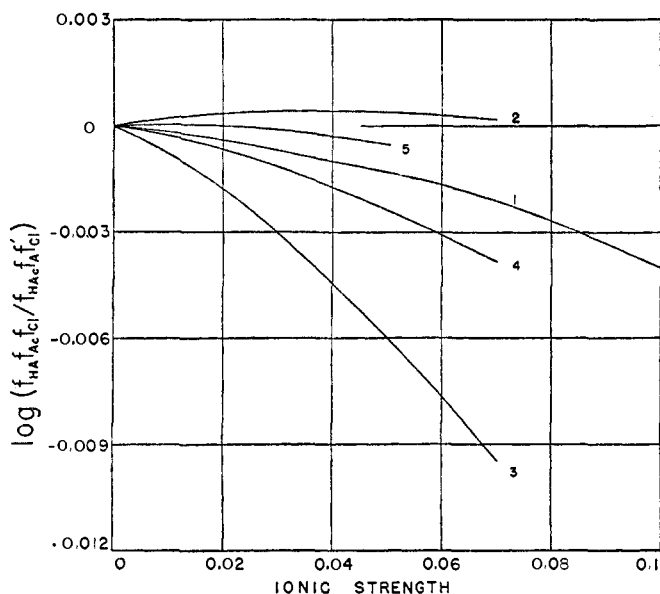


FIG. 9. Differences between $\log f_r$ for monobasic acid buffers with chloride and a reference buffer composed of equal molalities of acetic acid, sodium acetate, and sodium chloride plotted as a function of ionic strength. 1, formate, potassium salts (60); 2, propionate, sodium salts (59); 3, n-butyrate, sodium salts (67); 4, glycolate, potassium salts (116); 5, borate, sodium salts (107, 119).

molality of chloride equals that of the weak acid and its salt. The cation in each buffer is sodium or potassium. It is apparent that the quantity plotted as ordinate is the logarithm of the product of three quantities, all of which should be approximately unity. These are the ratios of the activity coefficients of two neutral molecules,[13] of two different univalent anions, and of the same ion (chloride) in two different solutions of the same ionic strength.

Figure 10 is a similar plot of differences between $\log f_r$ for six mixtures com-

[13] Randall and Failey (127) have compiled data on the activity coefficients of many neutral molecules in salt solutions. The ratio of the activity coefficients of two different neutral molecules in the same salt medium of moderate concentration is close to unity. The activity coefficient of acetic acid in sodium acetate is given by $\log f_{HAc} = -0.014 \mu$. In sodium chloride, on the contrary, $f_{HAc}$ is greater than 1.

posed of chloride and the primary and secondary anions of dibasic or polybasic
acids and log $f_r$ for a reference mixture containing equal molalities of potassium
dihydrogen phosphate, disodium hydrogen phosphate, and sodium chloride (8).
The buffer ratio is unity unless otherwise stated. The activity coefficient of
chloride ion in the reference mixture is again designated $f'_{Cl}$. Values of log $f_r$ at
each ionic strength were computed by equation 37 with the aid of $a^*$ and $\beta^*$
from the literature reference cited. The electromotive-force measurements of
Harned and Scholes (66) at 25°C. were used to obtain log $(f_{HCO_3}f_{Cl}/f_{CO_3})$ in mix-
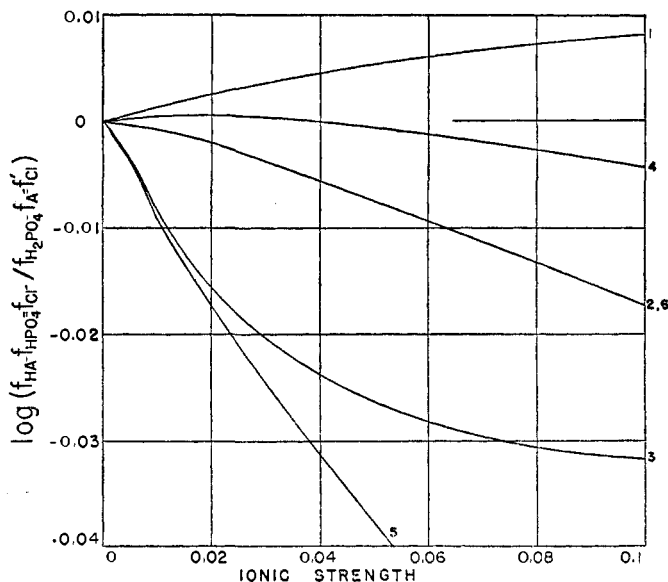


FIG. 10. Differences between log $f_r$ for mixtures of chloride and primary and secondary
anions of dibasic and polybasic acids and a reference buffer composed of equal molalities of
potassium dihydrogen phosphate, disodium hydrogen phosphate, and sodium chloride
plotted as a function of ionic strength. 1, phosphates, sodium salts (6); 2, malonates,
sodium salts (48); 3, carbonates, sodium salts (66); 4, phthalates, potassium salts (47);
5, potassium $p$-phenolsulfonate, sodium hydroxide, sodium chloride (12); 6, potassium
binoxalate, sodium oxalate, sodium chloride, 1:5:1 (125).

tures of sodium bicarbonate, sodium carbonate, and sodium chloride. These
values, fitted to equation 37, gave $a^* = 10.0$ and $\beta^* = 0.417$. Figures 9 and 10
reveal a greater uniformity, at intermediate ionic strengths, among the values
of log $f_r$ for systems of monobasic acids and their sodium and potassium salts
than is found for systems that are composed of the primary and secondary sodium
and potassium salts.

## B. Differences of paH

The approximate equality of the activity coefficients of ions of like charge in
the same medium suggests the possibility of determining differences of $-\log a_H$

among a series of buffer solutions of ionic strengths sufficiently high as to be experimentally accessible. The electromotive force, $E$, of the concentration cell,

$$H_2; \text{ reference buffer, NaCl, AgCl; Ag–Ag; AgCl, buffer, NaCl; } H_2 \quad \text{Cell XII}$$

when the molality of chloride is the same throughout, is given by

$$E/k = \text{paH}' - \text{paH}'' - \log (f'_{Cl}/f''_{Cl}) \tag{50}$$

where the single primes refer to the reference solution and the double primes to the buffer on the right of cell XII. The compositions of the buffer solutions would necessarily be so carefully matched that the last term of equation 50 could be assumed to be smaller than the desired accuracy of the difference of paH.

In terms of equation 29a, the difference of paH is given by

$$\text{paH}' - \text{paH}'' = pK' - pK'' - \log (m'_{HA}m''_A/m''_{HA}m'_A)$$
$$-\log (f'_{HA}f''_A f'_{Cl}/f''_{HA}f'_A f''_{Cl}) + \log (f'_{Cl}/f''_{Cl}) \tag{51}$$

The next to the last term of equation 51 is evidently $\log f''_r - \log f'_r$. It can be obtained readily from measurements of the E.M.F. of cell XII either in the presence of sodium chloride or, by extrapolation, in its absence. The ratio of the activity coefficient of chloride ion in the two media cannot be evaluated. One can, however, ascertain the limit of the ionic strength above which the next to the last term of equation 51 exceeds the desired accuracy, for example 0.003 unit, of the difference in paH. When the ionic strength is well below this upper limit, $\log (f'_{Cl}/f''_{Cl})$, which is part of this measured activity-coefficient term, can probably be assumed to be smaller than 0.003 also. The difference between the paH of the two solutions is then obtained from equation 50 or 51.

With two notable exceptions, namely, carbonates and phenolsulfonates, the buffer solutions composed of primary and secondary sodium or potassium salts (figure 10) yield approximately equal activity-coefficient terms at ionic strengths below 0.02. The monobasic acid series has the same degree of uniformity below about 0.03 (figure 9). The ionic strength of an equimolal buffer of the first type is, however, four times the molality of each buffer salt when chloride is absent. Buffer solutions prepared from weak monobasic acids can readily be used at ionic strengths as low as 0.01.

It is not impossible, then, to define a series of paH standards that covers a considerable range of acidity with a high degree of internal consistency. A series of monobasic acid buffer solutions appears most suitable. The differences of pH between each buffer and a member of the series arbitrarily chosen as a reference would correspond closely to differences in $-\log a_H$. The ionic strength would necessarily be less than 0.03 and identical for each solution. The buffers would likewise be identical with respect to kind and concentration of cation and concentration of neutral molecules. The problem of assigning a paH value to the reference solution will be considered in the next section.

### C. paH of the reference buffer

A determination of the paH of the reference buffer solution, for example, a mixture of acetic acid and sodium acetate, requires the evaluation of log $f_{Cl}$ in equation 29 or 29a. This can be done only by introducing an assumption. One of the most plausible, perhaps, is to assume that the activity coefficient of chloride ion in the reference buffer (with sodium chloride or in its absence) is equal to the mean activity coefficient of hydrochloric acid in a mixture of similar composition and identical ionic strength. Such an assertion is probably justifiable at an ionic strength of 0.01 or below (92, 97, 155). The value of log $f_{Cl}$ in 0.01 $m$ hydrochloric acid derived by Scatchard (136) and that computed by the MacInnes assumption (99) differ from the logarithm of the mean activity coefficient by only 0.002 or less. The buffers of known paH are restricted to this low range of ionic strengths, although accurate differences of paH may possibly be obtainable at somewhat higher concentrations.

The estimation of log $f_{Cl}^0$ in 0.01 $m$ acetic acid, 0.01 $m$ sodium acetate is accordingly made as follows. In a 0.01 $m$ solution of pure hydrochloric acid, $-\log f_{HCl}$ is 0.0434 (58, 128, 145). The medium effect of 0.01 $m$ acetic acid can be estimated from the measurements of Owen (118) to be considerably less than 0.001.[14] The concentration of hydrochloric acid, however, is zero in the reference buffer, and the molality of sodium ion is 0.01. The effect of sodium ions can be estimated from the data for mixtures of hydrochloric acid and sodium chloride. The electromotive-force data of Harned (53) permit a calculation of the change in activity coefficient at 0–40°C. produced by adding sodium chloride to hydrochloric acid at low ionic strengths. The value of $-\log f_{HCl}$ at 25°C. is increased by the following amounts when 0.01 mole of sodium chloride is substituted for 0.01 mole of hydrochloric acid: 0.0004 at an ionic strength of 0.06, 0.0008 at 0.03, and 0.0011 at 0.02. By extrapolation to an ionic strength of 0.01, $-\log f_{HCl}$ is found to be higher in 0.01 $m$ sodium chloride by 0.0014 than in 0.01 $m$ hydrochloric acid, that is, 0.0448. In the same way, $-\log f_{HCl}$ in 0.01 $m$ sodium chloride is found to be 0.0446 at 0°C. and 0.0459 at 40°C. The extrapolations were made on plots of these calculated differences as a function of the square root of the ionic strength.

The activity coefficient of chloride ion could be identified with the mean activity coefficient of sodium chloride in its pure 0.01 $m$ solution with equal justification. From the measurements of Brown and MacInnes (24), $-\log f_{NaCl}$ is 0.0441. The medium effect appears to be larger with sodium chloride than with hydrochloric acid (1) but can again be neglected when the concentration of non-electrolyte is 0.01 $m$. The mean activity coefficient of sodium chloride at other temperatures was calculated from its value at 25°C. with the aid of the relative partial molal heat content of sodium chloride from the measurements of Gulbransen and Robinson (37).

The activity coefficient of chloride ion in a buffer of the composition 0.01 $m$

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[14] Dioxane in the same concentration would produce a change of about 0.001 (64), and the effect of methanol would be entirely negligible (1).

HA and 0.01 $m$ NaA, where HA is a weak monobasic acid, is then arbitrarily set equal to the average of $-\log f^0_{HCl}$ and $-\log f_{NaCl}$ in a 0.01 $m$ solution of sodium chloride. At 0° and 40°C., these two quantities differ by 0.0020 and 0.0011, respectively. The values of $-\log f^0_{Cl}$ obtained in this manner are given by

$$-\log f^0_{Cl} = 0.0436 + 0.00004t \tag{52}$$

where $t$, the temperature in degrees Centigrade, lies between 0 and 40. At 0°, 25°, and 38°C., $-\log f^0_{Cl}$ is respectively 0.0436, 0.0446, and 0.0451. The paH value at 0.01 $\mu$ defined in this way is given by

$$\text{paH} \equiv -\log (f_H f_{Cl} m_H)^0 - 0.0436 - 0.00004t \tag{53}$$

The paH of the reference acetate buffer is computed from equation 29a with the aid of this defined value of $-\log f^0_{Cl}$. At ionic strengths below 0.1, log

TABLE 14

paH of buffer solutions composed of 0.01 M HA and 0.01 M NaA at 0°, 25°, and 38°C.

| A | paH AT | | |
|---|---|---|---|
| | 0°C. | 25°C. | 38°C. |
| Formate............................ | 3.760 | 3.727 | 3.737 |
| Acetate............................ | 4.741 | 4.714 | 4.724 |
| | 4.745* | 4.717* | 4.726* |
| Propionate.......................... | 4.853 | 4.831 | 4.844 |
| Borate†............................ | 9.466 | 9.190 | 9.093 |

* Computed by equation 53 from $-\log (f_H f_{Cl} m_H)^0$ given in table 6.
† 0.005 M borax.

$(f_{HAc} f_{Cl}/f_{Ac}) = -0.06\ \mu$ (56). Values of this quantity for formate, propionate, and borate buffer solutions are to be found in the literature (59, 60, 107, 119). The buffer ratio is determined by arithmetical approximations. The paH of four buffers computed by equations 29a and 52 at 0°, 25°, and 38°C. is given in table 14.

In only five instances can this paH be compared with paH derived from the cell with liquid junction. Hitchcock and Taylor (76) found 4.714 for the acetate buffer at 25°C., whereas MacInnes, Belcher, and Shedlovsky (102) give 4.700 for this temperature and 4.710 at 38°C. The corrected value[9] of Guggenheim and Schindler (36) for this solution is 4.713 at 25°C. The paH at 38°C. computed from the data of Hitchcock and Taylor (77) for the borax buffer, 9.093, is identical with that given in table 14.

The electromotive-force measurements given in table 5 for the 0.01 $m$ acetate buffer are about 0.2 mv. higher than the data of Harned and Ehlers (56, 57). The paH of this buffer computed from equation 53 and listed in table 13 is accordingly 0.003 unit higher than that calculated by equations 29a and 52. The measurements of the 0.1 $m$ acetate buffer are, however, in excellent agreement with

those of Harned and Ehlers at each temperature. The molar and molal scales of concentration can be used interchangeably, in this range of concentration, without sensible error.

The several paH scales that have been discussed here are essentially equivalent at ionic strengths as low as 0.01. The equations that define $p_3H$, $p_4H$, and $p_5H$ are inapplicable to buffers of the monobasic acid type, however, and the practical disadvantage of buffers of other types at such a low ionic strength is well recognized. A series of solutions of known paH but of different ionic character or composition need not necessarily yield a uniform calibration of a cell with liquid junction over a wide range of pH. In this respect, buffers of the type: 0.01 $M$ HA, 0.01 $M$ NaA, seem well suited for purposes of standardization. At this low ionic strength, the paH can be said to possess some measure of thermodynamic meaning.

Primary standards such as these can be used to redetermine the value of $E^{0'} + E_j$ in equation 11 and, with the aid of cells of type II or IV, the paH values of the many convenient secondary standards of somewhat higher concentrations and varying types. The computation of hydrogen-ion activity at high or even moderate ionic strengths is quite uncertain and probably will remain so.

### IX. SUMMARY

Unfortunately, the pH computed from the electromotive force of cells can only be defined as a unit on an arbitrary scale. Until the character of the ionic activity coefficient is precisely defined, the residual liquid-junction potential will remain indeterminate. Definitions of pH therefore rest upon arbitrary assumptions that enable the liquid-junction potential to be evaluated or eliminated or that permit the activity coefficient of a single ionic species to be derived from measurable combinations of activity coefficients.

In itself, the concentration of hydrogen ion is a very suitable measure of acidity. Activity coefficients appear in the equations for electromotive force, however, and pcH is not readily obtained from measurements of galvanic cells. By choice of different values for $E^{0'} + E_j$ in the equation

$$\text{pH} = \frac{E - (E^{0'} + E_j)}{k} \tag{54}$$

a family of pH scales can be defined. When $E^{0'} + E_j$ is taken to be 0.3376 at 25°C. for the cell with hydrogen and 0.1 $N$ calomel electrodes (cell II), the conventional scale defined by Sørensen (psH scale) results. The psH unit is satisfactory for reproducible comparisons of the work of different investigators, but it has no meaning in terms of chemical equilibria. Assignment of 0.3352 to $E^{0'} + E_j$ defines a unit that corresponds closely to $-\log a_H$, insofar as it can be estimated, in the thermodynamic equilibria for a number of weak monobasic acids. The general adoption of this activity scale and the paH unit seems warranted.

Measurement of the electromotive force of cells without liquid junction furnishes a means of calculating the paH of buffer mixtures composed of weak acids and their salts. At ionic strengths of 0.01 or below, these values are quite

reasonable, for the several plausible assumptions upon which the calculation of the single-ion activity coefficients is based are then substantially equivalent. At higher concentrations, appreciable differences among these several paH scales appear. As yet, only the pwH ($-\log a_H f_i$) retains its significance at all ionic strengths, and this unit is of limited usefulness in the practical determination of acidity.

The computation of paH from the electromotive force of cells without liquid junction in dilute solutions is valid for strong acids and mixtures of strong electrolytes as well as for buffered solutions over the entire pH range. For this reason, paH derived in this way is useful in the standardization of cells with liquid junction.

In view of the multiplicity of pH scales in use at the present time, all published pH values should be accompanied by a statement of the type of cell measured, of the standard potential used in computing the results, and of whether any attempt was made to eliminate the liquid-junction potential or to correct the electromotive force therefor. When the pH meter is employed, the pH values of the standard reference solutions with which the instrument was calibrated should be specified.

The pH can never possess the absolute significance of a true thermodynamic constant. It is therefore of primary importance that a single unequivocal definition of the pH scale be generally recognized. That the definition will perforce be stated in terms of operations and calculations is of secondary concern.

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