# Electrometric *p*H Determination

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## Zusammenfassung

Die geschichtliche Entwicklung einer praktischen *p*H-Skala für wässerige Lösungen wird kurz betrachtet. Im Lichte der modernen Theorie zeigt sich, daß die experimentell bewährten Methoden für die elektrometrische *p*H-Bestimmung nicht Werte ergeben, die einer theoretisch exakt begründeten *p*H-Skala entsprechen. Eine praktische *p*H-Skala muß deshalb unvermeidlich willkürlich oder konventionell sein, und es ist wichtig, die besonderen Bedingungen zu kennen und zu verstehen, unter denen *p*H-Messungen theoretisch interpretiert werden können. Es werden die Bemühungen, eine internationale *p*H-Skala festzulegen, behandelt. Die Möglichkeit der Festsetzung analoger brauchbarer Skalen für nichtwässerige und teilweise wässerige Medien wird ebenfalls erörtert. Die weitverbreitete Verwendung der *p*H-Messung in Forschung und

Industrie kann vor allem der von kommerzieller Seite vorwärts getriebenen Entwicklung von empfindlichen und dauerhaften Glaselektroden, von robusten Instrumenten zur Messung elektromotorischer Kräfte in Stromkreisen mit sehr hohem Widerstand und von raffinierten Anlagen zur automatischen Regulation des *p*H zugeschrieben werden. Es werden neueste Verbesserungen bei den *p*H-Geräten und bei der Meßtechnik sowie einige neuartige Anwendungsmöglichkeiten der *p*H-Kontrolle beschrieben.

The *p*H value of aqueous solutions occupies a place of unique importance in many fields of scientific endeavor today—in chemical analysis, in medical and biochemical research, and in the investigation and control of chemical equilibria. The wide application of *p*H measurements in the laboratory as well as their extensive use in the control of industrial processes is a tribute to the resourcefulness of the chemists and engineers of the companies engaged in the manufacture of *p*H instruments and equipment. These specialists have given us versatile, sturdy, and reliable electrodes useful over wide ranges of temperature, pressure, and *p*H. They have produced sensitive electronic meters of remarkable stability which are capable of accurate voltage measurements in circuits of enormous input resistance. Furthermore, they have devised ingenious automatic controllers able to adjust accurately the acidity of a process stream at a predetermined value, hour after hour and day after day.

While *p*H instrumentation was reaching its present high level of development, the fundamental nature of the *p*H scale was being examined, the *p*H unit was being defined in the most precise way consistent with the existing experimental techniques, and suitable standards to fix this scale were being chosen. It is the purpose of this review to summarize these parallel developments and in this manner to describe the present state of *p*H theory and the modern equipment available for electrometric *p*H determination.

## I. Development of the *p*H Concept

### *A. Evolution of the* p*H Scale*

It is noteworthy that the experimental method by which *p*H values are determined today differs in no fundamental respect from that prescribed by SØRENSEN when he first proposed the *p*H unit fifty years ago.[41] The practical *p*H cell may may be written as follows:

| | | | |
|---|---|---|---|
| Pt; $H_2$ (g) or Glass | Solution X | Saturated KCl | Calomel electrode (0.1 M or saturated) |

*j*

In 1909 the gaseous hydrogen electrode and the 0.1 M calomel reference electrode were used exclusively, whereas today the glass electrode (an excellent substitute for the hydrogen electrode over much of the *p*H range) and the saturated calomel electrode are usually preferred. The electromotive force ($E_x$) of this cell is now known to be formulated most conveniently in the following way:

$$E_x = E^{0\prime} + E_j - \frac{2{,}3026\,RT}{F} \log c_H \cdot f_H, \qquad (1)$$

where $E^{0\prime} + E_j$ is the 'standard potential' of the calomel reference electrode including the potential across the liquid-liquid junction ($j$), and $R$, $T$, and $F$ are the gas constant per mole, the temperature in degrees Kelvin, and the faraday, respectively. The symbol $c_H$ represents the hydrogen ion concentration, and $f_H$ is the hydrogen ion activity coefficient.

The imperfection of the theories of a half-century ago led SØRENSEN to write $c_H$ instead of $c_H f_H$ in the last term of Equation (1). He proceeded therefore to derive the substantially constant sum, $E^{0\prime} + E_j$, from a measurement of the E.M.F. ($E_s$) of this cell when a 'standard' solution (S) of known $c_H$ was used in place of the 'unknown' (X). Furthermore, it was quite logical to create the 'hydrogen ion exponent', which we now write *p*H, to express in a clear and simple manner the values of $-\log c_H$ computed from $E_x$ after $E^{0\prime} + E_j$ had been determined by a suitable standardization.

From modern thermodynamics it is known that the measurement of $E_x$ does not yield values of $c_H$, but rather values of a quantity formally represented by the product of $c_H$ and an activity coefficient of a single ionic species. This activity coefficient, $f_H$, like $E_j$, is not susceptible to independent definition. SØRENSEN and LINDERSTRØM-LANG[42] amended the definition to the form $pH = -\log c_H f_H$, but this new *p*H value also remains fixed only as long as $E_j$ is constant.

The introduction of some sort of mean activity coefficient in place of $f_H$ has sometimes been advocated, in order to make this definition acceptable to thermodynamic purists. GUGGENHEIM has pointed out that the experimental *p*H should be regarded as $-\log c_H f_?$, in recognition of the influence of adventitious changes in $E_j$.[24] Needless to say, these proposals do not alter the fact that the *p*H value is an inexact physical quantity. It has been said that 'we can't understand what we measure; we can't measure what we understand.'

Fortunately, there is good reason to believe that the liquid-junction potential is indeed substantially constant over much of the *p*H range ($2.5 < pH < 11.5$), provided that the Solutions X and S are both dilute aqueous solutions of simple ions and molecules. Under these conditions, we have by difference

$$pH(X) - pH(S) = \frac{E_x - E_s}{2{,}3026\,RT/F}, \qquad (2)$$

which is the operational definition of *p*H most widely used today.

### *B.* p*H Standardization*

The fruitful use of Equation (2) evidently requires one or more standard solutions of known or assigned *p*H. Whatever the arbitrary assignment of *p*H(S), the definition of *p*H given above furnishes a set of reproducible *p*H numbers and, hence, fulfills the most important

requirement of a standard scale. These *p*H values would satisfy many of the regulatory requirements of commerce in spite of the fact that they would have little or no clear meaning in terms of the fundamental chemical properties of the unknown mixtures. Most of the applications of *p*H measurements would be impossible if fundamental significance in a certain measure could not be imparted to the measured *p*H.

Salt bridges and liquid junctions are designed to minimize the liquid-junction potential. It is fair to assume that this boundary potential is substantially constant when (a) the concentration of neither the hydrogen ion nor hydroxide ion in solutions S and X exceeds about 0.005 M and (b) both S and X are aqueous solutions whose concentration does not exceed 0.1 M. Under these optimum conditions, then,

$$pH(X) - pH(S) \approx \log \frac{(c_H f_H)_s}{(c_H f_H)_x}. \qquad (3)$$

As already indicated, neither the hydrogen ion activity $(c_H f_H)$ or activity coefficient $(f_H)$ can be obtained exactly. Nevertheless, the difference of E.M.F. that appears on the right side of Equation (2) yields, in the ideal situation, a ratio of activities rather than ratio of concentrations. Although the exact value of $f_H$ in the standard solution is not known, a useful *conventional* *p*H scale can be established by defining $f_H$ in the standard solution in a reasonable manner.

At the National Bureau of Standards in the United States the *p*H (S) values of standard reference solutions have been based upon E.M.F. measurements of cells free from the experimental complications of the liquid junction, namely

$$Pt;\ H_2(g) \mid \text{Solution S, } KCl(c_{Cl}) \mid AgCl;\ Ag$$

The standard potential $(E^0)$ of this cell is known over the range 0 to 95 °C.[7] The quantity $-\log (c_H f_H f_{Cl})$ in the mixture of solution S and potassium chloride can therefore be obtained with very good accuracy:

$$-\log (c_H f_H f_{Cl}) = \frac{E - E^0}{2.3026\, RT/F} + \log c_{Cl}. \qquad (4)$$

Furthermore, if the measurements of each buffer solution are repeated with three or more small added concentrations of potassium chloride, the value of $-\log (c_H f_H f_{Cl})$ in the absence of added chloride can be obtained readily by extrapolation.

The arbitrary step, namely the estimation of the activity coefficient of chloride ion, must now be taken in order to derive $(c_H f_H)$:

$$pH(S) \equiv -\log c_H f_H = -\log (c_H f_H f_{Cl}) + \log f_{Cl}. \qquad (5)$$

In order to accomplish this, many reasonable estimates of the single ionic activity coefficient were considered. The corresponding values of *p*H (S) for equimolal phosphate buffer solutions were calculated, and the results are shown in Figure 1.[4]

In very dilute solutions, the Debye-Hückel equation is a guide to the magnitude of the activity coefficient. At ionic strengths as high as 0.1, however, specific effects of the sizes and chemical natures of the ions become evident, and the influence of the solute species on the properties of the solvent medium may have to be considered. In the range of moderate concentrations, the activity coefficient of chloride ion may reasonably be defined in terms of the measurable mean activity coefficient of potassium chloride or other chloride salt, or of hydrochloric acid at the appropriate ionic strength. These mean activity coefficients should preferably be the values in the particular buffer solution concerned, but the desired values are usually not known and sometimes are difficult or impossible to obtain.

In any case, the manner in which the activity coefficient of chloride ion changes with ionic strength between ionic strengths of 0 and 0.1 very likely approximates the behavior defined by the Debye-Hückel equation in its first-approximation form:

$$-\log f_{Cl} = \frac{A\sqrt{\mu}}{1 + Ba^*\sqrt{\mu}}, \qquad (6)$$

where $\mu$ is the ionic strength, $A$ and $B$ are constants, and $a^*$ is the 'ion-size parameter'. It will be remembered that the mean activity coefficients of most strong uni-univalent electrolytes up to 0.1 M can be satisfactorily represented by this equation. Furthermore, the ion-size parameter for most of these lies between 3 and 6. The several curves of the Figure were based upon conventions thought to be 'reasonable' in the light of these considerations.

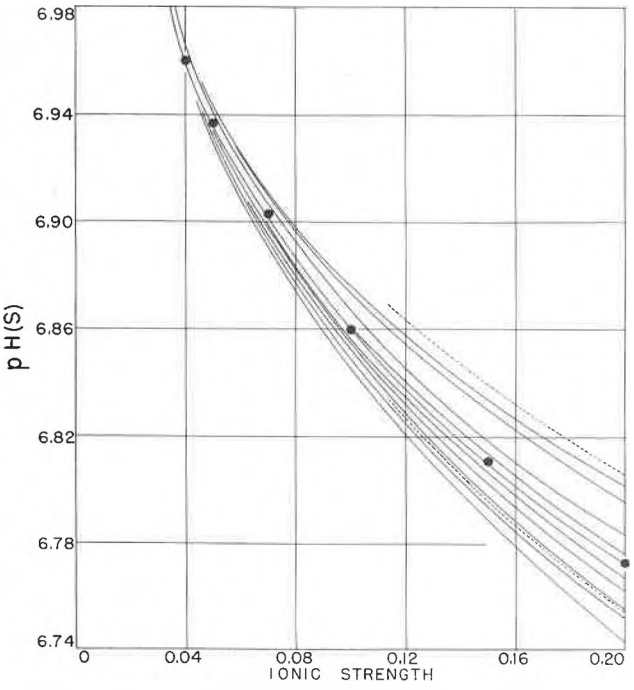


*Fig. 1.* *p*H (S) values for equimolal mixtures of $KH_2PO_4$ and $Na_2HPO_4$, based on different estimates of the activity coefficient of chloride ion

As Figure 1 illustrates, buffer solutions with ionic strengths of 0.1 or less can be assigned an 'average' *p*H(S) value (black dots) that will not be in serious conflict with any of these so-called reasonable conventions. The *p*H standard solutions selected by the National Bureau of Standards (NBS) are therefore rather dilute, and the *p*H is assigned an uncertainty of ± 0.01 unit. The materials can be purified easily, and solutions of the correct *p*H can readily be prepared by weight or by saturation. The solutions have adequate buffer capacity, the *p*H is not sensitive to dilution, and the change of *p*H with temperature lies within acceptable limits. These properties are summarized in Table 1. The *p*H(S) values are given in Table 2[11] and are plotted as a function of temperature in Figures 2 and 3.

Table 1: Properties of NBS standards

| Solution | Buffer value, moles per *p*H unit | Dilution value, $\Delta pH_{1/2}$ *p*H units for 1:1 dilution | Temperature coefficient, $dpH/dt$, *p*H units per deg C. |
|---|---|---|---|
| K tetroxalate, 0.05 M (*p*H 1.68) ..... | 0.070 | + 0.19 | + 0.001 |
| KH tartrate, saturated at 25 °C (*p*H 3.56) ..... | 0.027 | + 0.05 | − 0.0014 |
| KH phthalate, 0.05 M (*p*H 4.01) ..... | 0.016 | + 0.05 | + 0.0012 |
| $KH_2PO_4$, 0.025 M; $Na_2HPO_4$, 0.025 M (*p*H 6.86) ..... | 0.029 | + 0.08 | − 0.0028 |
| $Na_2B_4O_7$, 0.01 M (*p*H 9.18) ..... | 0.020 | + 0.01 | − 0.0082 |
| $Ca(OH)_2$, saturated at 25 °C (*p*H 12.45) ..... | 0.09 | − 0.28 | − 0.033 |

In establishing a sound useful procedure for the standardization of the *p*H cell, one must consider both the *p*H response of the glass electrode and the constancy of the liquid-junction potential. Most (but not all) glass electrodes display a linear *p*H response that corresponds well with the theoretical Nernst response between *p*H 3 and 10. Furthermore, the liquid-junction potential appears to maintain a fairly constant value in this same range of *p*H when the concentrations of the solutions (unknown X or standards $S_1$ and $S_2$) in contact with the bridge solution of saturated potassium chloride do not exceed 0.1 M.[10] Thus

$$\frac{E_1 - E_2}{pH(S_1) - pH(S_2)} = \frac{2.3026\,RT}{F} . \qquad (7)$$

The quantity on the right is known as the 'theoretical slope;' it has the value 59.16 mv/*p*H (reciprocal, 16.90 *p*H units/v) at 25 °C. We may conclude that standardization with a single buffer solution in the intermediate *p*H range would be sufficient, unless a need were felt to confirm the function of the glass electrode. In actuality, the glass membrane is fragile, and corrosion, accelerated by alkalies, is always proceeding when the membrane is in contact with aqueous solutions. Deterioration of the *p*H response precedes complete failure of the electrode and may easily go undetected unless a dual standardization is made routinely. In addition, the electrodes, 'unknown' solutions, and standard solutions should all be at the same temperature. It is desirable that one of the standards selected have a *p*H value close to that of the unknown, where possible.

Some glass electrodes display a linear non-theoretical response, especially when failure is imminent. In cases of this sort, accurate *p*H measurements can still be made

Table 2: *p*H(S) of NBS *p*H standards from 0 to 95 °C

| *t* | Secondary Standard | Primary Standards | | | | Secondary Standard |
|---|---|---|---|---|---|---|
| °C | 0.05 M K tetroxalate | KH tartrate (saturated at 25 °C) | 0.05 M KH phthalate | 0.025 M $KH_2PO_4$, 0.025 M $Na_2HPO_4$ | 0.01 M Borax | $Ca(OH)_2$ (saturated at 25 °C) |
| 0 | 1.67 | – | 4.01 | 6.98 | 9.46 | 13.43 |
| 5 | 1.67 | – | 4.01 | 6.95 | 9.39 | 13.21 |
| 10 | 1.67 | – | 4.00 | 6.92 | 9.33 | 13.00 |
| 15 | 1.67 | – | 4.00 | 6.90 | 9.27 | 12.81 |
| 20 | 1.68 | – | 4.00 | 6.88 | 9.22 | 12.63 |
| 25 | 1.68 | 3.56 | 4.01 | 6.86 | 9.18 | 12.45 |
| 30 | 1.69 | 3.55 | 4.01 | 6.85 | 9.14 | 12.30 |
| 35 | 1.69 | 3.55 | 4.02 | 6.84 | 9.10 | 12.14 |
| 40 | 1.70 | 3.54 | 4.03 | 6.84 | 9.07 | 11.99 |
| 45 | 1.70 | 3.55 | 4.04 | 6.83 | 9.04 | 11.84 |
| 50 | 1.71 | 3.55 | 4.06 | 6.83 | 9.01 | 11.70 |
| 55 | 1.72 | 3.56 | 4.07 | 6.84 | 8.99 | 11.58 |
| 60 | 1.73 | 3.56 | 4.09 | 6.84 | 8.96 | 11.45 |
| 70 | 1.75 | 3.58 | 4.12 | 6.85 | 8.93 | – |
| 80 | 1.77 | 3.61 | 4.16 | 6.86 | 8.89 | – |
| 90 | 1.80 | 3.65 | 4.20 | 6.88 | 8.85 | – |
| 95 | 1.81 | 3.68 | 4.23 | 6.89 | 8.83 | – |

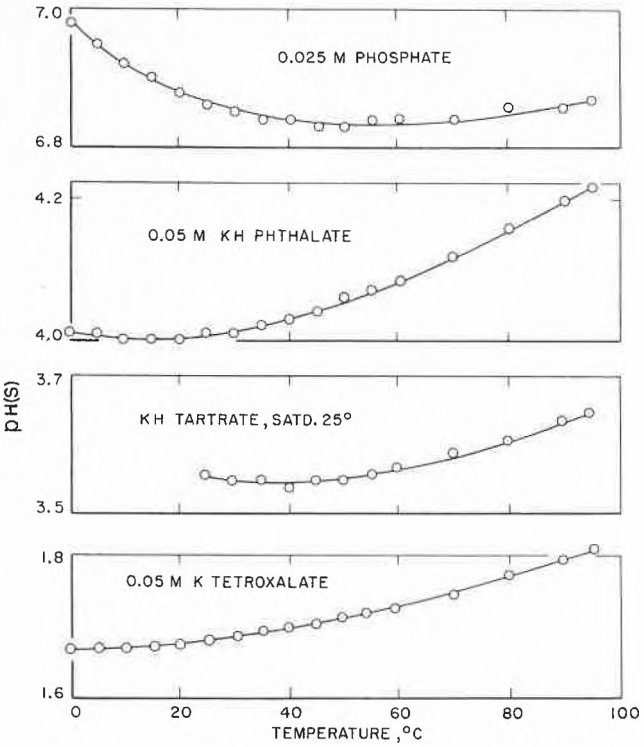


*Fig. 2.* $p$H (S) of NBS reference standards as a function of temperature. Acidic range

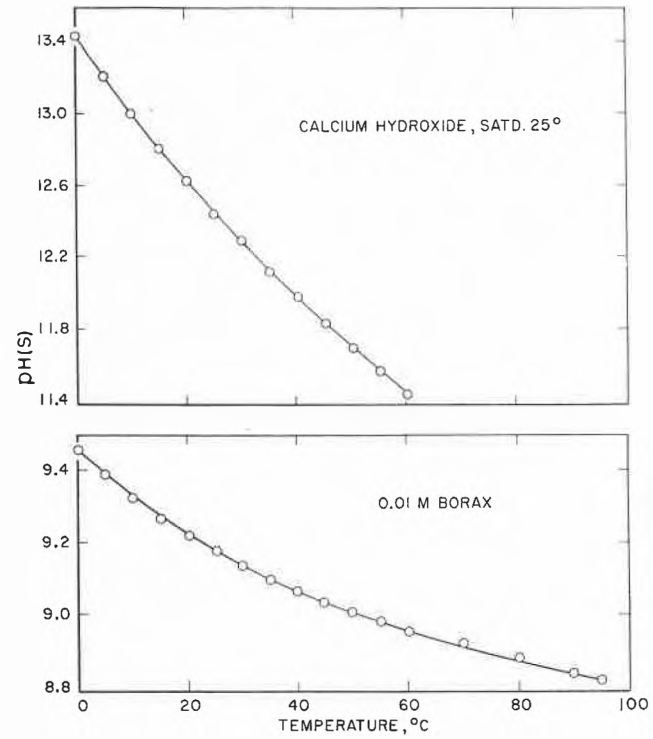


*Fig. 3.* $p$H (S) of NBS reference standards as a function of temperature. Alkaline range

by standardizing the $p$H cell with two solutions, one ($S_1$) with $p$H less than that of the 'unknown' (X) and one ($S_2$) with $p$H greater. The $p$H (X) is then obtained by interpolation:[8]

$$\frac{p\mathrm{H}\,(\mathrm{X}) - p\mathrm{H}\,(\mathrm{S}_1)}{p\mathrm{H}\,(\mathrm{S}_2) - p\mathrm{H}\,(\mathrm{S}_1)} = \frac{E_x - E_1}{E_2 - E_1}. \qquad (8)$$

A parallel situation indeed exists in highly acidic and in highly alkaline solutions, as a result not so much of defects in the glass-electrode response as of the changing liquid-junction potential.[10] As shown in Figure 4, the observed increase of E. M. F. when the borax buffer solu-

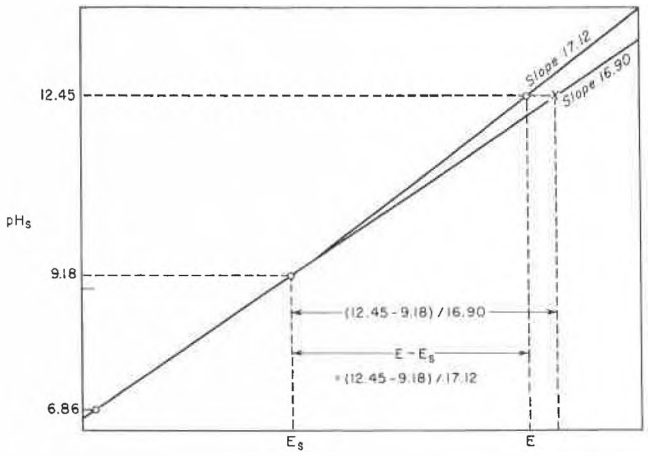


*Fig. 4.* Standardization in the highly alkaline $p$H range

tion ($p$H[S] = 9.18) is replaced by the saturated solution of calcium hydroxide ($p$H[S] = 12.45) is less than would be expected if the theoretical slope of 16.90 $p$H units/v were maintained. This experience is in accord with a simple picture of the phase boundary, the potential of which is governed primarily by the presence of appreciable quantities of the highly mobile hydroxide ions. In order to make the response of the $p$H instrument consistent with these two standards, converting measured volts to $p$H units in the proper ratio, it is necessary to utilize a slope of 17.12. This adjustment can be made on many $p$H meters by means of the manual temperature compensator.

Unfortunately, this procedure does not appear to be a practical means of extending the standard scale to very low and very high $p$H. Although the measured $p$H appears almost invariably to be too low in the region of high $p$H when the theoretical slope is accepted, the sign of the liquid-junction error in acid solutions seems no longer to be governed exclusively by the charge of the highly mobile (hydrogen) ions. Hence, $p$H (X) is sometimes too low and sometimes too high, if the cell without liquid junction is taken as an index of the 'correct' result. At the present time, therefore, it appears impossible to devise a refinement in $p$H standardization that will increase the usefulness of all practical $p$H measurements in the regions of low and high $p$H.

The NBS tetroxalate buffer and calcium hydroxide solution are therefore designated 'secondary standards,' to be used for confirmatory purposes and to fulfill special needs for solutions of known conventional hydrogen ion activity. At the present time, the four primary stand-

ards should be used to standardize the measurement of practical *p*H numbers over the entire range. Other secondary standards may have utility in special measuring situations. A secondary standard for blood *p*H measurements is under study in Great Britain.[32]

### *C. An International* p*H Scale*

The operational definition of the *p*H value as given in Equation (2) has achieved nearly universal acceptance. It is the basis of the recommended *p*H methods that have been promulgated in Great Britain,[12] in the United States,[1, 3] and in Japan.[29] The British and Japanese methods recognize only one primary standard (the 0.05 M solution of potassium hydrogen phthalate), and thus adopt the theoretical slope over the entire *p*H range. In addition, other solutions, designated secondary standards, are recommended for checking glass electrodes. In other respects, only minor differences between the procedures adopted by these three nations exist, and steps toward a complete harmonizing of these views are being taken under the aegis of the International Union of Pure and Applied Chemistry.[8]

It is to be hoped that recommendations based on the experience of these nations will be followed by other groups which may contemplate the drafting of a recommended standard. To the author's knowledge, no other national standards for *p*H methods have been adopted, although a move in this direction is reported to be under consideration in France.[44]

The recommandations that would form the basis for an international *p*H scale are in essence the following:[8]

1. that the symbol *p*H denote the experimental practical *p*H number, and that standard values based on a conventional hydrogen ion activity be denoted *p*H (S) or $pa_H$;
2. that the operational definition of *p*H (Equation 2) be adopted;
3. that the activity coefficient of chloride ion at ionic strengths not exceeding 0.1 be defined conventionally by Equation (6) with $Ba^* = 1.5$;
4. that the *p*H scale be fixed by one or more of the primary standards given in Table 2.

It should be noted that the British method prescribes the *p*H (S) of its primary standard (potassium hydrogen phthalate) to three decimal places. Furthermore, adoption of the third recommendation above would make it possible to assign *p*H (S) to all standards with a precision of about $\pm 0.002$ unit. It would then be necessary to intercompare all of the standards carefully to detect possible internal inconsistencies in the standard scale. These inconsistencies, examined with third-decimal accuracy, would doubtless be found to be influenced by the structure of the liquid junction. At 25 °C, at least, the discrepancies among the four primary standards do not appear to be large, as the data in Table 3 illustrate. The numbers given in the column headed '*p*H (liquid junction)' were determined by a hydrogen-calomel cell with liquid junction[10] and are based on a value of 6.863 for the the *p*H of the reference phosphate solution.

Alternative conventions, equally reasonable but probably no more convenient, could have been chosen instead of recommendation no. 3. VALENSI,[43] for example, prefers to consider the activity coefficient of chloride ion equal to the mean activity coefficient of potassium chloride in the buffer mixture, as measured with the dropping potassium amalgam electrode. This convention is applicable at high ionic strengths but less easily at low concentrations. Furthermore, it restricts somewhat the compositions of the standard solutions, for sodium ions and other cations reduced by potassium amalgam must be absent.

### *D. Interpretation of* p*H Values*

When the unknown solution matches the standard closely in composition and *p*H—that is, when the unknown is an aqueous solution of ionic strength less than 0.1, contains no large amounts of non-electrolytes, and has a *p*H between 2.5 and 11.5—there is reason to believe that the uncompensated part of the liquid-junction potential is small. Under these relatively ideal conditions, the measured *p*H may be expected to lie on the conventional scale of hydrogen ion activity fixed by the primary standards. Thus

$$pH = -\log c_H f_H \pm 0.02, \qquad (9)$$

where $f_H$ is an activity coefficient related to the $f_{Cl}$ defined by Equation (6) as follows:

$$f_H = \frac{f^2_{HCl}}{f_{Cl}}. \qquad (10)$$

The experimental *p*H values for dilute aqueous solutions, though admittedly not a measure of the 'true' single ion activity, will be consistent with a prescribed definition of ionic activity coefficients and will give correct thermodynamic results when properly used in equilibrium equations. Consequently they are of considerable

Table 3: Comparison of *p*H values from cells with and without a liquid junction

| Solution | $-\log(c_H f_H f_{Cl})$ | $-\log f_{Cl}$ (Eq. 6) | *p*H (S) | *p*H (liquid junction) |
|---|---|---|---|---|
| KH tartrate (saturated at 25 °C) | 3.635 | 0.078 | 3.557 | 3.564 |
| KH phthalate, 0.05 M | 4.093 | 0.087 | 4.006 | 4.007 |
| $KH_2PO_4$, 0.025 M; $Na_2HPO_4$, 0.025 M | 6.972 | 0.109 | 6.863 | (6.863)* |
| $Na_2B_4O_7$, 0.01 M | 9.240 | 0.059 | 9.181 | 9.183 |

* Reference solution

utility. It is obvious that no single functional relationship such as Equation (6) can describe the variation of $f_{Cl}$ with ionic strength with exactitude in differently constituted standard solutions and unknown solutions. A similar restriction to the application of measured $p$H values to chemical equilibria is inescapable.

Although it is impracticable to recognize specific differences of a secondary character, differences of electric charge are of primary importance and allowance must be made for them. The interpretation is facilitated by utilizing the valence relationships of the Debye-Hückel limiting law to relate the activity coefficients of other anions to that of chloride, namely

$$f^{-} = f_{Cl} \text{ and } f^{-2} = f^{4}_{Cl}.$$

In many important equilibria, notably the dissociation of monobasic weak acids, this collateral convention is all that is required. Thanks to a partial concellation of activity-coefficient corrections, the treatment is often very successful.

In the author's opinion, a universally accepted conventional definition of individual ionic activity coefficients is sorely needed. A formula of this sort would not only bring uniformity to the interpretation of $p$H measurements but would provide a sytematic basis for the tabulation of other electrochemical data as well.

Above an ionic strength of 0.1, an interpretation of the practical $p$H should be attempted only with a recognition that the liquid-junction potential probably no longer matches closely that of the standard solution. Even more important, perhaps, is the possibility, not provided for in Equation (6), that $f_{Cl}$ passes through a minimum between $\mu = 0.2$ and $\mu = 0.5$, as the mean activity coefficients of some uni-univalent chlorides are known to do. If interpretations of $p$H in solutions of $\mu > 0.1$ containing considerable sodium chloride are to be made, for example, it would be advisable, following DAVIES,[18] to add the term $-0.1\,\mu$ to the right side of Equation (6). Nevertheless, it is interesting to note that the right side of this equation is a reasonably satisfactory representation of the mean activity coefficient of potassium chloride even above $\mu = 0.1$.

Under conditions of constant ionic strength, when both the standard (S) and unknown (X) are predominantly composed of the same neutral salt (e.g. potassium chloride), it may be justifiable to consider the value of $f_H$ to be a constant. Hence, the difference of E.M.F., $E_x - E_s$, is an index of the difference of hydrogen ion concentration:

$$pcH(X) - pcH(S) = \frac{E_x - E_s}{2.3026\,RT/F}, \qquad (11)$$

where $pcH$ is defined as $-\log c_H$. To measure $pcH(X)$, a standard solution of known hydrogen ion concentration is needed. This procedure has been used with notable success by SCHWARZENBACH.[37]

*E. Nonaqueous and Partially Aqueous Media*

One of the most difficult and least understood problems facing the chemist who measures $p$H values routinely concerns the proper use of measurements made in media that are not entirely aqueous. The $p$H cell develops a reproducible E.M.F. in many solutions that contain little or no water. Hence, the computation of $p$H values for these media is fully justified by the breadth of operational definition embodied in Equation (2). The interpretation of these $p$H numbers in the manner suggested in the previous section, however, cannot lead to useful results when the solvent medium contains more than a few percent of a nonaqueous component. The fact that the hydrogen electrode and often the glass electrode function reproducibly and reversibly in some anhydrous media and in many partly aqueous solutions suggests that a quantity which may be termed the 'proton activity' has a definite value in these media. It is this quantity which BRØNSTED regarded as a manifestation of acidity in a fairly general sense, free from medium restrictions.[13] Although this concept is esthetically satisfying and of considerable academic interest, it cannot serve to establish a universal scale, because all comparisons of the acidity of two differently composed media involve an indeterminate phase-boundary potential.

BATES and SCHWARZENBACH[9] found, for example, that the practical $p$H of dilute solutions of strong acids and buffers in ethanol-water solvents follows only in a rough qualitative way the apparent changes indicated by other acidity functions which do not involve a liquid-junction potential. Their results for a mixture of hydrochloric acid (0.002 M) and sodium chloride (0.008 M) in solvents of composition varying from 0 to 100 vol. percent ethanol are plotted in Figure 5. As expected, the Hammett function $H_-$ and the quantity $-\log (c_H f_H f_{Cl})$, labeled $pw^{\circledast}$, vary similarly when the alcohol content is changed. The conventional $p$H value, however, behaves in a manner that seems incompatible with the definition $-\log c_H f_H$ and the form of the relatively reliable curves for $-\log (c_H f_H f_{Cl})$ and for the medium effect, $f^m$.

Nevertheless, there is good evidence that a determination of the *relative* acidity of dilute solutions in a particular nonaqueous medium may be quite successful, as long as the composition of the solvent does not change.[33] The hydrogen electrode, and often the glass electrode as well, is useful for this purpose. The establishment of reference solutions in each medium would follow the procedures outlined for the assignment of values to the aqueous $p$H standards, and no partiuclar difficulties should be encountered. The $p$H in each medium would be consistent with dissociation constants of the weak electrolytes present and with mean activity coefficients, both of these quantities being referred to the standard state corresponding to infinite dilution *in the particular medium.* One would then not have to deal with primary medium effects. This approach has been

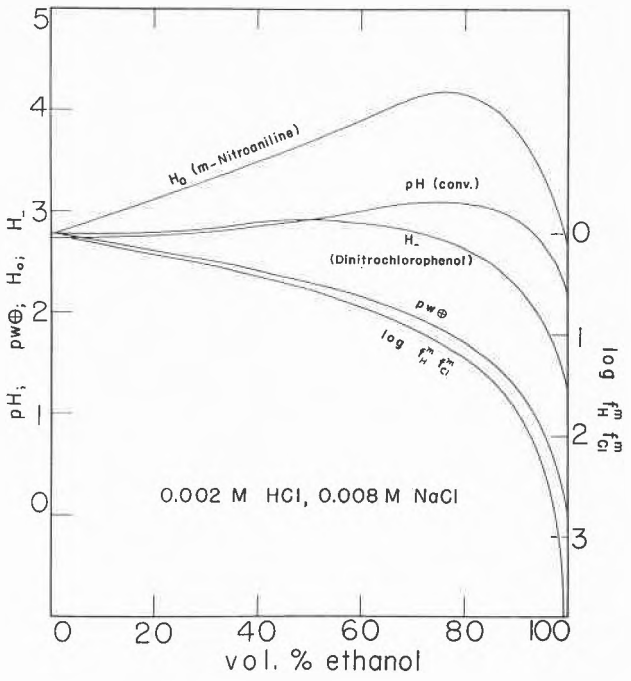


*Fig. 5.* Acidity functions for solutions of 0.002 M HCl, 0.008 M NaCl in ethanol-water mixtures. $H_0$ and $H_-$: Hammett acidity functions; $pw\oplus$: $-\log c_H f_H f_{Cl}$; $f^m$: the primary medium effect (ratio of the activity coefficient of the species at infinite dilution in the solvent medium to that at infinite dilution in pure water)

used to derive *p*H values for the Sørensen and McIlvaine buffers in methanol-water solvents containing 10, 30, and 50 vol. percent methanol.[34] For diverse solvents, one would like, of course, to measure *p*H values that would have meaning in terms of the *p*H obtained in aqueous media. A series of standard solutions whose *p*H values were all referred to the customary standard state for aqueous solutions would link all measurements to a common basis. Unfortunately, it does not appear possible to obtain these reference values at the present time.

It should perhaps be noted here that a universal *p*H scale for all media, if it could be achieved, might prove less useful than expected. The complexity of acid-base interactions in solvents of varied chemical natures is becoming increasingly evident. It appears unlikely that a single acid would react in the same way and to the same degree at identical *p*H values (or proton activities) in different solvents, for the *extent* of a chemical reaction is determined by factors which do not necessarily influence the electrometric measurement.[6] For the same reason, two acids of different structures and charge types in different solvents would probably not participate to the same extent in a reaction with a given base, even though the *p*H values of their solutions were the same. In view of these limitations, it seems unwise to attempt to relate acid-base phenomena in nonaqueous and partially aqueous media to the aqueous scale or to apply the term *p*H to these media in other than its operational sense.

## II. Recent Developments in *p*H Instrumentation

The remainder of this paper will be devoted to a description of some of the outstanding recent developments in electrodes, measuring circuits, and industrial *p*H measurement and control. It is manifestly impossible to mention here all of the excellent *p*H instruments that are currently offered commercially. The examples given are therefore to be considered as representative of the advanced designs of *p*H equipment now available.

Noteworthy improvements have been made in all aspects of *p*H measurement in the past ten years. New electrodes for special or unusual measuring conditions have been devised. Circuits for measuring the E.M.F. of the *p*H cell are not only more sensitive and stable than ever before but are capable of measuring accurately the E.M.F. of cells of enormous resistance. Modern measuring instruments can furnish a record of *p*H changes or, if desired, will actuate controllers which maintain the *p*H of the medium continually at a predetermined level.

Temperature errors in *p*H cells and means for their elimination are now understood more fully than ever before. For some time, manual and automatic compensation for the change of slope, 2.3026 $RT/F$ in Equation (7), has been commonplace, allowing direct conversion of E.M.F. to *p*H units on the dial of the instrument. Some progress has also been made in providing a direct instrumental compensation for changes in the standard potential of the *p*H cell with changes of temperature.[19] If this correction can be made successfully, it will remove the restriction that the temperatures of standardization and measurement must be the same, although changes in the asymmetry potential will still be of concern. The same objective could be accomplished by designing a completely symmetrical *p*H cell, with standard buffer and internal reference solution so chosen that the cell E.M.F. at the point of standardization is zero at all temperatures.[21] This possibility will be discussed further in a later section.

### *A. Glass Electrodes*

The utility of the glass electrode rests on the fact that the magnitude of the potential across the boundary between the glass membrane and the electrolytic solution is determined almost exclusively by the hydrogen ion concentration or activity of the solution. Before the hydrogen ion response can be developed, the glass membrane must be suitably conditioned by immersion in water or aqueous solution, preferably containing dilute acid. During this conditioning process alkali-metal cations, which occupy holes in the silicon-oxygen network of the glass, pass into the water phase and are replaced by hydrogen ions from the aqueous solution. These hydrogen ions find positions of great stability, it appears, within the glass surface. Water also penetrates the glass during the conditioning process, as indicated by a noticeable swelling of the glass surface.

Although the glass electrode is applied almost universally in the practical measurement of *p*H, the mechanism by which the electrode develops its potential has not yet been uniquely explained. It seems clear, however, that water is important in developing this potential and that some sort of exchange or transfer of hydrogen ions takes place between the conditioned surface and the solution in which the electrode is immersed. From the work of HUBBARD and his co-workers it is clear that the hygroscopicity of the glass is an important characteristic, as is also the durability.[26]

It has, indeed, long been believed that the solvent in which the glass electrode is immersed must contain a large percentage of water to give satisfactory results, or alternatively, that the electrode must be conditioned frequently in water before it can be used in a solvent of low water activity. Recent work has indicated, however, that the glass electrode is capable of giving accurate results in methanol-water solvents containing very little water.[2] Glass electrodes were stored in methanolic solvents and were not conditioned in pure water between measurements. In spite of this, the dissociation constants for acetic acid in methanol-water mixtures found from the glass electrode measurements were in good agreement with determinations based on conductivity measurements.[38] There is some evidence, however, that the glass electrode does not behave as satisfactorily in ethanol-water mixtures containing large proportions of ethanol.

Probably the three most serious limitations of the glass electrode are as follows: (1) The high electrical resistance and the large temperature coefficient of resistance; (2) The tendency of the glass surface to adsorb preferentially a variety of ions; and (3) The pronounced error displayed by many glass electrodes in alkaline solutions.

The electrical resistance of the average glass electrode at room temperature lies between 200 and 400 megohms. At 0 °C, however, the same electrode may have a resistance of 3,000 to 7,000 megohms. It is clear that the difficulty of making an accurate measurement of the surface potential of a given glass electrode is much greater at 0 than at 25 °C. Similarly, if this same electrode is used at 100 °C its resistance will be extremely low. In addition, the durability of the glass (which decreases as the resistance decreases) is likely to be correspondingly low, and the useful life of the electrode in solutions of high temperature will be quite short.

The glass surface is easily contaminated with ions, as well as fouled by films of colloids, proteins, and sludge. Since the *p*H response involves a surface reaction, adsorbed material may introduce errors which are particularly important when the solution is poorly buffered. The possibility that adsorption of acid may explain the error of the glass electrode in solutions of low *p*H has been suggested by SCHWABE and GLÖCKNER.[36]

A noteworthy study of the E.M.F. behavior of 15 electrode glasses has recently been made by SIMON and WEGMANN.[40] These authors have turned their attention to four properties of commercial electrodes, namely: the *p*H response in the intermediate range, the alkali error and its dependence upon time, the asymmetry potential, and the electrical resistance. The best of the commercial electrodes were found to have an alkaline error of only about 0.15 *p*H unit in 1 N sodium hydroxide at 25 °C. Indeed, electrodes fabricated from the new GB glass of Electronic Instruments Ltd. are said to have an error of only about one-third this figure.[32] It is thus evident that the problem of the alkaline error which has plagued the practical measurement of *p*H for three decades has largely been solved. This has been accomplished by the discovery of new and better glass compositions, in particular the substitution of lithium, barium, and cesium for the sodium and calcium of the early glass electrodes. The addition of uranium dioxide to the glass appears to lower the resistance considerably,[35] whereas germanium dioxide improves the workability.[39]

In the past decade there has been an increasing demand for accurate *p*H measurements at elevated temperatures. Most of the manufacturers of *p*H electrodes now offer glass electrodes suitable for use at long periods near or above 100 °C. The GB type of electrode supplied by Electronic Instruments Ltd. is recommended for temperatures as high as 160 °C. The greatest difficulty in the design of such electrodes appears to be the proper choice of internal reference solution and internal electrodes that will have the necessary stability over long periods of time.

The calomel electrode which is often used within the glass bulb is known to be unsuitable for continuous measurements at high temperatures.[30] The failure which begins at about 80 °C is believed to be due to a disproportionation reaction. The silver-silver chloride electrode can often be employed successfully, but the high solubility of silver chloride in relatively concentrated solutions of chloride detracts from the general usefulness of this electrode. FRICKE[21] has accordingly described a reference electrode consisting of 40% thallium amalgam in contact with solid thallous chloride and immersed in a solution saturated with potassium chloride. This electrode permits a completely symmetrical cell to be established, for the thallous chloride electrode is suitable as an external reference electrode and also as a reference within the glass bulb. In both uses, the electrode is in contact with a solution saturated with potassium chloride.

FRICKE has pointed out that, ideally, the *p*H cell intended for use at many temperatures should be symmetrical, and that the buffer solution with the glass bulb is filled should, if possible, have a zero temperature coefficient of *p*H. Inasmuch as the change of *p*H with temperature is governed primarily by the temperature coefficient of the dissociation constant of the weak acid or base of which the buffer is composed, it would seem difficult to achieve this objective. The experiments of

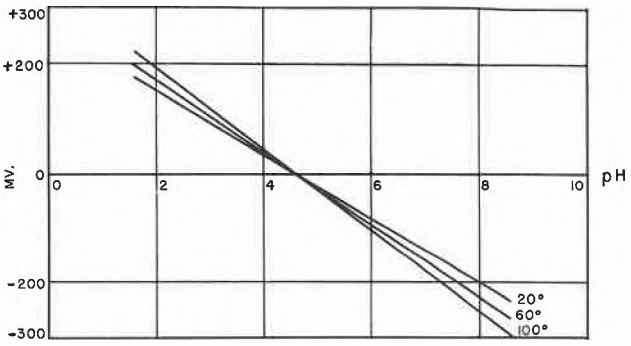


*Fig. 6.* Isotherms of a symmetrical *p*H cell

FRICKE have shown, however, that the temperature coefficient of *p*H of several buffer solutions is considerably reduced when the solution is saturated with potassium chloride. For example, it was found that an acetate buffer composed of acetic acid and sodium acetate each at a concentration of 1 N in a solution saturated with potassium chloride has a *p*H that varies only by a few hundredths of a unit between 20 and 100 °C.

The favorable electrical characteristics of this assembly are illustrated in Figure 6, where the E.M.F. (in mv) of the symmetrical cell at temperatures of 20, 60, and 100 °C is plotted as a funtion of *p*H. The slope of the line for each temperature is, of course, governed by the Nernst equation. Inasmuch as the cell is completely symmetrical and the *p*H of the internal reference buffer is substantially independent of temperature, all of these curves pass through a single point («Isothermenschnittpunkt») corresponding to the *p*H (4.6) of the buffer within the glass bulb.

An electrode composed of 2-percent cadmium amalgam in a *p*H 4.6 buffer that is N/3 in cadmium sulfate is also said to be a useful internal reference.[22] In conjunction with an external thallium amalgam-thallous chloride reference electrode, the assembly has an «Isothermenschnittpunkt» at *p*H 7.0.

The manufacturers of glass electrodes have developed many ingenious electrodes for special purposes during the past ten years. It is impossible to mention any considerable number of these; however, some of them are illustrated in Figure 7.

The miniature electrodes developed by Leeds & Northrup permit precise *p*H measurements to be made on volumes as small as a single drop. An electrode marketed by Polymetron Ltd. permits *p*H measurements to be made on surfaces of paper, leather, and other materials and on the skin. An electrode with a 2-meter lead developed by Ingold (Zurich) permits the direct measurement of *p*H in the stomach, the circuit being completed through a salt-bridge tube placed in the mouth. The Ingold «Agroprobe» electrode assembly permits measurements of moist soil to be made in the field. Though not a new development, the MacInnes-Belcher *p*H cell is still one of the most satisfactory designs for precise laboratory measurements. To the author's knowledge, however, this electrode is not yet supplied with glass membranes of low sodium error.

### *B. Reference Electrodes*

The function of the reference electrode in *p*H measurements is to maintain a constant potential with respect to which the potential of the *p*H-sensitive glass membrane is measured. The choice of type of reference electrode is dictated to some extent by the temperature at which the cell is to be used. The proper choice of reference electrode is also important in reducing the temperature

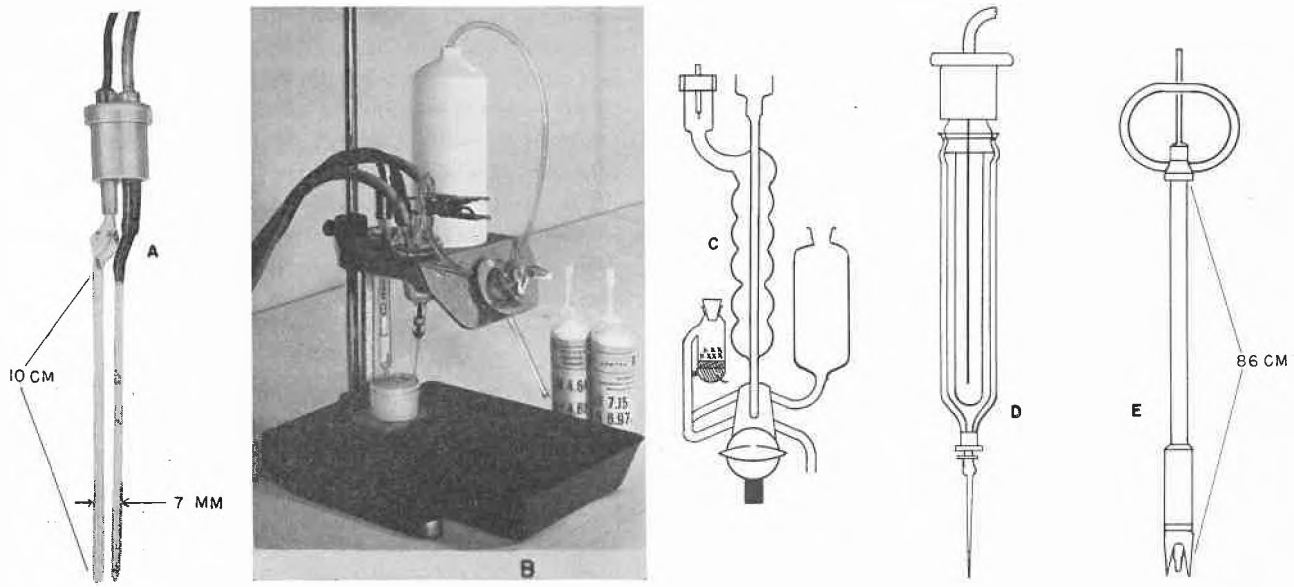


*Fig. 7.* Special types of glass electrode (courtesy of Leeds & Northrup Inc., Metrohm AG, Electronic Instruments Ltd., Ingold). *A* L & N Miniature; *B* Metrohm blood chain; *C* MacInnes-Belcher; *D* E.I.L. Hypodermic; *E* Ingold «Agroprobe»

coefficient of the cell as a whole, a consideration that is of particular importance when the cell is to be operated at elevated temperatures.

Reference electrodes do not show the diversity of types found for glass electrodes. The calomel type is by far the most popular, although an increasing tendency to favor other newer types is noted. In place of the calomel electrode, the silver-silver chloride electrode in a saturated potassium chloride solution is sometimes preferred. A mercury-mercurous sulfate electrode in a solution of sodium sulfate is useful when chlorides must be excluded. The thallium amalgam-thallous chloride electrode mentioned in the previous section is finding increasing application and should be well suited for measurements over a considerable temperature range.

Jenaer Glaswerk Schott und Gen. recommends calomel electrodes for *p*H measurements in the temperature range −10 to 80 °C and the silver-silver chloride electrode for the range −10 to 100 °C. For a wider range of temperatures extending from 0 to 135 °C, the Jena Company furnishes its thallium amalgam-thallous chloride reference (called the 'Thalamid electrode'). Ingold also provides a reference electrode especially designed for use at high temperatures, but the nature of this electrode is not revealed. Both the calomel and Thalamid electrodes appear to have a very small polarizability. The silver chloride electrode has the disadvantage that the solubility of silver chloride in strong solutions of potassium chloride becomes rather large at temperatures nearing 100 °C. There is some danger, therefore, that silver chloride may be dissolved completely from the electrode if an attempt is made to utilize this reference for extended periods at high temperatures. It has already been noted that the calomel electrode is unsuitable for extended use above 80 °C. Some of the newer glass-reference electrode combinations will, however, withstand numerous sterilization cycles which subject them to 2 atm. of steam pressure for one-half hour.

The design of the liquid junction is a matter of considerable importance if reproducible and stable *p*H measurements are to be obtained. It has long been believed that static junctions of cylindrical symmetry, allowing free diffusion, are the most reproducible. Unfortunately it is difficult to construct a practical, versatile liquid junction of this type. Consequently, most commercial reference electrodes are designed in such a way that the relatively dense saturated solution of potassium chloride flows slowly from the tip of the electrode into the solution. One exception to this design is to be found in the popular MacInnes-Belcher type of cell assembly, shown in Figure 7. In this cell, the liquid junction approaches cylindrical symmetry inasmuch as it is formed in the bore of a stopcock arranged so that the potassium chloride solution is below the solution whose *p*H is to be determined. With this exception, however, most commercial electrodes depend upon various arrangements to permit a retarded flow of potassium chloride solution into the solution in contact with the glass electrode.

Beckman Instruments, Inc., supplies three types of junction. An asbestos fiber sealed into the glass allows a very slow flow of bridge solution to take place. When the solution under investigation is of such a composition that the fiber might become blocked by a precipitate, a ground-glass sleeve is used to form the junction. A third type, recently introduced, consists of palladium annulus sealed into the glass. The very convenient Beckman combination assembly, in which the glass electrode is mounted within the cylindrical calomel-bridge tube, projecting a few mm from the lower end, utilizes a fiber junction.

The Leeds & Northrup Company has devised a liquid junction which has been termed the 'controlled-crack' liquid junction tube. The glass tube containing the saturated bridge solution has two very small apertures or cracks, through which the bridge solution leaks very slowly, at its lower end. As an added feature, the glass tube containing the bridge solution can be unscrewed from the electrode support. It is therefore readily possible to interchange calomel elements and to replace the bridge solution. When measurements are being made at several different temperatures, it may be advantageous to utilize a series of junction tubes each one of which is kept at a different temperature.

There is a recent trend to favor liquid junctions formed at ceramic diaphragms or ceramic plugs, and there is some reason to predict that commercial reference electrodes will gradually utilize this type of junction almost exclusively. The reference electrodes produced by Ingold and by Philips (Eindhoven) are of this type. The Jenaer Glaswerk produces reference electrodes with asbestos junctions and ground-glass junctions but recommends its ceramic diaphragm for normal conditions of use. The resistance of the diaphragm is of the order of 3,000 to 6,000 ohms.

Salt bridges made of porous glass and ion-exchange membranes have also been studied.[14] The former are fabricated from a leached but unfired Vycor produced by Corning Glass Works. The electrical characteristics of both types are favorable, but adsorption of fouling materials on the porous glass may constitute a problem. As expected, the junction potentials across the ion-exchange membranes are relatively large, but the membrane bridges appear to function without the passage of solution and hence may find use in special applications.

It should, perhaps, be noted that differences among liquid junctions of different designs often are not apparent when measurements are made in buffer solutions of intermediate *p*H. Deviations from the behavior of the best static junctions may be revealed only when the solution has a *p*H less than 2 or greater than 12. It is well known that the magnitude of the liquid junction potential is dependent not only on the mobilities of the ions at the liquid junction but upon their concentrations as

well. It is evident, therefore, that the liquid-junction error will be largest when the concentration of the unknown solution is quite different from that of the buffer solution, the *p*H being equal. In practical measurements, the error is not likely to be of great concern. The work of VALENSI,[43] however, suggests that some refinement in *p*H measurements might result from correlating the measured *p*H with the conductivity of the unknown solution.

Colloids and suspensions at the liquid junction may be the source of serious errors in *p*H measurements. Although the cause of this defect is not completely clear, it seems possible that the flowing electrodes of commercial design are less influenced by suspensions than is the case with those few liquid junctions of the static type.

MATTOCK has considered the sources of error in the design of liquid junctions[31] and has pointed out that for high reproducibility strict attention to thermal stability is imperative.[32] It is his belief that the so-called 'hysteresis errors' of saturated calomel electrodes are to be attributed largely to a failure to achieve complete temperature equilibrium.

### *C.* p*H Meters*

The *p*H meter is essentially a voltmeter of very high input resistance, designed in such a way that *p*H units can be read directly. During the past decade great progress has been made in electronic instrumentation. As a result of these developments, many excellent *p*H meters are now being manufactured in several different countries. Measurement techniques have been developed to such a degree that reproducible *p*H numbers can easily be obtained with a precision of a few thousandths of a unit. It is well to remember, however, that the fundamental meaning of the measured *p*H is considerably less certain than the accuracy with which the numbers can be obtained.

Among the criteria which have influenced the design of *p*H meters are the following:

(1) The measurement should be unaffected by the high resistance of the *p*H cell or by large changes in the magnitude of the resistance.
(2) The meter should have a provision for temperature compensation, preferably automatic.
(3) For many purposes, the *p*H meter should be operated by alternating current, and its operation should be independent of normal changes in the voltage of the power supply.
(4) The circuit constants should not be altered when the vacuum tubes are changed. In addition, it is often desirable that a recorder be connected to the measuring system and that the precision of the measurement should not be affected thereby.

There is considerable diversity in the circuitry of *p*H meters, and modern instruments cannot be rigorously classified by the characteristics of the circuit used. Three basic types of circuit, however, have played an important role in the development of the *p*H meter, and these will be explained briefly. These are (a) the null-detector method, (b) the direct-coupled feedback amplifier method, and (c) the frequency-conversion amplifier method. In actual practice, these types are not separate and distinct, but a variety of combinations exists. The characteristics of circuits and amplifiers suitable for accurate *p*H measurement have been discussed by HITCHCOX,[25] CLARK and PERLEY,[16] and WOLF.[45]

The null-detector method is one of the earliest and simplest and still one of the most satisfactory methods available. The *p*H cell is connected to a potentiometer standardized against a standard cell, and the null current is amplified by means of a D.C. amplifier to make it possible to operate a galvanometer or other indicator. Theoretically, the voltage of the *p*H cell may be exactly balanced against that of the potentiometer. Battery operation stabilizes the amplifier response, but special precautions to minimize grid current errors may be required. The selection of electrometer tubes has proved a successful means of avoiding a large grid current drain and its attendant errors.

The popular and reliable Beckman Model G meter and the Radiometer *p*H meter 4 are instruments of the null-detector type. In the Radiometer meter, the plate supply voltage and the filament current for the output tubes are developed by a transistor converter operated by 1.5 v batteries. Reproducibility of measurement to $\pm$ 0.001 unit is said to be achieved.

By the use of direct-coupled feedback amplifiers, *p*H meters can be made to indicate directly changes in the *p*H of the solution in the *p*H cell. This type of circuit also makes possible the operation of recorders. In a typical arrangement, an output voltage from the amplifier is fed back in opposition to the input voltage from the electrodes. This feedback voltage is proportional to the difference between the cell potential and the balancing voltage. When sufficient gain is employed, the current drawn from the electrodes is negligible, and the E.M.F. of the cell is measured by metering the feedback current. Changes in the power supply and in the characteristics of the tubes can be made negligible. They may have a considerable effect, however, on the zero reading, and special attention has to be given to the stability of the voltage supply for the D.C. amplifier in order to reduce the zero error. In addition, precautions may also have to be adopted to reduce grid-current errors.

The input resistance, grid current, and zero stability of a D.C. amplifier are largely governed by the quality of the electrometer tube. Differential amplifiers have accordingly been used successfully to improve the amplification characteristics. The basic principle consists in the arrangement of two identical amplifiers in such a way that their response to external signals is additive while that to internal noise or drift is subtractive.[25] This type of circuit has been used successfully in the Electronic Instruments Model 28 meter.

The Polymetron 42 B meter combines the accuracy of the potentiometer with the convenience of a direct-read-

ing meter. Partial compensation of the input signal is achieved by means of a potentiometric circuit with a standard cell. The residual voltage is read directly. Special stabilization of the fluctuations in the mains voltage is provided. Provision is made for direct connection to a recorder.

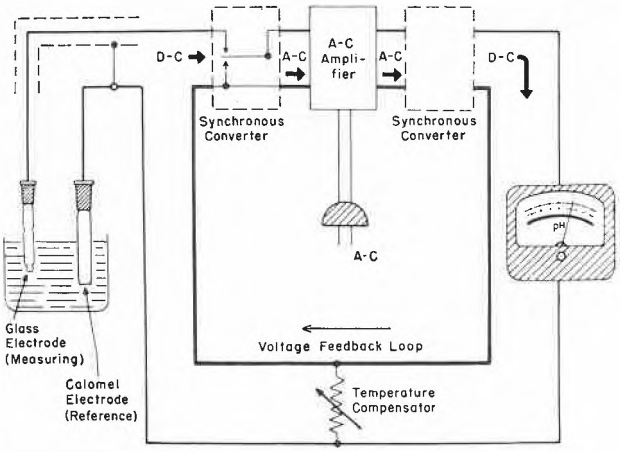


*Fig. 8.* Frequency-conversion amplifier of the chopper type (Leeds & Northrup stabilized *p*H indicator, courtesy of Leeds & Northrup Inc.)

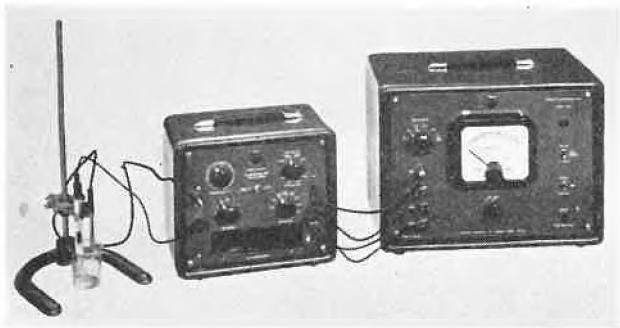

*Fig. 9.* Vibron *p*H-measuring unit and electrometer (courtesy of Electronic Instruments Ltd.)

The outstanding recent development in *p*H instrumentation is undoubtedly the introduction of frequency-conversion amplifiers making use of the chopper and the vibrating condenser. These amplifiers produce a pulsating signal, the A.C. component of which is extracted by a suitable filter network and fed to an A.C. amplifier of restricted band width. Both types of converter require high gain in the A.C. amplifier. The output may be reconverted to direct current if desired.

The noise generated by a mechanical chopper can readily be kept quite small in terms of the D.C. input voltage. The A.C. amplifier used in both types of instrument may have a very narrow band width; hence, a high degree of substantially noise-free amplication is practicable. After the A.C. signal is reconverted to D.C., the amplitude is great enough to swamp any subsequent low-frequency interference. Negative D.C. feedback is ordinarily used to stabilize the gain of the system as a whole.

Circuits of the frequency-conversion types provide excellent long-term stability as well as excellent discrimination. The input resistance of the dynamic capacitor, for example, is determined only by the quality of the insultation. Values as high as $10^{16}$ ohms are not unreasonable.

Several modern instruments make effective use of frequency-conversion amplifiers to achieve high stability and, in some instances, a sensitivity that may reach 0.1 mv (0.002 *p*H unit). Mechanical choppers are the heart of the direct-reading Radiometer Universal *p*H meter 22, the Knick laboratory *p*H meters, and the Leeds & Northrup stabilized *p*H indicator. The Metrohm Precision Compensator E 322 utilizes a chopper amplifier as a null indicator in a potentiometer circuit, and the Philips *p*H meter GM 4491 applies a vibrating condenser in a similar fashion. The circuit of the Leeds & Northrup instrument is shown schematically in Figure 8. The Cary electrometer and the Electronic Instruments Vibron electrometer incorporate vibrating condensers. The Vibron electrometer with its associated *p*H-measuring unit is shown in Figure 9.

Fortunately, the low grid-current drain of the newer instruments normally eliminates the 'IR-drop' error illustrated in Table 4.[5] As the Table shows, the resistance of the glass electrode has such a large temperature coefficient that an appreciable error may be incurred if a current greater than about $10^{-12}$ amp. is drawn from the cell. The IR drop at the temperature of the standard buffer solution can be compensated in the standardization procedure. If the temperature of the 'unknown' is different from that of the standard, however, an error equal to the *change* of the IR drop may be incurred.

Table 4: 'IR drop' in a typical *p*H cell

| *t* °C | *R* megohms | IR drop (*p*H units) at grid current of: | | |
|---|---|---|---|---|
| | | $1 \times 10^{-12}$ amp | $1 \times 10^{-11}$ amp | $5 \times 10^{-11}$ amp |
| 10 | 1,000 | 0.01 *p*H | 0.18 *p*H | 0.89 *p*H |
| 25 | 200 | 0.00 *p*H | 0.03 *p*H | 0.17 *p*H |
| 40 | 60 | 0.00 *p*H | 0.01 *p*H | 0.05 *p*H |

### *D. Automatic Titrators*

Laboratory titrators, which have been available for many years, are still being improved. Several models, such as the Metrohm Potentiograph E 336, provide for endpoint anticipation which governs the rate of addition of reagent by the slope of the titration curve, preventing overshoot. The Metrohm instrument can record the titration curve and the first-derivative curve as well.

Titrations which permit automatic sampling of industrial process fluids have recently become available. The Electronic Instruments Titromatic, for example, removes a sample from a pipeline, titrates it, records the result, and initiates a corrective action if necessary.

The Radiometer Titrigraph is designed to record titration data furnished by the Radiometer Titrator TTT-1. The two instruments are shown in Figure 10. As an added feature, this titration assembly will function as a 'pH-stat,' recording automatically the amount of

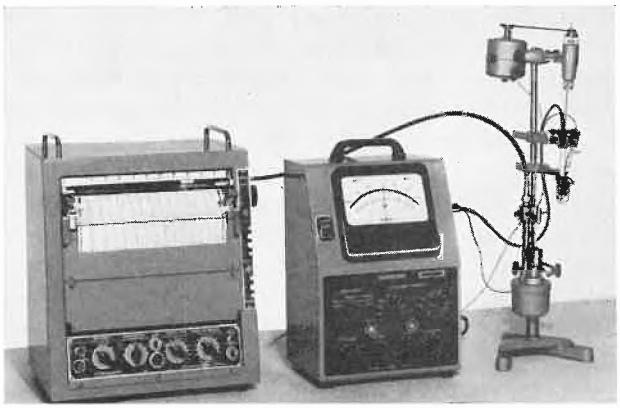

*Fig. 10.* Radiometer Titrator and Titrigraph (*p*H-stat) (courtesy of Radiometer)

reagent necessary to maintain constant *p*H. Titrations at constant *p*H, in which the volume of titrant is recorded as a function of time, are of considerable value in kinetic studies of enzyme systems and other dynamic biological processes.[28] The Polarad Automatic Recording Titrator manufactured by Polarad Electronics Corp., Long Island City, N.Y., not only functions as a *p*H-stat but is equipped to plot either the first-derivative or second-derivative curve.

### *E. Industrial* p*H Control*

The development of *p*H meters of high stability, of new sturdy, shock-proof glass electrodes, and of glass and reference electrodes capable of satisfactory operation at high temperatures and pressures has led to an expanding use of *p*H measurements in industrial control. Recorders of increased versatility are now available. If desired, the industrial *p*H measurement can be made completely automatic, with the aid of *p*H controllers of either the electric or pneumatic types. The mode of corrective action most suited to the problem at hand can be programmed by these ingenious instruments, and remarkably effective control is possible.

Each industrial control application is an individual problem. There are nonetheless certain fundamental principles that determine effective *p*H control, and these are becoming increasingly understood. These principles and their application in practical control situations have been capably discussed by CHAPLIN,[15] FARRINGTON,[20] and COLVER NUTTING.[17]

The essential elements in a control installation are the cells and electrodes, which together make up the sensing element; the *p*H meter, which measures the voltage developed in the *p*H cell; and the recorder or controller, which records or corrects the *p*H of the process solution.

Industrial *p*H cells are commonly of two types: immersion cells, designed to be immersed in open channels, flumes, and the like, and flow cells, which conduct the process solution in a closed channel past the electrodes. Immersion cells must incorporate some type of guard to protect the electrodes from damage. Flow cells are made from a variety of materials. Beckman Instruments Inc., for example, furnishes flow cells in porcelain, stainless steel, rubber and glass. Leeds & Northrup supplies a plastic flow cell as well as a stainless-steel flow chamber. Metallic chambers are useful in preventing errors caused by streaming potentials, which are sometimes a source of difficulty when the flow is rapid. It is often desirable to locate the measuring instrument at some distance from the process and to use the same measuring instrument for a number of sensing elements. Both of these objectives are possible with switching arrangements now available. It is readily possible to locate the meter at a distance of 150 meters from the cells.

One of the most common difficulties that plague industrial *p*H measurement and control is fouling of the electrodes by the process solution. The mechanical arrangement for cleaning electrodes devised by Ingold has found successful application in avoiding this difficulty, and the self-cleaning electrode assembly recently introduced by Polymetron AG appears to be a most useful and promising development. An immersion cell equipped with self-cleaning electrodes is shown at the left in Figure 11. The ultrasonic principle is used to remove films that accumulate on the electrodes. It has been found that neither the life of the electrodes nor the measured *p*H is influenced by use of this device.

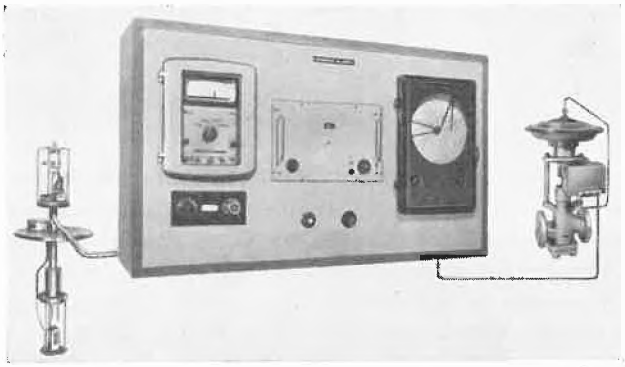

*Fig. 11.* Industrial installation for automatic measurement and control of *p*H of sewage, including (at left) self-cleaning electrode assembly of the ultrasonic type (courtesy of Polymetron AG)

The extension of industrial *p*H measurements to temperatures above 100 °C in aqueous systems has been possible only because of the development of glasses suitable for high-temperature measurements and of reference electrodes stable above 100 °C, equipped with liquid junctions capable of functioning at pressures above atmospheric. New compositions of glass of high durability and low error have solved the problem of a *p*H-responsive electrode for elevated temperatures. As we

have already seen, reference electrodes can be also devised for extended use under these special conditions.

Considerable attention has been given to the problem of obtaining a free-flowing liquid junction for elevated pressures. The Ingold company manufactures industrial reference electrodes provided with separate stock vessels for the potassium chloride solution which are equipped for pressure equalization up to 2 atm. In its industrial installations, Polymetron provides a differential pressure regulator which maintains the reference electrode and salt bridge at a pressure of 0.1 atm. in excess of that on the solution in contact with the glass electrode.

Likewise, the Leeds & Northrup Company has devised a reference electrode which utilizes a bell-jar principle; air trapped between the salt bridge and a surrounding tube is compressed as the pressure on the external solution increases. The increased air pressure is communicated to the interior of the reference electrode through a breather hole near the top of the salt-bridge tube. If the additional air needed at very high pressures is supplied, freeflowing junctions can be obtained at pressures as high as 7 atm. The manufacturers claim that this arrangement permits larger pressure fluctuations to be compensated than do other pressure-regulating devices.

INGRUBER[27] has developed a pressurized reference electrode. The calomel element is cooled by a jacket of circulating water, and there is a non-convective thermal junction in the salt bridge. A *p*H cell utilizing a glass electrode in conjunction with this reference performed satisfactorily at 200°C and a pressure of 14 atm. INGRUBER has also considered the matter of temperature corrections for measurements of *p*H cells with thermal gradients.

Controllers such as the Leeds & Northrup Model S Speedomax and Brown Elektronik furnish a detailed record of the process variable. They are able also to utilize control procedures of the three most useful types, namely (1) Proportional action, in which the amount of reagent added is proportional to the deviation of the *p*H from the desired control point, (2) Rate action, by which the amount of reagent added is governed by the *rate* of change of the *p*H, thereby overcoming a time lag in the process, and (3) Automatic reset, which keeps the control valve moving when a sustained demand, which would tend to balance the process above or below the control point, develops.

The solutions to some typical problems of industrial *p*H control have been summarized recently by GAUCHAT.[23] In electroplating installations, for example, the problem of stray currents has been solved by fabrication of a flow cell from a block of graphite. The cell is provided with holes for the electrodes and for the flowing solution. The graphite block simulates a Faraday cage. In quite a different situation, namely monitoring the acidity of heavy water, it was found necessary to modify the electrodes by using heavy water in preparing the buffer solution placed within the glass electrode as well as for the saturated potassium chloride solution of the reference electrode and the salt bridge.

An arrangement for the continuous measurement of *p*H and the automatic neutralization of sewage is shown in Figure 11. This assembly may be considered typical of many industrial control installations. At the left is an immersion cell with self-cleaning electrodes and at the right the pneumatically controlled valve which admits reagent to the process stream upon demand. The control panel houses the *p*H meter, ultrasonic generator, recorder, and pneumatic controller. With the use of the versatile components now available commercially, the problem of *p*H control in many complex industrial processes has been effectively solved.

The author takes pleasure in acknowledging the generous cooperation of the following companies and individuals: Electronic Instruments Ltd., Richmond, Surrey (Dr. G. MATTOCK); Jenaer Glaswerk Schott und Gen., Mainz (Dr. H. K. FRICKE); Leeds & Northrup, Inc., Philadelphia (Dr. E. L. ECKFELDT); Metrohm AG, Herisau (L. KUHN, B. SUHNER); Polymetron AG, Zürich (Ing. CH. L. GAUCHAT, Dr. H. JUCKER); Radiometer, Copenhagen (Ing. S. SCHRØDER); and Dr. W. SIMON, ETH, Zürich.

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