HYDROGEN-ION ACTIVITY

1. Introduction

In a world in which most chemical and biological reactions occur in aqueous media, it is well recognized that the hydrogen ion is of fundamental importance. Hydrogen ions are involved in a wide variety of natural and industrial reactions, and the equilibrium positions as well as the rates of these reactions are therefore dependent on hydrogen-ion concentration. The hydrogen ion is more correctly termed hydronium ion. The unhydrated proton does not exist in aqueous solution but rather is bound to several molecules of water. This ion, sometimes represented as $H(H_2O)_n^+$, is usually written simply as H^+. More important is the distinction between the hydrogen ion concentration and its activity. The hydrogen ion concentration, or total acidity, is obtained by titration and corresponds to the total concentration of hydrogen ions available in a solution, ie, free, unbound hydrogen ions as well as hydrogen ions associated with weak acids. The hydrogen ion activity refers to the effective concentration of unbound hydrogen ions, ie, the form which affects physicochemical reaction rates and equilibria. The effective concentration of hydrogen ion in solution is expressed in terms of pH, which is the negative logarithm of the hydrogen-ion activity, a_{H^+}

$$\mathrm{pH} = -\log_{10} a_{H^+} \tag{1}$$

The relationship between activity, a, and concentration, c, is

$$a = \gamma c \tag{2}$$

where the activity coefficient γ is a function of the ionic strength of the solution and approaches unity as the ionic strength decreases; ie, the difference between the activity and the concentration of hydrogen ion diminishes as the solution becomes more dilute. The pH of a solution may have little relationship to the titratable acidity of a solution that contains weak acids or buffering substances; the pH of a solution indicates only the free hydrogen-ion activity. If total acid concentration is to be determined, an acid–base titration must be performed.

Thermodynamically, the activity of a single ionic species is an inexact quantity, and a conventional pH scale has been adopted that is defined by reference to specific solutions with assigned pH(S) values. These reference solutions, in conjunction with equation 3, define the pH(X) of the sample solution.

$$\mathrm{pH}(X) = \mathrm{pH}(S) - \frac{(E_X - E_S)F}{2.303RT} \tag{3}$$

E_S is the electromotive force (emf) of the cell:

$$\text{reference electrode}|\mathrm{KCl}(\geq 3.5M)\|\text{solution } S|\mathrm{H_2(g)},\ \mathrm{Pt}$$

and E_X is the emf of the same cell when the reference buffer solution S is replaced by the sample solution X. The quantities R, T, and F are the gas constant, the thermodynamic temperature, and the Faraday constant, respectively.

For routine pH measurements, the hydrogen gas electrode [H_2(g),Pt] usually is replaced by a glass membrane electrode.

The availability of multiple pH(S) reference solutions makes possible an alternative definition of pH(X):

$$\mathrm{pH}(X) = \mathrm{pH}(S_1) + [\,\mathrm{pH}(S_2) - \mathrm{pH}(S_1)]\,\frac{(E_X - E_{S1})}{(E_{S2} - E_{S1})} \tag{4}$$

where E_{S1} and E_{S2} are the measured cell potentials when the sample solution X is replaced in the cell by the two reference solutions S_1 and S_2 such that the values E_{S1} and E_{S2} are on either side of, and as near as possible to, E_X. Equation 4 assumes linearity of the pH vs E response between the two reference solutions, whereas equation 3 assumes both linearity and ideal Nernstian response of the pH electrode. The two-point calibration procedure is recommended if a pH electrode other than the hydrogen gas electrode is used for the measurements.

2. pH Determination

Two methods are used to measure pH: electrometric and chemical indicator (1–7). The most common is electrometric and uses the commercial pH meter with a glass electrode. This procedure is based on the measurement of the difference between the pH of an unknown or test solution and that of a standard solution. The instrument measures the emf developed between the glass electrode and a reference electrode of constant potential. The difference in emf when the electrodes are removed from the standard solution and placed in the test solution is converted to a difference in pH. Electrodes based on metal–metal oxides, eg, antimony–antimony oxide (see ANTIMONY AND ANTIMONY ALLOYS; ANTIMONY COMPOUNDS), have also found use as pH sensors (8), especially for industrial applications where superior mechanical stability is needed (see SENSORS). However, because of the presence of the metallic element, these electrodes suffer from interferences by oxidation–reduction systems in the test solution.

More recently, two different types of nonglass pH electrodes have been described which have shown excellent pH-response behavior. In the neutral-carrier, ion-selective electrode type of potentiometric sensor, synthetic organic ionophores, selective for hydrogen ions, are immobilized in polymeric membranes (see MEMBRANE TECHNOLOGY) (9). These membranes are then used in more-or-less classical glass pH electrode configurations, although they have the advantages of being more easily fabricated into unique designs and are less prone to protein fouling in biological fluids. Another type of pH sensor is based on an integrated ion-selective electrode and insulated-gate field-effect transistor (10). These sensors (qv), usually termed ion-selective field-effect transistors (ISFETS), are based on the modulation of the transistor source-drain current by a potential (or charge) applied to the transistor gate region. In the case of a pH ISFET, this potential is produced by a pH-responsive material applied to the gate region and in contact with the test solution. The most successful materials for this purpose have been crystalline solids, such as silicon nitride or tantalum oxide, and polymeric membranes containing the ionophores selective for hydrogen ions. Sensors based on the ISFET principle have the potential for extreme miniaturization and multisensor arrays on a single transistor chip (see also ELECTROANALYTICAL TECHNIQUES).

The second method for measuring pH, the indicator method, has more limited applications. The success of this procedure depends on matching the color that is produced by the addition of a suitable indicator dye to a portion of the unknown solution with the color produced by adding the same quantity of the same dye to a series of standard solutions of known pH. Alternatively, the color is matched against a color comparison chart for the particular dye. The results obtained by the indicator method are less accurate relative to those obtained using a pH meter. The indicator method, however, is inexpensive and simple to apply. In addition to being used by direct addition to the test solution, indicator dyes can be immobilized onto paper strips, eg, litmus paper or, more recently, onto the distal end of fiber-optic probes which, when combined with spectrophotometric readout, provide more quantitative indicator-dye pH determinations.

2.1. Reference Buffer Solutions.

To define the pH scale and permit the calibration of pH measurement systems, a series of reference buffer solutions have been certified by the U.S. National Institute of Standards and Technology (NIST). The pH values at 25°C of these primary and secondary reference buffer solutions are listed in Table 1 (2). The pH 6.86 and 7.41 phosphate buffers have long been accepted as the primary reference standards for blood pH measurements. It is well known that the ionic strength of these buffers is significantly different from that of blood, thus biasing (however reproducibly) the pH measurement in blood owing to the residual liquid-junction potential. Two concentrations of two zwitterionic buffer systems, HEPES/HEPESate and MOPSO/MOPSOate, have been certified as pH buffers at ionic strengths comparable to that of blood and consequently should minimize the residual liquid-junction potential problem. The International Union of Pure and Applied Chemistry (IUPAC) recommends the NIST primary standards plus a series of operational standards, measured vs the phthalate reference value standard in a cell having liquid junction, for the definition of the pH scale (11).

2.2. Accuracy and Interpretation of Measured pH Values.

The acidity function which is the experimental basis for the assignment of pH, is reproducible within about 0.003 pH unit from 10 to 40°C. If the ionic strength is known, the assignment of numerical values to the activity coefficient of chloride ion does not add to the uncertainty. However, errors in the standard potential of the cell, in the composition of the buffer materials, and in the preparation of the solutions may raise the uncertainty to 0.005 pH unit.

The reproducibility of the practical scale that has been defined using the seven primary standards includes the possible inconsistencies introduced in the standardization of the instrument using seven different standards of different composition and concentration. These inconsistencies are the result of variations in the liquid-junction potential when one solution is replaced by another and are unavoidable. The accuracy of the practical scale from 10 to 40°C therefore appears to be from 0.008 to 0.01 pH unit.

Variations in the liquid-junction potential may be increased when the standard solutions are replaced by test solutions that do not closely match the standards with respect to the types and concentrations of solutes, or to the composition of the solvent. Under these circumstances, the pH remains a reproducible number, but it may have little or no meaning in terms of the conventional hydrogen-ion activity of the medium. The use of experimental pH numbers as a measure of the extent of acid–base reactions or to obtain thermodynamic equilibrium constants is justified only when the pH of the medium is between 2.5 and 11.5 and when the mixture is an aqueous solution of simple solutes in total concentration of ca $\leq 0.2\ M$.

2.3. Sources of Error. pH electrodes are subject to fewer interferences and other types of error than most potentiometric ionic-activity sensors, ie, ion-selective electrodes (see ELECTROANALYTICAL TECHNIQUES). However, pH electrodes must be used with an awareness of their particular response characteristics, as well as the potential sources of error that may affect other components of the measurement system, especially the reference electrode. Several common causes of measurement problems are electrode interferences and/or fouling of the pH sensor, sample matrix effects, reference electrode instability, and improper calibration of the measurement system (12).

In general, the potential of an electrochemical cell, E_{cell}, is the sum of three potential terms:

$$E_{\text{cell}} = E_{\text{pH}} - E_{\text{ref}} + E_{lj} \tag{5}$$

where E_{pH} and E_{ref} are the potentials of the pH and reference electrodes, respectively, and E_{lj} is the ubiquitous liquid-junction potential. After substitution of the Nernst equation for the pH electrode potential term in equation 5,

$$E_{\text{cell}} = E^{o}_{\text{pH}} - \frac{RT}{F} \ln a_H - E_{\text{ref}} + E_{lj} \tag{6}$$

it can be calculated that a 1 mV error in any of the potential terms corresponds to an error of ca 4% in the hydrogen-ion activity. Under carefully controlled experimental conditions, the potential of a pH cell can be measured with an uncertainty as small as 0.3 mV, which corresponds to a ±0.005 pH unit uncertainty.

The measurement of pH using the operational cell assumes that no residual liquid-junction potential is present when a standard buffer is compared to a solution of unknown pH. Although this may never be strictly true, especially for complex matrices, the residual liquid-junction potential can be minimized by the appropriate choice of a salt-bridge solution and calibration buffer solutions.

Other problems occur in the measurement of pH in unbuffered, low ionic strength media such as wet deposition (acid rain) and natural freshwaters (see AIR POLLUTION; GROUNDWATER MONITORING) (13). In these cases, studies have demonstrated that the principal sources of the measurement errors are associated with the performance of the reference electrode liquid junction, changes in the sample pH during storage, and the nature of the standards used in calibration. Considerable care must be exercised in all aspects of the measurement process to assure the quality of the pH values on these types of samples.

3. pH Measurement Systems

3.1. Glass Electrodes. The glass electrode is the hydrogen-ion sensor in most pH-measurement systems. The pH-responsive surface of the glass electrode consists of a thin membrane formed from a special glass that, after suitable conditioning, develops a surface potential that is an accurate index of the acidity of the solution in which the electrode is immersed. To permit changes in the potential of the active surface of the glass membrane to be measured, an inner reference electrode of constant potential is placed in the internal compartment of the glass membrane. The inner reference compartment contains a solution that has a stable hydrogen-ion concentration and counterions to which the inner electrode is reversible. The choice of the inner cell components has a bearing on the temperature coefficient of the emf of the pH assembly. The inner cell commonly consists of a silver–silver chloride electrode or calomel electrode in a buffered chloride solution.

Immersion electrodes are the most common glass electrodes. These are roughly cylindrical and consist of a barrel or stem of inert glass that is sealed at the lower end to a tip, which is often hemispherical, of special pH-responsive glass. The tip is completely immersed in the solution during measurements. Miniature and microelectrodes are also used widely, particularly in physiological studies. Capillary electrodes permit the use of small samples and provide protection from exposure to air during the measurements, eg, for the determination of blood pH. This type of electrode may be provided with a water jacket for temperature control.

The membrane of pH-responsive glass usually is made as thin as is consistent with adequate mechanical strength. Nevertheless, its electrical resistance is high, eg, 10–250 Mω. Therefore, an electronic amplifier must be used to obtain adequate accuracy in the measurement of the surface potential of a glass electrode. The versatility of the glass electrode results from its mechanism of operation, which is one of proton exchange rather than electron transfer; hence, oxidizing and reducing agents in the solution do not affect the pH response.

Most modern electrode glasses contain mixtures of silicon dioxide [7631-86-9], either sodium oxide [1312-59-3] or lithium oxide [12057-24-8], and either calcium oxide [1305-78-8], barium oxide [1304-28-5], cesium oxide [12018-61-0], or lanthanum oxide [1312-81-8]. The latter oxides are added to reduce spurious response to alkali metal ions in high pH solutions. The composition of the glass has a profound effect on the electrical resistance, the chemical durability of the pH-sensitive surface, and the accuracy of the pH response in alkaline solutions (see GLASS). Both the electrical and the chemical resistance of the electrode glasses decrease rapidly with a rise in temperature. Therefore, it is difficult to design an electrode that is sufficiently durable for extended use at high temperatures and yet, when used at room temperature, free from the sluggish response often characteristic of pH cells of excessively high resistance. Most manufacturers use different glass compositions for electrodes, depending on their intended use.

The mechanism of the glass electrode response is not entirely understood. It is clear, however, that when a freshly blown membrane of pH-responsive glass is first conditioned in water, the sodium or lithium ions that occupy the interstices of the silicon–oxygen network in the glass surface are exchanged for protons from the water. The protons find stable sites in the conditioned gel layer of the glass surface. Exchange of the labile protons between these sites and the solution phase appears to be the mechanism by which the surface potential reflects changes in the acidity of the external solution. When the glass electrode and the hydrogen gas electrode are immersed in the same solution, the potentials usually differ by a constant amount, even though the pH of the medium is raised from 1 to 10 or greater. In this range, the potential of a glass electrode, E_g, may be written

$$E_g = E_g^o + \frac{RT}{F} \ln a_{H^+} \tag{7}$$

where E_{g}^{o} is the standard (formal) potential of that particular glass electrode on the hydrogen scale.

Departures from the ideal behavior expressed by equation 7 usually are found in alkaline solutions containing alkali metal ions in appreciable concentration, and often in solutions of strong acids. The supposition that the alkaline error is associated with the development of an imperfect response to alkali metal ions is substantiated by the successful design of cation-sensitive electrodes that are used to determine sodium, silver, and other monovalent cations (3).

The advantage of the lithium glasses over the sodium glasses in the reduction of alkaline error is attributed to the smaller size of the proton sites remaining after elution of the lithium ions from the glass surface. This view is consistent with the relative magnitudes of the alkaline errors for various cations. These errors decrease rapidly as the diameter of the cation becomes larger. The error observed in concentrated solutions of the strong acids is characterized by a marked drift of potential with time, which is thought to result from the penetration of acid anions, as well as protons, into the glass surface (14).

The immersion of glass electrodes in strongly dehydrating media should be avoided. If the electrode is used in solvents of low water activity, frequent conditioning in water is advisable, as dehydration of the gel layer of the surface causes a progressive alteration in the electrode potential with a consequent drift of the measured pH. Slow dissolution of the pH-sensitive membrane is unavoidable, and it eventually leads to mechanical failure. Standardization of the electrode with two buffer solutions is the best means of early detection of incipient electrode failure.

Fouling of the pH sensor may occur in solutions containing surface-active constituents that coat the electrode surface and may result in sluggish response and drift of the pH reading. Prolonged measurements in blood, sludges, and various industrial process materials and wastes can cause such drift. Therefore, it is necessary to clean the membrane mechanically or chemically at intervals that are consistent with the magnitude of the effect and the precision of the results required.

3.2. Reference Electrodes and Liquid Junctions. The electrical circuit of the pH cell is completed through a salt bridge that usually consists of a concentrated solution of potassium chloride [7447-40-7]. The solution makes contact at one end with the test solution and at the other with a reference electrode of constant potential. The liquid junction is formed at the area of contact between the salt bridge and the test solution. The mercury–mercurous chloride electrode, the calomel electrode, provides a highly reproducible potential in the potassium chloride bridge solution and is the most widely used reference electrode. However, mercurous chloride is converted readily into mercuric ion and mercury when in contact with concentrated potassium chloride solutions above 80°C. This disproportionation reaction causes an unstable potential with calomel electrodes. Therefore, the silver–silver chloride electrode and the thallium amalgam–thallous chloride electrode often are preferred for measurements above 80°C. However, because silver chloride is relatively soluble in concentrated solutions of potassium chloride, the solution in the electrode chamber must be saturated with silver chloride.

The commercially used reference electrode–salt bridge combination usually is of the immersion type. The salt-bridge chamber usually surrounds the electrode element. Some provision is made to allow a slow leakage of the bridge solution out of the tip of the electrode to establish the liquid junction with the standard solution or test solution in the pH cell. An opening is usually provided through which the electrode chamber may be refilled with the salt-bridge solution. Various devices are used to impede the outflow of bridge solution, eg, fibers, porous ceramics, capillaries, ground-glass joints, and controlled cracks. Such commercial electrodes normally give very satisfactory results, but there is some evidence that the type and structure of the junction may affect the reference potential when measurements are made at very low pH and, possibly, at high alkalinities.

Combination electrodes have increased in use and are a consolidation of the glass and reference electrodes in a single probe, usually in a concentric arrangement, with the reference electrode compartment surrounding the pH sensor. The advantages of combination electrodes include the convenience of using a single probe and the ability to measure small volumes of sample solution or in restricted-access containers, eg, test tubes and narrow-neck flasks. In addition, the surrounding electrolyte solution in the reference electrode compartment provides excellent electrical shielding of the pH sensor, which reduces noise and susceptibility to polarization.

Theoretical considerations favor liquid junctions by which cylindrical symmetry and a steady state of ionic diffusion are achieved. Special cells in which a stable junction can be achieved are not difficult to construct and are available commercially. A solution of potassium chloride that is saturated at room temperature usually is used for the salt bridge. It has been shown that the higher the concentration of the solution of potassium chloride, the more effective the bridge solution is in reducing the liquid-junction potential (15). Also, the saturated calomel reference electrode is stable, reproducible, and easy to prepare. However, the saturated electrode is not without its disadvantages. For example, it shows a marked hysteresis with changes of temperature. After long periods and on temperature lowering, the salt-bridge chamber may become filled with large crystals of potassium chloride that block the flow of bridge solution and thereby impair the reproducibility of the junction potential and raise the resistance of the cell. A slightly undersaturated (eg, 3.5 *M*) solution of potassium chloride is preferred.

Samples that contain suspended matter are among the most difficult types from which to obtain accurate pH readings because of the so-called suspension effect, ie, the suspended particles produce abnormal liquid-junction potentials at the reference electrode (16). This effect is especially noticeable with soil slurries, pastes, and other types of colloidal suspensions. In the case of a slurry that separates into two layers, pH differences of several units may result, depending on the placement of the electrodes in the layers. Internal consistency is achieved by pH measurement using carefully prescribed measurement protocols, as has been used in the determination of soil pH (17).

Another effect that may result in spurious pH readings is caused by streaming potentials. Presumably, these are attributable to changes in the reference electrode liquid junction that are caused by variations in the flow rate of the sample solution. Factors that affect the observed pH include the magnitude of the flow-rate changes, the geometry of the electrode system, and the concentration of the salt-bridge electrolyte; therefore, this problem may be avoided by maintaining constant flow and geometry characteristics and calibrating the system under operating conditions that are identical to those of the sample measurement.

3.3. pH Instrumentation. The pH meter is an electronic voltmeter that provides a direct conversion of voltage differences to differences of pH at the measurement temperature. One class of instruments is the direct-reading analogue, a deflection meter having a large scale calibrated in mV and pH units. Most modern direct-reading meters have digital displays of the emf or pH. The types range from very inexpensive meters that read to the nearest 0.1 pH unit to research models capable of measuring pH with a precision of 0.001 pH unit and drifting less than 0.003 pH unit over 24 h; however, the fundamental meaning of these measured values is considerably less certain than the precision of the measurement.

Because of the very large resistance of the glass membrane in a conventional pH electrode, an input amplifier of high impedance (usually 10^{12}–10^{14} ω) is required to avoid errors in the pH (or mV) readings. Most pH meters have field-effect transistor amplifiers that typically exhibit bias currents of only a pico-ampere (10^{-12} ampere), which, for an electrode resistance of 100 Mω, results in an emf error of only 0.1 mV (0.002 pH unit).

In addition, most devices provide operator control of settings for temperature and/or response slope, isopotential point, zero or standardization, and function (pH, mV, or monovalent–bivalent cation–anion). Microprocessors are incorporated in advanced-design meters to facilitate calibration, calculation of measurement parameters, and automatic temperature compensation. Furthermore, pH meters are provided with output connectors for continuous readout via a strip-chart recorder and often with binary-coded decimal output for computer interconnections or connection to a printer. Although the accuracy of the measurement is not increased by the use of a recorder, the readability of the displayed pH (on analogue models) can be expanded, and recording provides a permanent record and also information on response and equilibrium times during measurement (5).

3.4. Temperature Effects. The emf, E, of a pH cell may be written

$$E = E_g^{o'} - k\text{pH} \tag{8}$$

where k is the Nernst factor (2.303 RT)/F, and $E_{\text{g}}^{o'}$ includes the liquid-junction potential and the half-cell emf on the reference side of the glass membrane. Changes of temperature alter the scale slope because k is proportional to T. The scale position also is changed because the standard potential is temperature dependent: $E_{\text{g}}^{o'}$ is usually a quadratic function of the temperature.

The objective of temperature compensation in a pH meter is to nullify changes in emf from any source except changes in the true pH of the test solution. Nearly all pH meters provide automatic or manual adjustment for the change of k with T. If correction is not made for the change of standard potential, however, the instrument must always be standardized at the temperature at which the pH is to be determined. In industrial pH control, standardization of the assembly at the temperature of the measurements is not always possible, and compensation for shift of the scale position, though imperfect, is useful. If the value of $E_{\text{g}}^{o'}$ were a linear function of T, it would be easy to show that the straight lines representing the variation of E and pH at different temperatures would intersect at a point, the isopotential point or pH$_i$. Even though $E_{\text{g}}^{o'}$ does not usually vary linearly with T, these plots intersect at about pH$_i$ when the range of temperatures is narrow. By providing a temperature-dependent bias potential of kpH$_i$, an approximate correction for the change of the standard potential with temperature can be applied automatically (1,5).

4. Nonaqueous Solvents

The activity of the hydrogen ion is affected by the properties of the solvent in which it is measured. Scales of pH only apply to the medium, ie, the solvent or mixed solvents, eg, water–alcohol, for which the scales are developed. The comparison of the pH values of a buffer in aqueous solution to one in a nonaqueous solvent has neither direct quantitative nor thermodynamic significance. Consequently, operational pH scales must be developed for the individual solvent systems. In certain cases, correlation to the aqueous pH scale can be made, but in others, pH values are used only as relative indicators of the hydrogen-ion activity.

Other difficulties of measuring pH in nonaqueous solvents are the complications that result from dehydration of the glass pH membrane, increased sample resistance, and large liquid-junction potentials. These effects are complex and highly dependent on the type of solvent or mixture used (1,5).

5. Indicator pH Measurements

The indicator method is especially convenient when the pH of a well-buffered colorless solution must be measured at room temperature with an accuracy no greater than 0.5 pH unit. Under optimum conditions an accuracy of 0.2 pH unit is obtainable. A list of representative acid–base indicators is given in Table 2 with the corresponding transformation ranges. A more complete listing, including the theory of the indicator color change and of the salt effect, is also available (1).

Because they are weak acids or bases, the indicators may affect the pH of the sample, especially in the case of a poorly buffered solution. Variations in the ionic strength or solvent composition, or both, also can produce large uncertainties in pH measurements, presumably caused by changes in the equilibria of the indicator species. Specific chemical reactions also may occur between solutes in the sample and the indicator species to produce appreciable pH errors. Examples of such interferences include binding of the indicator forms by proteins and colloidal substances and direct reaction with sample components, eg, oxidizing agents and heavy-metal ions.

6. Industrial Process Control

Specialized equipment for industrial measurements and automatic control have been developed (18) (see PROCESS CONTROL). In general, the pH of an industrial process need not be controlled with great accuracy. Consequently, frequent standardization of the cell assembly may be unnecessary. On the other hand, the ambient conditions, eg, temperature and humidity, under which the industrial control measurements are made, may be such that the pH meter must be much more robust than those intended for laboratory use. To avoid costly downtime for repairs, pH instruments may be constructed of modular units, permitting rapid removal and replacement of a defective subssembly.

The pH meter usually is coupled to a data recording device and often to a pneumatic or electric controller. The controller governs the addition of reagent so that the pH of the process stream is maintained at the desired level.

Immersion-cell assemblies are designed for continuous pH measurement in tanks, troughs, or other vessels containing process solutions at different levels under various conditions of agitation and pressure. The electrodes are protected from mechanical damage and are sometimes provided with devices to remove surface deposits as they accumulate. Process flow chambers are designed to introduce the pH electrodes directly into piped sample streams or bypass sample loops that may be pressurized. Electrode chambers of both types usually contain a temperature-sensing element that controls the temperature-compensating circuits of the measuring instrument.

Glass electrodes for process control do not differ materially from those used for pH measurements in the laboratory, but the emphasis in industrial application is on rugged construction to withstand both mechanical stresses and high pressures. Pressurized salt bridges, which ensure slow leakage of bridge solution into the process stream even under very high pressures, have been developed. For less severe process monitoring conditions, reference electrodes are available with no-flow polymeric or gel-filled junctions that can be used without external pressurization.

BIBLIOGRAPHY

“Hydrogen-Ion Concentration” in *ECT* 1st ed., Vol. 7, pp. 711–726, by R. G. Bates and E. R. Smith, National Bureau of Standards; in *ECT* 2nd ed., Vol. 11, pp. 380–390, by R. G. Bates, National Bureau of Standards; “Hydrogen-Ion Activity” in *ECT* 3rd ed., Vol. 13, pp. 1–11, by R. A. Durst, National Bureau of Standards, and R. G. Bates, University of Florida.

CITED PUBLICATIONS

1. R. G. Bates, *Determination of pH, Theory and Practice*, 2nd ed., Wiley-Interscience, New York, 1973.
2. Y. C. Wu, W. F. Koch, and R. A. Durst, *Standardization of pH Measurements*, National Bureau of Standards Special Publication 260-53, U.S. Government Printing Office, Washington, D.C., 1988; National Institute of Standards and Technology, Gaithersburg, Md., private communication, 1993.
3. G. Eisenman, ed., *Glass Electrodes for Hydrogen and Other Cations*, Marcel Dekker, New York, 1967.
4. G. Mattock, *pH Measurement and Titration*, Macmillan, New York, 1961.
5. C. C. Westcott, *pH Measurements*, Academic Press, Inc., New York, 1978.
6. *pH of Aqueous Solutions with the Glass Electrode*, ASTM method E70-77, American Society for Testing and Materials, Philadelphia, Pa., 1977.
7. H. Galster, *pH Measurement: Fundamentals, Methods, Applications, Instrumentation*, VCH, New York, 1991.
8. S. Glab and co-workers, *Crit. Rev. Anal. Chem.* **21**, 29 (1989).
9. D. Ammann and co-workers, *Ion-Selective Electrode Rev.* **5**, 3 (1983).
10. J. Janata, *Chem. Rev.* **90**, 691 (1990); J. Janata and R. J. Huber, eds., *Solid State Chemical Sensors*, Academic Press, Inc., New York, 1985; G. F. Blackburn, in A. P. F. Turner, I. Karube, and G. S. Wilson, eds., *Biosensors*, Oxford University Press, Oxford, 1987.
11. A. K. Covington, R. G. Bates, and R. A. Durst, *Pure Applied Chem.* **57**, 531 (1985).
12. R. A. Durst, in H. Freiser, ed., *Ion-Selective Electrodes in Analytical Chemistry*, Plenum Publishing, New York, 1978, “Chapt. 5”.
13. R. A. Durst, W. Davison, and W. F. Koch, *Pure Appl. Chem.* **66**, 649 (1994).
14. K. Schwabe, in H. W. Nürnberg, ed., *Electroanalytical Chemistry*, John Wiley & Sons, Inc., New York, 1974, “Chapt. 7”.
15. E. A. Guggenheim, *J. Am. Chem. Soc.* **52**, 1315 (1930).
16. H. Jenny and co-workers, *Science* **112**, 164 (1950).
17. A. M. Pommer, in Ref. 3, Chapt. 14.
18. F. G. Shinskey, *pH and pIon: Control in Process and Waste Streams*, John Wiley & Sons, Inc., New York, 1973.

GENERAL REFERENCES

Refs. (1–7) are also general references.

Richard A. Durst
Cornell University

Roger G. Bates
University of Florida

Table 1. **Solution pH Standards, Molality Scale**[a]

Composition[b]	Solution pH at 25°C
Primary standards	
potassium hydrogen tartrate (saturated at 25°C)	3.557
0.05 m potassium dihydrogen citrate	3.776
0.05 m potassium hydrogen phthalate	4.006
0.025 m KH_2PO_4 + 0.025 m Na_2HPO_4	6.863
0.008695 m KH_2PO_4 + 0.03043 m Na_2HPO_4	7.410
0.01 m $Na_2B_4O_7 \cdot 10H_2O$	9.180
0.025 m $NaHCO_3$ + 0.025 m Na_2CO_3	10.011
Secondary standards	
0.05 m potassium tetraoxalate dihydrate	1.681
0.05 m HEPES + 0.05 m NaHEPESate	7.503
0.08 m HEPES + 0.08 m NaHEPESate	7.516
0.05 m MOPSO + 0.05 m NaMOPSOate	6.867
0.08 m MOPSO + 0.08 m NaMOPSOate	6.865
0.01667 m TRIS + 0.05 m TRIS·HCl	7.699
$Ca(OH)_2$ (saturated at 25°C)	12.454

[a] Ref. 2.

[b] HEPES = $N - 2 -$ hydroxyethylpiperazine $- N' - 2 -$ ethanesulfonic acid [7365-45-9]; MOPSO = $3 - (N -$ morpholino$) - 2 -$ hydroxypropane sulfonic acid [68399-77-9]; and TRIS = trisparl0; hydroxymethylparr0; aminomethane [77-86-1].

Table 2. **Acid–Base Indicators**

		Color	
Indicator	pH Range	Acid	Base
acid cresol red [1733-12-6]	0.2–1.8	red	yellow
methyl violet [8004-87-3]	0.5–1.5	yellow	blue
acid thymol blue [76-61-9]	1.2–2.8	red	yellow
bromophenol blue [115-39-9]	3.0–4.6	yellow	blue
methyl orange [547-58-0]	3.2–4.4	red	yellow
bromocresol green [76-60-8]	3.8–5.4	yellow	blue
methyl red [493-52-7]	4.4–6.2	red	yellow
bromocresol purple [115-40-2]	5.2–6.8	yellow	purple
bromothymol blue [76-59-5]	6.0–7.6	yellow	blue
phenol red [143-74-8]	6.6–8.2	yellow	red
cresol red [1733-12-6]	7.2–8.8	yellow	red
thymol blue [76-61-9]	8.0–9.6	yellow	blue
phenolphthalein [77-09-8]	8.2–9.8	colorless	red
tolyl red [6410-10-2]	10.0–11.6	red	yellow
parazo orange [547-57-9]	11.0–12.6	yellow	orange
trinitrobenzoic acid [129-66-8]	12.0–13.4	colorless	orange