

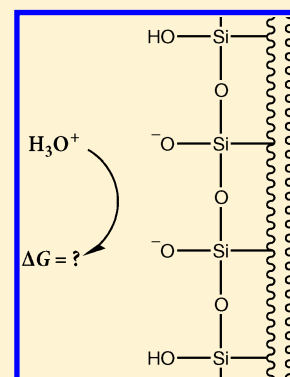
Development of the Glass Electrode and the pH Response

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ABSTRACT: The glass electrode is the most commonly used device to access the pH of an aqueous solution. It attains highly accurate measurements via simple and well-established procedures. However, the reasons why the glass electrode potential scales with hydrogen ion concentration according to almost Nernstian potential values have been long-standing challenges to explain. Only in the past 50 years has an understanding of the glass electrode response to pH been achieved, as elucidated by Nikolsky and Baucke and other researchers. In essence, the potential of a glass electrode derives from a solid–liquid electrolyte ionic process that entails both hydrated glass surface groups and diverse ions in solution. Thus, a process that is deceptively complicated—and usually overlooked—underpins a boundary potential difference. This notwithstanding, other interpretations of the glass electrode response have been contributed. Most notably, Cheng has viewed the device as an electrical circuit condenser responding to adsorbed hydrogen or hydroxyl ions. In addition, Morrison has attributed the glass electrode response to a double layer surface–liquid interface potential. The purpose of this article is to portray an unusual mix of complexity and viewpoint disparity over the years. Knowledge and appreciation of this mix offer a more complete picture for students and educators of aqueous solution chemistry. This information is most appropriate to lecture and laboratory courses on quantitative analysis.

KEYWORDS: Upper-Division Undergraduate, Analytical Chemistry, Textbooks/Reference Books, Acids/Bases, Aqueous Solution Chemistry, Electrochemistry, Ion Exchange, Ion Selective Electrodes, Oxidation/Reduction, Quantitative Analysis



The scene is a familiar one in high school and college labs. Students conduct acid–base titrations while writing down pH values: 4.52, 4.58, 4.61, and so forth. The latter appear as digital readout of plug-in or hand-held devices. Teachers clarify matters:

- what the devices really measure are electrical *potentials*, not concentrations per se,
- what the potentials respond to are solution activities which depend on H^+ and other ions plus temperature, and
- there is a natural uncertainty associated with these and more experimental variables. In short, the backdrop for pH is substantially more complicated than implied by three-digit readouts.

This *Journal* has done much justice to the subject. A statement by Gorman in 1940 augers perhaps the educational contributions and motivations of succeeding years: “The fact that pH is merely an index number which more or less approximates $-\log(C_{H^+}f_{\pm})$ must not be construed to mean that the concept is useless or that the vast accumulation of data gathered with the aid of the concept is worthless”.¹ Here Gorman is referring to the hydrogen ion molar concentration C_{H^+} weighted by an activity coefficient f_{\pm} . And to cite just a few of those contributions, the pH concept has been fleshed out in physical and historical terms by Kolb and other authors.^{2–5} The weighty subjects of scientific truth, paradoxes, and philosophy have centered the acid–base discussions of Hawkes, McCarty, and Vitz, and, most recently, de Levie.^{6–8} A century of pH was both lauded and summarized two years ago by Meyers.⁹ In the same volume, two of the present authors and a colleague

addressed the issue of hydrogen ion solvation.¹⁰ The same matter was taken up shortly thereafter by Silverstein.¹¹

So what do educators and students need to gather about pH at this point? In these authors’ opinion, it is the mechanistic uncertainty and viewpoint disparity of the workhorse sensing devices, namely glass electrodes. What instructors have conveyed to their clientele about the electrode workings has been remarkably fluid across the first century. This has been touched upon by Cheng in this *Journal* and at least two well-established undergraduate texts.^{12–14} Fluidity may well be the case for the second century judging from the literature and the electrode’s complexity. Thus, the purpose of this writing is to enhance knowledge and appreciation of the glass electrode’s mechanistic uncertainty. The plug-ins and hand-helds of everyday labs prove more complicated than meets the eye or instructor’s chalk talk.

■ GLASS ELECTRODES AND FOUNDATION STUDIES

The glass electrode is most commonly used to attain highly accurate pH measurements. From its first application, however, the potential response to H^+ has been a conundrum to explain. For good reason: it is difficult to fathom why such a potential response follows almost identically that of the hydrogen electrode. Is the response mimicry coincidental? Do the two electrode types share a nuanced and fundamental chemistry? These questions are easy to ignore, but have loomed nonetheless.

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Not surprisingly, the properties of glass interfaced with aqueous solutions have fascinated chemists since the era of Leyden jars and membrane prototypes. This has been discussed in detail by Moore et al.¹⁵ Also to be noted, Cremer charted the electrical response of glass membranes to variable hydrogen ion concentrations as early as 1906.¹⁶ His recordings transpired almost twenty years after Nernst applied the hydrogen electrode to $[H^+]$ determinations.¹⁷ In 1909, Haber and Klemensiewicz undertook systematic studies of glass membranes.¹⁸ They observed the electrochemical signals and their dependence on $[H^+]$. The same researchers established that the signals could be pinned down using electrometers of high input resistance. However, the wider employment of glass electrodes proved contingent not only on the engineering of sufficiently robust membranes, but also on the technology surrounding electronic measurements. Devices had to be capable of tracking the small currents attenuated by the high resistivity of glass membranes. In 1930, MacInnes and Dole reported that the composition of the most suitable glass electrode, Corning 015, had the percent composition $22Na_2O \cdot 6CaO \cdot 72SiO_2$.¹⁹ Dole was later to reflect in this *Journal* about the significance and pathway of this accomplishment.²⁰ Suffice to say that the precision and range of mixing alternatives attest to the research and development directed at glass electrodes during those years.

During the early to mid-20th century, researchers throughout the world continued to develop glass electrodes that were sensitive not only to H^+ , but also to other cations. Over time, glass afforded the premier composition that was highly selective for H^+ and conferred the greatest concentration response. There was a down side, however, in that the electrodes were difficult to use: the high electrical resistance of glass rendered them dismally poor circuit elements. Consequently, prior to the development of vacuum tube voltmeters, measurements were carried out using galvanometric and potentiometric techniques.^{15,21}

Two milestones of vacuum tube circuitry set the stage for commercial pH meters. In 1922, K. H. Goode in his master's degree research employed the newly developed triode, descendent from the audion. He constructed a continuous-reading titration apparatus for the determination of hydrogen ion concentration by using the hydrogen ion electrode.^{22,23} Almost concurrently, Elder and Wright completed a undergraduate thesis at the University of Illinois. For their project, they developed a pH meter that featured a glass electrode as the sensing device. Their instrument took novel advantage of vacuum tubes of that era. In so doing, it resolved the resistance problems presented by and indeed plaguing glass electrodes.^{24,25}

In 1935, A. O. Beckman used the fruits of Goode's and Elder and Wright's research by employing the triode. The outcome was the first and famous commercial production of pH meters. Vincent Dole, professor emeritus, in a symposium hosted by the Rockefeller Institute in 1985 commented: "With the instrumentation of the Beckman pH meter in 1940, every laboratory could estimate pH of solution almost as easily as measuring its temperature."²⁶ Who could argue otherwise yesterday and today?

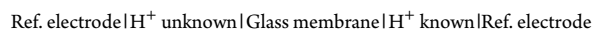
pH is accessed in modern day labs by substituting the glass electrode in place of the hydrogen electrode. This follows the strategy and design of the original Sorensen cell. pH is determined by comparing a reference standard buffer solution with the sample of interest as recommended by the U.S.

National Bureau of Standards.^{27–32} The measured pH of the sample is expressed by

$$pH = pH_s + (E - E_s) \left(\frac{F}{2.30RT} \right) \quad (1)$$

where F , R , and T have their usual electrochemical meanings: the Faraday constant, the gas constant, and absolute temperature, respectively. E and E_s refer to the cell potentials (voltages) of the "unknown" and standard reference solution, respectively; pH_s applies to the latter system. Equation 1 provides what can be viewed as the *operational* definition of pH. Just as important, eq 1 defines pH operationally as recommended by the Union of Pure and Applied Chemistry.^{27–32} And in words that need to be emphasized to students, the long-familiar term pH is more than merely a synonym for $-\log[H^+]$; ditto for $-\log(C_{H^+}f_{\pm})$ (Gormon's terminology¹). In practice, E_s is determined by careful measurements of the hydrogen cell potential in the *absence* of a liquid junction. In turn, values can be arrived at via glass electrodes with an accuracy of better than 0.01 pH units. Students, educators, and researchers are the clear beneficiaries.

Now, for the past 100 years, researchers have probed more deeply the glass membrane potential change with the change of the hydrogen ion as represented by the cell:



Note the critical property: the glass electrode does *not* exhibit the transfer of electrons in the potential-determining reaction as in the case of the hydrogen electrode; this underpins the conundrums: precisely how does the thing work? And comparing glass and hydrogen electrodes is arguably like comparing apples and oranges.

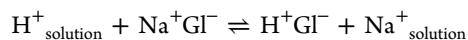
At the same time, glass electrodes have over the years presented the so-called alkaline error under conditions of high solution pH. Shortly after Haber and Klemensiewicz's 1909 publication, Donnan observed that alkali halides could be separated from proteins by the use of a membrane.^{18,33} The diffusion across the membrane effected an electrochemical potential known in modern day as the Donnan boundary potential. Not surprisingly then, the potential response of a glass membrane to the change of hydrogen ion concentration was modeled initially using the Donnan boundary potential—it was by far the most attractive idea at the time. In this viewpoint, it was assumed that *both* hydrogen and sodium ions pass *through* the glass membrane. Therefore, the observed potential was attributed to the *difference* between the diffusion rates of disparate ions through the membrane. Although this theory successfully predicted the pH response of the glass electrode in acidic and basic solutions, the penetration of H^+ through the membrane was subsequently disproved. Also, it was soon questionable whether the glass electrode response to the change of hydrogen ion in solution followed the logarithm relationship prescribed by the Nernst equation. In short, the glass electrode was widely vaunted for its capabilities. However, the explanations for its physical workings were tenuous at best and erroneous at worst.

Other attempts were made to explain the glass electrode potential, in particular its dependence on changes in the hydrogen ion concentration. Several viewpoints earned wide acceptance over the years such as the ion exchange and adsorption-potential theories. In 1937, Nikolsky proposed the ion exchange equilibrium theory.³⁴ Here the hydrous glass layer of the membrane is regarded as facilitating the exchange of

sodium ions with hydrogen ions in solution. The exchange controls the boundary potential with respect to the hydrogen ion:



Thus, the ion exchange on *both* sides (i.e., 1 and 2) of the membrane adheres to the equilibrium condition:



This condition dictates the potential difference E_m between opposite sides of the membrane where the sodium ion concentrations are far less those of hydrogen ions. Along this line of thought, E_m adopts the mathematical form:

$$E_m = c + \frac{RT}{F} \ln \left(\frac{a_{1\text{H}^+} \cdot a'_{2\text{H}^+}}{a'_{1\text{H}^+} \cdot a_{2\text{H}^+}} \right) \quad (2)$$

In eq 2, $a_{1\text{H}^+}$ and $a_{2\text{H}^+}$ refer to the hydrogen ion activities in solution. Their primed counterparts, $a'_{1\text{H}^+}$ and $a'_{2\text{H}^+}$, represent the activities of hydrogen ions in the double layer. Also in eq 2 (and throughout the article), c is a constant governed by the potentials of the reference electrodes; it is affected by the electrolyte junction and asymmetry effects. As is usual, eq 2 can be simplified by assuming the hydrogen ion concentration to be constant on one side of the glass membrane and by taking the hydrogen ion activities *in* the membrane and on both sides to be the same as in the double layer. Then the boundary potential, E_b , is directly related to the hydrogen ion activity of the unknown solution, viz.

$$\begin{aligned} E_b &= c' + \frac{RT}{F} \cdot \ln(a_{\text{H}^+}) \\ &= c' + \frac{2.30RT}{F} \cdot \log_{10}(a_{\text{H}^+}) \end{aligned} \quad (3)$$

Equation 3 proves generally valid for systems with $\text{pH} \leq 9$ where c' is yet another constant. For conditions where $\text{pH} \geq 9$, the diffusion of sodium ions becomes important, especially with increasing Na^+ concentration. This situation is reflected significantly in the boundary potential. Nikolsky assumed that equilibrium is maintained between the surface layers of the glass and the surrounding solution and that the electrochemical potential μ adopts the following elementary form, regardless of the phase:

$$\mu = \mu_i + zF\Psi \quad (4)$$

In eq 4, μ_i is the electrochemical potential of the ion having net electric charge z ; Ψ represents the electrostatic potential of the *heterogeneous* phase. In effect, the equilibrium state is obtained when the hydrogen ion and sodium ion (the typical metal ion in experiments) potentials become equal. Also to be noted, the Galvani potential on the one side of the membrane is quantified by:

$$E_{\text{Galvani}} = \Psi_{\text{glass}} - \Psi_{\text{solution}} \quad (5)$$

Nikolsky considered the number of exchange sites available to H^+ and Na^+ in the glass surface layer. He derived an equation for the Galvani potential, E_G , that took into account the ion exchange effects:

$$E_G = c + \frac{RT}{F} \cdot \ln(a_{\text{H}^+} + K' \cdot a_{\text{Na}^+}) \quad (6)$$

Then by eq 6, Nikolsky identified K' as the equilibrium constant for the H^+ and Na^+ exchange process.³⁴ Importantly, the calculated potentials proved in agreement with the experimental values when the hydrogen ion concentrations far exceeded those of sodium ions, and vice versa. Vexingly, however, the calculated potentials did *not* agree with data acquired under conditions where the hydrogen and sodium ion concentrations were comparable. Nonetheless, this representation of the glass electrode and its workings was widely accepted and disseminated in classrooms and laboratories for over seventy years. It was the educational canon of pH measurement.

Much to his credit, Nikolsky revised the “simple” ion exchange theory in 1957 by incorporating assumptions related to the homogeneity of ionic bonds and the constancy of ionic sites.³⁵ In particular, he modeled the electrode systems as featuring a kind of generic binding site R^- along with weakly dissociating iogenic groups such as $[\text{SiO}_{3/2}]\text{OH}$ and $[\text{SiO}_{3/2}]\text{M}$. Here M refers to the metal in the analytical application at hand. This approach led to a not-so-simple equation for the electrode potential:

$$\begin{aligned} E &= c + \frac{RT}{2F} \cdot \ln(a_{\text{H}^+} + K_{\text{H}^+\text{Na}^+}^{\text{exchange}} \cdot a_{\text{Na}^+}) + \frac{RT}{2F} \\ &\quad \cdot \ln \left(a_{\text{H}^+} + \left\{ \frac{K_{\text{H}^+}}{K_{\text{Na}^+}} \right\} \cdot K_{\text{H}^+\text{Na}^+}^{\text{exchange}} \cdot a_{\text{Na}^+} \right) \end{aligned} \quad (7)$$

In eq 7, k_{H^+} and k_{Na^+} represent the dissociation constants of $-\text{SiOH}$ and $-\text{SiO-Metal}$ ion groups; c is a constant as per usual. Equation 7 proved accurate under conditions where the hydrogen and sodium ion concentrations were comparable—a long-standing problem was finally addressed! And following Nikolsky, researchers Eisenman, Rudin, and Cosby traveled further with ion exchange chemistry and eq 7.³⁶ The following result based on their efforts offers still better agreement with experimental data:

$$E_G = c + \frac{nRT}{F} \cdot \ln[a_{\text{H}^+}^{1/n} + (K' \cdot a_{\text{M}^+})^{1/n}] \quad (8)$$

In eq 8, K' and n serve as empirical parameters characteristic of ion pairs in solution as well as the glass composition.

At this point, it should be noted that the alkaline error is significant given the sodium ions and sodium oxide in the glass composition. Further, it has been shown that the response to hydrogen ions can be enhanced for high pH environments by replacing sodium oxide (Na_2O) with lithium oxide (Li_2O). As is always the case, the selectivity of a glass electrode for various cations hinges on the composition of glass. It is important to include, however, that the ion exchange that underpins the phase boundary potential (i.e., in which H^+ ions exchange with Na^+ ions) has been seriously questioned. This is because the place switching of Na^+ with H^+ in solution fails to effect a change of the *net* charge in the double layer. The authors reiterate here the complexity and mechanistic uncertainty surrounding glass electrodes. These traits maintain in spite of the dependable employment by chemists.

We point out still other interpretations of the glass boundary potential. In 1941, Haugaard questioned the interpretation of the glass boundary potential.³⁷ He stated: “thermodynamics alone cannot tell us the mechanism of the process.” Bockris in 1970 opined: “that most electrochemists were still trying to do the impossible, i.e., to treat the highly thermodynamically

irreversible electrode reactions.”³⁸ And perhaps amusingly, he referred to this period as the “Great Nernst Hiatus”.

Durst in 1967 presented in this *Journal* that the response of the glass membrane is due to “an ion exchange process in the gel layer of the glass membrane producing a phase boundary potential that determines the pH response of the electrode and not a diffusion of hydrogen ions through the entire glass membrane.”³⁹ Thus, the potential in response to the pH of the test solution changes simply by 0.0591 V per pH unit at temperature 25 °C. And further translation: pH measurements using a glass electrode are underpinned by *adsorption*, not redox events in solution.

The adsorption–potential theory held that an adsorbed layer of hydrogen ions on the glass surface causes a potential drop at the glass–solution interface. The effect stems from the chemical potential difference between free and adsorbed ions.⁴⁰ However, this theory was unable to account for the glass electrode behavior in strongly acidic or basic solutions. Moreover, it predicted potential changes of *less than* 0.0591 V per pH unit.

The extensive investigations of the glass electrode over a sixty-year period have been discussed by numerous authors. Investigations of the glass electrode have been elaborated upon in quite a few books as well. Among the most classic, Bates has provided an exhaustive summary of hydrogen ion research, covering the period from its beginning in 1909 to 1967.⁴¹ Bates’ work has served as a seminal guide for generations of students, educators, and research chemists in the interpretation of the glass electrode response to hydrogen ions.

■ GLASS ELECTRODES AND PRESENT DAY

Even though the response of the glass electrode has been intensely studied—and has provided reliable pH measurements—a clear explanation of the mechanism appeared lacking even as late as the 1970s. Fortunately, improved analytical techniques of the past few decades have furnished a far better understanding of the glass electrode activity.

Belyustin, in a recent comprehensive review (which includes 147 references) on the centenary of the glass electrode, presents an up-to-date summary not only of the historical development but, also, on the theoretical studies.⁴² He also presents some of the extensive research conducted by electrochemistry groups at St. Petersburg State University, among other institutions.

Belyustin summarizes work dealing with charge transport mechanisms and the potential dynamics in the transition region from one cation function to another. He presents as well an approach of his own and other researchers pertaining to the glass chemical resistance and interaction of the silicon-oxide network. Briefly, the interactions that enter into pH measurements are focused at the glass–solution interface with water controlling the surface layer hydrolysis. Condensation promotes the interdiffusion and aggregation of water molecules in the leached area. Belyustin duly noted the contributions by Buck, Brant, and Regnitz who investigated the response of intact (ideal) glass membranes and hydrated films. The latter studies focused on both kinetics and electronics. In so doing, the chemists established response time constants τ_i in the range of few to 100 ms and capacitance values C_i on the order of 50 pF/cm²—in other words, the glass electrode is by no means a time-independent device. The same review attended to the electrokinetic experiments of Wikby who, by means of dc pulse techniques, determined time constants τ_i for the hydrogen ion

interaction with the glass membrane, the change of resistance R_p , and activation energies for the so-called “fast” process, namely

$$-\Delta H = 15.4 \pm 0.6 \text{ kcal/mol}$$

By contrast, the “slow” process demonstrated activation energy of

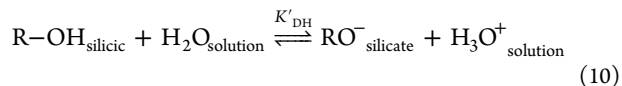
$$-\Delta H = 24.4 \pm 3.5 \text{ kcal/mol}$$

Translation: the chemistry of the glass electrode is by no means barrier-free and kinetically trivial. Belyustin, in addition, briefly reviewed Baucke’s fundamental investigations of glass electrode surfaces. The tools utilized included IBSCA (ion bombardment for spectrochemical analysis) and NRA (nuclear reaction analysis) techniques. Clearly the technology for probing glass electrodes has advanced substantially since the days of Nernst and Haber.

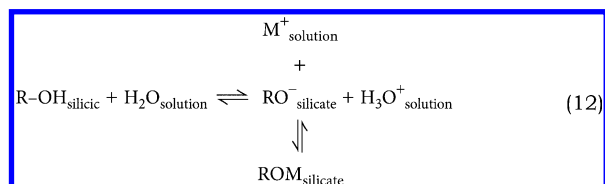
For over four decades, Baucke has conducted research pertaining to the glass electrode and its response to hydrogen ions.^{43,44} He has enhanced our understanding of what transpires at the hydrated glass electrode surface and the ionic environment in solution. Baucke’s view is that the glass electrode diverges from metal–metal ion redox electrodes (e.g., calomel), which operate specifically via electron transfer. By contrast, the glass electrode potential derives from a solid–liquid electrolyte interaction. It is a *dynamic ionic* process that is ultimately responsible for the potential difference. Thus, for an understanding the glass electrode workings, the student, educator, and research chemist must look substantially beyond equilibrium thermodynamics and time-independent principles. Baucke has concluded that there exists a *dynamic equilibrium* between the glass surface groups and the ions in aqueous solution. In turn, a dissociation mechanism sets up a potential *on* the glass membrane; the same mechanism governs the potential difference *between* the glass and solution. Negatively charged groups present a net-charge density at the glass surface. In turn, they generate a negative potential ϵ_m of the glass membrane relative to the solution. These ideas can be encapsulated in a two-variable mathematical function: the electrical potential dependent on both the hydrogen ion and metal ion concentrations, viz.

$$\epsilon_m = f(\text{pH}, \text{pM}) \quad (9)$$

Within the function, pH and pM have their usual respective meaning, namely, $-\log[\text{H}^+]$ and $-\log[\text{M}^+]$. Baucke, in attending to the relevant thermodynamic equations, considered separately the *dissociation* of silicic acid groups and *association* of silicate groups in the glass surface:



The subscripts attached to the equilibrium constants distinguish the dissociation and association mechanisms while M^+ represents a metal ion such as lithium, sodium, or potassium. By combining the above equations, Baucke convincingly demonstrated from the “crossed equilibrium” that the anionic form of the surface groups links the equilibrium equations as shown:



The equilibrium constants K'_{DH} and K'_{AM} for the dissociation and association mechanisms turn out to have extremely different magnitudes. Thus, in most cases, *only* the *single* equilibrium eq 10 or eq 11, of the “crossed equilibrium” process is valid. This also means that, in acidic solution, the thermodynamics of eq 10 is characterized by zero electrochemical Gibbs energy change:

$$\overline{\Delta G}_{\text{DH}} = \Delta G_{\text{DH}}^{\circ} + RT \ln \left(\frac{a'_{\text{R}^-} \cdot a_{\text{H}_3\text{O}^+}}{a'_{\text{RH}} \cdot a_{\text{H}_2\text{O}}} \right) - F\varepsilon_{\text{m}} = 0 \quad (13)$$

In eq 13, $\Delta G_{\text{DH}}^{\circ}$ represents the standard dissociation chemical energy change and ε_{m} is the potential difference between glass and solution, equivalent to $\Psi_{\text{glass}} - \Psi_{\text{solution}}$. The activities a'_{R} and a'_{RH} pertain to the glass surface groups. Rearrangement and substitution applied to eq 13 yields the pH dependent membrane potential

$$\begin{aligned}
 \varepsilon_{\text{m}} = & \frac{-2.303RT}{F} \log(K_{\text{DH}}) + \frac{-2.303RT}{F} \log \left(\frac{a'_{\text{R}^-}}{a'_{\text{RH}} \cdot a_{\text{H}_2\text{O}}} \right) \\
 & - \left(\frac{2.303RT}{F} \right) \cdot \text{pH}
 \end{aligned} \quad (14)$$

A similar expression for the membrane potential is obtained for the conditions where the metal ions far outnumber H^+ . In the transition region, the pH adheres to the following representation and can be derived using the association standard Gibbs energy change:

$$\Delta G_{\text{AM}}^{\circ} = G_{\text{SiOM}}^{\circ} - G_{\text{SiO}^-}^{\circ} - G_{\text{M}^+}^{\circ} = -RT \ln(K'_{\text{AM}}) = -F\varepsilon_{\text{M}}^{\circ} \quad (15)$$

In eq 15, $\Delta G_{\text{AM}}^{\circ}$ is directly related to the association constant K'_{AM} and $\varepsilon_{\text{M}}^{\circ}$ is the membrane potential between the glass electrode and the aqueous solution in the standard state. In turn, the potential of the electrochemical cell is:

$$\begin{aligned}
 E = & \sum \varepsilon_n + \varepsilon_{\text{M}}^{\circ'} - \left(\frac{2.303RT}{F} \right) \cdot \text{pM} \\
 = & E_{\text{M}}^{\circ} - \left(\frac{2.303RT}{F} \right) \cdot \text{pM}
 \end{aligned} \quad (16)$$

where $\varepsilon_{\text{M}}^{\circ'}$ is the *modified* standard state potential of the glass membrane. Calculations of pH in the transition region involve the respective dissociation and association constants K''_{DM} and K'_{AM} leading to the expression

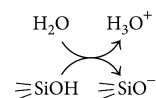
$$\varepsilon_{\text{m}} = \varepsilon_{\text{M}}^{\circ'} + \frac{2.303RT}{F} \cdot \log(a_{\text{H}_3\text{O}^+} + K''_{\text{DM}} \cdot K'_{\text{AM}} \cdot a_{\text{M}^+}) \quad (17)$$

The potential of the electrochemical cell in the transition region is

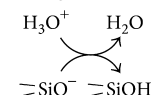
$$E = E_{\text{H}}^{\circ} + \frac{2.303RT}{F} \cdot \log(a_{\text{H}_3\text{O}^+} + K''_{\text{DM}} \cdot K'_{\text{AM}} \cdot a_{\text{M}^+}) \quad (18)$$

The derivation of the above equations is elaborated upon by Baucke in his fundamental papers.^{43,44} Furthermore, Baucke established the kinetic basis of the membrane potential. He

assumed that the electrochemical phase boundary equilibrium is dynamic, proceeding with equal rates, corresponding to equal anodic and cathodic current densities. The latter two quantities are typically represented by symbols I_+ and I_- , respectively. The stability of the phase depends on the magnitude of the current density: the larger the exchange current, the less polarizable is the phase boundary potential. The anodic proton exchange reaction of a glass membrane is



The cathodic proton exchange reaction can be represented as



Concomitantly, the exchange current density I_{oH} is given by the Butler–Volmer equation:

$$\begin{aligned}
 I_{\text{oH}} = I_{\text{H}^+} &= Fk_{\text{H}^+} C'_{\text{SiOH}} \cdot C_{\text{H}_2\text{O}} \cdot \exp \left[\frac{\alpha F \varepsilon_{\text{m}}}{RT} \right] \\
 = I_{\text{H}^-} &= Fk_{\text{H}^-} C'_{\text{SiO}^-} \cdot C_{\text{H}_3\text{O}^+} \cdot \exp \left[\frac{-(1-\alpha) F \varepsilon_{\text{m}}}{RT} \right]
 \end{aligned} \quad (19)$$

The k_{H^+} and k_{H^-} are anodic and cathodic rate constants, respectively; ε_{m} is the equilibrium membrane potential while α is the transfer coefficient. In eq 19, C'_{SiOH} , $C_{\text{H}_2\text{O}}$, C'_{SiO^-} , $C_{\text{H}_3\text{O}^+}$ s all refer to concentration quantities. Rearrangement of eq 19 yields

$$\varepsilon_{\text{m}} = \frac{-RT}{F} \cdot \ln \left(\frac{k_{\text{H}^+}}{k_{\text{H}^-}} \right) + \frac{RT}{F} \cdot \ln \left(\frac{C'_{\text{SiO}^-} \cdot C_{\text{H}_3\text{O}^+}}{C'_{\text{SiOH}} \cdot C_{\text{H}_2\text{O}}} \right) \quad (20)$$

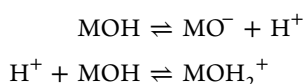
■ GLASS ELECTRODES AND ALTERNATE VIEWPOINTS

In 1980 Cheng proposed an intriguing hypothesis that considered the glass electrode as a *capacitor* rather than a battery element.^{12,45} The glass electrode was represented as having a “zwitterionic” surface where both cations and anions can be adsorbed. Thus, the glass membrane may be regarded as a double-layer capacitor that sustains a potential difference $\Delta E = E_{\text{outer}} - E_{\text{inner}}$ between the outer and inner membrane surfaces. The potential on each side of membrane, $E = q/C = (q \cdot d)/(\kappa \cdot A \cdot \varepsilon)$, is inversely proportional to the permittivity ε , area A of the electrode, and dielectric constant κ ; the potential scales with the product of the electric charge q and the membrane thickness d . More simply stated, the potential is inversely proportional to the capacitance C and proportional to the charge q . In short, Cheng posited that the measured potential scales simply with the number of adsorbed ions; there are *no* redox events with which to contend. The potential increases with the adsorption of metal cations and hydrogen ions whereas it decreases with the adsorption of anions such as hydroxide. Below the isoelectronic point of the glass membrane, or so-called point of zero charge (pzc) at approximately pH = 6, the membrane adsorbs hydrogen ions; above pzc the membrane adsorbs hydroxyl ions. Note the provocative idea in play: Cheng considered the glass electrode not only as a hydrogen ion electrode, but also as a hydroxyl ion electrode. For students and educators, the term “protode”

would be inappropriate for the glass electrode as in the yesteryear point of view.

Cheng appealed to the Gouy–Chapman double layer adsorption of the hydrogen ion model. Here, the charge region extends out from the electrode well into the solution. The adsorption of ions into the double layer was represented by Poisson–Boltzmann equations. However, Cheng’s adsorption-capacitor theory deviated somewhat from the observed values. Christian, in an analytical chemistry textbook, offers that Cheng’s “theory has not been generally accepted, but it presents some compelling arguments and experimental results to make this an interesting theory”.⁴⁶

Also in modern times, Morrison has weighed the response of the silica surface concerning proton ion adsorption and the potential developed in the Helmholtz double layer via pH changes.⁴⁷ Along this line of thinking, silica is viewed as an insulator with two distinct sites $(M^+)(OH^-)$ and MOH . The sites can accept or release a proton from solution:



The Gibbs energies for the reactions include the term $-qV_H$, where V_H represents the Helmholtz electrical potential and the quantity charge q times V_H is a measure of the Helmholtz energy. This is necessary because the proton performs work against the Helmholtz potential so as to become adsorbed on the glass surface. Accommodation via $+qV_H$ is also made of the energy released with the positive Helmholtz potential difference. This leads to the following two ratios:

$$\frac{[(MO^-)(H^+)]}{[MOH]} = \exp\left[\frac{-(\Delta G_a - qV_H)}{k_B T}\right] \quad (21)$$

$$\frac{[MOH_2^+]}{[(H^+)(MOH)]} = \exp\left[\frac{-(\Delta G_b + qV_H)}{k_B T}\right] \quad (22)$$

In eqs 21 and 22, the ΔG ’s quantify the Gibbs energy parts that do not depend on V_H ; k_B refers to the Boltzmann constant. In turn, the potential energy qV_H is related to pH of solution by the following equation

$$qV_H = 2.30k_B T \cdot \left[\left(\frac{\Delta G_a - \Delta G_b}{2} \right) - pH \right] + 2.30k_B T \cdot \log\left(\frac{[MOH_2^+]}{[MO^-]}\right)^{1/2} \quad (23)$$

At the point of zero charge (pzc, the state at which the glass electrode potential is zero), the following condition holds:

$$qV_H = 2.30k_B T \cdot [pzc - pH] + 2.30k_B T \cdot \log\left(\frac{[MOH_2^+]}{[MO^-]}\right)^{1/2} \quad (24)$$

Thus, the long-famous slope of 59 mV/pH unit is obtained so long as the second term on the right in eqs 23 and 24 is independent of pH. This condition will hold provided the solid is highly ionic, the sites on its surface are strongly charged, and that MOH_2^+ and MO^- both constitute a large fraction of a monolayer.

SUMMARY

The glass electrode is internationally accepted as the premier device for measuring $[H^+]$ in aqueous solutions. It is effective over a wide range of ion concentrations and operating conditions. Students, educators, and professionals rely on its facility, and not just in chemistry labs. As with all sensing electrodes, however, the fidelity is unable to maintain at all concentrations. Most notably, glass electrodes fail to furnish accurate readings at two ends of the spectrum: very concentrated and very dilute hydrogen ion solutions. This along with the other attributes presented in this article are probably uncommon knowledge or insufficiently appreciated in classrooms and teaching labs.

Across the century, there have been several models for the surface activities of silicate glasses that compose the electrodes. Each viewpoint has logged a convincing argument regarding electrochemical mechanisms and the electrode behavior in solution. Each model shares one thing in common, namely, that it supports an incontestable and time-honored stoichiometry. Along the way, appreciation of the glass electrode has been buttressed from multiple perspectives. Yet as captured deftly by the literature, pH measurements are so much more than the digital readout of plug-in and hand-held equipment. Educators field questions daily about laboratory instrumentation: how do NMR machines, mass spectrometers, and microbalances work? Regarding pH electrodes, the small, inexpensive devices also merit more than a short answer to questions about their workings.

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Notes

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