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On Calibration of pH Meters

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Abstract: The calibration of pH meters including the pH glass electrode, ISE electrodes, buffers, and the general background for calibration are reviewed. Understanding of basic concepts of pH, pOH, and electrode mechanism is emphasized. New concepts of pH, pOH, as well as critical examination of activity, and activity coefficients are given. The emergence of new solid state pH electrodes and replacement of the salt bridge with a conducting wire have opened up a new horizon for pH measurements. A pH buffer solution with a conducting wire may be used as a stable reference electrode. The misleading unlimited linear Nernstian slope should be discarded. Calibration curves with 3 nonlinear portions for the entire 0—14 pH range due to the isoelectric point change effect are explained. The potential measurement with stirring or unstirring and effects by double layer (DL) and triple layer (TL) will be discussed.

Keywords: electrochemistry, electrode, pH measurement

Introduction

Most instrumental methods of analysis are relative. Instruments register a signal due to some physical or chemical property of the solution. For example, pH meters measure the electrode potential which must be related to the $[H^+]$ or $[OH^-]$ of the solution by comparison against known $[H^+]$ or $[OH^-]$ standard buffers. In other words, the pH meter must be calibrated in order to obtain accurate results. A standard procedure for calibrating pH meters is to prepare a linear working curve known as a calibration curve by plotting the measured potential as a function of pH or pOH. Many calibration descriptions in the literature are rather confusion and misleading. This paper will discuss some basic concepts of pH, pOH, pH glass electrodes, reference electrodes, standard buffers, and pH meters.

Without correct definitions of certain terms relating to pH and an understanding of the mechanisms of the pH glass electrode, students are easily confused and do not know how to calibrate the pH meter correctly. The following is a discussion of some commonly encountered errors and misconceptions about pH meter calibration instructions found in many quantitative analytical textbooks [1-4] and some handbooks written by companies for users of their pH meters and electrodes [5-7].

The term "pH" was proposed as a simple form for expressing low $[H^+]$ in very dilute acid solutions. For the LaF_3 electrode, it should be called as the La/F ISE (ion selective electrode). Similarly, the pH glass electrode should be called as the H/OH ISE. It is incorrect to extend pH to alkaline solutions because there are practically no H^+ ions in alkaline solutions. The function of the pH electrode in an alkaline solution is to detect OH^- ions, not H^+ ions. One may argue that pH + pOH = pK_w = 14. However, this equation is incorrect because pK_w = 14 only for pure water at 25 ^oC, not for any other temperature, acid solutions or alkaline solutions. We have particularly called attention to the important role of OH^- in alkaline solutions [8]. We should use the term "pOH" for alkaline solutions and calibrate the "pOH" meter accordingly. One may argue again that the terms "pH" and "pH meter" have been used ubiquitously for almost one century, why do we need to change now? Our answer is that the change is for scientific exactness and proper interpretation of results. The analytical chemistry textbooks commonly offer the acid – base theories of Arrhrenius, Brønsted, and Lewis. Most of them prefer the Brønsted and Lewis concepts; some just ignore Arrhenius altogether. We prefer Arrhenius who emphasized the role of hydroxide and the presence of water in the properties of acids and bases. What are the definitions of acids and bases? Brønsted's theory neglects the role played by OH^- and Lewis' theory is too broad to be meaningful, since practically all chemical reactions deal with electron transfers. Recently the IUPAC raised the entire question of pH (*Anal. Chem.*, Sept. **1997)** and the resulting controversy (*Anal. Chem.*, April **1998**). The situation is becoming confused. We would like to explore a better and more logic way to teach pH and pOH correctly to our students so that they can obtain a good understanding of the concepts.

Students are generally taught to pay attention to activity rather than concentration for purposes of greater accuracy. The activity concept has been questioned [9,31]. What is the difference in definition between α_{H^+} and $[H^+]$? In fact, they are the same, because $[H^+]$ indicates only free proton concentration and does not include protonated ligands. We don't need useless activity coefficients which, just using parameters, insufficiently correct the effect of ligand complexation with proton or hydroxide and often give misinformation. This ligand effect may also be applied to the concept of ionic strength. Any ligand interacting with H^+ or OH^-, upon reaching a certain concentration, will decrease the effective $[H^+]$ of $[OH^-]$. Because ligand complexation cannot be simply compensated for by the introduction of an activity coefficient, there is no point in having students needlessly deal with activity and activity coefficients. In certain cases, the ligand effect in a complicated mixture can be eliminated by the standard addition calibration.

Theory: Nernst Equation, Slope, and Modified Boltzmann Equation

The redox-based Nernst equation has been misused for membrane electrodes, including the pH glass electrode, because it fails to explain their mechanisms and interference. Bockris called the misuse of Nernst equation for the over potential as "The Greatest Nernst Hiatus" [35]. Cheng called the second Nernst hiatus for its use to the ISE potential [8]. It provides misinformation to the effect

that infinite linear relationship (slope) exists between the potential and pH. The nonlinear portions in the calibration curve are generally ignored and called the "acid and alkaline errors" [31] (Figure 1). This gives a serious impression to students that the theoretical Nernstian slope is correct and (erroneously) the facts are wrong [31]. Students may ask why do we need to correct the facts to suit the hypothetical Nernstian slope? The misleading Nernstian slope has been explained as a common slope unrelated to the membrane electrode mechanism [14]. Furthermore, there is a slight deviation from linear in the curve between pH 6-8 for two reasons: First, the glass electrode responds to H^+ ions in the acid solution and OH^- ions in the alkaline solution. In other words, there are actually two calibration curves, one for H^+ and one for OH^-, connected together (Figure 2). Second, this deviation is attributed to the glass composition that determines the isoelectric point of the glass. Normally, addition of metal oxides to the glass for increasing its conductivity will reduce its isoelectric point to below pH 7 (approximately 5-6). Consequently, the potential of the common pH electrode glass in water is not zero at pH 7.0 as commonly assumed in the literature [7,15], but instead is more negative. We should keep this in mind when carrying out the calibration. For this reason, it might be serious to trust a reading of pH 7.001 considering that the pH meter with the common pH glass electrode might not be exactly pH 7.0, possibly slightly higher than pH 7.0 because the glass requires extra OH^- ions to be electrically neutral [10,28]. So a pH meter claiming to be accurate to pH 7.001 or 7.0001 would be subject to doubt. Further research in this area is needed. In actual calibration, we do not expect to have a perfect linear calibration curve, especially in the strong acid, strong alkaline, and neutral regions (Figure 3). In other words, the linear Nernstian slope, *i.e.*, 59 mV/pH for the entire calibration curve, does not exist. This is based on the Freudlich isothermal and the Boltzmann distribution equation [14]. Understanding the mechanism is most important. Little attention should be given to slope and thermodynamics because they do not contribute to understanding the mechanism. Many factors affect the calibration slope [14]. It is acceptable to use the 60 mV/pH slope calibration curve for ordinary purposes. However, for purposes of greater accuracy, it is only necessary to carry out a portion of the calibration curve near the sample pH using known buffers, not the entire 0 to 14 pH range. We are reminded of the limitation of pH meters. The Nernst equation was derived from the galvanic cell for the same ion species; on the other hand, the Boltzmann equation may deal with different ion species.

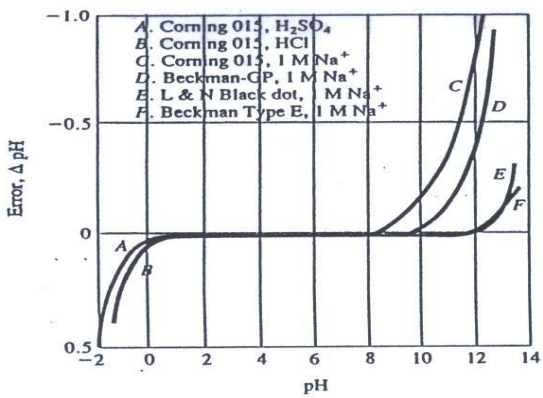

Figure 1. Acid and alkaline error for selected glass electrodes at 25 C. (from R. G. Bates, Determination of pH, 2nd ed., p. 365. New York: Wiley 1973).

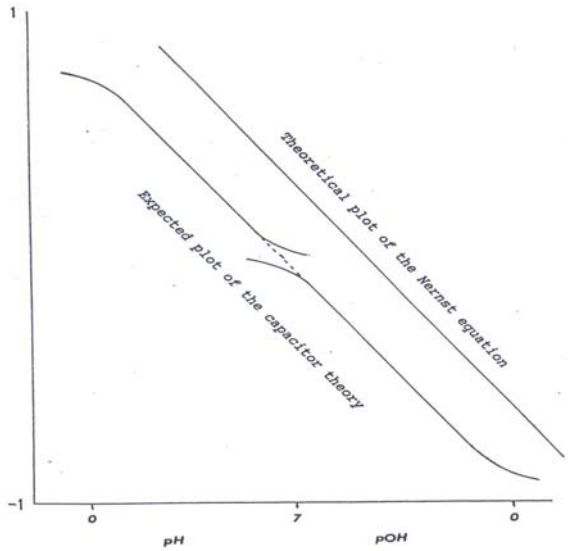

Figure 2. Theoretical and expected plot of the Nerst equation and the capacitor.

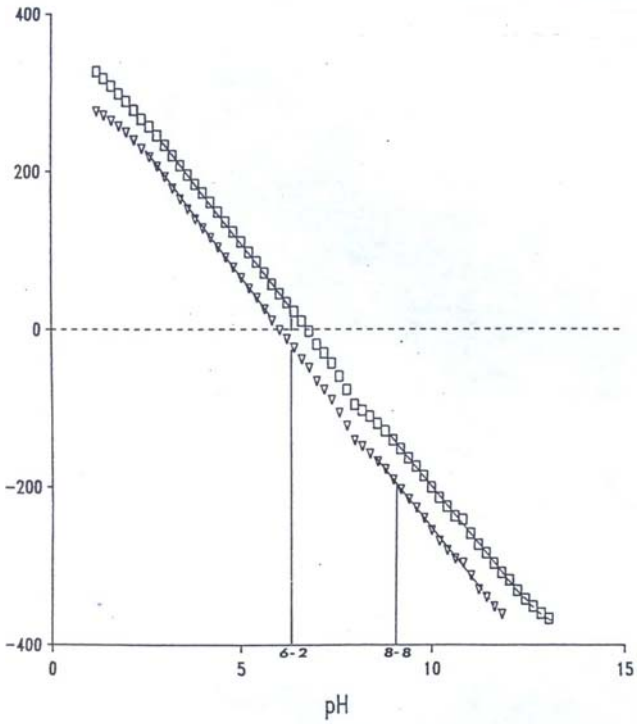

Figure 3. Potential vs. pH plot of buffers (CRC) Fisher glass electrode (cat.# 13-639-3); ∇ Fisher glass electrode (cat.# 13-639-1).

The electrode potential mechanism for nonfaradaic potentiometry has been proposed with the Boltzmann equation under a stirred condition:

$$N_i / N_o = \exp (- z_i e E) / KT$$

where N_i, N_o, z_i, e, and E are ions charges on the electrode surface and solution, electron charge, and potential, respectively. K and T are constants. In considering the counter-ion triple layer (cit) effect, the modified Boltzmann equation has been proposed [29,36]:

$$E_{not\ stirred} = 2.3\,(KT / z_{\pm} e)\log\,(N_i / N_o) - E_{cit}.$$

The original Boltzmann distribution equation did not include the cit effect which was only recently discovered. Also, the $z_{\pm}$ denotes the ion net charge.

Experimental

pH Meter

The pH measurement is potentiometric, that is, it explains the relationship between the electrode potential and the solution. In the literature it is common to see the Nernst equation used to explain such a relationship. The meter truthfully responds to the potential, it indirectly and mathematically converts the potential to the pH scale according to the questionable linear Nernst slope. It does not correct the nonlinear deviations in the strong acid, strong alkaline, and neutral regions. As a pH meter produces numerical numbers calculated following a certain scale, we must scrutinize whether this calculated pH scale is reliable or not. This is when a calibration is needed. This is a very serious matter in teaching pH measurement to our students that over emphasizing resolution and accuracy in pH measurements can be misleading, because the accuracy of pH measurements relies on precision calibration of pH glass electrodes, reference electrodes and buffers. Emphasis on a pH of 0.001 in a product means more for advertising value than actual scientific accuracy. It has been proposed for some time that a meter be made that has both pH and pOH scales, with corrections for the three nonlinear compensations [10,34]. The potential amplification may offer more sensitive readings on greater electrode charge density [27].

Temperature

As indicated in the Boltzmann equation, temperature affects ionic adsorption and distribution at the electrode interface and the ΔG thermodynamic effect. It is questionable whether the pH manufacturer can actually compensate for both effects of temperature without knowing the mechanisms of pH measurement [6,7,14,34]. We should realize that the effects of temperature on the pH electrode and the reference electrode are not the same [29,35]. Furthermore, the temperature under normal testing conditions within a few degree variation will not be a problem unless in strong acid or strong alkaline solutions. At much higher temperatures, the combined pH electrodes should not be used to measure pH. Instead, place the reference in a separate beaker containing a constant KCl solution with a conducting wire such as graphite, fiber, Pt, or Ag in place of the salt bridge (Figure 4). The calibration should be carried out under the same conditions, the reference electrode should be kept under a constant room temperature, and a constant potential should be maintained. The temperature with two functions affects the potential slope and the thickness of double layer and triple layers that determine the electrode potentials [29,35].

Stirring

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The stirring effect on pH measurement is well known. Chemists are confused by conflicting recommendations [1-7]. Many studies on the stirring effect have been reported [17,18]. The DL and TL at the electrode interface affect the electrode potential, and the stirring disturbs both layers [36]. Recommendations are to stir the solution to achieve a uniform solution, then stop stirring and perform the measurement. The calibration should be carried out with standard buffers under the same conditions without stirring. Since stirring speed affects the potential, close attention should be given to the flow injection analysis using ISE. The application of a pressure in an electrode solution should give rise to a potential difference and a corresponding electric field. This is the phenomenon known as the streaming potential [19] that has been applied to the stirring effect [2-4]. At 25°C, the streaming potential for an aqueous solution is represented by [19]:

$$\Phi = P \ \zeta / k \ (10^{-6})$$

where P is measured in mm Hg and Φ (streaming potential) and ζ (zeta potential) are in mV. Based on the stirring effect on the membrane potential, it may be possible to determine the liquid flow velocity by measuring the membrane potential with a known solution. A calibration curve obtained under stirring will give a higher than 59 mV/pH slope, because the stirring spins off counter-ions in the TL making the positive potential higher and the negative potential lower [29, 35]. The streaming potential deals with a colloid solution having zeta potential. On the other hand, the stirring effect deals with a pure solution to spin off the counter-ion triple layer by centrifugal force from the same solution.

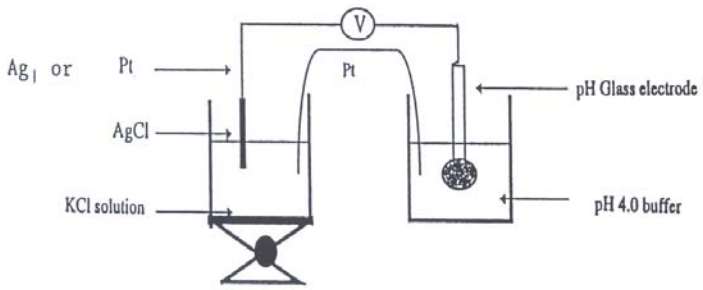

Figure 4. Experimental set up. Ag/AgCl or Pt/AgCl electrode is dipped progressively in a solution of KCl. Potentials are measured against a constant pH glass electrode.

Reference Electrode

Calomel and Ag/AgCl are the common used reference electrodes. In consideration of the environment, however, the calomel electrode is rarely used today. In literature, practically all reference electrodes have been described as redox potentials instead of capacitor potentials [20,21]. The whole pH measuring circuit consists of an indicator electrode, glass electrode, and a reference electrode that are immersed in the sample solution. In order to obtain a definite pH value, the reference electrode must have a stable potential that is independent of the sample solution. Ideally, no reaction between the sample solution and the reference electrode should occur. Some parameters such as temperature,

stirring, and KCl concentration, *etc.*, do not have the same effect on the reference electrode as on the indicator electrode [17,18,35]. To obtain accurate results, it is suggested that the reference electrode be immersed in a separate container containing a constant KCl solution and a conducting wire (replacing the salt bridge) (Figure 4). It is particularly important to separate the reference electrode from the indicator electrode in the cases under unusual conditions such as high temperature, high pressure, being in a fermentation broth, *etc*., such a separation offers another advantage that it will avoid any possible interaction between KCl and the sample solution. The double junction reference electrode is also unneeded. It is interesting to point out that without the new capacitor mechanism for both the glass electrode and reference electrode and the use of a conducting wire to replace the salt bridge, an accurate pH measurement of samples under extreme conditions would hardly be possible. It should be noted that AgCl is easily reduced under the light, resulting in reduced surface sites for Cl^- adsorption and changing the potential. It is also desirable to cover the Ag/AgCl electrode in a separate container from the light. The Ag may be replaced by another conductor such as Al or graphite. The replacement of the salt bridge with a conducting wire is really a breakthrough to achieve a stable reference electrode potential. It is still desirable to develop new and improved reference electrodes that are simple and stable under all conditions. Here, we may suggest an unconventional option of any stable solution to replace the Ag/AgCl or SCE as a reference electrode, for example, a pH electrode with a buffer solution in a separate container [29]. It can serve as a stable reference electrode for pH and pI measurement.

Junction Potential

There has been some misrepresentation in the literature about junction potentials. They are not redox phenomena, but are capacitors at the interface where a difference in charge density between two phases exists [8, 10]. The junction potential problem is generally not serious and can for most part be eliminated by close calibration. But for colloidal solutions containing negatively charged particles stuck to the electrode surface causing extra negative potentials, we might call this a problem of junction potentials. The fine colloidal particles tend to be adsorbed on the electrode surface as anions. That is what we call the suspension effect. The junction potential problem still exists if the pH of the two solutions is the same, because the different charge densities in the interface may be caused by ions other than H^+ or OH^-. The junction potential may cause measurement problems in biochemical samples. In certain cases, junction potentials may be eliminated by grounding or discharging.

Discussions

Standard Buffer

Standard buffers are extremely important because they are the basis for calibration. They are generally available in the compositions proposed by the NIST. In the past, they were prepared based on misused Nernst equation that, for instance, does not consider the phosphate to be involved in any redox reaction with the glass electrode [32,33]. Now, we have to question whether these buffers are accurate and how precise they are. Can we use the NIST standard pH 7.00 buffers to calibrate the pH

electrode to 7.001? Buffers prepared based on the Henderson-Hasselbach equation containing weak acid or base that is often a ligand to complex the metal contained at the glass surface. A ligand like phosphate may be adsorbed on the glass as a metal complex causing extra negatively charges, particularly when its concentration is high [34]. Usually rare earth oxides are added to the glass to improve its conductivity. Many buffers on the market are phosphates, so be alert of their possible interference from them or other ions in the calibration [16,22,26]. New mechanism, concepts, and technique are available for buffer research. The accuracy of the buffers prepared based on the Henderson-Hasselbach equation depends on the accuracy of pK_a or pK_b values. The latter in turn depends on accuracy of pH measurement. It appears in a cycle. In buffer research, first the correct isoelectric point of the glass electrode should be determined, not assumed to be pH 7.00 as commonly believed. Careful research on our standard buffers is urgently needed. It will be a time consuming job to recheck some possibly questionable pK_a and pK_b values. We may start to work with dilute known acid and base solutions to check the electrode response. We may suggest that the manufacturers will show the isoelectric point of their glass electrodes sold to the customers.

Sensitivity

As stated previously, a sensitivity of 0.001 pH for most pH meters seems to be a little exaggerated without considering limitations of the glass electrode due to many parameters surrounding the glass surface, interface, double and triple layers, etc. [14]. If we consider capacity for voltage measurement to be 0.1 mV with the 60 mV/pH slope, the meter sensitivity will be 1/60 x 0.1 = 0.0017 pH. This is the calculated ideal sensitivity that does not take into consideration of practical factors affecting the slope. It is rather doubtful that any pH meter can really measure a sample pH value of 7.001. In addition, the nonlinear portion in the neutral range should be considered. Sensitivity to pH 0.01 may be reasonable in the calibration [4,5,7]. We rarely look for sensitivity to pH 0.001. From this point of view, it is unnecessary to cite the slope as 0.05916 V/pH. In practice, we seldom obtain a 59.16 mV/pH calibration slope. If a more sensitive slope is desired, the amplification technique may be tried [27,28,30]. Amplification with 4 pH electrodes could give 230 mV/pH slope [27]! We could read 7.0004 pH on the pH meter. More research in this area is suggested. Contrary to electronic amplification, this is chemical amplification based on the increase in the capacitor electrode surface charge density, $E_{total} = E_1 + E_2 + \ldots E_n$.

Suspension Effect

The suspension effect has been reported and explained [23]. The negatively charged colloidal particles cause the higher pH values. It is better to remove colloidal particles from the sample with filtration, centrifuging, or other technique. The pH of clay soils may be easily estimated by using pH paper or dye. The acid soil samples usually cause no problem in pH meter measurement because H^+ coagulates with the colloidal clay. Suspension, emulsions, and foams should cause problems for pH measurements. Careful attention should be given when measuring pH or pI in biochemical samples. The polyaniline solid state pH electrode might be a better choice [30]. This needs to be tested.

Glass Electrode

The modern concept and mechanism of the pH glass electrode has been reported [8,25]. It is a capacitor rather than a half cell as commonly described in the literature. Understanding the mechanism correctly is important as it helps point out and remedy errors and teaches one to calibrate. Traditionally the pH glass electrode has been considered as a half-cell that can be explained by the Nernst equation. Many misleading concepts and mechanisms of the pH glass electrode have been disproved by experiments [8,10,11]. The solid state pH glass electrodes [12,13] demonstrate there is no need to have an internal solution inside the glass tubing, so long as there is a stable capacitor at the inner glass surface. The internal solution that serves as a conductor may be replaced with a conducting wire. The emergence of solid state pH glass electrodes has been revolutionary, overthrowing misleading concepts and mechanisms held in the past about the pH glass electrode. Thickness, shape, surface, property and composition of glass will affect its response to the potential or slope. Various types of non-glass pH electrodes are available for special purposes [27-30].

Limitations of the pH Glass Electrode

The new mechanism tells us that the membrane electrode potential reading from the charge density, i.e., the potential development is limited by the number of active sites available for adsorption. This explains the nonlinear calibration at high acid and alkaline concentrations, and why a high concentrations of electrolytes, even normally non-interfering ions may also be slightly adsorbed. In addition, a minimum number of adsorbed ions are required on the surface to show the potential (or the linear slope). This also raises the question of how small an ultramicro electrode can be made. Different membrane surfaces with various numbers of active sites, as well as different sizes of ions, and thickness of the membrane determines slope size. We must realize that the glass electrode is not perfect and specific for H^+ and OH^-; it can also adsorb or react with other ions at high concentrations. The calibration can find the calibration limit. The glass electrode can be damaged by strong alkaline solution, HF, contamination, scratches and high temperatures. We noted papers on measuring surface pH [24]. There is no such thing as surface pH. It is a misleading term because by definition pH is related to $[H^+]$. Concentration is a three dimensional term and surface is a two dimensional term. We can only measure the surface charge density and refer to the solution concentration. The glass electrode should only be allowed to touch solution, not solid surface. To touch the glass electrode surface by a solid wire would discharge the potential.

Frequency of Calibration

The pH meter should be calibrated at least two points close to the expected pH of the sample solution every 2-3 hours. A pH electrode is expected to last approximately 3 years under normal conditions [7]. A separate sealed Ag/AgCl could last much longer. Before calibration, the glass electrode should be cleaned with water; if necessary, acid, or organic solvent may be used. If there are solid particles on the glass they should be carefully removed with a wet paper towel and the glass

rinsed with water. When the electrode is not in use, it should be immersed in water. Since the electrode is a capacitor it can be readily grounded with a fine wire. Gently touch the electrode surface to see whether the pH meter goes to zero potential. By disconnecting it and recharging slowly (for about one minute) you can be sure of the time required to reach equilibrium.

Summary

It is important to have a firm understanding of the mechanism involved in pH measurements. Only then is it possible to have reliable calibration. Without basic knowledge of the mechanism, one would lack the judgment necessary to make corrections. First of all, electrode potential originates in the adsorption of H^+ or OH^- at the electrode surface according to the Freundlich isothermal and the Boltzmann distribution equation, not the misused linear Nernst equation. Emphasis has been made on three nonlinear curves. Also, the pH calibration curve is a combination of two calibration curves: namely the pH and the pOH curves. A slight deviation in the range of pH 6-8 is discussed. The pH glass electrode, reference electrode, and pH meter are the most important components of pH measurement. Other conditions, such as standard buffers, stirring, temperature, etc. are also discussed. The glass and reference electrodes often cause unstable or inaccurate readings. A new type of reference electrode and the use of a conducting wire to replace the salt bridge are suggested for more accurate and stable pH measurements. A simple ISE or pH electrode with a buffer in a separate container as a stable reference electrode for pH or pI measurement is suggested. For general purposes a linear calibration curve may be acceptable in the pH 2-10 range. For more precise calibration, make a few points of calibration near the pH of interest with accurate buffers. The potential amplification is suggested for higher sensitivity. The standard buffers depend on accurate pK_a and pK_b, that depend on accurate pH measurements. More research for better buffers is suggested. Paying more attention to the interference from the use of phosphate as a buffer is discussed. The suspension effect has been reported and explained [23]. Pay attention to pH and pI measurements for biochemical samples which contain colloids and contact the membrane surfaces.

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