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A Report on the National Bureau of Standards pH Standards

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In 1980, the research program in pH was re-established at the National Bureau of Standards (NBS). This report describes the state of this research, as well as the state of the NBS pH standards. The thermodynamic definition and the determination of pH are elaborated. The problems of liquid junction potentials encountered in the practical determination of pH are discussed. The goal of the research program in pH is to develop and maintain a unified pH scale based on clearly stated thermodynamic criteria, with a wide range of applicability to practical pH measurements.

Key words: activity; activity coefficient; buffers; galvanic cell; glass electrode; hydrogen ion; liquid junction; pH; silver/silver chloride electrode; Standard Reference Materials; standards; thermodynamics.

1. Introduction

The negative logarithm of the hydrogen ion activity is commonly known as pH [1][1]. This term is associated with the effective concentration of hydrogen ion. The importance of this quantity lies in the fact that it is the measure of the chemical reactivity of the acid and alkali in aqueous solutions. It is used extensively in monitoring agricultural and industrial processes. Functionally, pH lies at the base of many chemical synthetic processes and is essential in many analytical measurements. In biological and biochemical research, pH is important because it is fundamental to natural processes. In short, pH is intrinsic to life itself.

The determination of pH is based on physicochemical principles and can be performed by various techniques such as colorimetry, conductivity, and potentiometry. Of these, the potentiometric or the electromotive force (emf) method is the simplest, the most accurate, and hence the most widely used. This is particularly true since the invention and commercialization of the hydrogen ion sensitive glass electrode.

The employment of the glass electrode for determining pH generally requires the following arrangement:

Glass electrode | Test solution ‖
Salt bridge solution | Reference electrode (I)

where the single vertical bar is the electrode-solution interface and the double vertical bar is a liquid junction denoting an interface between the test solution and the salt bridge solution, the latter having an ion in common with the reference electrode. From the measured electromotive force of cell (I) the pH may be computed via the following equation:

$$\mathrm{pH} \equiv \log a_{\mathrm{H}} = \frac{E-(E^{\circ}_{\mathrm{pH}}+E_{\mathrm{j}})}{RT\ \ln 10/F} = \frac{E-E^{\circ\prime}_{\mathrm{pH}}}{k} \qquad (1)$$

where a_{H} = the hydrogen ion activity (the charge, +, is dropped for convenience)
E = the observed emf of the cell
E°_{pH} = a constant, dependent on temperature and pressure and the types of electrodes used

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[1]Numbers in brackets indicate literature references at the end of this paper. It should be noted here that the original definition was in terms of hydrogen ion concentration. It was S. P. L. Sorenson and K. Linderstrom-Lang (Compt. Rend. Trav. Carlsberg 15, 40, 1924) who first proposed hydrogen ion activity in the definition.

Ej = the liquid junction potential of the given cell
R = the gas constant
T = the kelvin temperature
F = the faraday constant
k = $(RT\ln 10)/F$
$E^{\circ\prime}_{pH} = E^{\circ}_{pH} + Ej$

The last quantity, $E^{\circ\prime}_{pH}$, cannot be accurately evaluated. However if $E^{\circ\prime}_{pH}$ is assumed to be constant for a given system [2], and if a solution of known pH [pH(S)] is available, then the pH of an unknown solution [pH(X)] can be determined by using cell (I) twice: first with solution S, then with solution X and calculating the pH(X) from the difference in the respectively measured emf's as follows:

$$pH(X) = pH(S) + \frac{E_X - E_S}{k}. \quad (2)$$

If pH(X) differs significantly from pH(S) or if the emf response of the system differs from the ideal Nernstian response of 1 pH unit per volt ($RT\ln 10/F$), then two pH standards (S1 and S2) should be used. The value of pH(X) can be computed according to eq (3):

$$pH(X) = pH(S1) + \frac{E_X - E_{S1}}{E_{S2} - E_{S1}}[pH(S2) - pH(S1)]. \quad (3)$$

The choice of the two buffers S1 and S2 should be such that pH(X) falls between the values pH(S1) and pH(S2). Such is the practical determination of pH today.

Therefore, the availability of standard pH solutions is a necessary condition for the application of eq (2). Moreover, according to the application of Henderson's or Planck's equation for the approximation of the liquid junction potential, Ej [3–5], the standard pH solution should be made as similar to the test solution as possible with respect to pH and composition. Under such conditions the assumption regarding the constancy of $E^{\circ\prime}_{pH}$ is sound. Since in practice the conventional pH scale spans 14 pH units, several pH standards are required for establishing calibration points over the entire pH range.

In the United States, pH standards are promulgated and maintained by the National Bureau of Standards (NBS). Many foreign countries have also adopted the NBS approach to pH standardization. This work has been performed at NBS since the late 1930s [6] through the issuance of Standard Reference Materials. This approach, as well as the materials and values for the NBS pH buffer standards, have been accepted internationally. The theory and practices which are at the base of the certification process undergo periodic critical examination at NBS to remain current with new developments and technology and to be responsive to changing and expanding national needs. A detailed discussion of the theory, the process, and the refinement of the evaluation and certification of pH standards at the NBS follows.

2. Thermodynamic Foundation of pH

The use of pH in the expression $pH = -\log a_H$ is purely a formalism because a_H, a single (hydrogen) ion activity, is indeterminate. The ultimate definition of pH should be made in terms of determinable quantities.

One way of determining the pH of a weak acid (HA) may be from the dissociation constant, K_a, of the acid, assuming K_a is known or can be independently determined:

$$K_a = \frac{a_H a_A}{a_{HA}} = \frac{a_H m_A \gamma_A}{m_{HA}\gamma_{HA}} \quad (4)$$

and

$$pH = pKa + \log\frac{m_A}{m_{HA}} + \log\frac{\gamma_A}{\gamma_{HA}}. \quad (5)$$

With the aid of the Debye-Hückel equation [7, 8]

$$\log \gamma_i = -AZ_i^2\sqrt{I}/(1 + B\mathring{a}_i\sqrt{I}) + bI \quad (6)$$

where m = molality of the constituents
γ_i = activity coefficient of the ith species
I = $\frac{1}{2}\Sigma m_i Z_i^2$. (This is the definition of ionic strength only if the electrolyte is fully dissociated. Otherwise, the degree of dissociation, α, should be included. Thus $I = \frac{1}{2}\Sigma \alpha m_i Z_i^2$, *e.g.*, I for 0.05 m potassium acid phthalate (KHP) at 25 °C is not 0.05 but 0.0533 [9].)
Z_i = ionic charge of the ith ion
A and B = constants dependent on the temperature and dielectric constant of the solvent
$\mathring{a}_i$ = the ionic size
b = an adjustable parameter

On the other hand, the pH of the same acid can be determined without the knowledge of K_a, using a galvanic cell without liquid junction, sometimes called the Harned cell:

$$Pt, H_2\ (1\ atm.)|HA(m), KCl(m')|AgCl,Ag. \quad (II)$$

The emf of this cell at one atmosphere (101.325 kPa) of hydrogen pressure is given by

$$E = E^{\circ}_{Ag,AgCl} - \frac{RT}{F}\ln m_H m_{Cl}\gamma_H\gamma_{Cl} \quad (7)$$

where m's are molalities, γ's the activity coefficients, R,T,F have their usual significance, and E is the measured emf. $E^{\circ}_{Ag,AgCl}$ is the potential of the silver-silver chloride electrode measured relative to the "standard hydrogen electrode," i.e.,

$$\tfrac{1}{2}H_2(g)=H^+ + e \tag{8}$$

and

$$E=E^{\circ}_{H}-\frac{RT}{F}\ln\frac{a_{H^+}}{p_{H_2}^{1/2}} \tag{9}$$

where p is the pressure of the H_2 gas. When $p=p^{\circ}\equiv 1$, atmosphere and $a_{H^+}=a^{\circ}_{H^+}\equiv 1$, then, $E=E^{\circ}_{H}$. Since half-cell potentials cannot be measured independently, it has been established by convention that $E^{\circ}_{H}=0$ at p°_{H} and at all temperatures. All other half-cell potentials are computed in relation to $E^{\circ}_{H}=0$.

By putting all the known quantities together on the right hand side, eq (7) may be rewritten as

$$-\log a_H\gamma_{Cl}=\frac{E-E^{\circ}}{k}+\log m_{Cl}\,. \tag{10}$$

Since by definition $\gamma_{Cl}=1$ as m goes to zero, by plotting the right hand side of eq (10) vs m_{Cl} and extrapolating to $m_{Cl}=0$, the limiting value of the acidity function can be expressed as $-\log(a_H\gamma_{Cl})^{\circ}_I$ [9]. This value corresponds to the acidity function at the particular ionic strength, I, of the weak acid HA and

$$pH=-\log(a_H\gamma_{Cl})^{\circ}_I+\log\gamma_{(at\ I)}\,. \tag{11}$$

The last term of eq (11) may be evaluated from eq (6). Therefore, all the quantities related to pH, either from the dissociation constant or from the emf of galvanic cells without liquid junction, can be determined. Hence, within this framework the term pH is defined.

It should be noted that the application of eq (6) for the evaluation of the activity coefficients requires assumptions outside the domain of thermodynamics. However, it has been experimentally proved that this equation is a suitable approximation for the activity coefficient function of strong electrolytes up to 1 molal concentration [10,11] and therefore the use of this equation is justified for the determination of pH at ionic strength lower than 1 molal.

As the ionic strength decreases, the b-term in eq (6) becomes insignificant, and the influence of $\mathring{a}_i$ also decreases. By selecting a value for $B\mathring{a}_i$ (for example 1.5, as recommended by the Bates-Guggenheim convention [12,13] at the ionic strength of around 0.1 molal), the resultant uncertainty in pH is less than 0.005 pH unit, even if $B\mathring{a}_i$ is varied by as much as 10%. The ionic strength of the standard pH solutions certified by NBS is $\leqslant 0.1$. Thus the Bates-Guggenheim convention,

$$\log\gamma_i=-\frac{Az_i\sqrt{I}}{1+1.5\sqrt{I}} \tag{12}$$

is justified within the present experimental uncertainty (see table 1), and is applicable to the certification of the NBS primary buffer standards.

New demands for pH standards of ionic strength greater than 0.1 molal, such as that for seawater, render the use of Bates-Guggenheim convention inapplicable. In these cases eq (6) must be used, and the values of $\mathring{a}_i$ and b must be determined experimentally.

3. NBS Standardization of pH Solutions

The standardization of pH solutions was initiated at NBS in the late 1930's when Hamer [14] suggested the use of a galvanic cell without a liquid junction, similar to cell II, for the purpose. Later Hamer and Acree [6] proved experimentally the applicability of cell II for the determination of pH. Early in the 1940's, Bates et al. [15] published a list of provisional pH values of standard buffers. In the following years the experimental setup and the treatment of data were significantly refined as the state of the art of measurement advanced.

The principle of the determination of pH and the thermodynamics of the establishment of a pH scale have been discussed in section 2. Because of the complexity of ionic interactions in electrolyte solutions, the knowledge of ionic activity or activity coefficients has been advanced little in recent years. The only improvements that have occurred in the determination of pH have been in the methods of measurement. Among various methods for determining pH, Hamer et al. [6,14] and later Bates [12,16] have ably demonstrated that a galvanic cell without a liquid junction,

$$Pt,\ H_2(1\ atm)\,|\,H^+\ solution,\ KCl(m)\,|\,AgCl,Ag \tag{II}$$

is the best suited for the purpose. A detailed experimental account has been given by Durst [17].

Since eq (7) is used for the determination of pH, it is necessary to know $E^{\circ}_{Ag,AgCl}$. The value of $E^{\circ}_{Ag,AgCl}$ is determined, using the following cell [10]:

$$Pt,\ H_2(1\ atm)\,|\,HCl(m)\,|\,AgCl,Ag \tag{III}$$

and the equation

$$E^{\circ}_{Ag,AgCl} = E_{cell} - E^{\circ}_{H} \quad (13)$$

where $E^{\circ}_{H} \equiv 0$, under the conditions described in the previous section. However, the best values of E° reported for this cell disagree by 0.2 mV or more [18,19]. This indicates that not all silver-silver chloride electrodes behave identically. Therefore, for the most accurate pH work, the E° value of each individual Ag,AgCl electrode must be determined in cell III and the stability of each electrode firmly established before it may be used in cell II.

Using cell II, relying on thermodynamic principles, and by adopting the Bates-Guggenheim convention, the NBS has certified seven primary and three secondary pH standards. They are listed in table 1. The uncertainty associated with each of the primary standards is 0.005 pH and the uncertainty of the secondary standards is 0.01 pH.

The widespread use of cell I for practical pH measurements necessitates the use of pH standards that are traceable to the primary standards for calibration purposes. The work at NBS satisfies this need by providing definitively calibrated and certified pH standards.

The advantages and shortcomings of cell I have been discussed in section 1. Nevertheless, it is of interest to examine the data obtained with cell I by using a combination glass electrode to test the internal consistency of the NBS pH standards. The results are shown in table 2. The maximum deviation among all pH(S) listed in table 2 is 0.002 pH units. The NBS pH scale is internally consistent to at least that extent, thus confirming the usefulness of the approximations and conventions described in the first part of this report.

4. The Operational Determination of pH and the Problem of Liquid Junction.

The operational definition of pH entails the measurement of pH with cell I and the comparison of the pH of the unknown solution with that of the standard as shown in eq (2). Such comparison assumes the constancy of the liquid junction potential, E_j, in eq (1). This assumption has only limited validity. In some instances significant errors may be introduced in the pH determination by this assumption.

The problem of liquid junction potential has been the

Table 2. Internal consistency of the NBS pH scale.

Standard Solution	25 °C	ΔpH
1:1 Phosphate		
pH(S)	6.863	
pH(meas)	6.861	+0.002
Tartrate		
pH(S)	3.639	
pH(meas)	3.638	+0.001
Phthalate		
pH(S)	4.004	
pH(meas)	4.006	−0.002
Borax		
pH(S)	9.183	
pH(meas)	9.184	−0.001
Carbonate		
pH(S)	10.014	
pH(meas)	10.014	+0.000

Table 1. NBS pH Standards.

Solution composition (molality)	pH(S) at 25 °C	Temperature range (°C)	SRM
Primary Standards:*			
potassium hydrogen tartrate (satd. at 25 °C)	3.557	25 to 95	188
0.05 *m* potassium dihydrogen citrate	3.776	0 to 50	
0.05 *m* potassium acid phthalate	4.006	0 to 50	185f
0.025 *m* KH_2PO_4+0.025 *m* Na_2HPO_4	6.863	0 to 50	186Id/186IId
0.008695 *m* KH_2PO_4+0.03043 *m* Na_2HPO_4	7.410	0 to 50	186Id/186IId
0.01 *m* $Na_2B_4O_7 \cdot 10\ H_2O$	9.180	0 to 50	187c
0.025 *m* $NaHCO_3$+0.025 *m* Na_2CO_3	10.010	0 to 50	191a/192a
Secondary Standards:**			
0.05 *m* potassium tetroxalate · $2H_2O$	1.679	0 to 95	189
0.01667 *m* tris***+0.05 *m* tris · HCl	7.699	0 to 50	922/923
$Ca(OH)_2$ (satd. at 25 °C)	12.454	0 to 60	

*Experimental uncertainty: ±0.005 pH
**Experimental uncertainty: ±0.01 pH
***tris: tris(hydroxymethyl)aminomethane.

subject of numerous studies [2,14,20,21] which indicate that the liquid junction potential is not a thermodynamic quantity, i.e., that the liquid junction potential, Ej, cannot be specifically defined. For example, Ej depends on the concentration of the salt bridge and on the temperature, but no functional correlation has been found. Ej also varies with specific electrolytes, such as strong and weak acids. Furthermore, it changes with the geometrical structure and the manner in which the junction of the salt bridge is formed [14,20]. Therefore, Ej cannot be determined exactly and eq (2) cannot be considered a rigorous thermodynamic definition of pH.

For the reasons outlined above, one cannot in general assume Ej to be constant in determining pH in solutions of unknown nature. It has been reported that the uncertainty in determining pH in acid rai . [22] and in biological fluids [23], using a combination glass electrode in cell I, is significant, often as large as 0.5 pH.

5. Research on pH

An active research program in pH has been established at NBS to maintain the standards used for pH calibration, to respond to changing needs in this important determination, and to advance the science in tune with advances in chemical and electronic technology. This research effort includes both basic and applied studies and its diversity is illustrated by two projects now in progress.

Basic research is being conducted to establish firmly the standard potential ($E°$) of the Ag,AgCl electrochemical couple which is often used as the reference electrode in pH measurements. As alluded to in a previous section, there are variations in the measured $E°$ of different preparations of Ag,AgCl electrodes. Recently, Bates [18] has reported that from over 30 independent measurements, values for $E°$ of Ag,AgCl determined in cells without liquid junction vary from 0.2222 to 0.2228 V at 25 °C. The range is 0.0006 V, which amounts to differences of approximately 0.01 pH unit.

Variations in $E°$ of such magnitude (0.6 mV)must be caused by the Ag,AgCl electrode itself, because the other factors in the system for determining $E°$ can be systematically eliminated. In fact, experts decided in 1956 to assign an uncertainty of 0.2 mV to the $E°$ measurements for this electrode [24]. The sources of problems associated with this electrode have been investigated by numerous workers in electrochemistry. The areas studied have included methodology, electrode preparation, and operational precautions. However, there is still need to define the characteristics of this electrode to reduce the uncertainties associated with pH measurements done on SRM's at NBS.

When classical experiments [19, wherein references cited] were repeated, it was observed that oxygen interacted with the electrode and was probably the major cause of the observed variations in $E°$. Although this observation was not new, the effect has never been fully discussed and investigated. To verify the effect of oxygen on the behavior of the electrode, we conducted the following experiments:

A. Electrode Preparation: A thermal electrolytic type of preparation was selected because the method is sim ple and results in an electrode with minimal (or least) contamination. Classical procedures were followed, except when electrodes were purposely exposed to either laboratory air or an argon atmosphere.

B. Cell EMF Measurement: The cell setup, temperature control, and measuring device were similar to those described by Durst [17] with minor modifications. Special care was taken to have the electrode and HCl solution under either laboratory air or an argon atmosphere. Measurements were made immediately after the preparation of the electrodes.

Four sets of experimental conditions were compared:

(a) $E_{el(O)}-S(O)$ (c) $E_{el(Ar)}-S(O)$
(b) $E_{el(O)}-S(Ar)$ (d) $E_{el(Ar)}-S(Ar)$

where el(O)=electrode exposed to air, el(Ar)=electrode exposed to argon, S(O)=HCl solution saturated with air, S(Ar)=HCl solution saturated with argon. The ranges of results for approximately 100 electrode measurements under the four sets of experimental conditons respectively are:

(a) $E°=0.22260$ to 0.22350 V
(b) $E°=0.22250$ to 0.22260 V
(c) $E°=0.22240$ to 0.22250 V
(d) $E°=0.22230$ to 0.22240 V.

The results indicate that oxygen does have an effect on the $E°$ for the Ag,AgCl electrode, and is most pronounced in those measurements made with electrodes exposed to an oxygen atmosphere. The higher potentials observed for such electrodes are probably due to mixed potentials from electrochemical couples other than silver-silver chloride, silver-silver oxide, for instance. However, the long term stability could not be maintained and the overall reproducibility for each set was only ±0.05 mV as compared with 0.01 to 0.02 mV as reported in the literature [10,19,25][2]. Work is continuing

[2]It was pointed out by Hamer [26] that Harned and his students used "limited" solutions and filled their cells under vacuum to get rid of the "air effect." Harned and Ehlers [27] thus obtained $E°=0.22239$ int. volts. On the present scale this becomes 0.22247 V which is in good agreement with conditions (c).

in the areas of oxygen adsorption and desorption measurements to determine quantitatively the effects of oxygen on $E°$. This work is necessary to lower the uncertainties in existing pH measurements.

In the second project, work is proceeding to develop matrix-specific pH standards to augment the primary buffer standards currently available. The major reason for these new standards is to take into account residual liquid junction potentials and to minimize their effect. It has been shown conclusively that these effects can seriously bias pH readings, especially if the ionic strengths of the standards and the test solutions are significantly different [22].

Research is now underway to test the feasibility of providing matrix-specific pH standards for selected applications, focusing initially on low ionic strength solutions such as acidic precipitation in the environment.

Recently an interlaboratory test was conducted to test the efficiency of using dilute solutions of a strong acid as working standards for pH measurements in acidic precipitation. The results of this test confirm the problems with residual liquid junction potentials and indicate that the strong acid standards (specific for this application) greatly minimize the problem. It is anticipated that in late 1984 NBS will issue a Research Material (RM) which will incorporate these findings and represent the first attempt at matrix-specific pH standards. The effort will be expanded to include matrices such as seawater, biological fluids, and eventually, non-aqueous media. This new generation of pH standards will be consistent with the current NBS pH scale and will be as thermodynamically meaningful as possible. This should avoid the confusion that would be caused by several inconsistent pH scales.

The ultimate goal of the NBS research program on pH is to develop and maintain a unified pH scale based on clearly stated thermodynamic criteria, with a wide range of applicability to practical pH measurements. The present projects form the foundation for this goal and will lead to intensive investigations into activity coefficients and the concept of single ion activities.

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