Revised Standard Values for pH Measurements from 0 to 95 °C

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Seven standard solutions serve to fix the NBS conventional activity scale of pH (termed $p\text{H}_s$) from 0 to 95° C. The original emf data have been re-examined and the values of the acidity function $p(a_{\text{H}}\gamma_{\text{Cl}})$, from which $p\text{H}_s$ is derived, have been recalculated with the use of a single consistent set of standard potentials and electrochemical constants. The convention proposed recently by Bates and Guggenheim for the numerical evaluation of the individual activity coefficient of chloride ion in the buffer solutions has been adopted, and by this means $p\text{H}_s$ values to the third decimal have been assigned. These "experimental" $p\text{H}_s$ values in the temperature range 0 to 95 °C have been smoothed as a function of temperature by least-squares treatment. The properties and uses of the standards are discussed and directions for the preparation of the solutions are given.

1. Introduction

For a number of years the National Bureau of Standards has recommended a standard pH scale defined in terms of six reference points (see, for example, [1][1]). A seventh standard (E below) has recently been established to aid in the accurate measurement of pH in the physiologically important range pH 7 to 8 [2]. The compositions of these seven solutions are as follows, where m is molality:

A, potassium tetroxalate, 0.05 m,

B, potassium hydrogen tartrate, saturated at 25 °C,

C, potassium hydrogen phthalate, 0.05 m,

D, a solution 0.025 m with respect to both potassium dihydrogen phosphate and disodium hydrogen phosphate,

E, a solution 0.008695 m with respect to potassium dihydrogen phosphate and 0.03043 m with respect to disodium hydrogen phosphate,

F, borax, 0.01 m,

G, calcium hydroxide, saturated at 25 °C.

The assignment of pH values to these standards has been described in detail in earlier papers (citations are given in [1]). The necessity of estimating the individual activity coefficient of chloride ion in each reference solution deprives the standard pH value (termed $p\text{H}_s$) of exact fundamental meaning. The numerical value of this activity coefficient must rest upon an arbitrary convention, chosen in part for its reasonableness but largely for its utility [3].

Heretofore, the assigned pH values have been made consistent with several reasonable conventions for the single ionic activity coefficient of chloride ion. In order to do this, pH values had to be assigned with only second decimal accuracy. Recently, however, the adoption of a single convention has been recommended [4]. For the assignment of standard pH values it has thus been proposed that the activity coefficient of chloride ion (γ_{Cl}) be defined by the equation

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[1] Figures in brackets indicate the literature references at the end of this paper.

$$\log \gamma_{\text{Cl}} = \frac{-AI^{1/2}}{1+1.5I^{1/2}}, \tag{1}$$

where I is the ionic strength and A is a parameter of the Debye-Hückel theory having a different value at each temperature. It was intended that this convention be applied when I is equal to, or less than, 0.1.

This convention is both simple and useful. It is also reasonable in that it makes the activity coefficient of chloride ion nearly equal to the mean ionic activity coefficient of sodium chloride in its pure aqueous solution of ionic strength I. Furthermore, the values of $p\text{H}_s$ for the four standards in the intermediate pH range, obtained by the use of this convention, agree quite well with the experimental pH values furnished by a pH cell with liquid junction standardized with the phosphate buffer at pH 6.865, as the following data illustrate [5]:

Standard	$p\text{H}_s$ at 25° C	pH (l.j.) at 25° C
B, tartrate	3. 557	3. 566
C, phthalate	4. 008	4. 009
D, phosphate	6. 865	[a] (6. 865)
F, borax	9. 180	9. 185

[a] Reference value.

The values of $-\log (\gamma_{\text{H}}\gamma_{\text{Cl}}m_{\text{H}})$ or $p(a_{\text{H}}\gamma_{\text{Cl}})$, used to derive $p\text{H}_s$, can be obtained with an accuracy of a few thousandths of a unit. With the adoption of the new convention it becomes possible to assign $p\text{H}_s$ values with an accuracy dependent only upon the precision of the primary data. The reproducibility of the pH of the standards justifies this move.

It is the purpose of this paper to report a critical re-examination of the original emf data, a recalculation of the values of $p(a_{\text{H}}\gamma_{\text{Cl}})$ with the use of consistent values for the natural constants involved, and finally an assignment of $p\text{H}_s$ values given to the third decimal place in terms of the new convention for γ_{Cl}. The properties of the seven standard

solutions are summarized, and instructions for the preparation and use of the solutions are given.

2. Method

The acidity function $p(a_H\gamma_{Cl})$ is calculated from the electromotive force (E) of cells containing hydrogen and silver–silver chloride electrodes by the equation

$$p(a_H\gamma_{Cl}) \equiv -\log (\gamma_H\gamma_{Cl}m_H) = \frac{E-E^\circ}{2.30259RT/F} + \log m_{Cl}, \qquad (2)$$

where E° is the standard potential of the cell [6], F is the Faraday, R is the gas constant, and T is the temperature in degrees Kelvin.[2] The pH_s of the chloride-free buffer solution is computed from the equation

$$pH_s = p(a_H\gamma_{Cl})^\circ + \log \gamma_{Cl}^\circ, \qquad (3)$$

where $p(a_H\gamma_{Cl})^\circ$ is the value of $p(a_H\gamma_{Cl})$ in the limit of zero concentration of added chloride. Similarly, γ°_{Cl} is the limit of γ_{Cl} as the concentration of chloride in the buffer solution is reduced to zero. Values of $p(a_H\gamma_{Cl})^\circ$ are obtained readily by extrapolation of emf data obtained for the same buffer solution with two or more added small concentrations of a soluble chloride; γ°_{Cl} is computed by the convention set forth in eq (1).

The values of E°, $2.30259RT/F$, and of the Debye-Hückel slope A on the molal scale from 0 to 95 °C are summarized in table 1. For this calculation, R was taken to be 8.3147 j mole^{-1} deg^{-1}, F was taken to be 96,495.4 coulomb equiv^{-1}, while T is t °C$+273.150$ [7]. It should be noted that the recent shift to the carbon 12 scale of atomic weights is without effect on the magnitude of the quantity $2.30259RT/F$, inasmuch as R and F are changed in the same proportion. The values of A have been recalculated by Robinson and Stokes [8] with the use of a recent redetermination of the dielectric constant of water [9]. Their figures, given for the volume scale of concentration, have been converted to the molal scale through multiplication by $\sqrt{d^\circ}$, where d° is the density of pure water. All emf values recorded prior to January 1, 1948, have been corrected to absolute volts through multiplication by the conversion factor 1.00033 [10].

The recalculated values of $p(a_H\gamma_{Cl})^\circ$ for the seven standard buffer solutions from 0 to 95 °C are collected in table 2. The pH_s values given in table 3 were calculated from these values of $p(a_H\gamma_{Cl})^\circ$ together with the convention for γ_{Cl} given in eq (1).

The relation between pH_s for each buffer solution and the absolute temperature T was found to be represented closely by a four-constant equation of the form

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[2] This acidity function was formerly called pwH (see [3] and later papers).

TABLE 1. *Values of* E°, $2.30259RT/F$, *and the Debye-Hückel slope* A *(molal scale) from 0 to 95 °C*

t	E°	$2.30259RT/F$	A
°C	v	v	
0	0.23655	0.054195	0.4918
5	.23413	.055187	.4952
10	.23142	.056183	.4988
15	.22857	.057171	.5026
20	.22557	.058163	.5066
25	.22234	.059155	.5108
30	.21904	.060147	.5150
35	.21565	.061139	.5196
40	.21208	.062131	.5242
45	.20835	.063123	.5291
50	.20449	.064115	.5341
55	.20056	.065107	.5393
60	.19649	.066099	.5448
70	.18782	.068083	.5562
80	.17873	.070067	.5685
90	.16952	.072051	.5817
95	.16511	.073043	.5886

$$pH_s = \frac{A}{T} + B + CT + DT^2. \qquad (4)$$

The constants A, B, C, and D of this empirical equation were obtained for each of the buffer solutions with the aid of the IBM 704 computer. They are summarized in table 4, the last column of which gives the standard deviation of a single value of pH_s based on the deviations from the least-squares line. The "recommended" values of pH_s are those calculated by eq (4) and, hence, smoothed temperature-wise. The summary given in table 5 includes pH_s for 38° C, in view of the frequent use of this temperature in biological studies.

A consideration of the standard deviations of the values of $p(a_H\gamma_{Cl})^\circ$ given in table 2 (where available) together with the fit of pH_s to eq (4) as represented by the standard deviations given in table 4, leads to the following estimated limits to the effects of random errors in the recommended standard pH_s values: 0.003 for the range 0 to 60 °C and 0.005 for the range 60 to 95 °C. If, in addition, 0.002 is allowed for the maximum uncertainty in the constants of eq (2) below 60 °C and 0.003 above 60 °C, the total uncertainties in pH_s (table 5) become 0.005 unit (0 to 60 °C) and 0.008 unit (60 to 95 °C).

3. Properties of the Standards

Compositions on the molal scale of the solutions to which pH_s values have been assigned are given above. Furthermore, the pH_s represents $-\log a_H$, where a_H is an activity in molal units. It is nonetheless usually convenient to prepare buffer solutions by volume methods rather than weight methods, and it has been noted in earlier publications that the error in pH_s that results from use of an x *molar* solution in place of the prescribed x *molal* solution is negligible, in view of the tolerance of ±0.01 unit placed on the values of pH_s. If, however, third-decimal accuracy is to be ascribed to the values of pH_s, the compositions of the solutions must be adjusted somewhat more carefully.

TABLE 2. *Values of $p(a_H \gamma_{Cl})°$ for seven standard buffer solutions from 0 to 95 °C*

t	A	B	C	D	E	F	G
	Tetroxalate	Tartrate	Phthalate	Phosphate	Phosphate	Borax	Calcium hydroxide
°C							
0	1.765	----------	4.090	7.091	7.640	9.522	13.510
5	1.764	----------	4.084	7.057	7.605	9.450	13.291
10	1.765	----------	4.082	7.029	7.579	9.390	13.088
15	1.769	----------	4.083	7.006	7.555	9.336	12.893
20	1.773	----------	4.087	6.988	7.537	9.287	12.712
25	1.780	3.637	4.096	6.974	7.523	9.240	12.537
30	1.785	3.631	4.104	6.965	7.511	9.200	12.381
35	1.792	3.628	4.113	6.956	7.498	9.162	12.219
40	1.797	3.627	4.125	6.951	7.493	9.130	12.070
45	1.803	3.628	4.138	6.949	7.486	9.100	11.926
50	1.811	3.631	4.155	6.948	7.482	9.072	11.790
55	1.819	3.639	4.172	6.950	----------	9.044	11.661
60	1.824(1.827)	3.647(3.643)	4.188(4.175)	6.954(6.948)	----------	9.021(9.026)	11.540
70	1.849	3.664	4.219	6.962	----------	8.990	----------
80	1.877	3.698	4.259	6.979	----------	8.953	----------
90	1.904	3.738	4.301	7.001	----------	8.920	----------
95	1.919	3.767	4.331	7.014	----------	8.899	----------
Reference, 0 to 60 °C	[11]	[12]	[13]	[14]	[2]	[15]	[16]
Reference, 60 to 95 °C (value at 60 °C enclosed in parentheses)	[1]	[1]	[1]	[1]		[1]	

TABLE 3. *"Experimental" values of pH_s for seven standard buffer solutions from 0 to 95 °C*

t	A	B	C	D	E	F	G
	Tetroxalate	Tartrate	Phthalate	Phosphate	Phosphate	Borax	Calcium hydroxide
°C							
0	1.669	----------	4.006	6.986	7.534	9.465	13.425
5	1.667	----------	3.999	6.951	7.499	9.392	13.206
10	1.667	----------	3.996	6.922	7.472	9.332	13.003
15	1.671	----------	3.997	6.898	7.447	9.277	12.808
20	1.674	----------	4.000	6.879	7.429	9.228	12.627
25	1.680	3.558	4.008	6.864	7.414	9.180	12.452
30	1.685	3.552	4.016	6.855	7.400	9.140	12.296
35	1.691	3.548	4.024	6.845	7.387	9.101	12.133
40	1.695	3.546	4.035	6.839	7.381	9.069	11.984
45	1.700	3.547	4.047	6.836	7.373	9.038	11.839
50	1.707	3.549	4.063	6.833	7.367	9.010	11.703
55	1.714	3.556	4.080	6.834	----------	8.981	11.573
60	1.719(1.722)	3.563(3.559)	4.095(4.082)	6.837(6.831)	----------	8.957(8.962)	11.451
70	1.742	3.578	4.124	6.843	----------	8.925	----------
80	1.767	3.610	4.162	6.857	----------	8.887	----------
90	1.792	3.648	4.202	6.876	----------	8.852	----------
95	1.806	3.676	4.231	6.888	----------	8.830	----------

The density of each of the seven standard solutions at 25 °C is listed in table 6, together with the corresponding molarity of each of the buffer components. The fifth column of the table gives the dilution value [17] or change of pH_s resulting from dilution of the buffer with an equal volume of pure water. The difference of pH_s between two solutions of numerically equal molality and molarity can therefore be derived, and it is given in the sixth column of the table. The Van Slyke buffer value, $\beta = db/dpH$ (where db is an increment of strong acid or strong base, in equivalents, added to 1 liter of buffer solution) [18], is given in the seventh column and the temperature coefficient of the pH_s value in the last column.

It is evident from the results given in table 6 that only the tetroxalate solution and the calcium hydroxide solution (solutions A and G) have sufficiently large dilution values to require that a distinction between molal (m) and molar (M) scales be made. Indeed, this difference is of only academic interest as it applies to the standard solution of calcium hydroxide, which is a saturated solution prepared without the necessity of weighing the calcium hydroxide itself. On the other hand, the pH_s of a 0.05 M solution of potassium tetroxalate is lower by about 0.003 unit than that of the standard 0.05 m solution, and allowance should be made for this difference.

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Table 4. *Values of the constants of the equation:* $pH_s = A/T + B + CT + DT^2$, *for seven standard buffer solutions from 0 to 95 °C*

Solution	Temperature range	A	B	C	$10^5 D$	Standard deviation
	°C					
A, Tetroxalate	0 to 95	−362.76	6.1765	−0.018710	2.5847	0.0019
B, Tartrate	25 to 95	−1727.96	23.7406	−.075947	9.2873	.0016
C, Phthalate	0 to 95	1678.30	−9.8357	0.034946	−2.4804	.0027
D, Phosphate	0 to 95	3459.39	−21.0574	.073301	−6.2266	.0017
E, Phosphate	0 to 50	5706.61	−43.9428	.154785	−15.6745	.0011
F, Borax	0 to 95	5259.02	−33.1064	.114826	−10.7860	.0025
G, Calcium hydroxide	0 to 60	7613.65	−38.5892	.119217	−11.2918	.0028

Table 5. *Recommended standard values of* pH_s, *calculated by eq* (4)

t	A	B	C	D	E	F	G
	Tetroxalate	Tartrate	Phthalate	Phosphate	Phosphate	Borax	Calcium hydroxide
°C							
0	1.666	----------	4.003	6.984	7.534	9.464	13.423
5	1.668	----------	3.999	6.951	7.500	9.395	13.207
10	1.670	----------	3.998	6.923	7.472	9.332	13.003
15	1.672	----------	3.999	6.900	7.448	9.276	12.810
20	1.675	----------	4.002	6.881	7.429	9.225	12.627
25	1.679	3.557	4.008	6.865	7.413	9.180	12.454
30	1.683	3.552	4.015	6.853	7.400	9.139	12.289
35	1.688	3.549	4.024	6.844	7.389	9.102	12.133
38	1.691	3.548	4.030	6.840	7.384	9.081	12.043
40	1.694	3.547	4.035	6.838	7.380	9.068	11.984
45	1.700	3.547	4.047	6.834	7.373	9.038	11.841
50	1.707	3.549	4.060	6.833	7.367	9.011	11.705
55	1.715	3.554	4.075	6.834	----------	8.985	11.574
60	1.723	3.560	4.091	6.836	----------	8.962	11.449
70	1.743	3.580	4.126	6.845	----------	8.921	----------
80	1.766	3.609	4.164	6.859	----------	8.885	----------
90	1.792	3.650	4.205	6.877	----------	8.850	----------
95	1.806	3.674	4.227	6.886	----------	8.833	----------

Table 6. *Properties of seven standard buffer solutions at 25 °C*

Solution	m	Density	Molarity	Dilution value, $\Delta pH_{1/2}$	$^a \Delta pH_s$	Buffer value, β	Temperature coeff., dpH_s/dt
		g/ml				equiv./pH	units/°C
A, Tetroxalate	0.05	1.0032	0.04962	+0.186	−0.0028	0.070	+0.001
B, Tartrate	.0341	1.0036	.034	+.049	−.0003	.027	−.0014
C, Phthalate	.05	1.0017	.04958	+.052	−.0009	.016	+.0012
D, Phosphate	b.025	1.0028	b.02490	+.080	−.0006	.029	−.0028
E, Phosphate	c.008695	1.0020	c.008665	e+.07	−.0005	.016	−.0028
	d.03043		d.03032				
F, Borax	.01	0.9996	.009971	+.01	−.0001	.020	−.0082
G, Calcium hydroxide	.0203	0.9991	.02025	−.28	+.0014	.09	−.033

a $\Delta pH_s = pHs$ (*M Molar* solution) $-pH_s$ (*m molal* solution).
b Concentration of each phosphate salt.
c KH_2PO_4.
d Na_2HPO_4.
e Calculated value.

Accordingly, from the molarities given in table 6 have been calculated the weights of buffer substance that should be taken in order to prepare (by volume methods) 1 liter of buffer solution of the prescribed molality at 25 °C. The weights (in air near sea level) are given in table 7. The preparation of a sample of calcium hydroxide suitable for use as a standard buffer substance has been described in an earlier paper [16]. The other buffer substances are available as certified standard samples from the National Bureau of Standards. Carbon dioxide-free water should be used to prepare the standards composed of phosphate salts or borax.

Table 7. *Compositions of seven standard buffer solutions*

Weight of buffer substance (in air) per liter of buffer solution at 25 °C

Solution		Buffer substance	Weight in air
			g
A, Tetroxalate,	0.05 m	$KH_3(C_2O_4)_2 \cdot 2H_2O$	12.61
B, Tartrate,	about 0.034 m	$KHC_4H_4O_6$	Saturated at 25 °C
C, Phthalate,	0.05 m	$KHC_8H_4O_4$	10.12
D, Phosphate,	0.025 m	KH_2PO_4	3.39
	0.025 m	Na_2HPO_4	3.53
E, Phosphate,	0.008695 m	KH_2PO_4	1.179
	0.03043 m	Na_2HPO_4	4.30
F, Borax,	0.01 m	$Na_2B_4O_7 \cdot 10H_2O$	3.80
G, Calcium hydroxide,	0.0203 m	$Ca(OH)_2$	(Saturated at 25 °C)

4. Discussion

It is evident from the foregoing sections that the NBS standard pH scale can be characterized as a scale of conventional hydrogen ion activity (on the molal scale), defined in terms of certain specified standard solutions. The special nature of these standard values is indicated by use of the symbol pH$_s$ or pH(S) to avoid confusion with the pH, a quantity that is determined operationally, usually by a pH cell with a liquid junction and a glass electrode. Although the precise meaning of pH$_s$ is set forth in eqs (1) and (2), it cannot be said that experimental pH values possess this same significance in the same degree. The unavoidable variations in the liquid-junction potential are largely responsible for the indeterminate nature of operational pH values. Only under certain very restricted experimental conditions is it wise to attempt an interpretation of pH values in terms of the conventional scale of pH$_s$.

The pH response of glass electrodes (that is, the change in the surface potential with change of pH) is often somewhat less than the theoretical Nernst slope. Fortunately, however, the voltage response is usually linear with pH over considerable ranges. For these reasons, two or more standards are needed to furnish a useful calibration of the glass electrode function. The pH values of "unknowns" X then are determined, in effect, by interpolation between two electromotive forces (E_1 and E_2) furnished by two standard solutions, S_1 and S_2 [4]:

$$\frac{p\text{H}(X) - p\text{H}(S_1)}{p\text{H}(S_2) - p\text{H}(S_1)} = \frac{E_X - E_1}{E_2 - E_1}. \tag{5}$$

This procedure serves admirably for the standardization of pH cells with a glass electrode between a lower limit of about pH 2.5 and an upper limit of about pH 11.5, corrections for the alkaline error of the glass electrode being applied where necessary. With the availability of the tetroxalate standard and the calcium hydroxide standard, it seemed possible to extend this standardization procedure to pH 1.7 at the low end and to pH 12.4 at the high end [19].

If this procedure were followed, however, the calibration of the assembly would correct not only for deficiencies in the response of the glass electrode but also for the variability of the liquid-junction potential when a standard of intermediate pH is replaced by the tetroxalate solution or by the calcium hydroxide solution. It may be anticipated that the response of the glass electrode will be nearly the same in all solutions of pH 1.7 or in all solutions of pH 12.4, but it is a well-known fact that the liquid-junction potential does not necessarily show this regularity and cannot, therefore, be effectively "calibrated out."

For the standardization of glass electrode assemblies with a liquid junction, therefore, a distinction has been made between "primary standards" and "secondary standards." The five solutions of pH 3.5 to 9.5 are considered to be *primary* standards intended for establishing the response of glass electrode pH cells. On the other hand, the tetroxalate solution and the calcium hydroxide solution are considered to be *secondary* standards, for confirmatory purposes, only when the usual pH cell is used. Experiments have shown that a pH assembly with liquid junction, standardized in the approved fashion in the intermediate range of pH, will indicate a pH value for the tetroxalate solution that is about 0.03 unit lower than the value of pH$_s$ given in table 5 [20].

Similarly, the calcium hydroxide solution will also have a pH value about 0.03 unit lower than pH$_s$ [16]. (The equality of these two figures is, of course, fortuitous.) In spite of these deviations, it should be realized that the pH$_s$ values of these two solutions are as accurate as those for the other five, and all seven may be used with equal confidence when the variability of the liquid-junction potential is not a factor.

Inasmuch as pH$_s$ is assigned independently for each buffer solution, the possibility of the existence of inconsistencies in the standardization of practical pH assemblies, even in the intermediate pH range, must be recognized. These inconsistencies, if they exist, would be attributable to one or both of the following causes: The first is the unavoidable oversimplification inherent in eq (1), which recognizes a single formula for the variation of γ_{Cl} with I in seven solutions of different compositions. The second is that the concentrations and mobilities of the ions in the several buffer solutions are different. No effort has been made to match the buffer solutions carefully in these respects, since the "unknowns" cannot in any case be expected to match the standards.

At any rate, the concentrated solution of potassium chloride used as a bridge solution, together with a properly designed junction, can be depended upon to smooth out variations in the liquid-junction potential rather successfully between pH 3.5 and 10.5. The data reproduced in section 1 of this paper indicate that the inconsistency is not large for one particular design of liquid junction of the free-diffusion type. Further studies are, however, desirable at other temperatures and for other junctions, including those of the commercial types most commonly used.

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