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Standards for *p*H Measurements from 60° to 95° C

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The NBS standard *p*H scale is defined in terms of several reference solutions whose *p*H values ($p\mathrm{H_S}$) have heretofore been assigned only in the range 0° to 60° C. Recent measurements of the standard potential of the silver–silver-chloride electrode at temperatures above 60° now permit this scale to be extended to 95° C.

Electromotive-force measurements of cells with hydrogen and silver–silver-chloride electrodes and containing buffer-chloride solutions are reported in this paper for the range 60° to 95° C. The assignment of $p\mathrm{H_S}$ values to the following five reference solutions is described: 0.05-*m* potassium tetroxalate; potassium hydrogen tartrate (saturated at 25° C); 0.05-*m* potassium hydrogen phthalate; 0.025-*m* potassium dihydrogen phosphate; 0.025-*m* disodium hydrogen phosphate; and 0.01-*m* borax.

1. Introduction

The Bureau has recommended a standard *p*H scale defined in terms of several reference points. The primary standards which fix the points on this scale are six in number and cover the *p*H range 1.6 to 12.5 at 25° C. Their compositions are as follows: A 0.05-*m* solution of potassium tetroxalate ($p\mathrm{H_S}$ 1.68 [1] [1]); a solution saturated with potassium hydrogen tartrate at 25° C ($p\mathrm{H_S}$ 3.56 [2]); 0.05-*m* potassium hydrogen phthalate ($p\mathrm{H_S}$ 4.01 [3]); a solution 0.025-*m* with respect to both potassium dihydrogen phosphate, and disodium hydrogen phosphate ($p\mathrm{H_S}$ 6.86 [4]); 0.01-*m* borax (sodium tetraborate, $p\mathrm{H_S}$ 9.18 [5]); and a solution saturated with calcium hydroxide at 25° C ($p\mathrm{H_S}$ 12.45 [6]).

In earlier published work, the $p\mathrm{H_S}$ values of five of these reference standards have been determined at intervals of 5 deg from 0° to 60° C, permitting the standardization of *p*H equipment over a rather wide range of temperatures. At the time when most of these values were obtained, standards at higher temperatures were precluded by a lack of data for the standard potential of the silver–silver-chloride electrode, or other reference electrode, above 60° C. A need on the part of commerce and industry for accurate standards for measuring *p*H at temperatures up to 95° C, however, led the authors to undertake a determination of this important electrode potential in the range 60° to 95° C [7]. The $p\mathrm{H_S}$ values of all but one of these standards have now been extended to this high range of temperature. Calcium hydroxide has a negative temperature coefficient of solubility, and a separation of solid material was sometimes observed when a solution saturated at 25° C was heated to temperatures above 60° C. Furthermore, the poor stability of those cells in which precipitation did not occur made precise measurements extremely difficult. For these reasons, $p\mathrm{H_S}$ values have not been assigned to the calcium hydroxide standard in this extended temperature range.

2. Method of Assigning $p\mathrm{H_S}$

The procedure by which the standard *p*H values have been assigned to the standard reference solutions has been set forth in earlier publications [1 to 6, 8, 9]. There are three steps in the procedure: (1) Measurement of the emf of the cell Pt; H_2(g), standard reference solution, KCl (*m*), AgCl; Ag. This cell contains the reference solution in which a soluble chloride (usually potassium chloride) is present at one of three selected low, accurately known, molalities (*m*). From the emf (*E*), the standard potential of the silver–silver-chloride electrode ($-E^\circ$ [7]), and natural constants, values of the quantity $pw\mathrm{H}$ are calculated by the formula

$$pw\mathrm{H}\equiv\frac{(E-E^\circ)F}{2.3026RT}+\log m \tag{1}$$

in which F is the faraday, R the gas constant, and T the temperature on the Kelvin scale; (2) the effect of the added chloride on the value of $pw\mathrm{H}$ is removed by extrapolation to $m=0$, in order to obtain the limiting value, $pw\mathrm{H}^\circ$; (3) the standard *p*H values, termed $p\mathrm{H_S}$, are calculated from $pw\mathrm{H}^\circ$ and a conventional definition of the activity coefficient of chloride ion, f_{Cl}:

$$p\mathrm{H_S}=pw\mathrm{H}^\circ+\log f_{\mathrm{Cl}}. \tag{2}$$

The single ionic activity coefficient, f_{Cl}, is related in some arbitrary manner to mean activity coefficients, which are either experimentally determined or calculated from equations, like that of Debye and Hückel [10], believed to be valid for dilute solutions. For this step it is necessary to know the ionic strength of the solution.

3. Experimental Procedures

In view of the high vapor pressure of water in the cell solutions at these elevated temperatures, each cell vessel was provided with a saturator consisting of three chambers in series [11], in addition to the single saturating chamber that was a part of the vessel itself [12]. The hydrogen gas bubbled through

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

a total depth of nearly 30 cm of solution before entering the hydrogen electrode compartment of the cell. By this means, vapor-liquid equilibrium was believed to be established at all of the temperatures. The smallest volume of hydrogen sufficient to separate the solution from the rubber stopper holding the electrodes was allowed to remain in the silver–silver-chloride electrode compartment at the time the cell was filled.

The constant temperature bath was filled with a commercial heavy mineral oil of U. S. P. grade. Temperatures were measured with a platinum resistance thermometer, and are believed to have been fixed at the nominal values within ±0.05° C. In order to correct the observed emf to 1 atm partial pressure of hydrogen, the vapor pressures of the solutions were taken to be the same as those of pure water. The pressure corrections at 60° to 95° C, in millivolts, have been tabulated elsewhere [9].

The cell solutions were prepared from weighed amounts of the buffer materials (NBS Standard Samples), and from potassium chloride solutions of the desired molality. Dissolved oxygen was removed by bubbling pure hydrogen through the solutions for 2 hr before the cells were filled. Concentrations were expressed on the molal scale (moles per kilogram of water) exclusively, inasmuch as the molality remains unchanged when the temperature of the solution is altered. The dilution effect on the *p*H of these standard solutions is small. Hence, in practice it is permissible to regard the buffer concentrations given in the tables as either *molarities* or *molalities*. The error exceeds 0.001 *p*H unit only for the tetroxalate solution, where it may amount to 0.002 unit.

The preparation of the electrodes has been described elsewhere [9]. The hydrogen electrodes used in the phthalate solutions were coated with palladium black to minimize reduction of the solute. In other details, the procedure followed closely that of the study of hydrochloric acid solutions at 60° to 95° C. [7].

The duration of stability of these cells is considerably reduced at elevated temperatures, particularly when the cell solutions are alkaline. For this reason, the cells were brought to initial equilibrium at room temperature, and the measurements at 60° to 95° C were completed within 8 hr after the temperature of the bath was raised.

4. Results

The measurements were made at three low molalities (m), namely 0.015, 0.010, and 0.005, of potassium chloride. It has been found that the values of *pw*H for a given buffer solution, computed by eq (1), usually vary linearly with m below $m=0.015$. Although most of the measurements at high temperatures were of insufficient precision to provide an independent test of linearity, nevertheless, a straight line, located by the method of least squares, was drawn through the values of *pw*H. The intercept of this line

$$pw\mathrm{H}=pw\mathrm{H}^{\circ}+am \qquad (3)$$

with the axis at $m=0$ is *pw*H°, and the slope of the line is designated a.

The experimental data, which were rather numerous, are summarized in table 1. In the next to the last column is given the value of σ, the standard deviation of a single "observed" value of *pw*H from the calculated value, and in the last column is found σ_i, the standard deviation of *pw*H°, the intercept.

TABLE 1. *Summary of data and calculated values of pw*H°

Reference solution	Temperature	Number of cells for $m_{\mathrm{KCl}}=$			Constants of eq (3)		Standard deviations	
		0.005	0.010	0.015	*pw*H°	a	σ	σ_i
	° *C*							
0.05-*m* potassium tetroxalate	60	3	2	2	1.827	0.28	0.003	0.003
	70	3	2	2	1.849	.35	.003	.003
	80	3	2	2	1.877	.34	.002	.002
	90	3	2	2	1.904	.16	.012	.011
	95	3	2	2	1.919	.01	.011	.010
Potassium hydrogen tartrate, saturated at 25° C	60	5	4	2	3.643	−.42	.002	.002
	70	5	4	2	3.664	−.20	.003	.002
	80	5	4	2	3.698	−.60	.002	.002
	90	5	4	2	3.738	−.25	.003	.002
	95	5	4	2	3.767	−1.56	.005	.004
0.05-*m* potassium hydrogen phthalate	60	6	4	5	4.175	−.05	.005	.003
	70	4	3	3	4.219	−.03	.007	.005
	80	4	3	3	4.259	−.01	.006	.005
	90	4	3	3	4.301	+.01	.006	.005
	95	6	4	5	4.331	.04	.005	.003
0.025-*m* potassium dihydrogen phosphate, 0.025-*m* disodium hydrogen phosphate	60	5	4	2	6.948	−.97	.005	.004
	70	5	4	2	6.962	−.64	.004	.003
	80	5	4	2	6.979	−.29	.004	.003
	90	5	4	2	7.001	+.05	.005	.003
	95	5	4	2	7.014	.03	.004	.003
0.01-*m* borax	60	5	5	3	9.026	.04	.005	.003
	70	5	5	3	8.990	.20	.004	.003
	80	5	5	3	8.953	.90	.003	.002
	90	5	5	3	8.920	1.19	.005	.003
	95	5	5	3	8.899	1.77	.012	.009

5. Calculation of $p\mathrm{H}_{\mathrm{S}}$

Several different conventions for the estimation of the activity coefficient of chloride ion, f_{Cl} in eq (2), have been used in assigning $p\mathrm{H}_{\mathrm{S}}$ values to the six NBS standards. Inasmuch as this coefficient has no independent thermodynamic definition, one convention cannot be termed "more correct" than another. In fairness, all of these may be called "reasonable", and it is fortunate that all lead to identical $p\mathrm{H}$ values at very low concentrations and to values that differ by only about ± 0.01 unit at an ionic strength of 0.1 [8, 9]. The assignment of $p\mathrm{H}_{\mathrm{S}}$ values with an accuracy of ± 0.001 unit must await the universal acceptance of a single convention for the estimation of the individual ionic activity coefficients needed in the evaluation of electrochemical data.

Mean activity coefficients of the electrolytes present in buffer solutions are ordinarily unknown; hence, assumed relationships among the activity coefficients of the ions in these mixtures are not usually a fruitful means of evaluating f_{Cl}. It is just as satisfactory, and more convenient, to estimate f_{Cl} by the Debye-Hückel equation

$$\log f_{\mathrm{Cl}} = \frac{-A\sqrt{\mu}}{1+Ba^*\sqrt{\mu}} \qquad (4)$$

where A and B are constants for the water medium at a particular temperature, μ is the ionic strength, and a^* is an "ion-size parameter". When the latter is given a value of 4 to 6, the right side of eq (4) reproduces the logarithm of the mean activity coefficient of many uniunivalent strong electrolytes very successfully.

In order to use eq (4) to calculate $p\mathrm{H}_{\mathrm{S}}$ at elevated temperatures, it is necessary to know, within about 10 percent, the ionic strength of the buffer solution at 60° to 95° C. The evaluation was accomplished as follows for the five buffer solutions:

1. 0.05-*m* potassium tetroxalate: in the earlier work [1], the ionic strength of the 0.05-*m* solution was found to be 0.077 at 0° C and 0.074 at 60° C. This change was not only small, but approximately linear; hence, the values of the ionic strength at 60° to 95° C were obtained by extrapolation, and an average value of 0.073 was selected.

2. Potassium hydrogen tartrate, saturated at 25° C: the equation for the calculation of the ionic strength is given in an earlier paper [2]. The ratio of the dissociation constants, K_2/K_1, needed in the calculation, was estimated with the required accuracy from the known ratio in the range 0° to 60° C [13] by extrapolation to the higher temperatures. In this way, it was shown that the ionic strength of the tartrate solution saturated at 25° C is practically constant at 0.04 in the temperature range 25° to 95° C.

3. 0.05-*m* potassium hydrogen phthalate: the ionic strength of this solution between 25° and 60° C was calculated from the compositions listed by Hamer, Pinching, and Acree [3], and found to change only 0.3 percent when the temperature is increased by 35° C. The ionic strengths were plotted, and the curve extended to 95° C. An average value of 0.053 was chosen for the range 60° to 95° C.

4. 0.025-*m* potassium dihydrogen phosphate, 0.025-*m* disodium hydrogen phosphate: inasmuch as negligible amounts of free hydrogen and hydroxyl ions are present in these solutions, the ionic strength is constant at 0.1 from 0° to 95° C.

5. 0.01-*m* borax: the ionic strength is 0.02 and is unchanged by the increased degree of hydrolysis at the elevated temperatures. The formation of polyboric acids is not believed to be sufficiently extensive at this low concentration and relatively high $p\mathrm{H}$ to affect the ionic strength appreciably [5].

These values of the ionic strength were used to compute $p\mathrm{H}_{\mathrm{S}}$ by eq (2) with the aid of the conventional definition of f_{Cl} embodied in eq (4). The ion-size parameter a^* of the latter equation was given two values, 4 and 6, and the values of $p\mathrm{H}_{\mathrm{S}}$ given in table 2 are the mean of the two results to the nearest 0.01 unit. The $p\mathrm{H}_{\mathrm{S}}$ of the six NBS standards for all the temperatures at which an assignment of $p\mathrm{H}_{\mathrm{S}}$ has been made are plotted in figures 1 and 2, and are included in table 2 for the convenience of the reader.

The reference solutions should be preserved at room temperature, where they are known to be stable for several weeks, and portions heated to the elevated temperatures as needed for the standardization of $p\mathrm{H}$ equipment.

TABLE 2. *$p\mathrm{H}_{\mathrm{s}}$ of the six reference solutions*[a] *from 0° to 95° C*

t	0.05-*m* K tetroxalate	KH tartrate, (saturated at 25° C)	0.05-*m* KH phthalate	0.025-*m* KH_2PO_4, 0.025-*m* Na_2HPO_4	0.01-*m* borax	$Ca(OH)_2$, (saturated at 25° C)
0	1.67	--------	4.01	6.98	9.46	13.43
5	1.67	--------	4.01	6.95	9.39	13.21
10	1.67	--------	4.00	6.92	9.33	13.00
15	1.67	--------	4.00	6.90	9.27	12.81
20	1.68	--------	4.00	6.88	9.22	12.63
25	1.68	3.56	4.01	6.86	9.18	12.45
30	1.69	3.55	4.01	6.85	9.14	12.30
35	1.69	3.55	4.02	6.84	9.10	12.14
40	1.70	3.54	4.03	6.84	9.07	11.99
45	1.70	3.55	4.04	6.83	9.04	11.84
50	1.71	3.55	4.06	6.83	9.01	11.70
55	1.72	3.56	4.07	6.84	8.99	11.58
60	1.72	3.56	4.09	6.84	8.96	11.45
70	1.74	3.58	4.12	6.85	8.93	--------
80	1.77	3.61	4.16	6.86	8.89	--------
90	1.80	3.65	4.20	6.88	8.85	--------
95	1.81	3.68	4.23	6.89	8.83	--------

[a] In the preparation of the buffer solutions, it is usually more convenient to dissolve the buffer substance in water and dilute to a given volume in a volumetric flask than to add a known weight of water. As noted above, the $p\mathrm{H}_{\mathrm{s}}$ of solutions, whose *molarities* at 25° C are the same numerically as the *molalities* given in table 2, will not differ appreciably from the values listed.

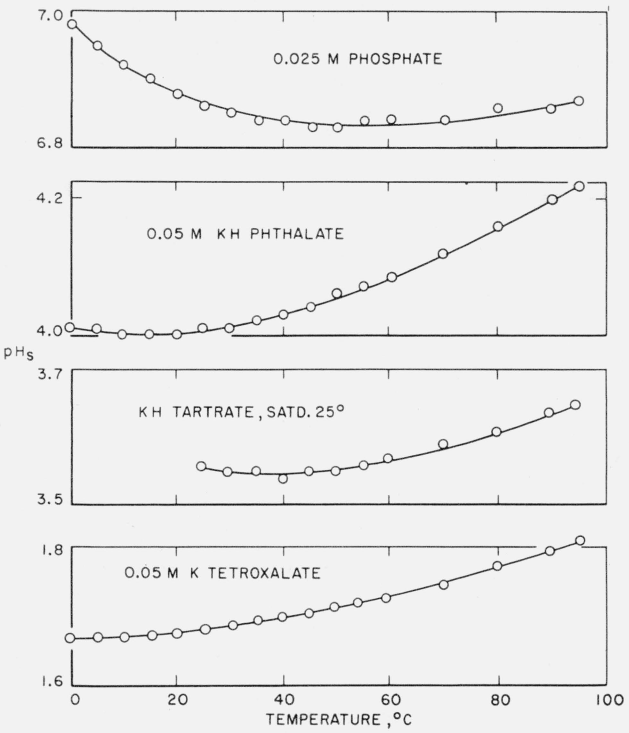

Figure 1. *pH_S of the NBS tetroxalate, tartrate, phthalate, and phosphate standards at 0° to 95° C.*

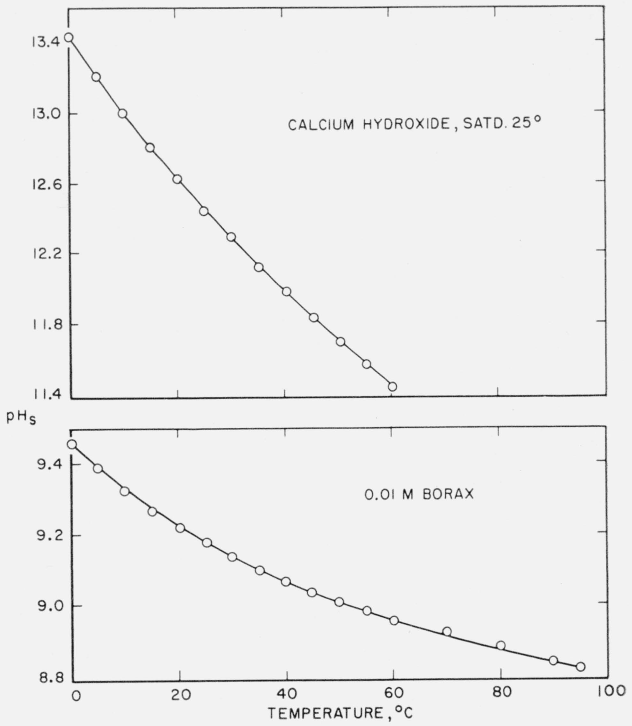

Figure 2. *pH_S of the NBS borax and calcium hydroxide standards from 0° to 95° C.*

6. References

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