

Two New Standards for the pH Scale¹

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Two new primary standards for the NBS pH scale, supplementing the five already available, are proposed. The new reference solutions are the 0.05 molal solution of potassium dihydrogen citrate and a mixture of sodium bicarbonate and sodium carbonate, each 0.025 molal. The citrate solution has a pH of 3.776 at 25 °C and is more stable under certain conditions than either the tartrate or phthalate standards. The carbonate solution has a pH of 10.012 at 25 °C. It therefore extends the NBS pH scale above its present upper limit of 9.180 at this temperature. Reference values pH(S), based on emf measurements of cells with hydrogen electrodes and silver-silver chloride electrodes, have been assigned to these two standard solutions at 11 temperatures from 0 to 50 °C.

Key Words: Acidity; carbonate; citrate; emf; hydrogen electrode; pH; standards for pH.

1. Introduction

At present, the NBS standard pH scale is fixed in the range 3.5 to 9.5 by means of five primary standard solutions. The five reference solutions which define this conventional activity scale are listed in table 1 with the corresponding standard pH, designated pH(S), at 25 °C [1].²

The least suitable of the five primary standards is the solution of potassium hydrogen tartrate. Its chief disadvantage is its tendency to support the growth of molds [2]. Molds usually appear in the tartrate solution after a few days, and the pH may increase by as much as 0.1 unit. Likewise neither the phthalate solution nor the borax solution is an ideal pH standard. Although the former probably is used most extensively of all the primary pH standards, it has the disadvantage of being unstable in contact with the platinum-hydrogen electrode [3]. Since phthalate absorbs strongly in the ultraviolet region of the spectrum, this solution also finds limited application in many spectrophotometric methods for the determination of dissociation constants and in other studies of acid-base behavior.

Borax (sodium tetraborate decahydrate) has been found to lose some of its water of crystallization during storage. More important, the ionic strength of the solution is not as well known as might be desired, as a consequence of the tendency of boric acid to polymerize in solution. It is accordingly difficult to calculate pH(S) with certainty, as the calculation requires a

TABLE 1. Primary standards of the NBS pH scale

Material	Molality	pH(S) at 25 °C
KHC ₄ H ₄ O ₆ (tartrate).....	satd. at 25 °C	3.557
KHC ₈ H ₄ O ₄ (phthalate).....	0.05	4.008
KH ₂ PO ₄	0.025	6.865
Na ₂ HPO ₄	0.025	
KH ₂ PO ₄	0.008695	7.413
Na ₂ HPO ₄	0.03043	
Na ₂ B ₄ O ₇ · 10H ₂ O (borax).....	0.01	9.180

knowledge of the ionic strength. Furthermore, an alkaline standard with a pH higher than that of the borax standard (9.18 at 25 °C) would be most useful. In view of the increasing uncertainties of the glass electrode response as the pH rises above 10, it would be most desirable to have an additional standard with pH(S) of 10 or greater.⁴

The precise, electromotive force measurements leading to the assignment of pH(S) values to a solution 0.05 molal in potassium dihydrogen citrate and to another solution 0.025 molal in both sodium bicarbonate and sodium carbonate from 0 to 50 °C are described in this paper. These two reference solutions supplement the present primary standards, extending the standard scale to pH 10 at 25 °C and facilitating the standardization of hydrogen electrode pH cells at the lower end of the standard scale. In addition, the citrate solution can often be used advantageously in spectrophotometric studies where the phthalate solution is excluded.

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² Figures in brackets indicate the literature references at the end of this paper.

2. Experimental Procedures

2.1. Potassium Dihydrogen Citrate

The potassium dihydrogen citrate was prepared and purified by M. Paabo according to the procedure given by Kolthoff [4]. Anhydrous granular citric acid, 1 mole of which was dissolved in 80 cm³ of hot water, was neutralized with anhydrous reagent-grade potassium carbonate which had been dried previously at 205 °C. The recrystallized product was analyzed coulometrically and was found to assay 99.999 percent, with an uncertainty of 0.005 percent.

2.2. Carbonate Salts

The sodium carbonate ("primary standard" grade) was dried at 250 °C for 90 min and stored over calcium chloride and Drierite. Reagent-grade sodium bicarbonate was dried over a mixture of molecular sieves and Drierite for about two days at room temperature. Coulometric assay of these salts gave the following results: NaHCO₃, 99.95 percent; Na₂CO₃, 99.97 percent.

2.3. Methods and Results

With a few minor exceptions, the experimental techniques for the conduct of the precise emf measurements, including the design of the cells and the preparation of the electrodes, were the same as those described earlier [5, 6]. The solutions were prepared by weight from the buffer salts, a sample of fused potassium chloride low in bromide [7], and distilled water with a conductance less than $0.8 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$. It was essential that the water used in preparing the carbonate solution be purged with carbon dioxide-free nitrogen before the salts were dissolved in it. A slow increase in emf with time, observed in the cells containing the carbonate buffer, was minimized by discontinuing the hydrogen flow overnight during the course of the experiments. This drift was probably due to the removal of carbon dioxide from the buffer solution by the constant passage of hydrogen gas over long periods of time.

The emf of the following cells without liquid junction was measured at 11 temperatures from 0 to 50 °C:

Pt;H₂(g, 1 atm), KH₂ citrate (0.05m), KCl (*m*_{Cl}), AgCl;Ag

and

Pt;H₂(g, 1 atm), NaHCO₃ (0.025m), Na₂CO₃ (0.025m), KCl (*m*_{Cl}), AgCl;Ag

where *m*_{Cl} was 0.005, 0.01, or 0.015 mol kg⁻¹. The measured values of the emf, corrected to a partial pressure of hydrogen of 1 atm, are summarized in table 2. Each entry in the table is the average emf of four to seven individual cells. In general, values for the individual cells varied from the average by several hundredths of a millivolt in the citrate series to a

maximum of over 0.1 mV for some of the cells containing the carbonate buffer.

Values of the acidity function $p(a_H\gamma_{Cl})$ were calculated from the measured emf (*E*) of each cell at each of the three chloride concentrations by the equation

$$p(a_H\gamma_{Cl}) \equiv -\log(\gamma_H\gamma_{Cl}m_H) = \frac{(E - E^\circ)F}{RT \ln 10} + \log m_{Cl} \quad (1)$$

The standard emf E° of the cell is known over the temperature range of the measurements [8]. Limiting values of $p(a_H\gamma_{Cl})$, designated $p(a_H\gamma_{Cl})^\circ$, in the absence of chloride were obtained by extrapolating the average $p(a_H\gamma_{Cl})$ for each buffer-chloride mixture as a function of *m*_{Cl} to *m*_{Cl}=0. These limiting acidity functions are listed in tables 3 and 4. The extrapolation at 25 °C is shown in figure 1.

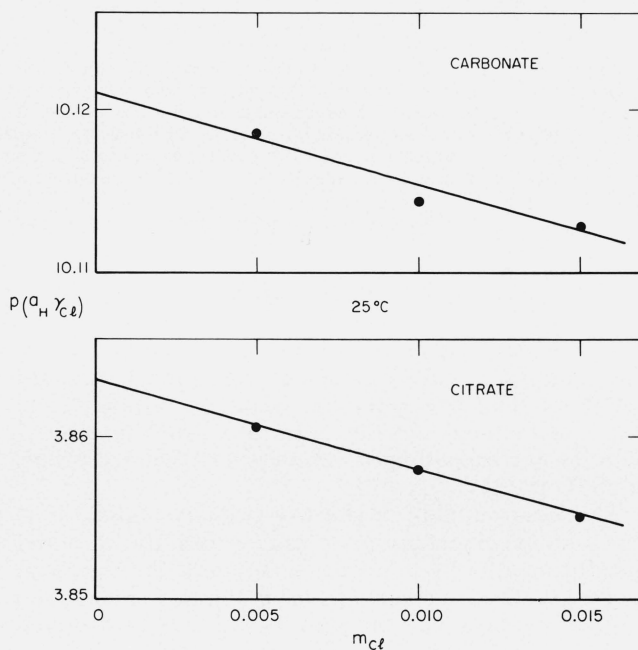


FIGURE 1. The acidity function $p(a_H\gamma_{Cl})$ at 25 °C plotted as a function of the molality of chloride.

An iterative procedure was used to calculate the ionic strengths. For this purpose, the three dissociation constants of citric acid [9], the second constant for carbonic acid [10], and the ionization constant of water [11] were used. The activity coefficient γ_i of each univalent ion *i* was taken equal to that for chloride as given by the convention [12]

$$-\log \gamma_{Cl^-} = \frac{A\sqrt{I}}{1 + 1.5\sqrt{I}} \quad (2)$$

in which *A* is the Debye-Hückel slope [6] and *I* is the ionic strength. Activity coefficients of bivalent and trivalent ions were approximated by $(\gamma_{Cl^-})^4$ and $(\gamma_{Cl^-})^9$, respectively, in accord with the valence factor in the Debye-Hückel equation. The activity coefficients and

TABLE 2. *Emf (E) of the cell Pt:H₂ (g, 1 atm), buffer-KCl soln., AgCl:Ag from 0 to 50 °C, in volts*

KCl molality	E ₀	E ₅	E ₁₀	E ₁₅	E ₂₀	E ₂₅	E ₃₀	E ₃₅	E ₄₀	E ₄₅	E ₅₀
Buffer: Potassium dihydrogen citrate (0.05 molal)											
0.015	0.54889	0.55086	0.55274	0.55463	0.55648	0.55828	0.56011	0.56190	0.56366	0.56539	0.56710
.01	.55851	.56062	.56272	.56477	.56688	.56878	.57087	.57277	.57478	.57666	.57849
.005	.57509	.57751	.57990	.58224	.58458	.58686	.58915	.59142	.59366	.59587	.59807
Buffer: NaHCO ₃ (0.025 molal), Na ₂ CO ₃ (0.025 molal)											
0.015	0.89957	0.90514	0.91094	0.91679	0.92261	0.92844	0.93435	0.94026	0.94621	0.95210	0.95803
.01	.90921	.91513	.92109	.92709	.93310	.93903	.94512	.95123	.95738	.96334	.96951
.005	.92558	.93199	.93822	.94451	.95085	.95707	.96349	.96991	.97633	.98289	.98908

TABLE 3. *Assignment of pH(S) values to the 0.05 molal solution of potassium dihydrogen citrate from 0 to 50 °C*

<i>t</i>	<i>p</i> (<i>a_H</i> γ _{Cl}) ⁰	<i>I</i>	−log γ _{Cl} [−]	<i>p</i> <i>a_H</i>	pH(S) (calc.)
°C					
0	3.948 ₁	0.0527	0.0840	3.864	3.863
5	3.923 ₈	.0526	.0845	3.839	3.840
10	3.904 ₂	.0526	.0851	3.819	3.820
15	3.887 ₄	.0526	.0858	3.802	3.802
20	3.874 ₃	.0526	.0865	3.788	3.788
25	3.863 ₅	.0526	.0872	3.776	3.776
30	3.854 ₈	.0526	.0879	3.767	3.766
35	3.847 ₂	.0525	.0886	3.759	3.759
40	3.843 ₁	.0525	.0894	3.754	3.753
45	3.840 ₄	.0524	.0902	3.750	3.750
50	3.839 ₉	.0524	.0910	3.749	3.749

TABLE 4. *Assignment of pH(S) values to the solution 0.025 molal with respect to both sodium bicarbonate and sodium carbonate from 0 to 50 °C*

<i>t</i>	<i>p</i> (<i>a_H</i> γ _{Cl}) ⁰	<i>I</i>	−log γ _{Cl} [−]	<i>p</i> <i>a_H</i>	pH(S) (calc.)
°C					
0	10.426 ₁	0.1	0.1055	10.321	10.317
5	10.348 ₈	.1	.1062	10.243	10.245
10	10.285 ₁	.0999	.1070	10.178	10.179
15	10.223 ₇	.0999	.1078	10.116	10.118
20	10.168 ₄	.0999	.1086	10.060	10.062
25	10.121 ₀	.0999	.1095	10.012	10.012
30	10.078 ₈	.0998	.1104	9.968	9.966
35	10.039 ₂	.0998	.1114	9.928	9.925
40	10.004 ₆	.0997	.1123	9.892	9.889
45	9.969 ₀	.0996	.1133	9.856	9.856
50	9.939 ₆	.0995	.1144	9.825	9.828

the ionic strength were calculated by successive approximations until neither varied by more than 1×10^{-6} from one approximation to the next. The calculations were simplified by the use of a time-shared computer with Dartmouth BASIC language.

A method for the resolution of overlapping dissociation constants has been described [9, 13] which simplifies the estimation of the ionic strength. The values of *I* for the citrate solution obtained by this method agreed to about 0.001 with those resulting from the iterative procedure.

The conventional *p**a_H* values for the citrate buffer are given in table 3 along with related data from which they were derived. A similar summary for the carbonate buffer is given in table 4. In both instances, the *p**a_H* was calculated from *p*(*a_H*γ_{Cl})⁰ by the equation

$$p a_H = p(a_H \gamma_{Cl})^0 + \log \gamma_{Cl}^- \quad (3)$$

where γ_{Cl}[−] was defined by eq (2). In the NBS procedure for establishing pH standards, the conventional *p**a_H* is taken equal to the standard value pH(S) of the operational definition of pH.

3. Discussion

The pH(S) values for the two new standards are plotted as a function of temperature in figure 2. The method of least squares and OMNITAB were utilized to fit pH(S) to an equation of the form

$$pH(S) = \frac{A}{T} + B + CT \quad (4)$$

where *T* is the temperature in kelvins. The constants of this equation are listed in table 5, and the calculated pH(S) is included in tables 3 and 4. The standard deviation of the "experimental" pH(S) from the smoothed curve represented by eq (4) is 0.0007 unit for the citrate buffer and 0.0026 unit for the carbonate buffer.

The citrate is highly recommended as an additional primary pH standard by the long-term stability of both the solid potassium dihydrogen citrate and its aqueous solution and by the stability of citrate solutions in contact with the hydrogen electrode. In addition, this reference solution is convenient to prepare, as only one salt need be weighed. The pH(S) value assigned to the 0.05*m* solution of this salt at 25 °C is 3.776.

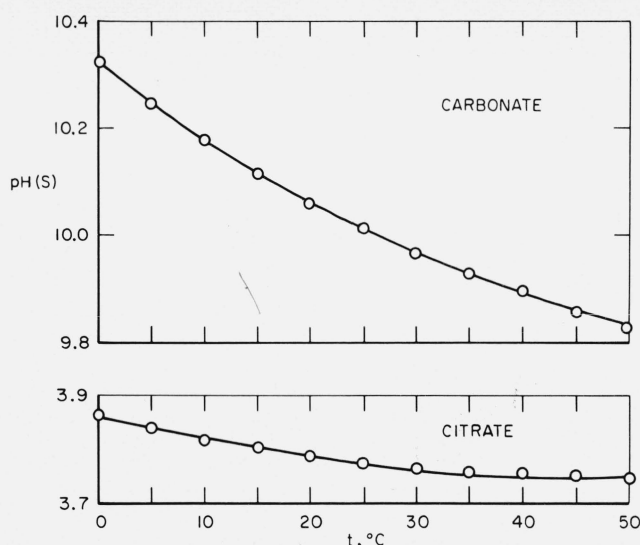


FIGURE 2. $\text{pH}(\text{S})$ for the citrate and carbonate standards plotted as a function of temperature.

TABLE 5. Constants of eq (4)

	Citrate standard	Carbonate standard
A	1280.4	2557.1
B	-4.1650	-4.2846
C	0.012230	0.019185

The carbonate buffer, 0.025 molal in sodium bicarbonate and sodium carbonate, is a useful primary standard for the high pH region. This solution is reasonably stable if protected from atmospheric carbon dioxide. Its assigned $\text{pH}(\text{S})$ is 10.012 at 25 °C.

The uncertainty of the assigned values of $\text{pH}(\text{S})$ can be estimated by combining the standard errors of the intercepts $p(a_{\text{H}^+\gamma_{\text{Cl}}})^\circ$ given in tables 3 and 4 with the estimated uncertainty in the standard emf and natural constants used in the calculation of $p(a_{\text{H}^+\gamma_{\text{Cl}}})$ and with the standard deviation of the experimental $\text{pH}(\text{S})$ from eq (4). The standard emf is known to better than 0.1 mV (0.0017 in pH) and, for all practical purposes, the values of R , T , and F contribute a negligible amount to the uncertainty of $\text{pH}(\text{S})$. Furthermore, the convention set forth in eq (2) is considered to be exact. The standard deviations of $p(a_{\text{H}^+\gamma_{\text{Cl}}})$ ranged from 0.0001 to 0.0015, while the standard deviation of the values of $\text{pH}(\text{S})$ from eq (4) was 0.0007 for the citrate buffer and 0.0026 for the carbonate buffer. Although the manner in which these individual errors are combined is to some extent a subjective matter, the total uncertainty in $\text{pH}(\text{S})$ is estimated to lie between 0.002 and 0.005 unit, being least for the citrate buffer near 25 °C and greatest for the carbonate buffer at 0 and 50 °C.

The group of primary pH standards that define the NBS scale should exhibit a satisfactory consistency when intercompared in any pH meter with liquid junction. If the standard scale of pH were not internally consistent, the experimental values of an

"unknown" solution would depend upon the particular reference solution chosen to standardize the measuring instrument. Evidently no exact consistency can be expected when a liquid-junction potential is involved, because the standards have different ionic strengths and contain different ionic species whose mobilities are not the same.

To reveal the extent of the consistency, the new citrate and carbonate standards were intercompared with the equimolal phosphate standard [$\text{pH}(\text{S}) = 6.865$ at 25 °C] in a cell where two hydrogen electrodes were separated by a bridge of saturated potassium chloride solution [14]. The results displayed in figure 3 show that the pH indicated by this cell with liquid junction is higher than the assigned $\text{pH}(\text{S})$ for the citrate standard and lower for the carbonate standard. In each instance, the difference may amount to 0.01 pH unit in the temperature range 10 to 45 °C.

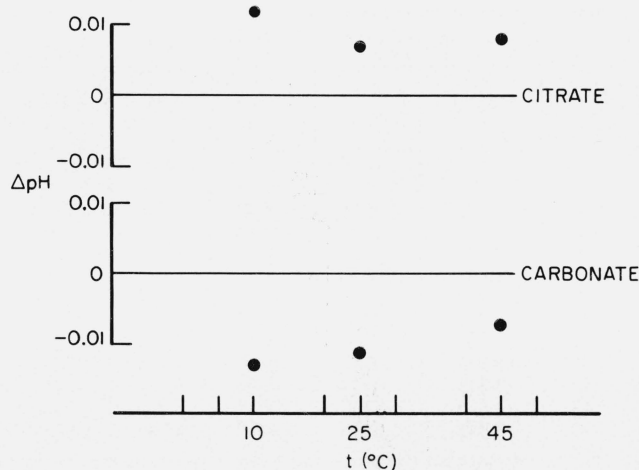


FIGURE 3. Internal consistency of the standard pH scale. Comparison of the new pH standards with the equimolal phosphate standard [$\text{pH}(\text{S}) = 6.865$ at 25 °C].

The citrate reference solution is most conveniently prepared by dissolving 11.41 g of pure potassium dihydrogen citrate in water and diluting to 1 liter at 25 °C. The carbonate reference solution can be made by dissolving 2.092 g of sodium bicarbonate and 2.640 g of sodium carbonate in carbon-dioxide-free water and diluting to 1 liter at 25 °C. The weights given above are weights in air. The compositions, densities, dilution values [15], buffer values [16], and pH-temperature coefficients for the two new pH standard solutions are summarized in table 6.

TABLE 6. Properties of two standard reference solutions at 25 °C

	Citrate standard	Carbonate standard
Molality.....	0.05	0.025 (each salt)
Molarity.....	0.04958	0.02492 (each salt)
Density, g ml ⁻¹	1.00294	1.00135
Dilution value.....	+0.024	+0.079
Buffer value.....	0.034	0.029
$d\text{pH}/dt$	-0.0022	-0.0096

The authors are indebted to George Marinenko for performing the coulometric analyses of the buffer salts.

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